Properties of $Sr_3Cr_2O_7$ synthesized under High Pressure and High Temperature

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Supervisors : M. Nunez-Regueiro & P. Toulemonde

Common properties of high temperature superconductors

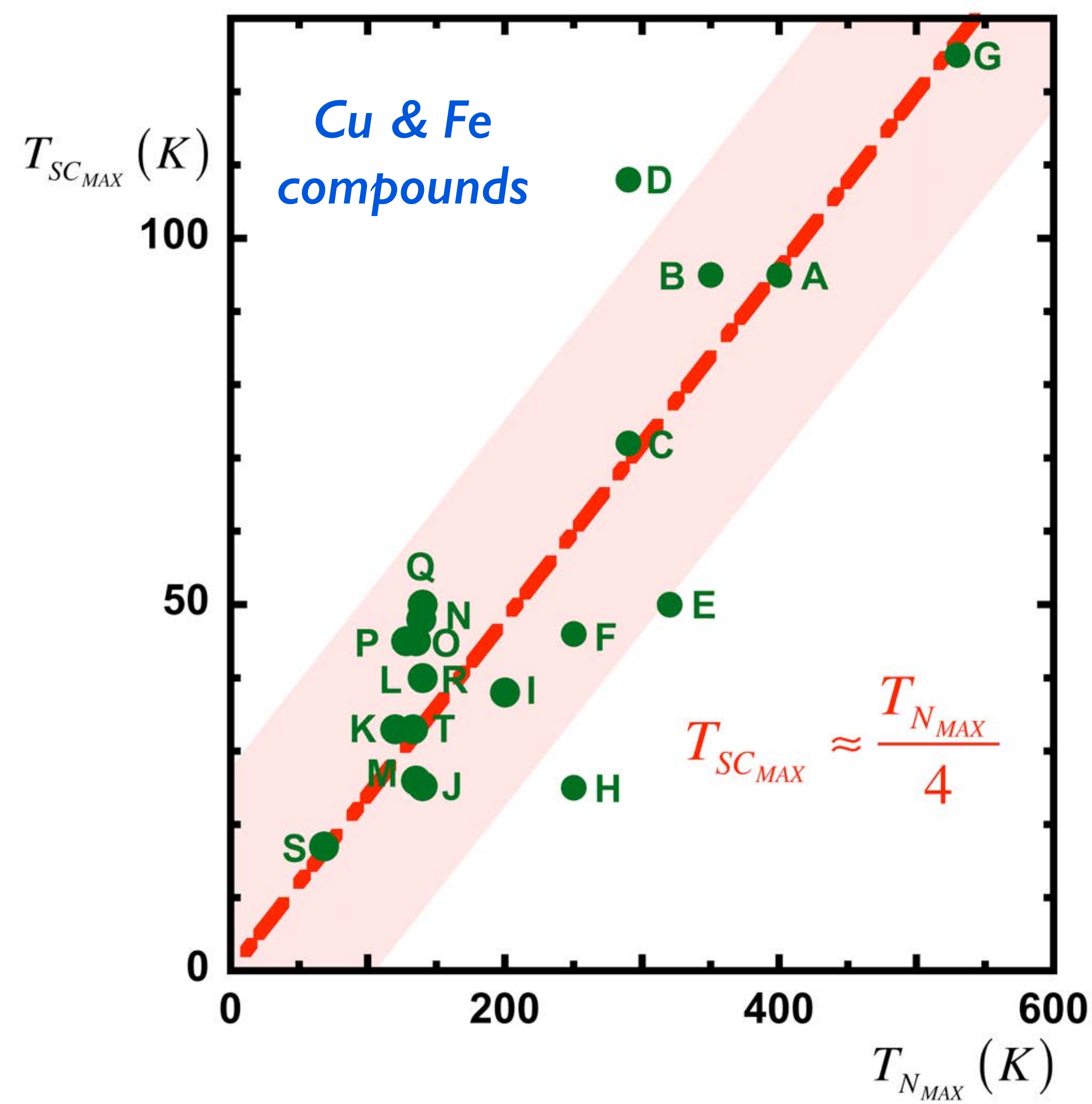
Layered (2D compounds)

AFM parent compound

High T_N

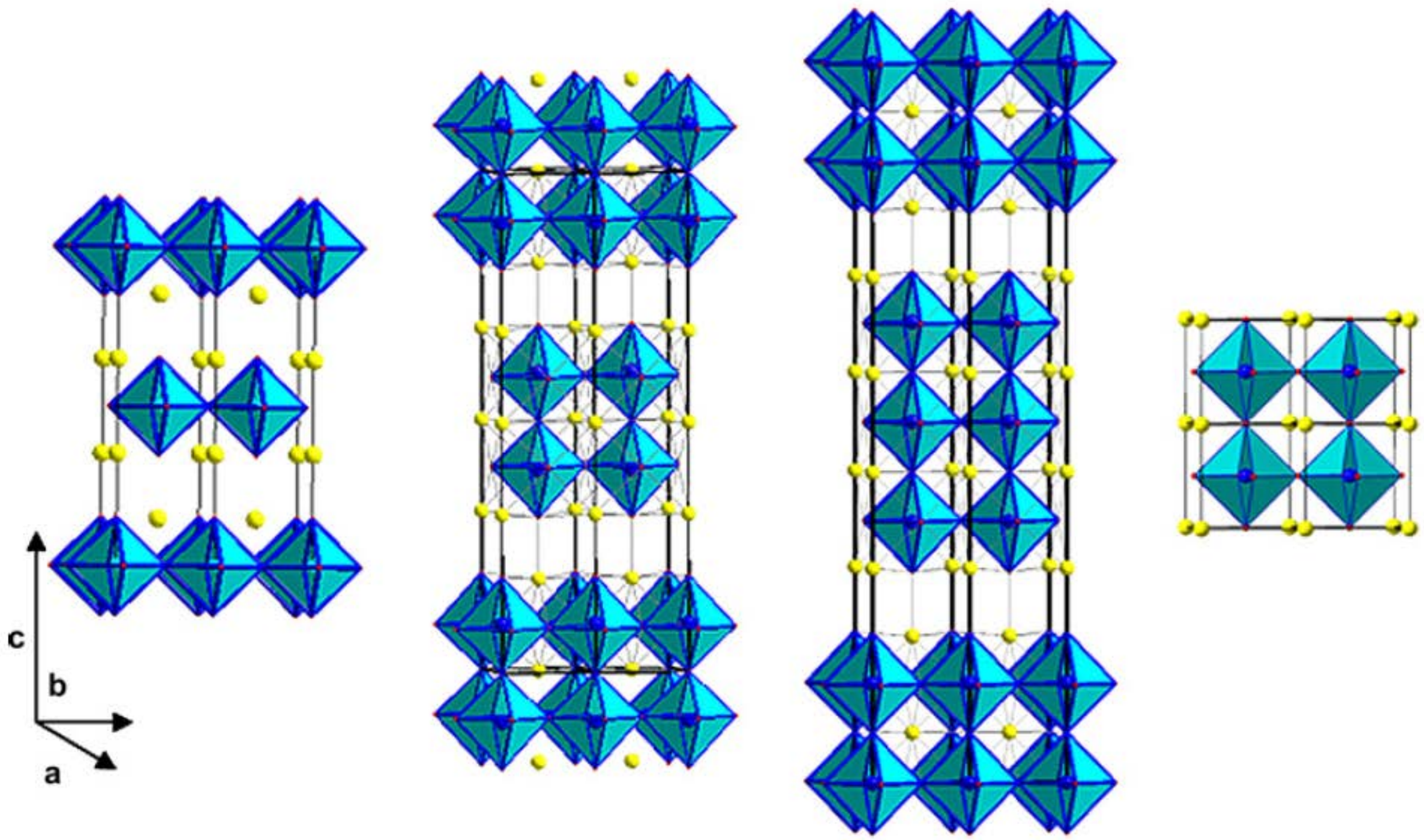
Low Magnetic Moment

candidates based on :
V, Cr, Mn, Fe, Co, Ni, Cu



A) *YBa2Cu3Ox*; B) *Bi2Sr2MCu2O8+d* C) *Hg*-1245; D) *Hg*-1245 ; E) *La2CuO4+ y* ;
F) *SSr2CuO2F2*; G)*CaxSr*1-x*CuO*2; H)*Nd*1-x*CexCuO*4;I) *Sr*1-*xKxFe2As*2 ;
J) *BaFe*2- *xCoxAs*2; K) Ca1- xNaxFe2As2; L) Ba1-xKxFe2As2 ; M) LaFeAsO1- xFx;
N) PrFeAsO1- xFx; O) SmFeAsO1- xFx ; P) GdFeAsO1- xFx ; Q) NdFeAsO1- xFx; R)
CeFeAsO1-xFx; S) *Fe*1+ *x* (*Te*1-*xSex*) ; T) *KyFe*2-*xSe*2

Ruddlesden-Popper phases : $\mathbf{Sr_{n+1}Cr_nO_{3n+1}}$



Cr^{IV}

e^- config. : $3d^2$

n= 1	n=2	n=3	n= ∞
Sr_2CrO_4	$Sr_3Cr_2O_7$	$Sr_4Cr_3O_{10}$	$SrCrO_3$

n : number of Perovskite layers

J.A. Kafalas and J.M. Longo, J. Sol. St. Chem. ***4****, 55 (1972).*

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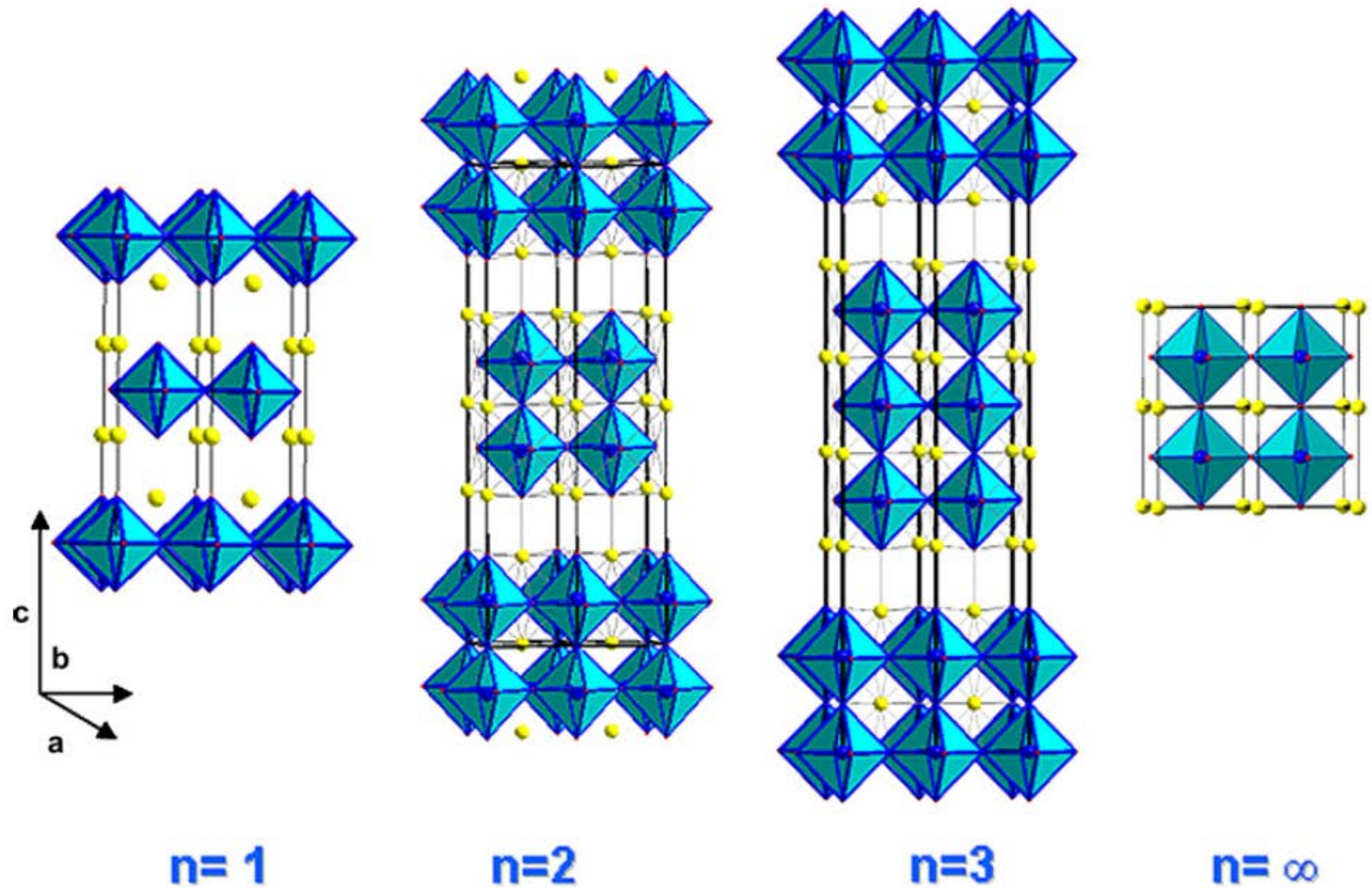

Difficult synthesis conditions : High Pressure/Temperature phases !

Sr_2CrO_4 **$Sr_3Cr_2O_7$** $Sr_4Cr_3O_{10}$ **$SrCrO_3$**

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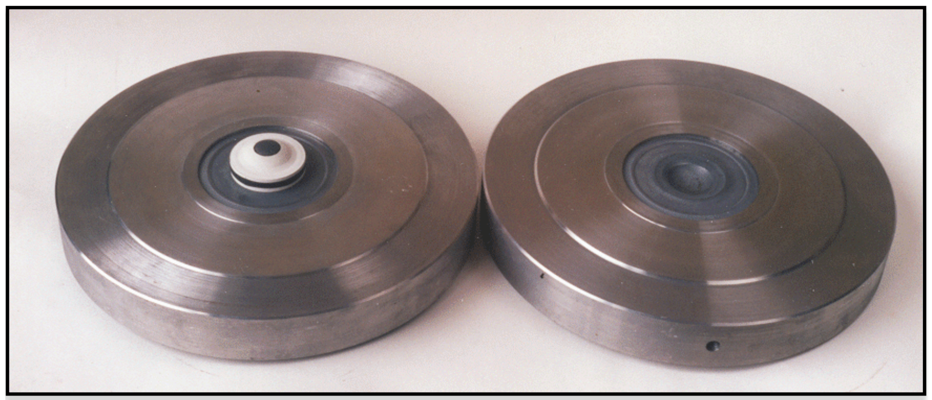
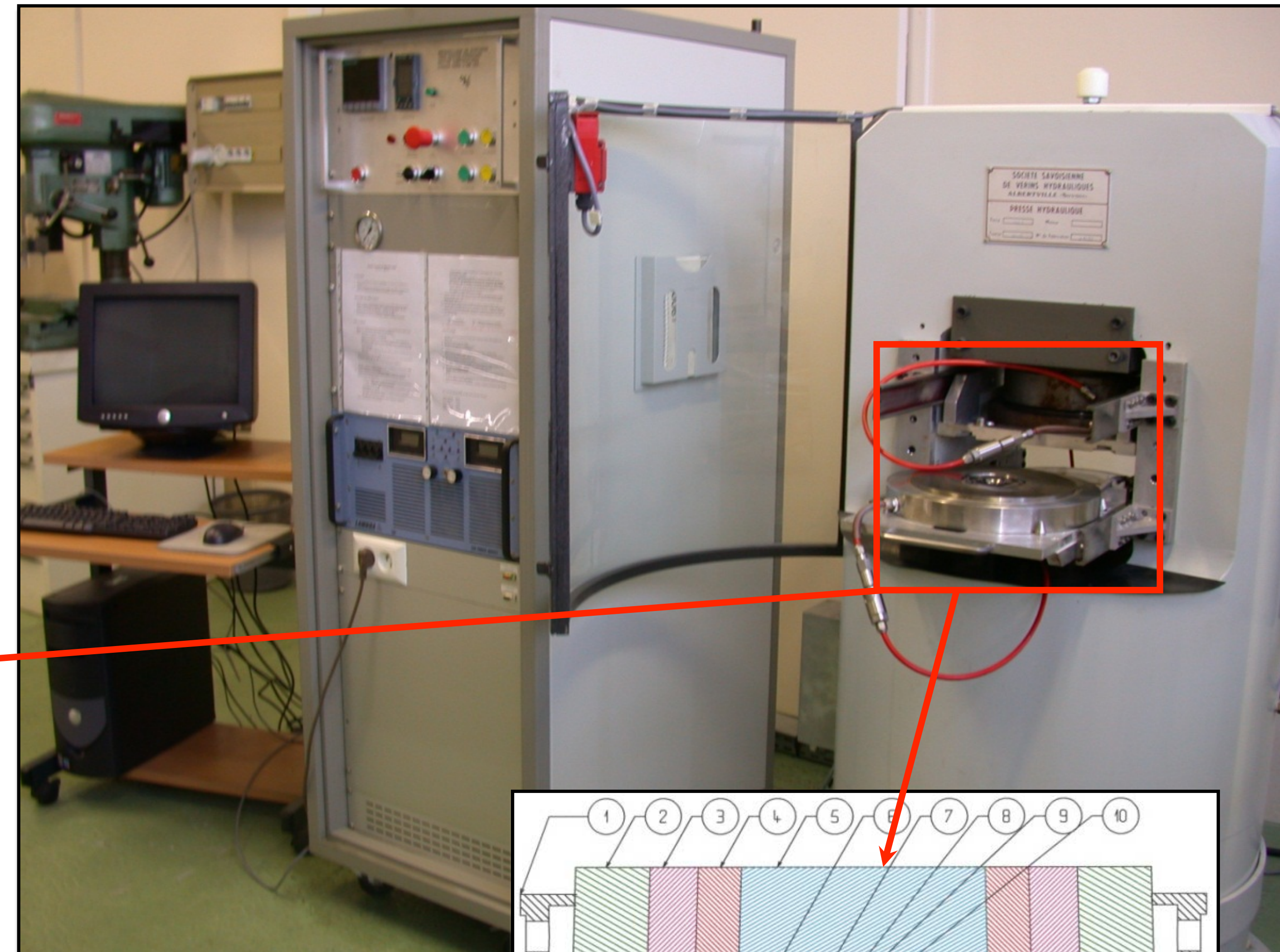
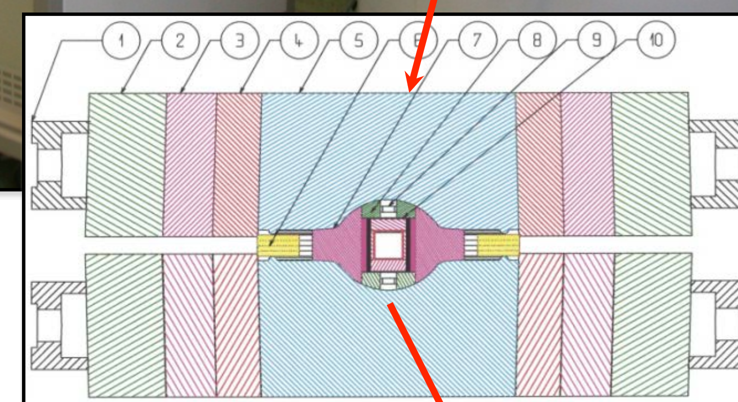
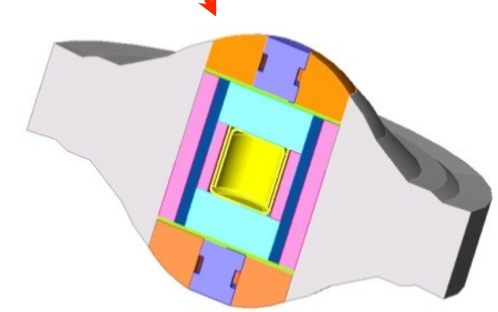
High Pressure & High Temperature Synthesis







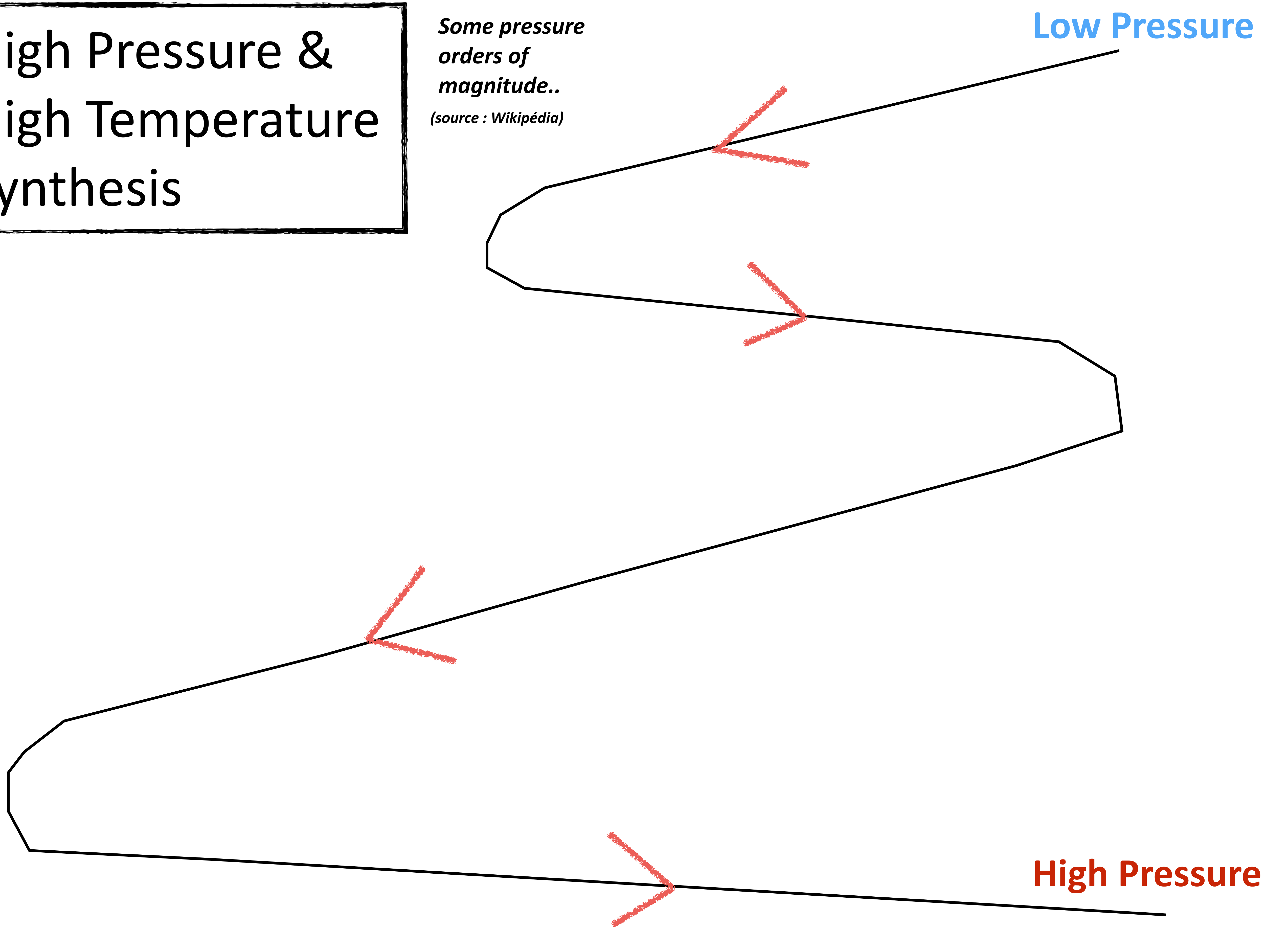


T_{max} ~ 1500°C.	Belt	Conac	
Cells diameter	12 mm	40mm	28mm
Capsule volume (Au,Pt,acier,CuBe,Ta,BN)	0.04 cm^3	0.8 cm^3	0.2 cm^3
Mass product	160 mg	2 g	0.5 g
Pressure range	0 - 8 GPa	0 - 5.5 GPa	0 - 7 GPa

High Pressure & High Temperature Synthesis

Some pressure orders of magnitude..

(source : Wikipédia)



High Pressure & High Temperature Synthesis

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10^{-15} Pa

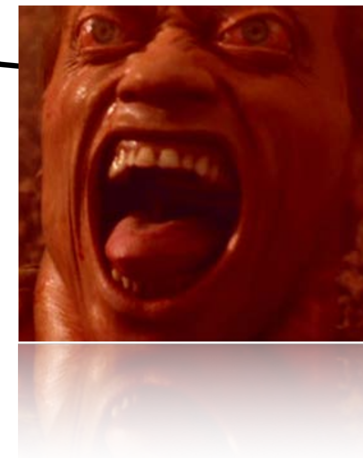
between stars in the Milky Way

10^{-5} Pa

threshold of human hearing

10^{2} Pa

threshold of pain pressure level for sound (~130dB)



6.3 kPa

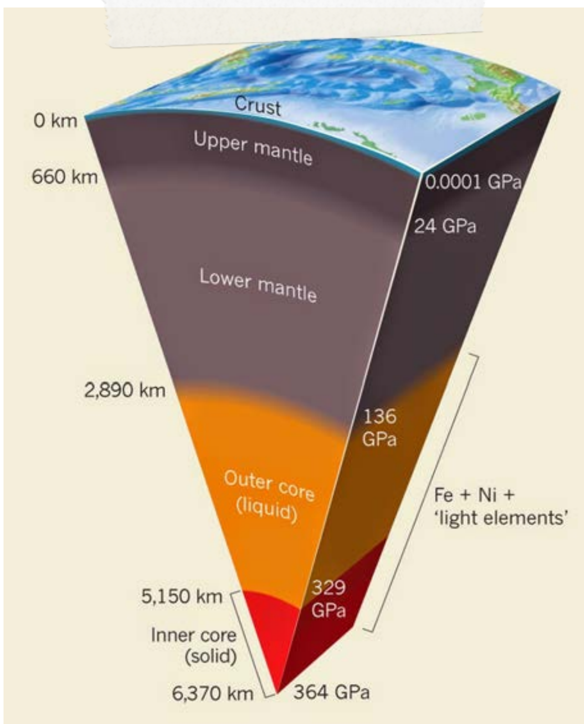
Pressure where water boils at normal human body temperature (37°C)

10^{5} Pa

pressure on hands of a (good) weightlifter

1 MPa

average human bite

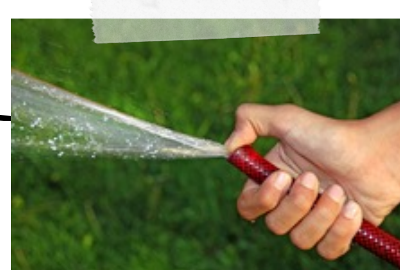


100 MPa

at bottom of Mariana trench (around 11km)

69 GPa

highest water jet pressure

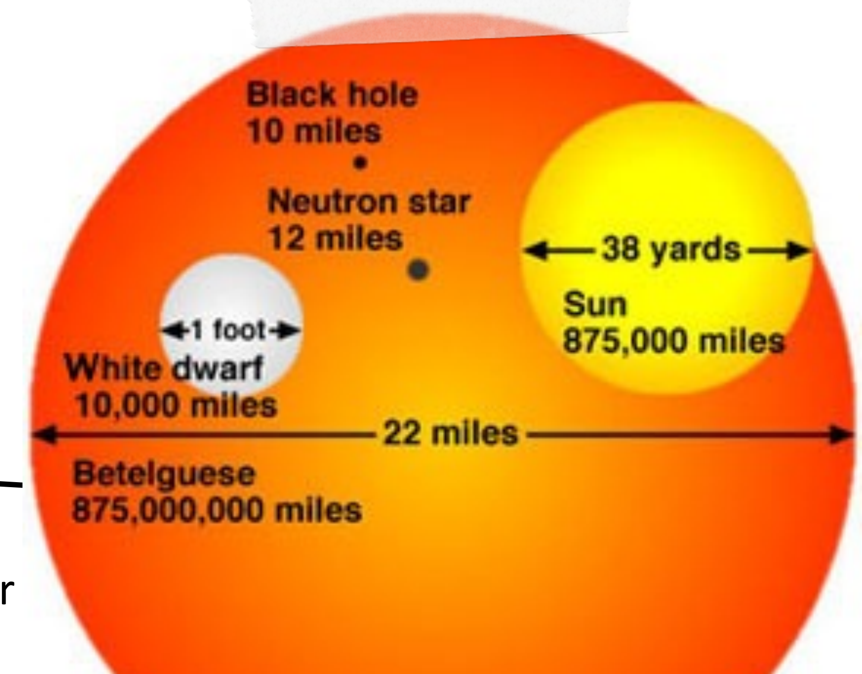


10^{16} Pa

inside core of the Sun

10^{34} Pa

inside a neutron star



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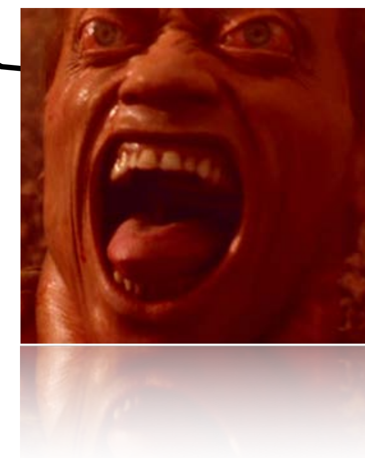

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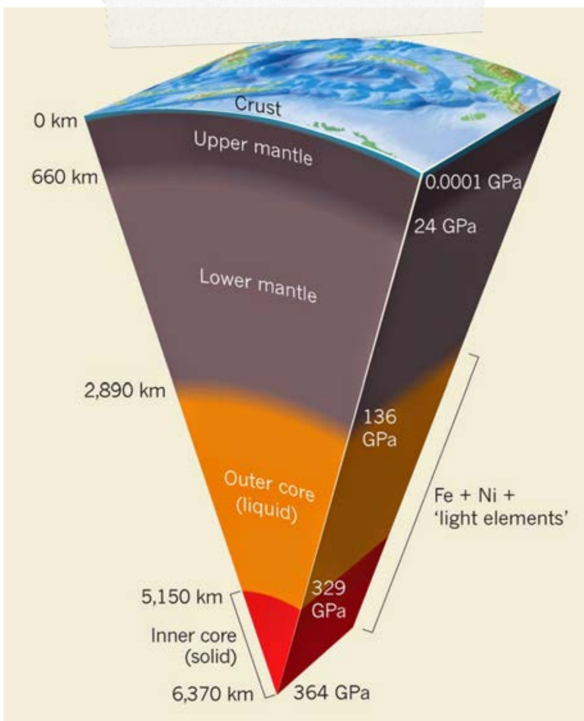
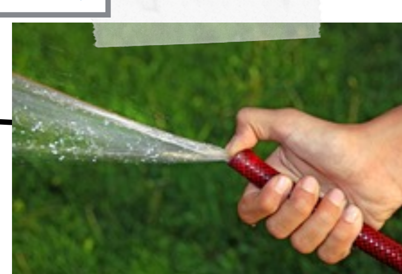


Our samples
~6 GPa / 1100°C
25km depth (Middle Crust)



69 GPa
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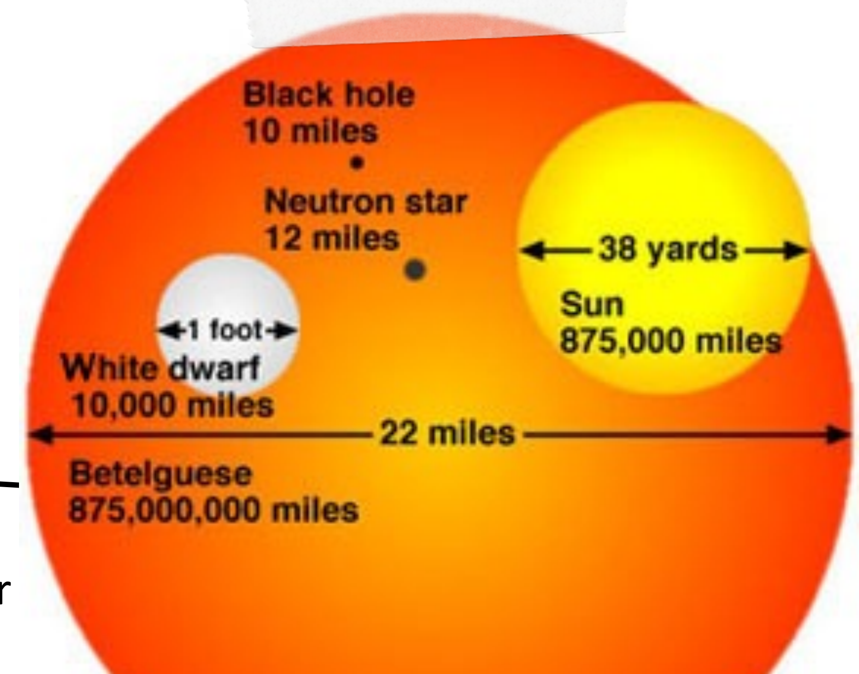

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Introduction : Perovskite $SrCrO_3$

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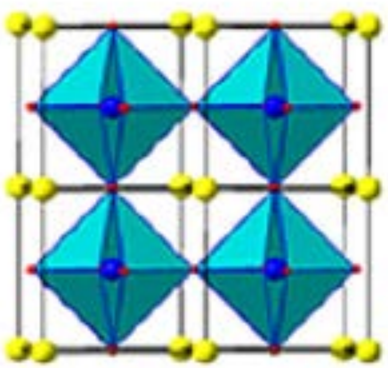
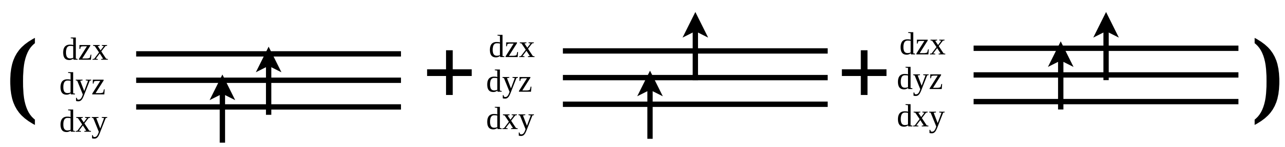


T>40K

cubic

paramagnetic

orbital degenerescence



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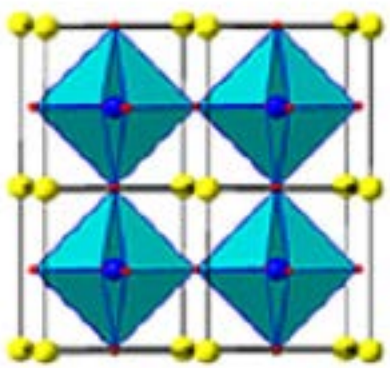

T>40K
cubic
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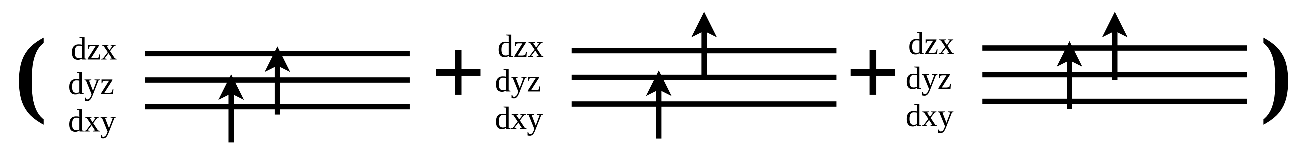
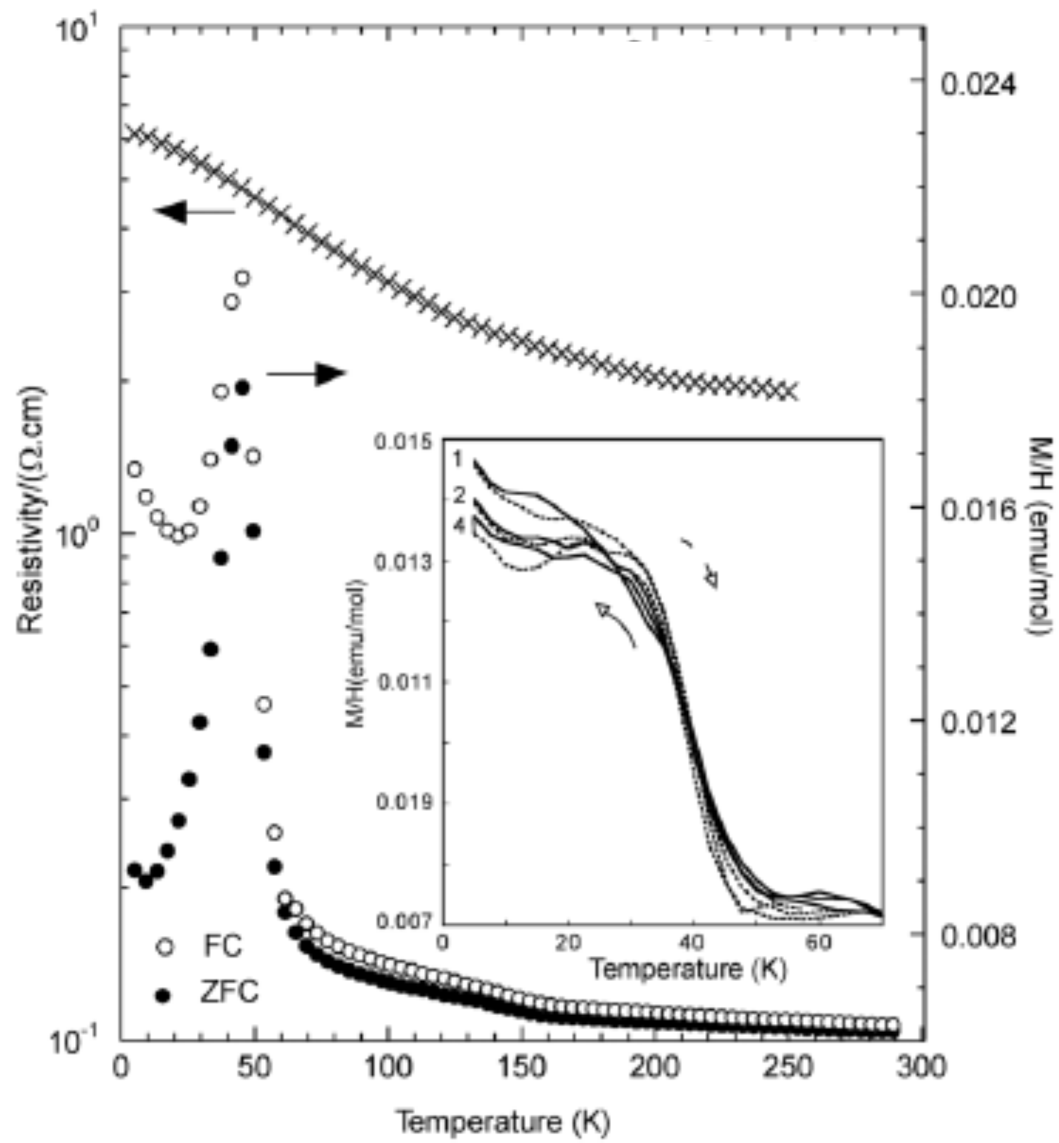


Neutron powder diffraction
Ortega *et al.*, PRL **99** (2007) 255701



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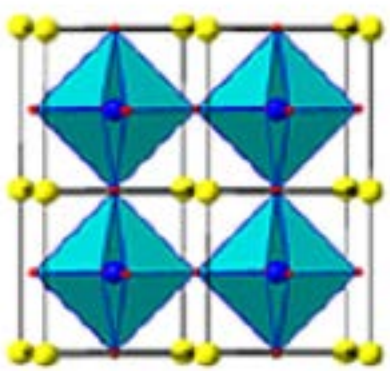

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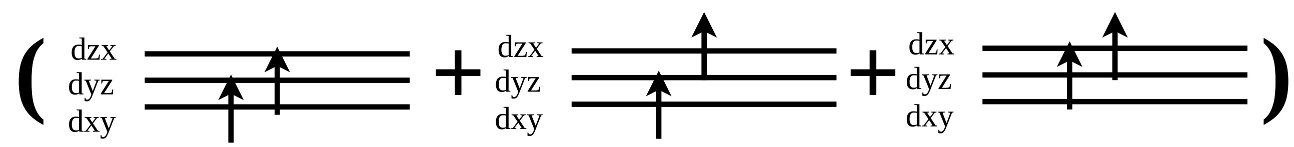

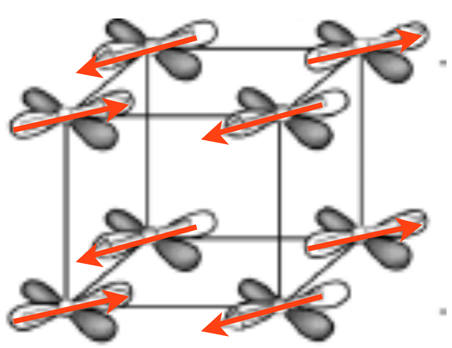

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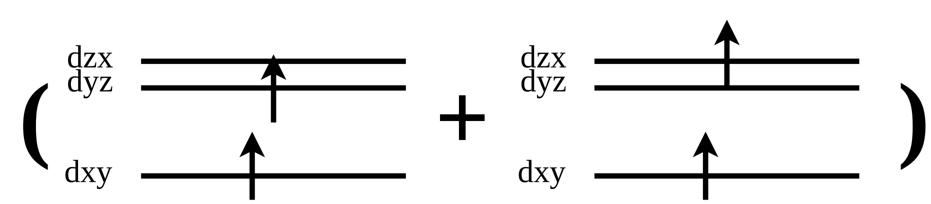
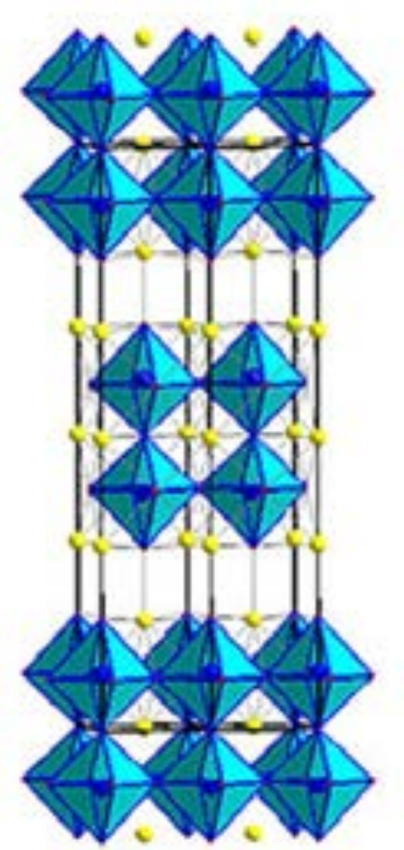
T<40K
tetragonal c/a=0.992
antiferromagnetic order
partial orbital order



$Sr_3Cr_2O_7$

Sr327
I4/mmm



a ~ 3.82 Å

c ~ 20.14 Å

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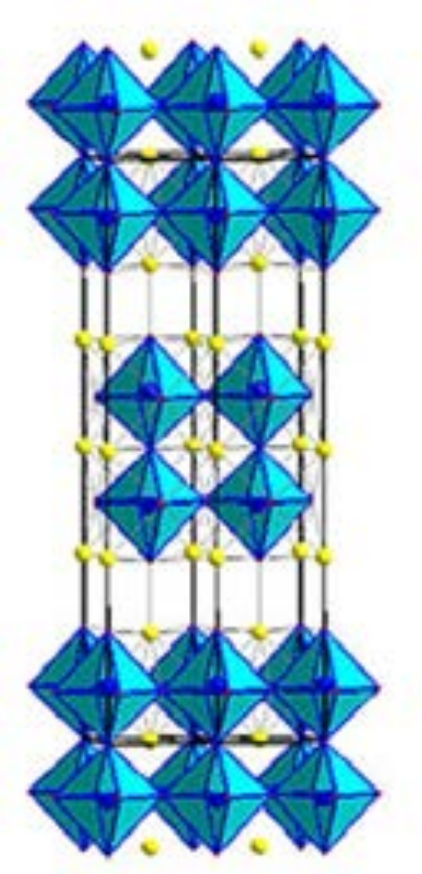

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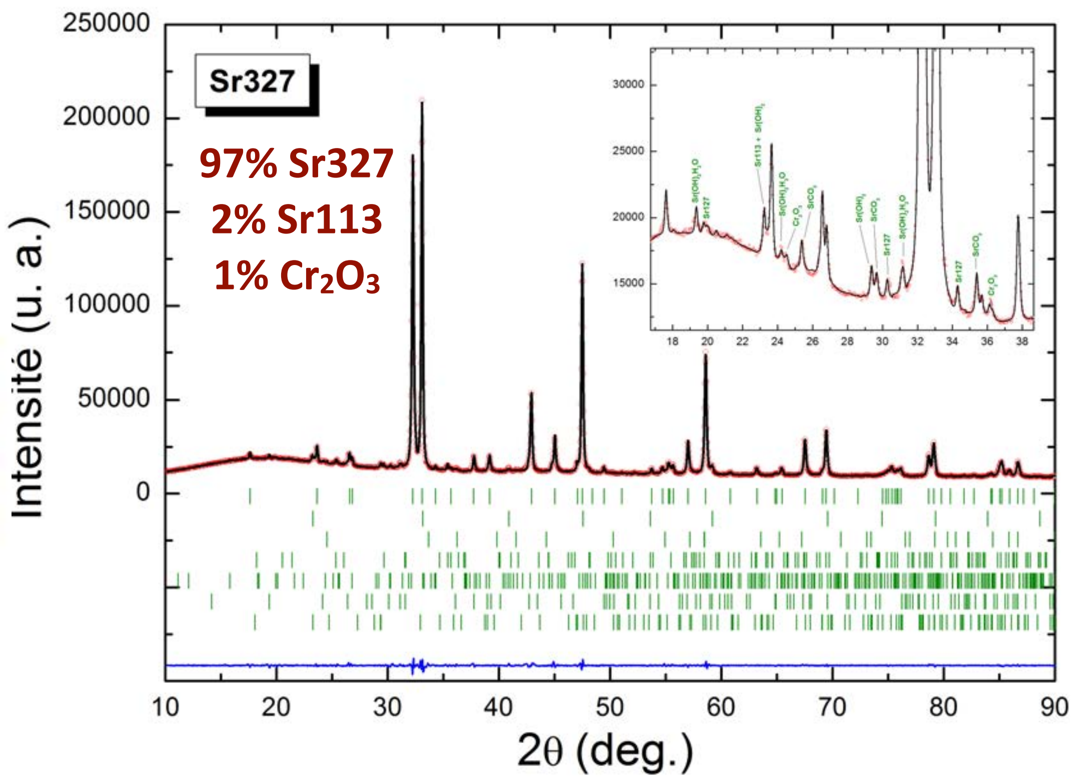
X-ray diffraction



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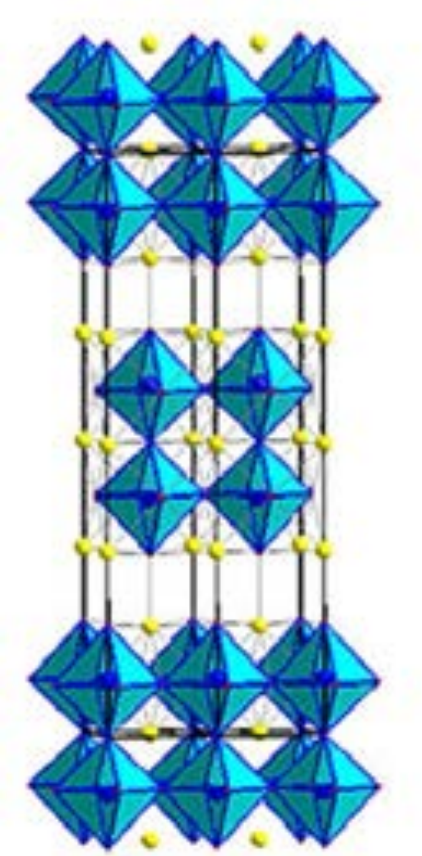

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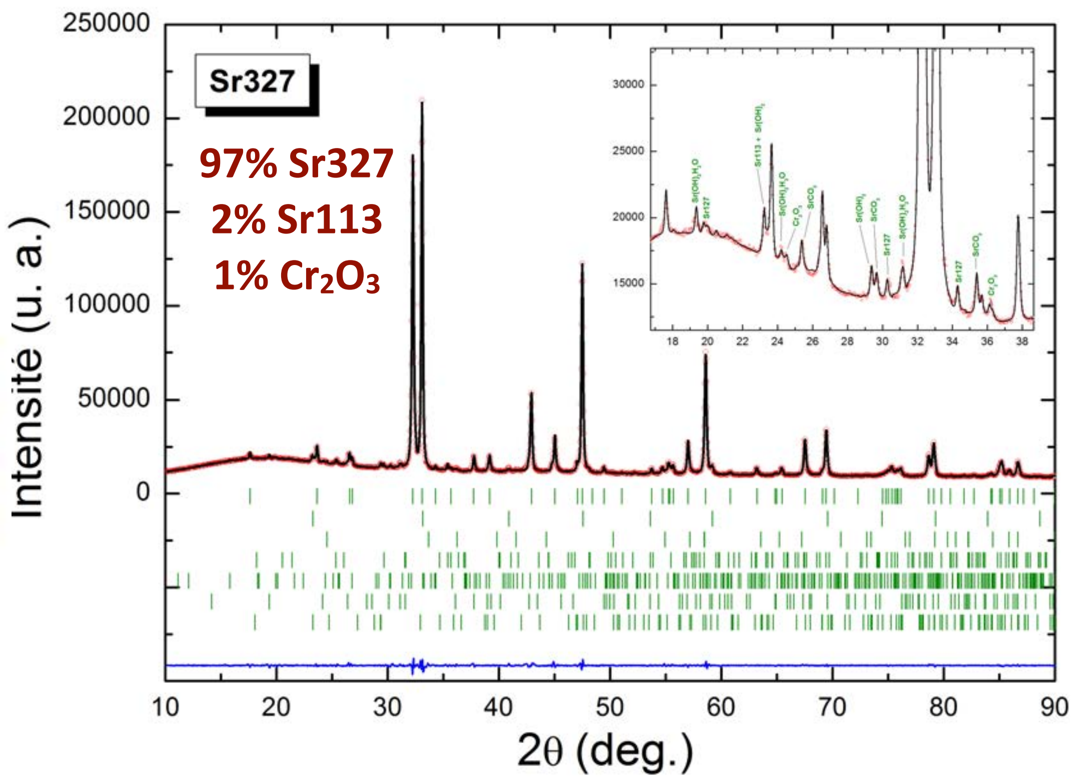
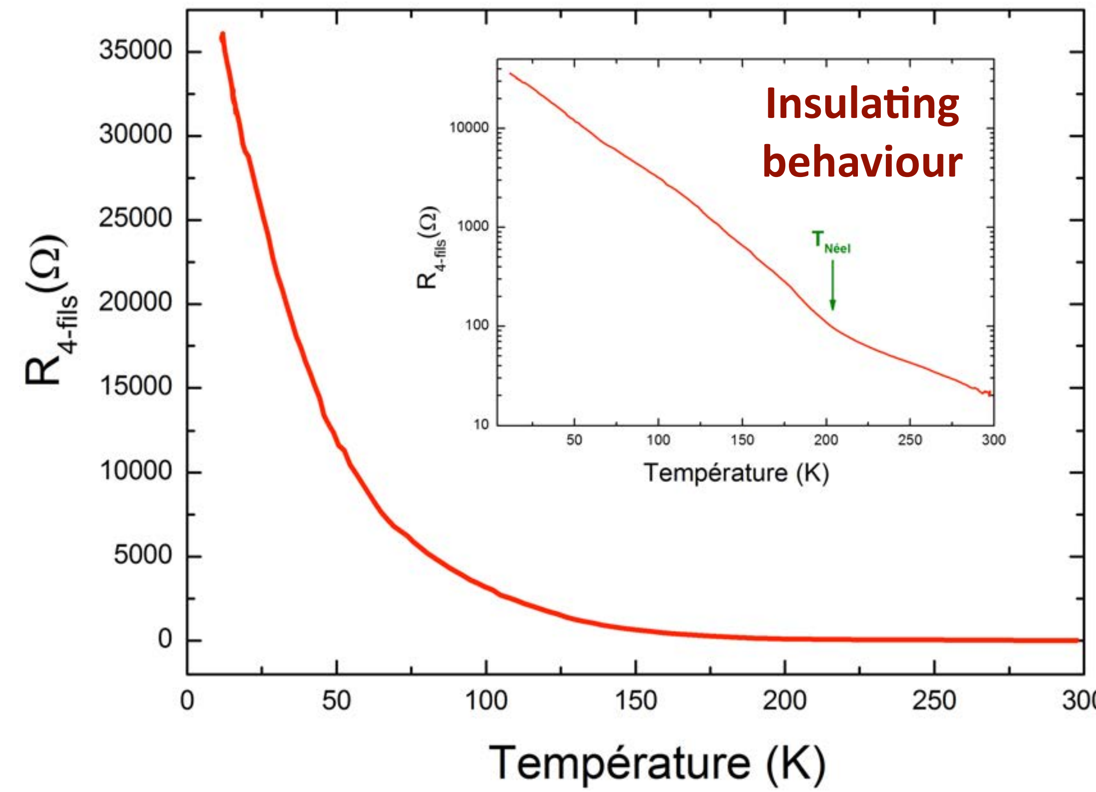
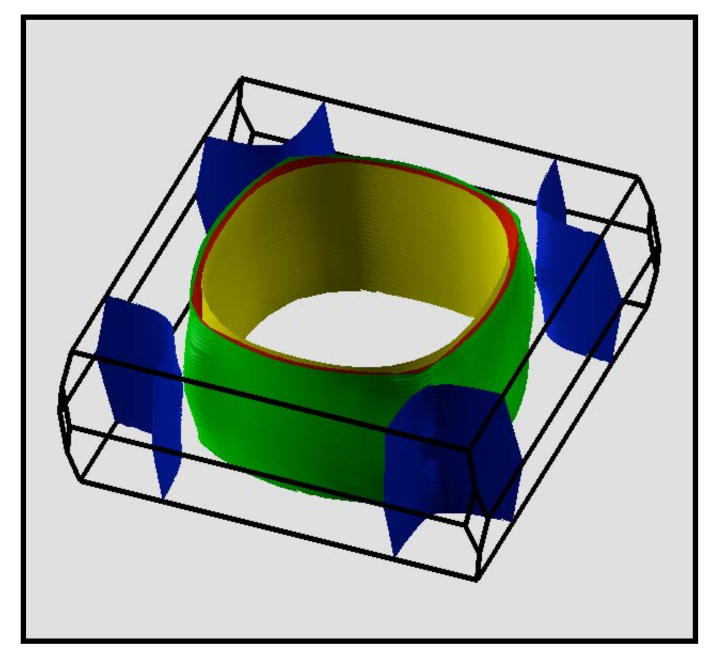


Transport measurement



Calculations give metallic (without magnetism & U)



Ruben Weht

$Sr_3Cr_2O_7$

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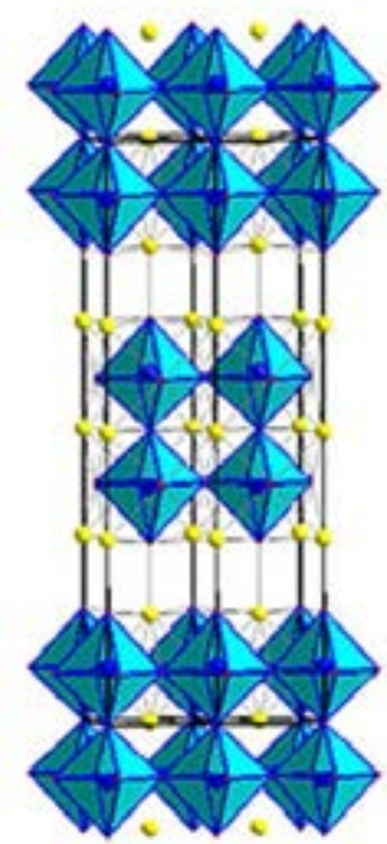

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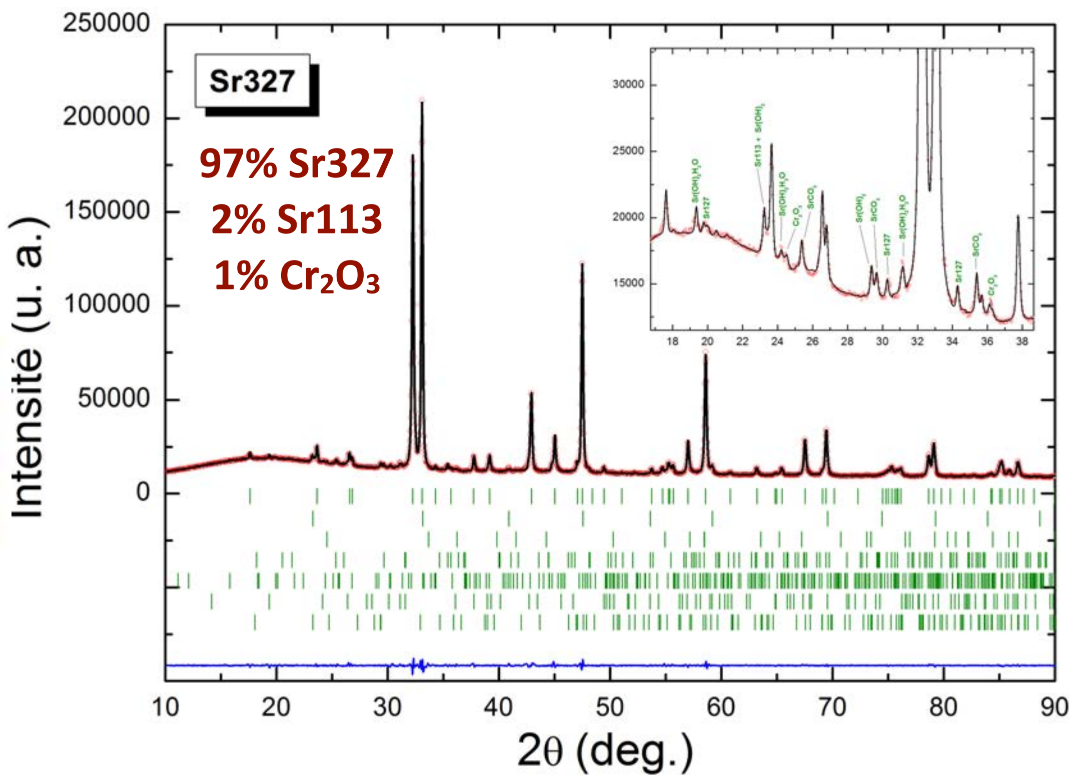

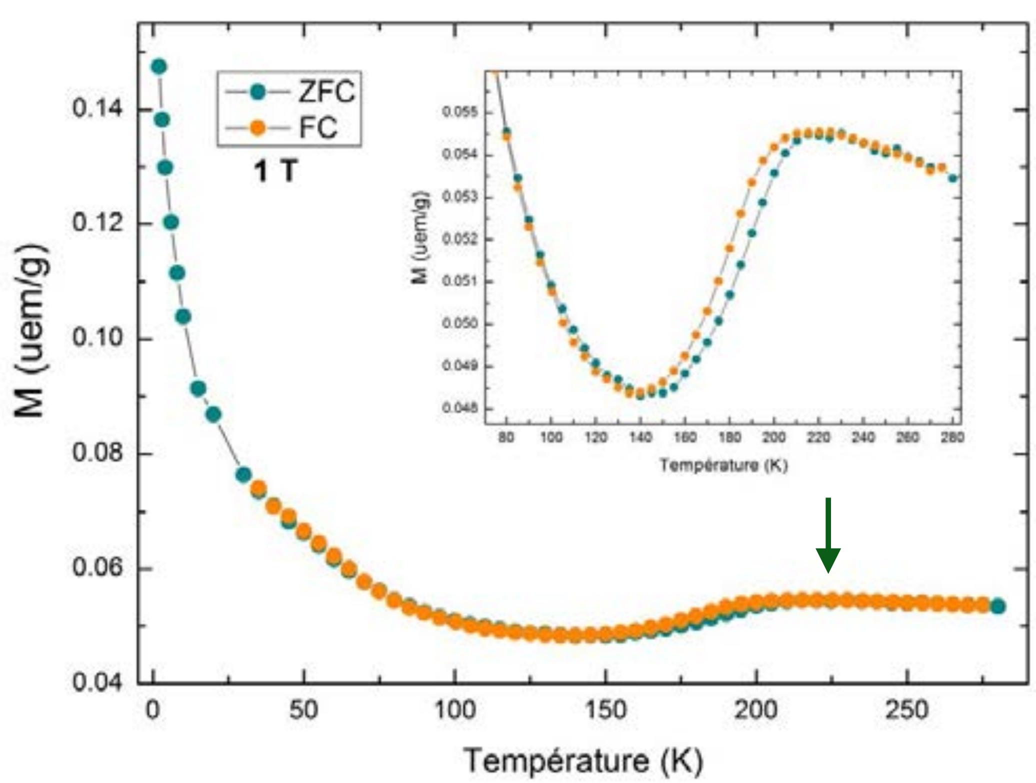

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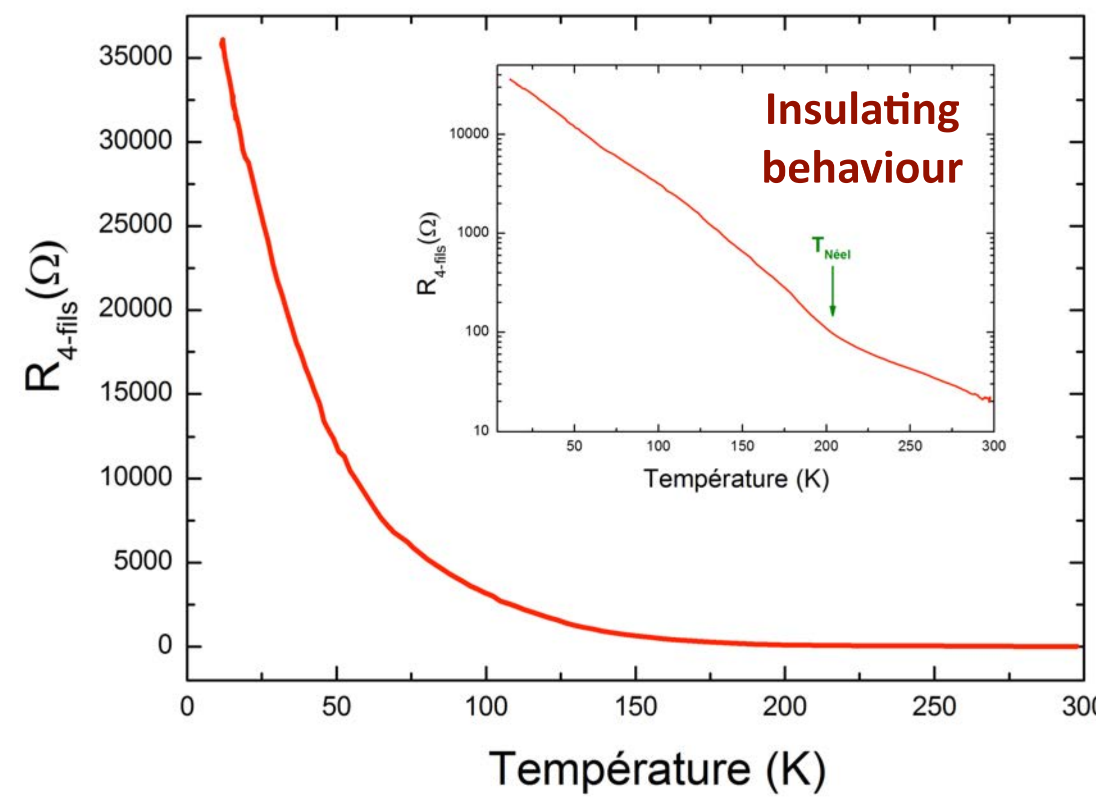
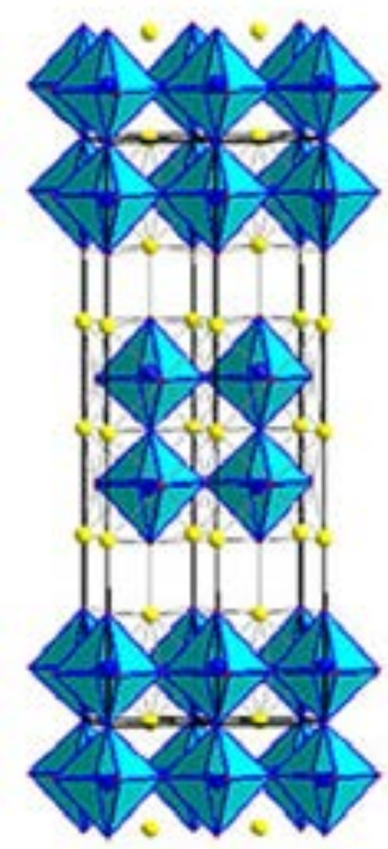


AFM

$T_{Néel}$ = 210K

$Sr_3Cr_2O_7$

Sr327
I4/mmm



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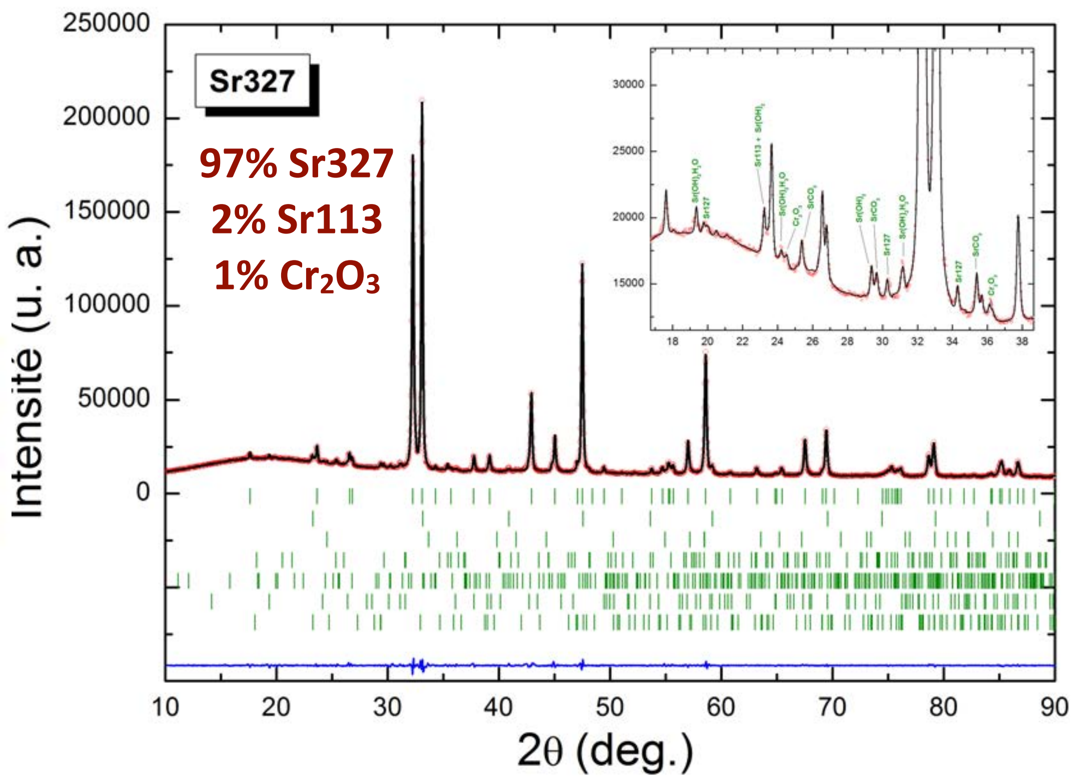

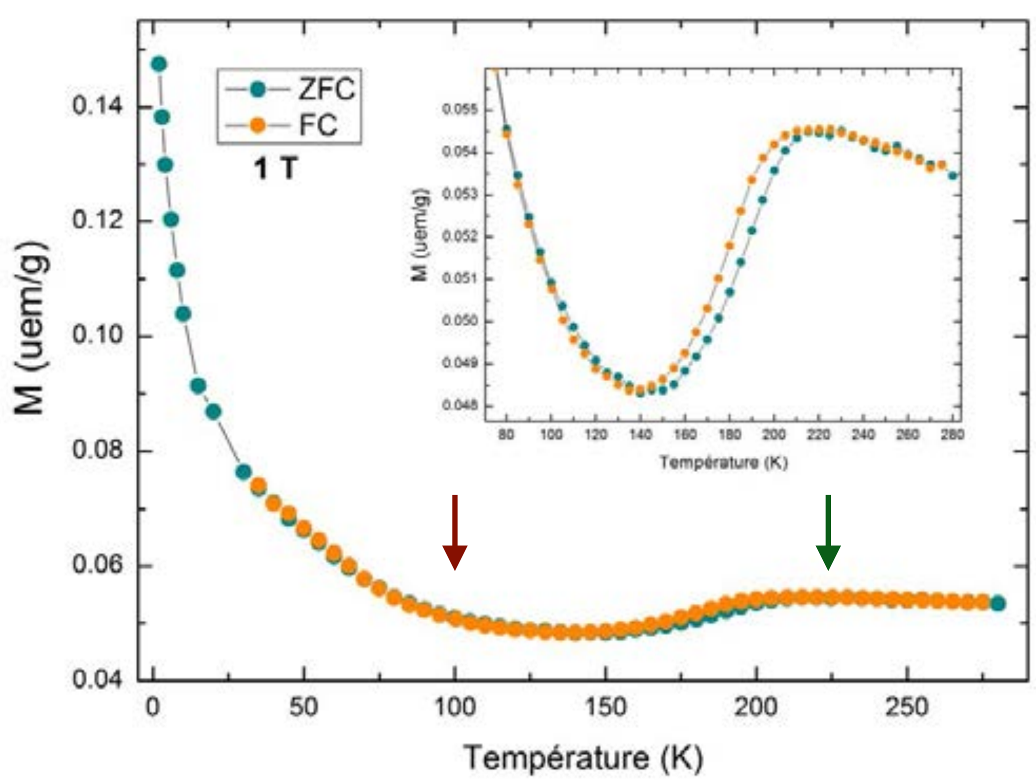

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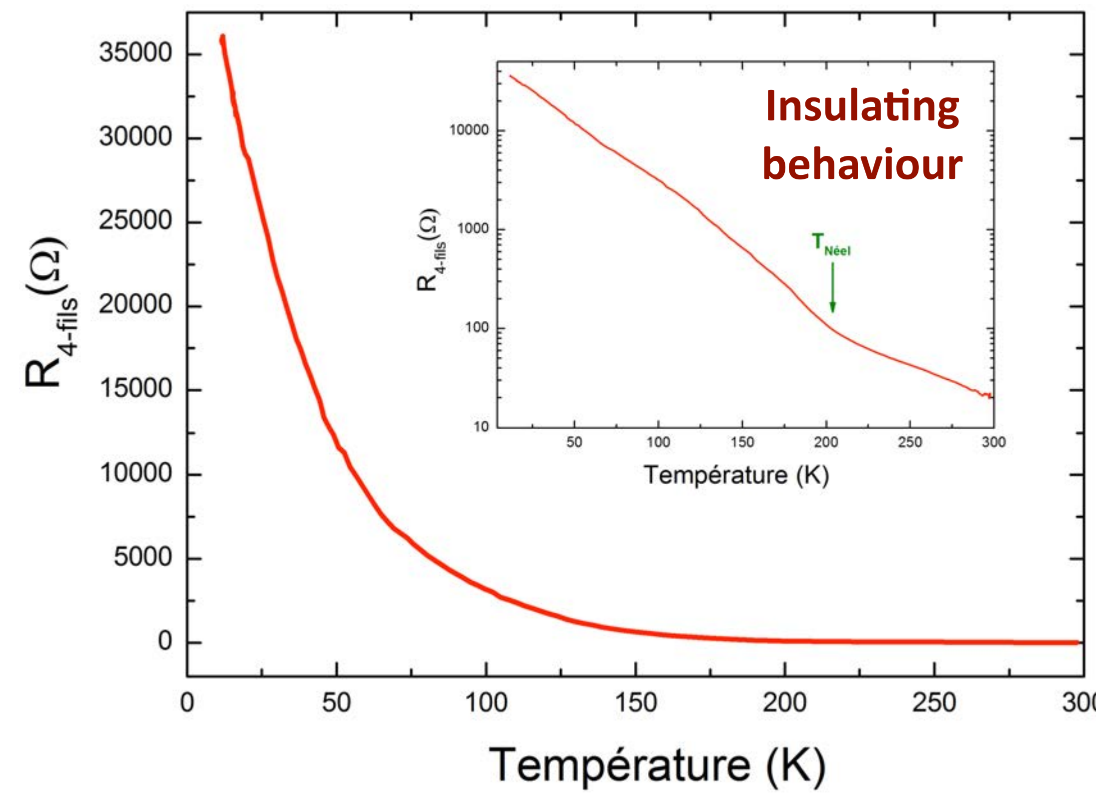

AFM

$T_{Néel}$ = 210K

anomaly
T = 100K ?

$Sr_3Cr_2O_7$

Neutron Powder diffraction

ILL, D1B & D2B instruments

$Sr_3Cr_2O_7$

Neutron Powder diffraction

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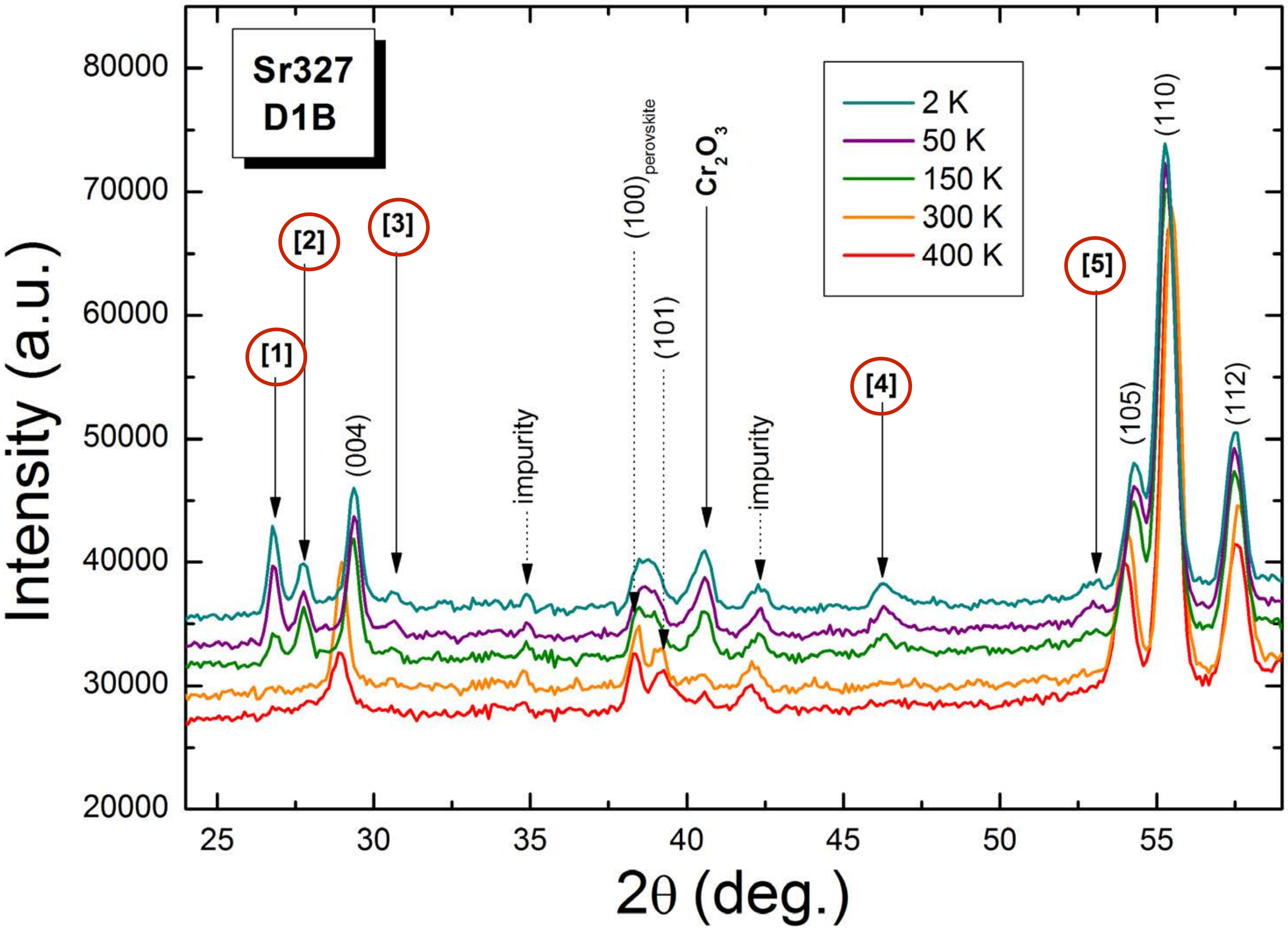

Magnetic peaks appearance between 300 & 150 K

$Sr_3Cr_2O_7$

Neutron Powder diffraction

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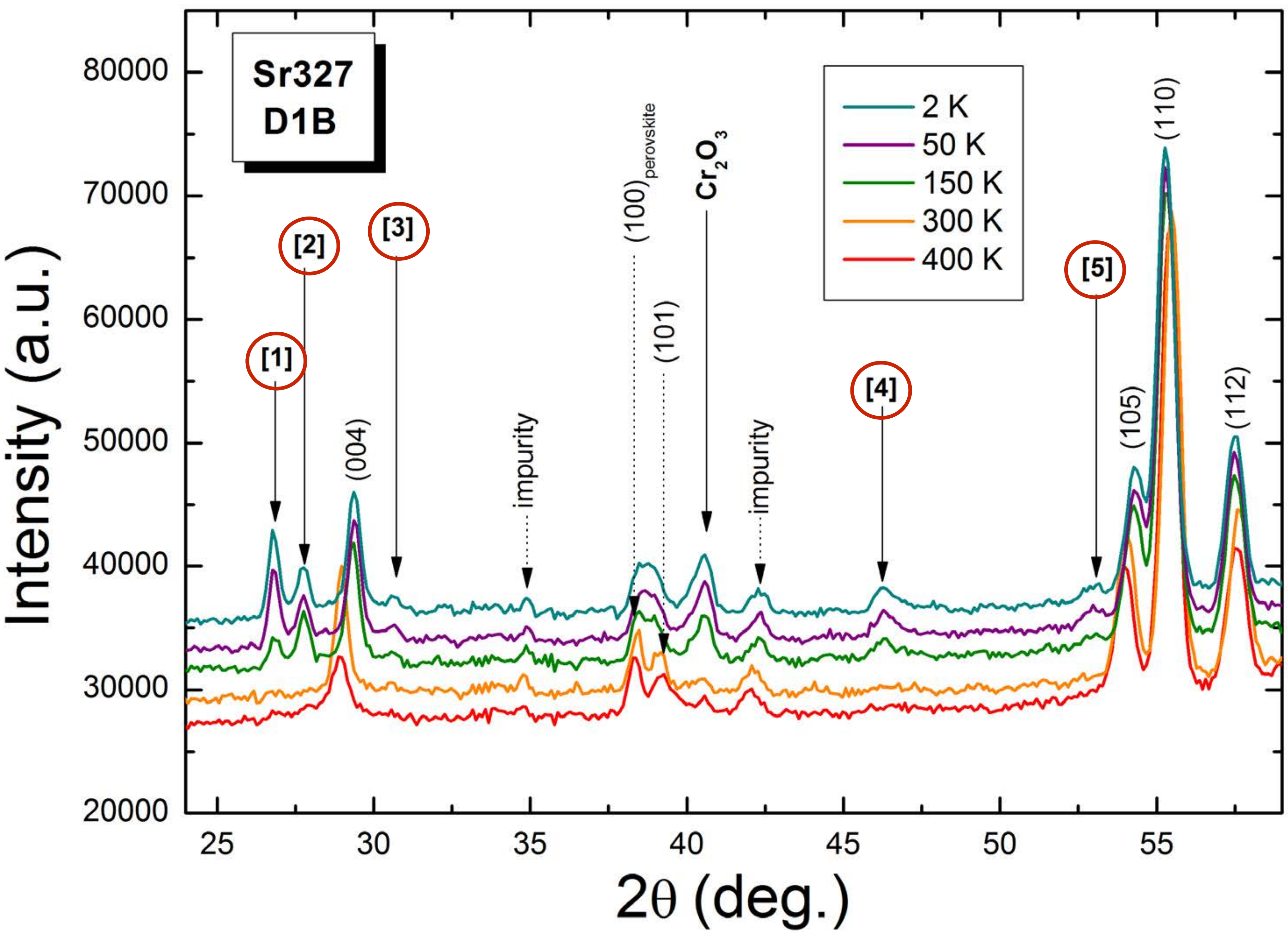

Magnetic peaks appearance between
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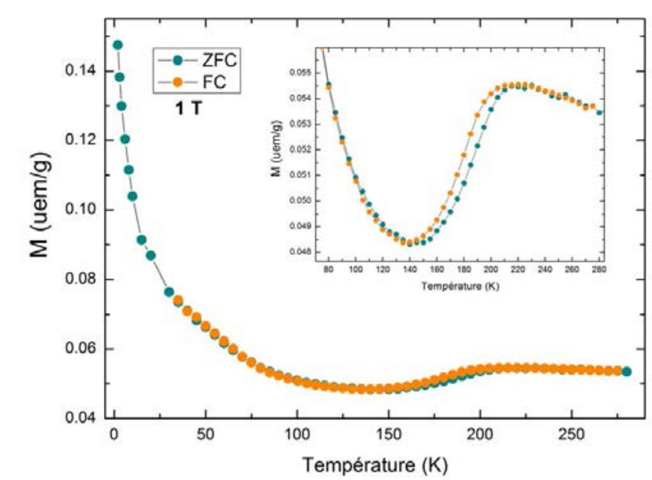
OK with $T_{Néel}$ = 210 K



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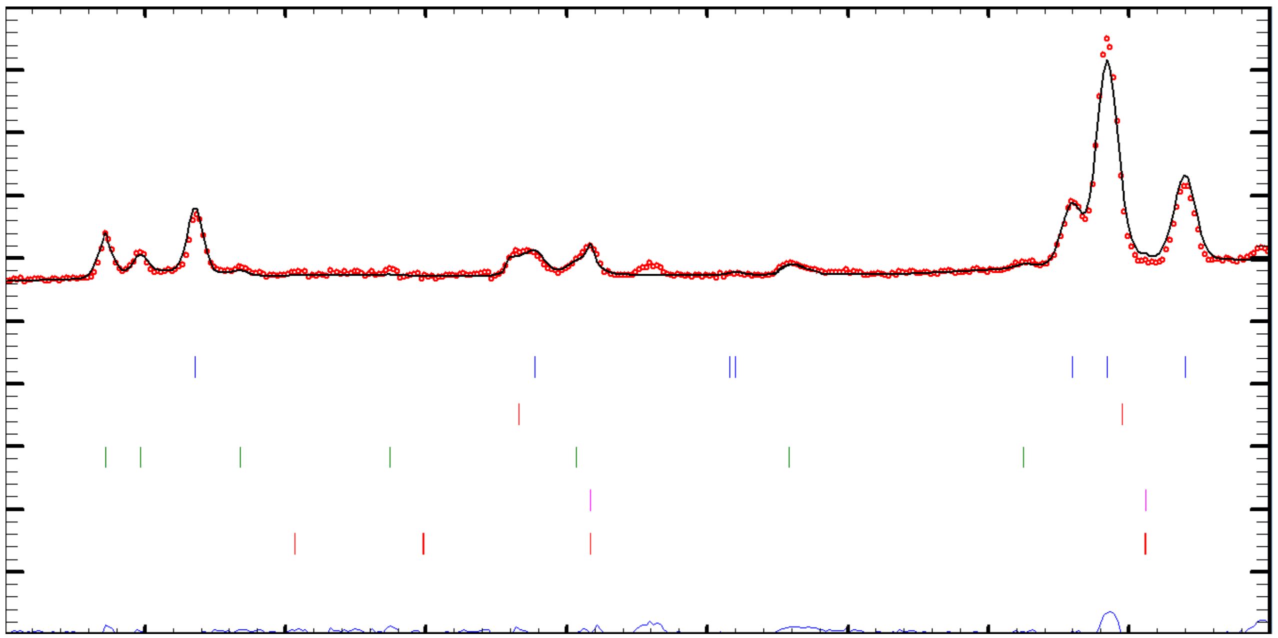

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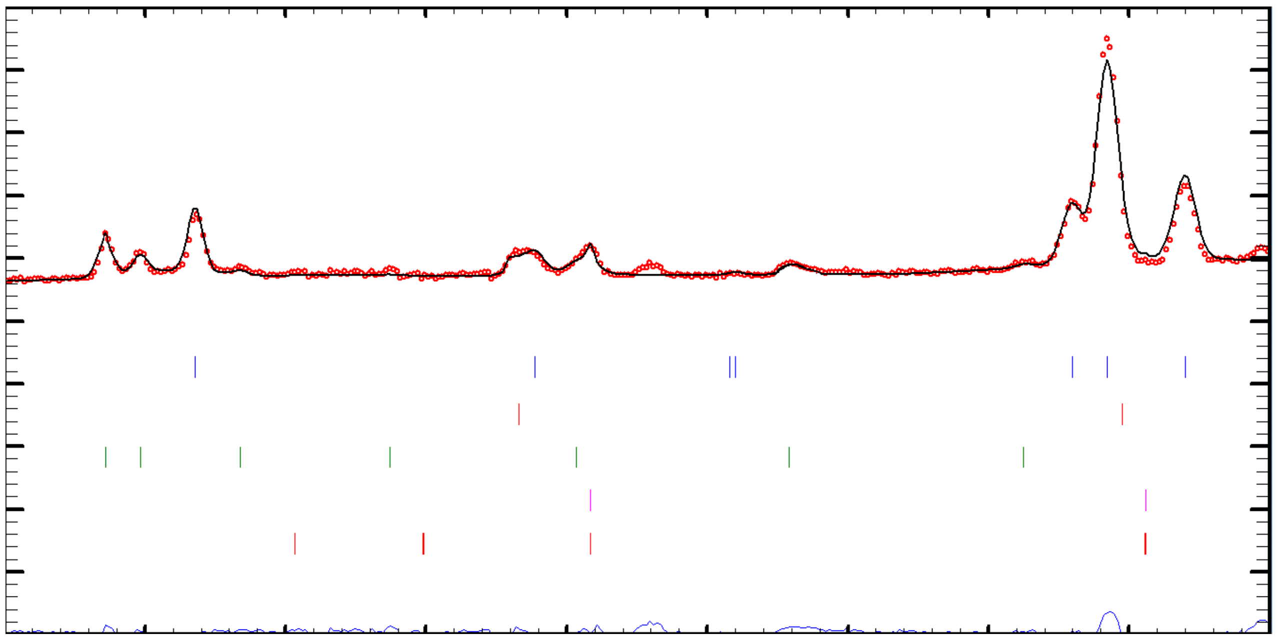
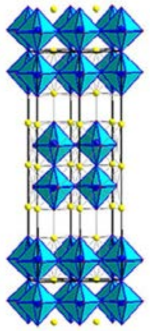
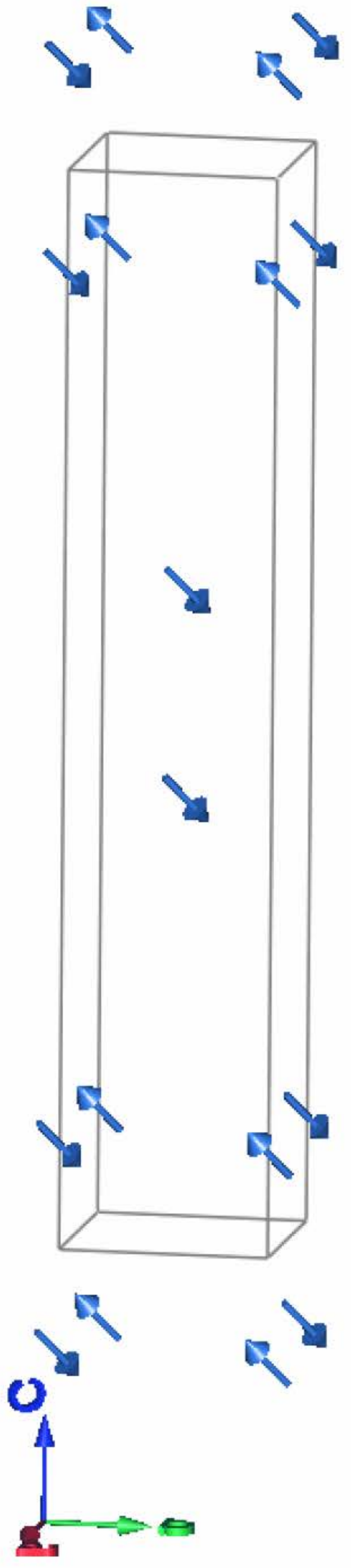


Magnetic phase refinement





$Sr_3Cr_2O_7$

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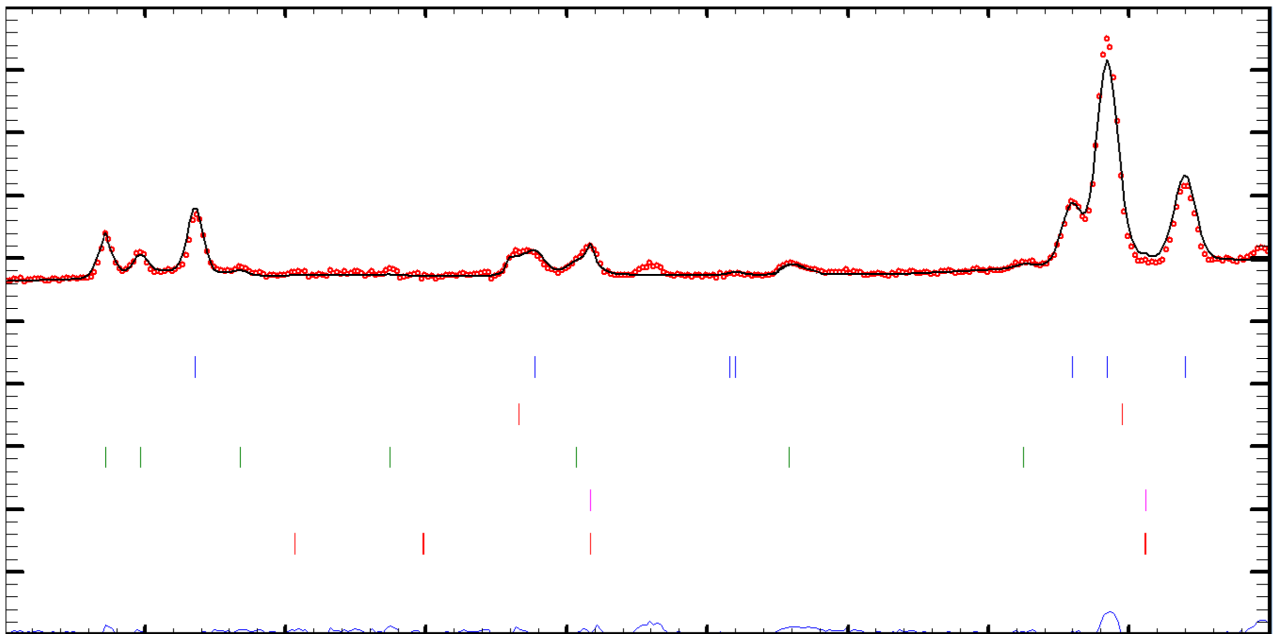

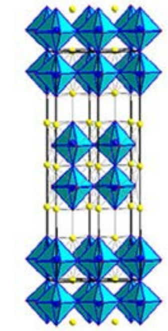

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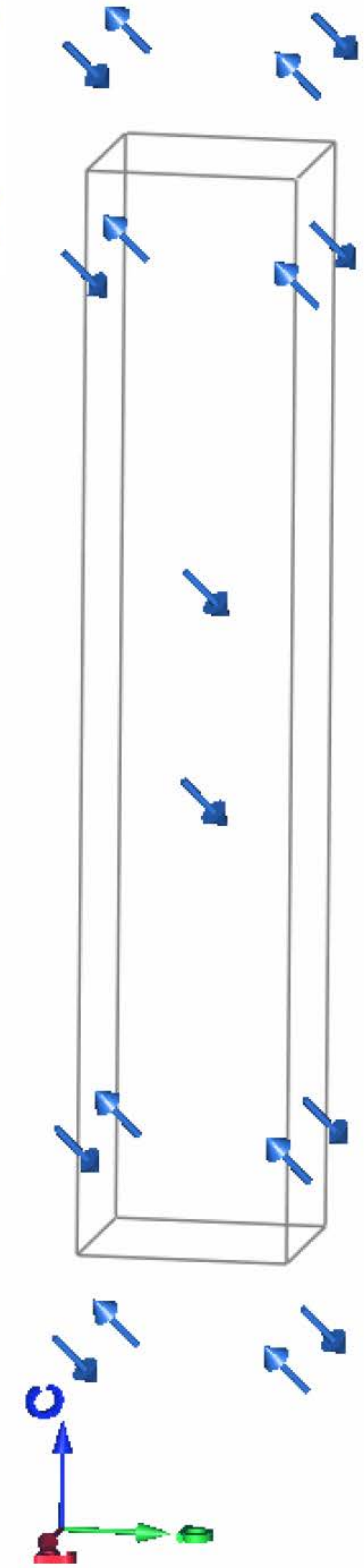
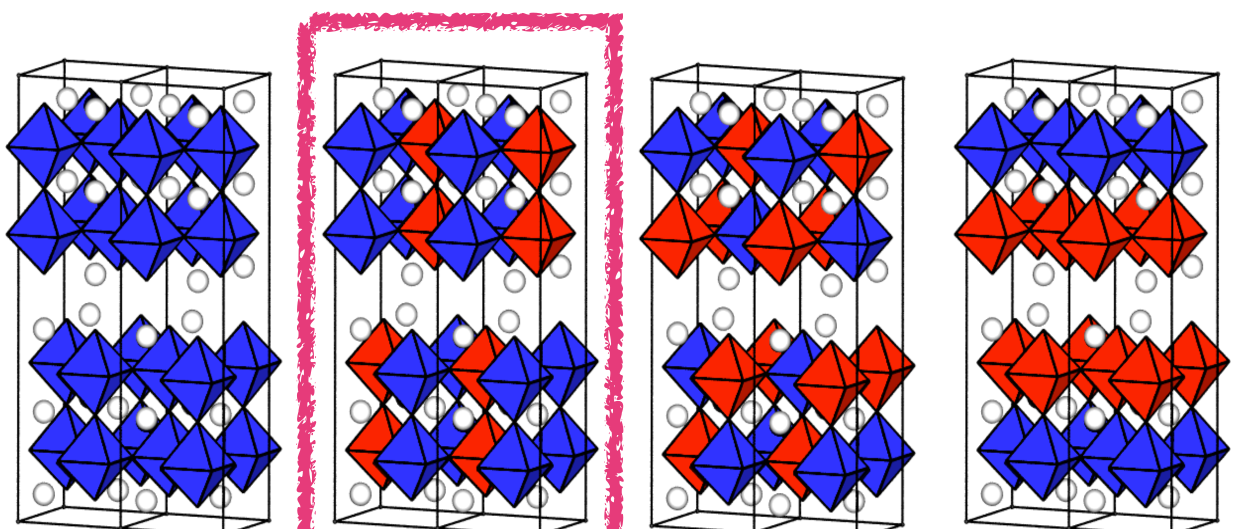




DE = 0
DE(FM-PM)= -2.8 eV)

DE = -115 meV

DE = -87 meV

DE = -94 meV

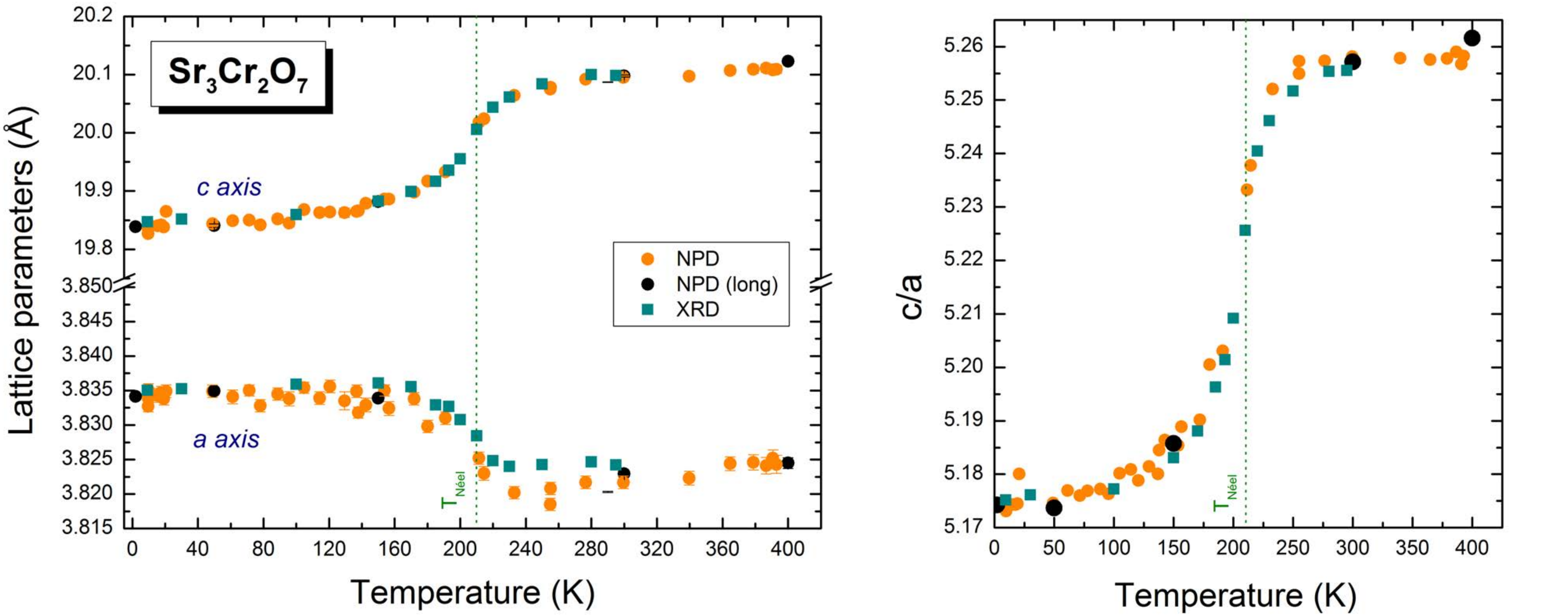
Calculated and measured magnetic structure coincide

$Sr_3Cr_2O_7$

Neutron Powder diffraction

ILL, D1B & D2B instruments

D1B : Claire Colin & Vivian Nassif
D2B : Emmanuelle Suard



Huge anomaly at T_N : strong magneto-structural coupling

c axis : -1.33%

a axis : +0.33%

$Sr_3Cr_2O_7$

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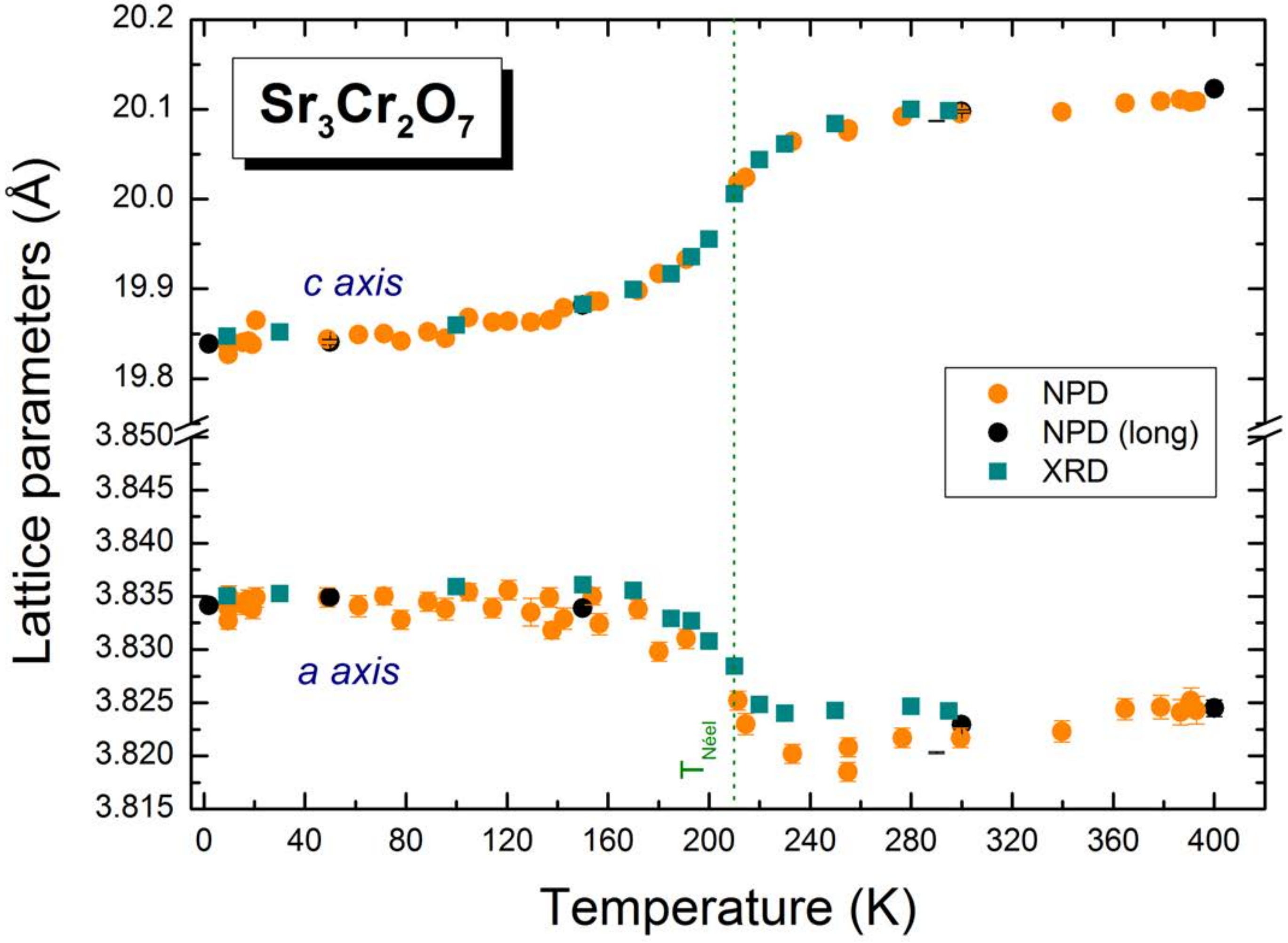

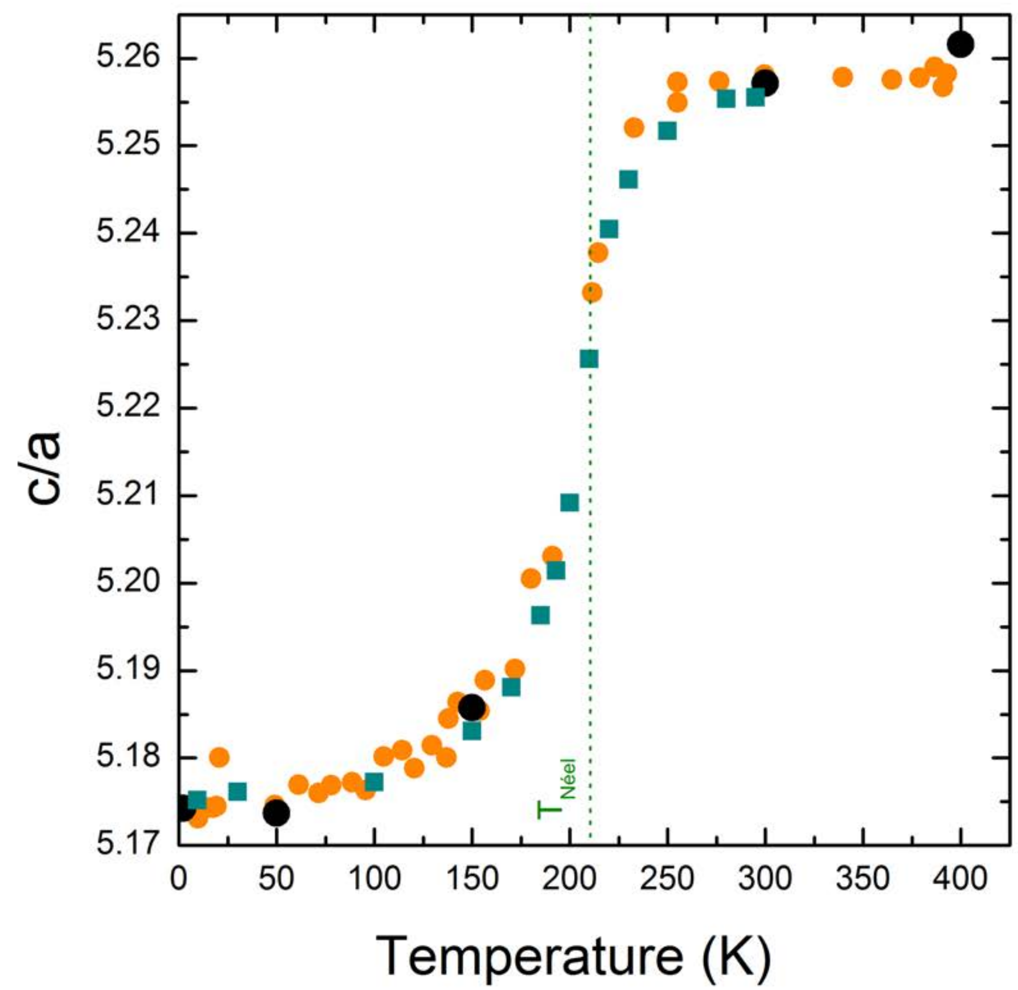

Huge anomaly at T_N : strong magneto-structural coupling

c axis : -1.33%

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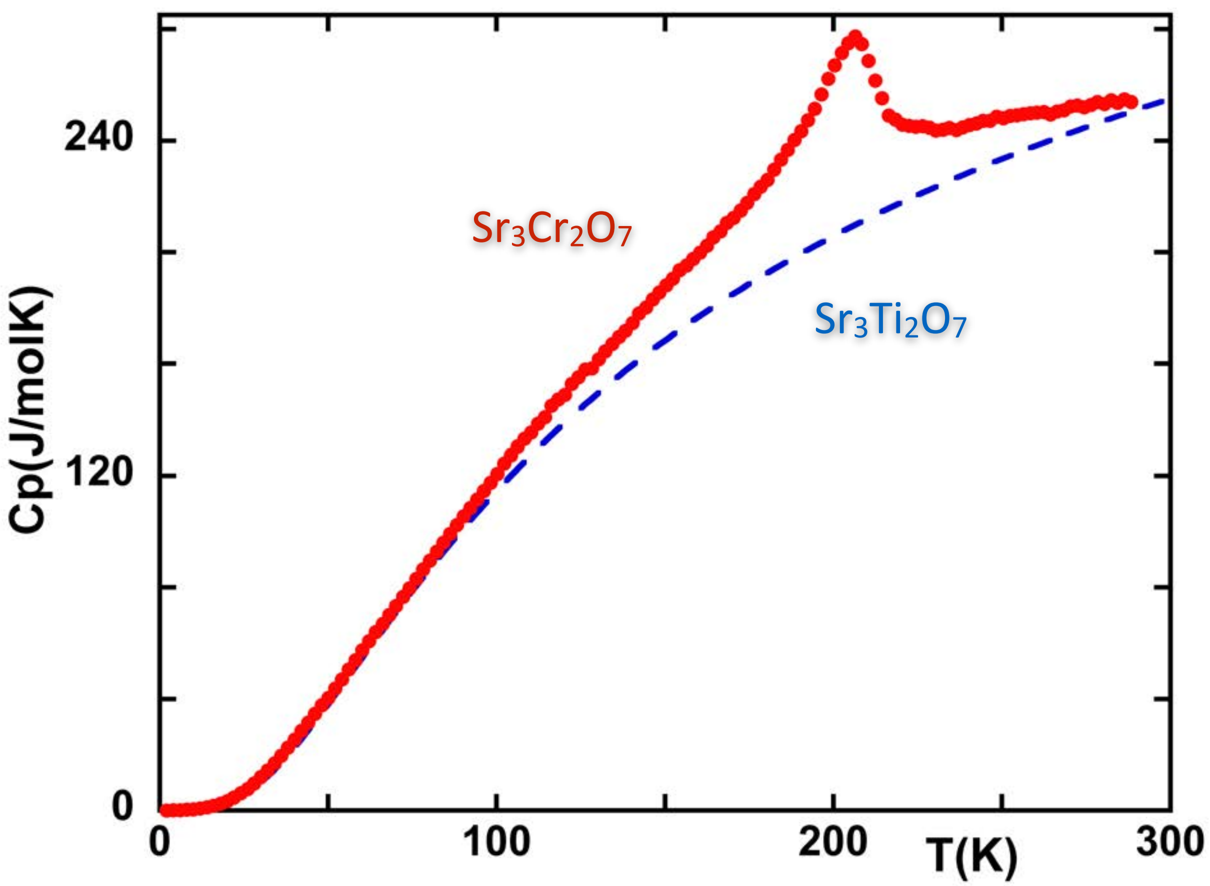
$LaMnO_3$: a +0.8% at $T_{Néel}$=141K
b -0.05%

$CaCrO_3$: c +0.5% at $T_{Néel}$=90K

$Sr_3Cr_2O_7$

Specific Heat



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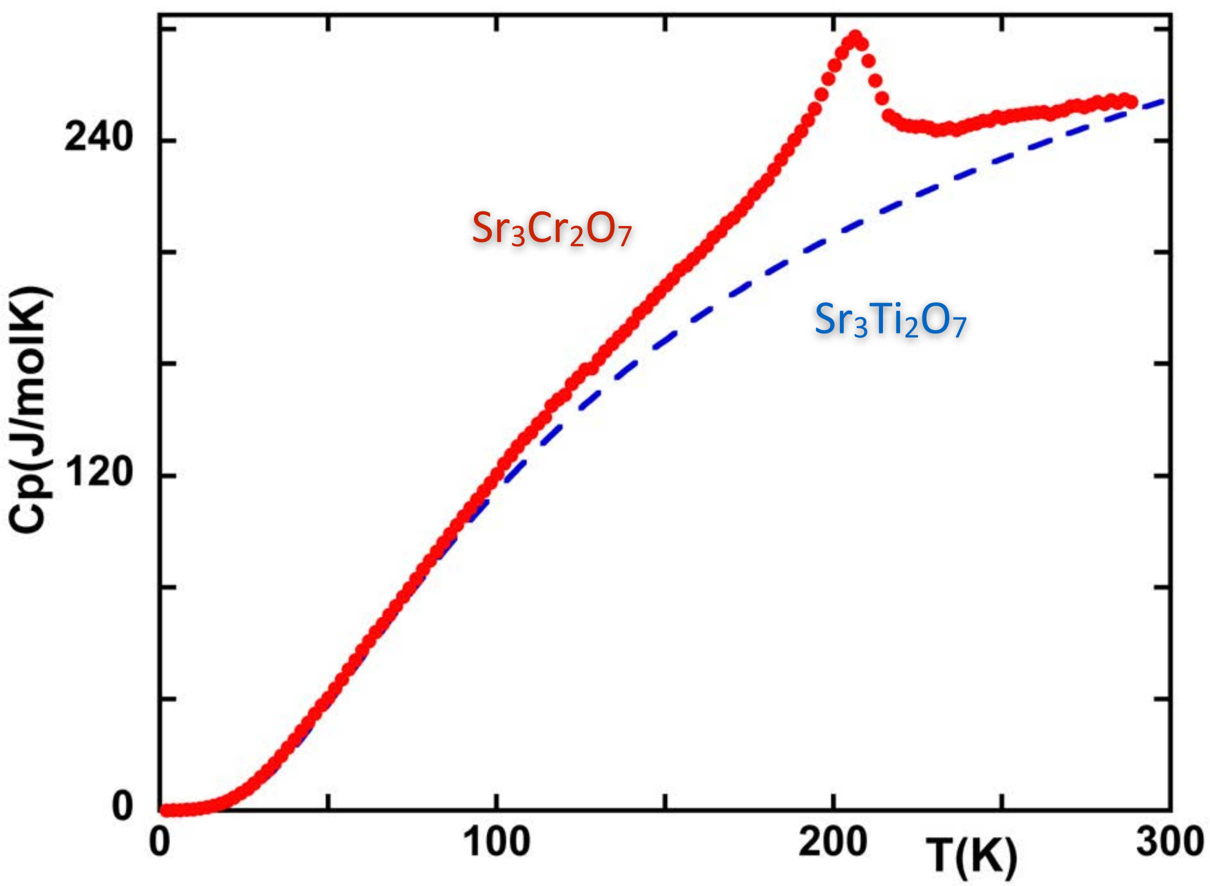
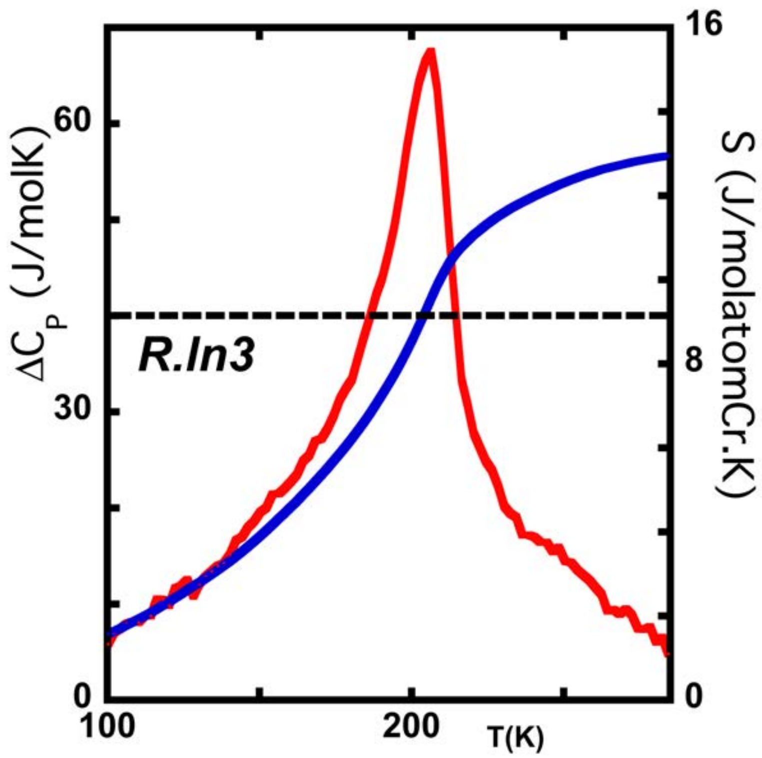
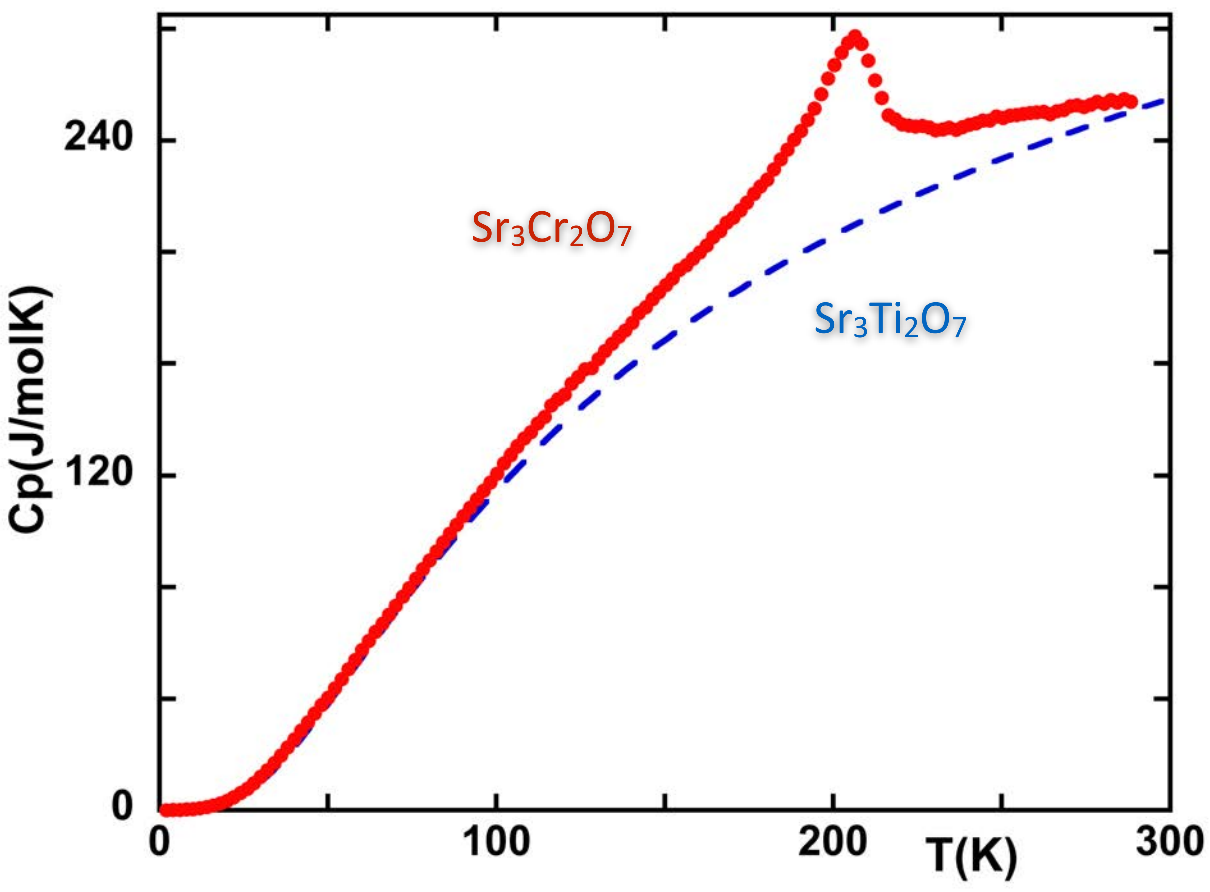
Specific Heat

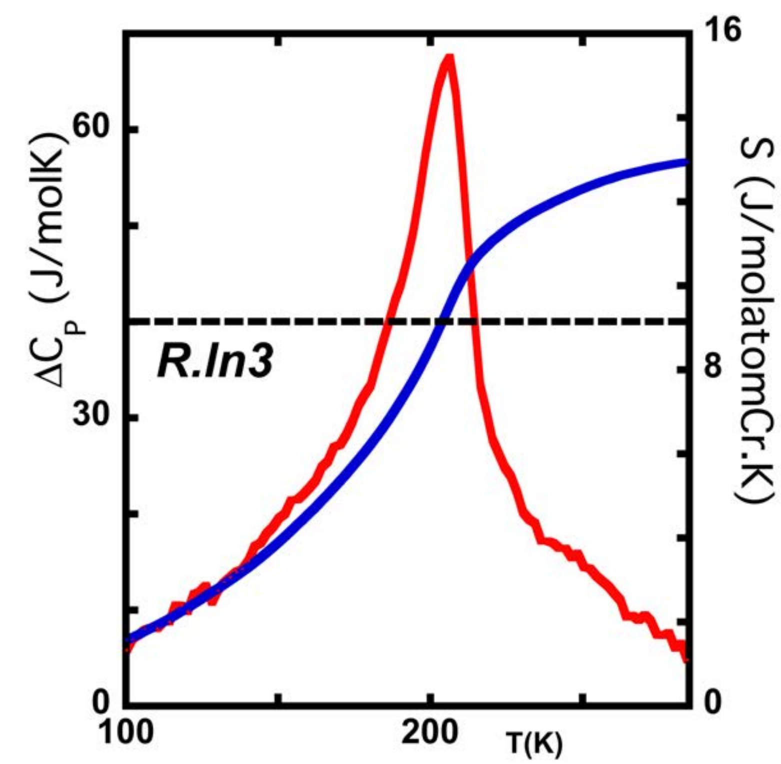




$Sr_3Cr_2O_7$

Specific Heat



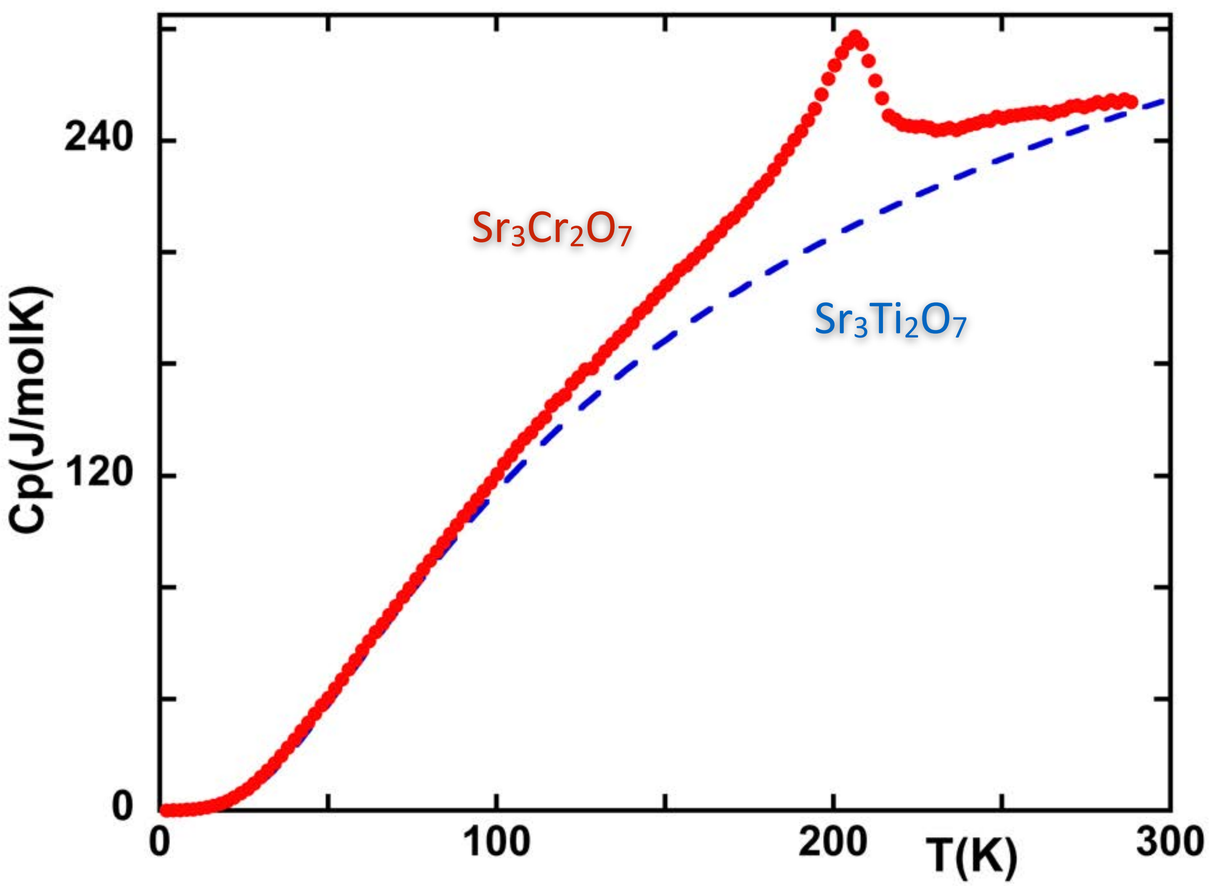


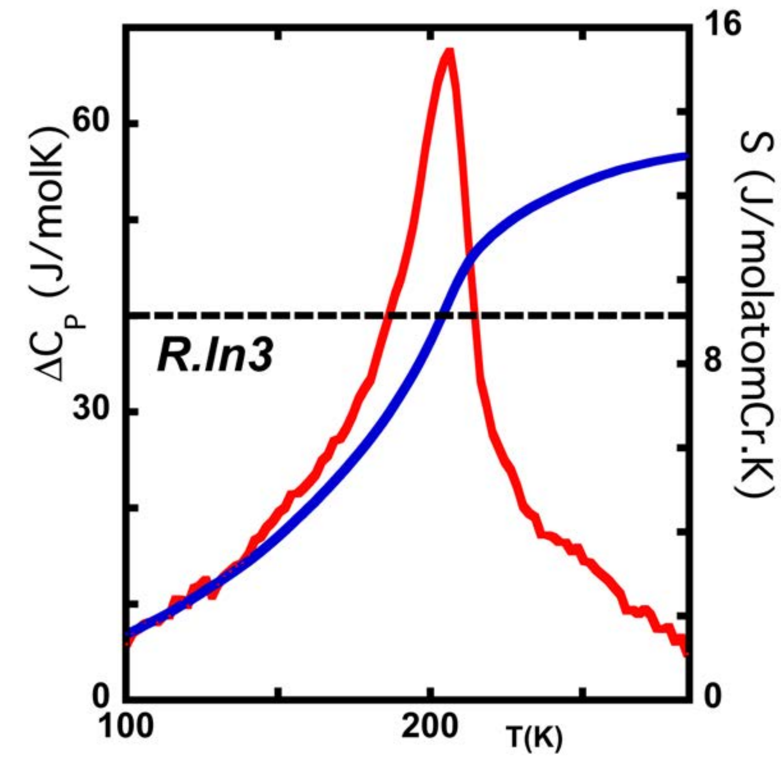
Transition entropy : near to **R*ln*6**

(if only magnetic ordering : R*ln3)*

$Sr_3Cr_2O_7$

Specific Heat





Transition entropy : near to **R*ln*6**

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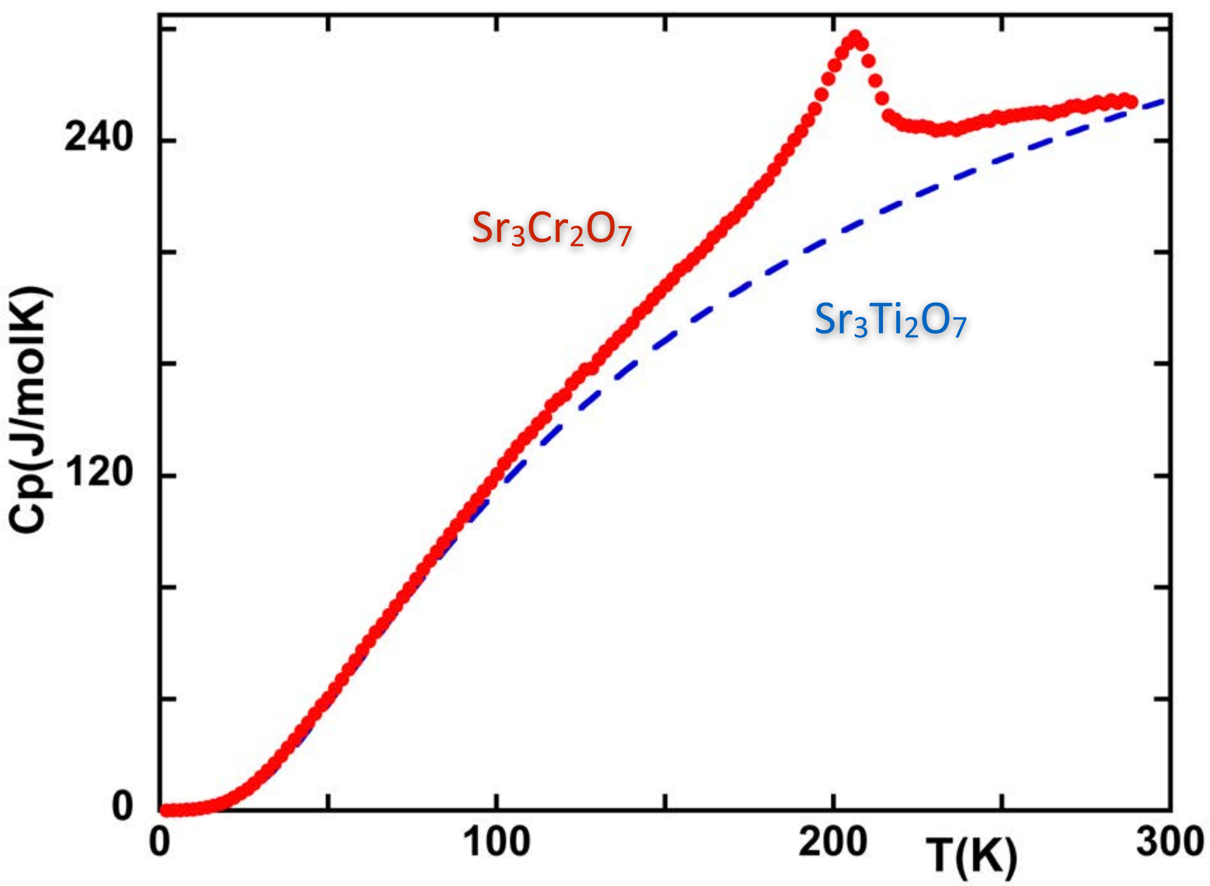
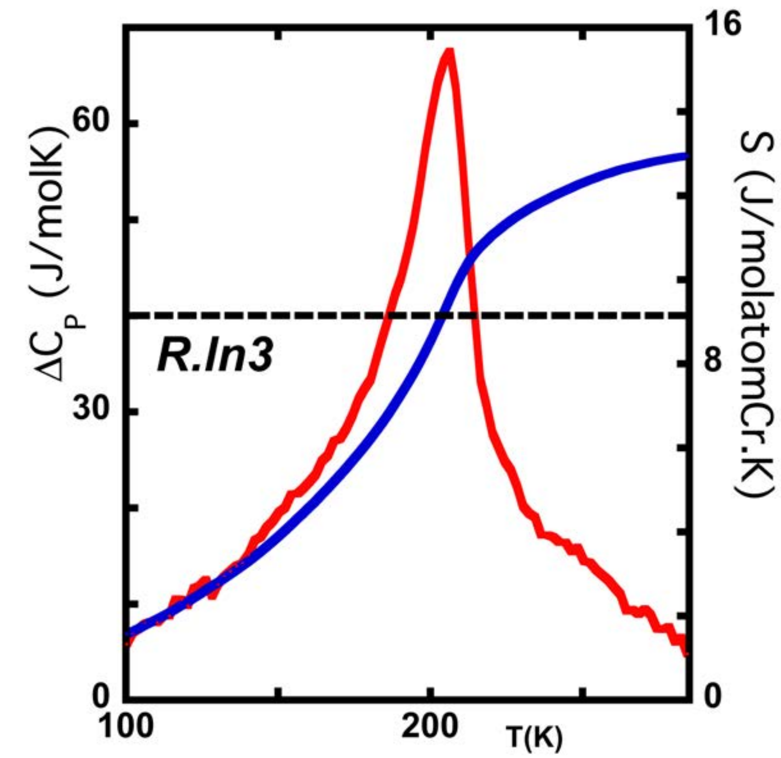
Magnetic AND Orbital Ordering

$Sr_3Cr_2O_7$

Specific Heat





Transition entropy : near to **R*ln*6**

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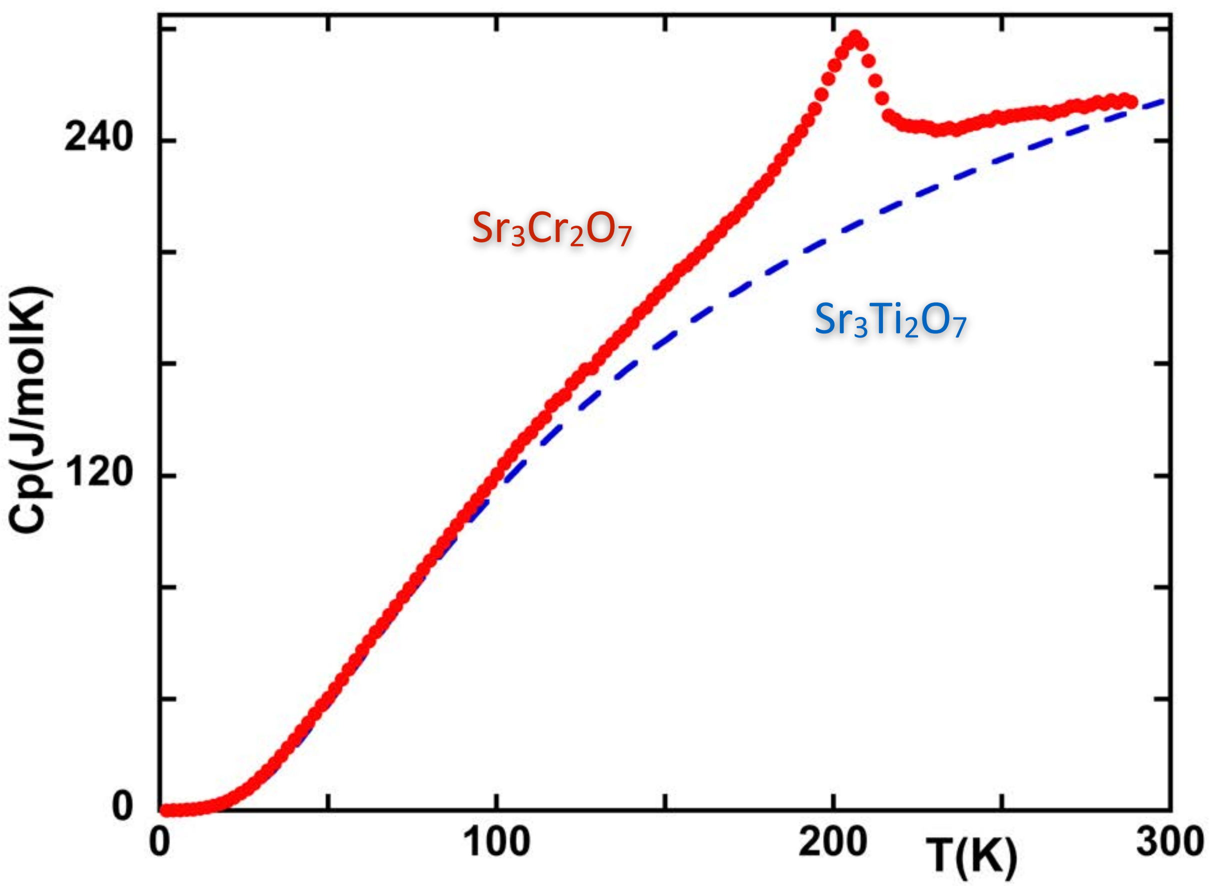
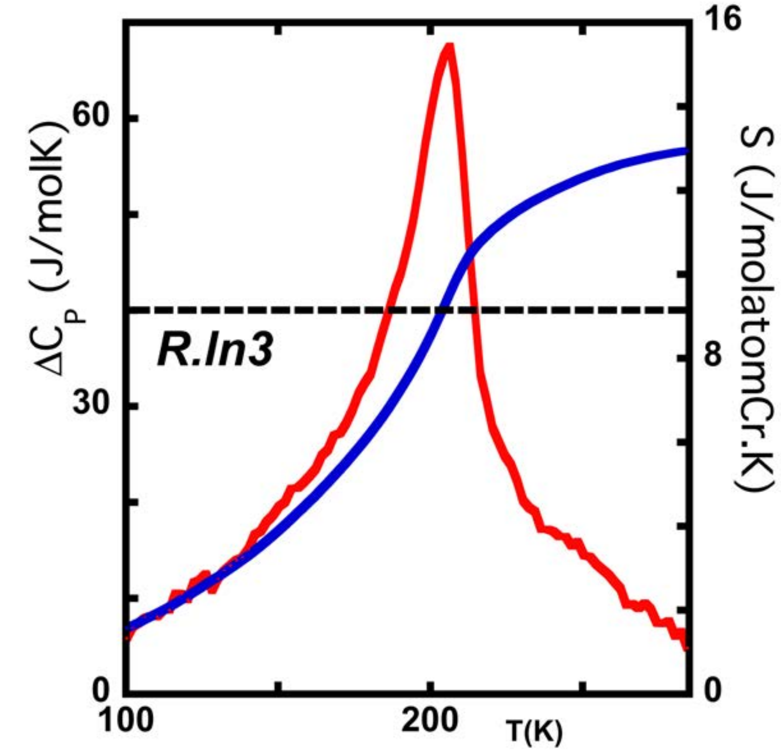
Magnetic AND Orbital Ordering

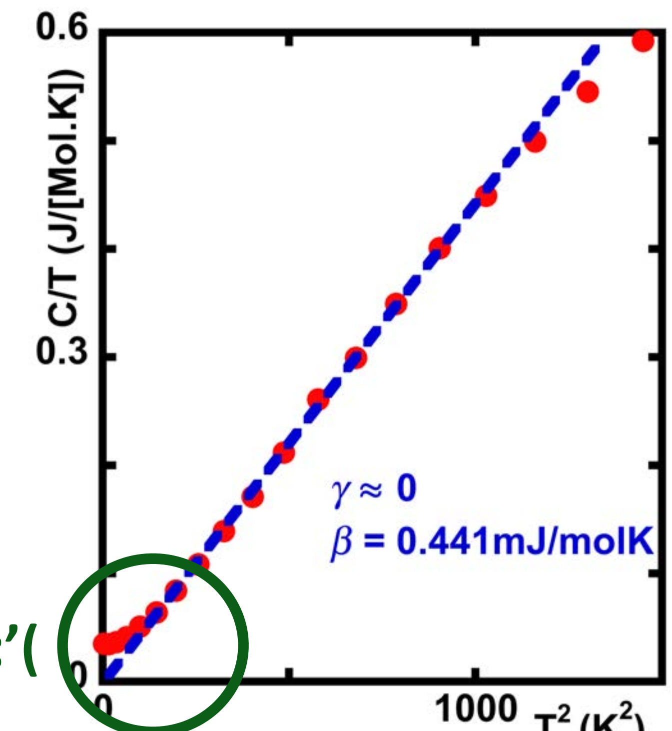
partial or full?

$Sr_3Cr_2O_7$

Specific Heat







Transition entropy : near to **R*ln*6**

(if only magnetic ordering : R*ln3*)

Magnetic AND Orbital Ordering

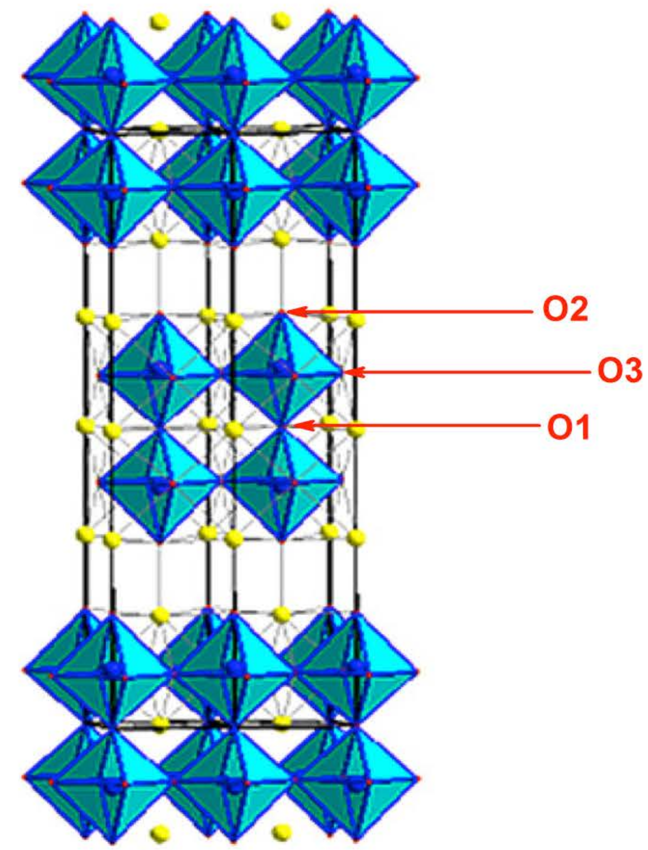
partial or full?

non metallic :'(

$Sr_3Cr_2O_7$

Neutron Powder diffraction

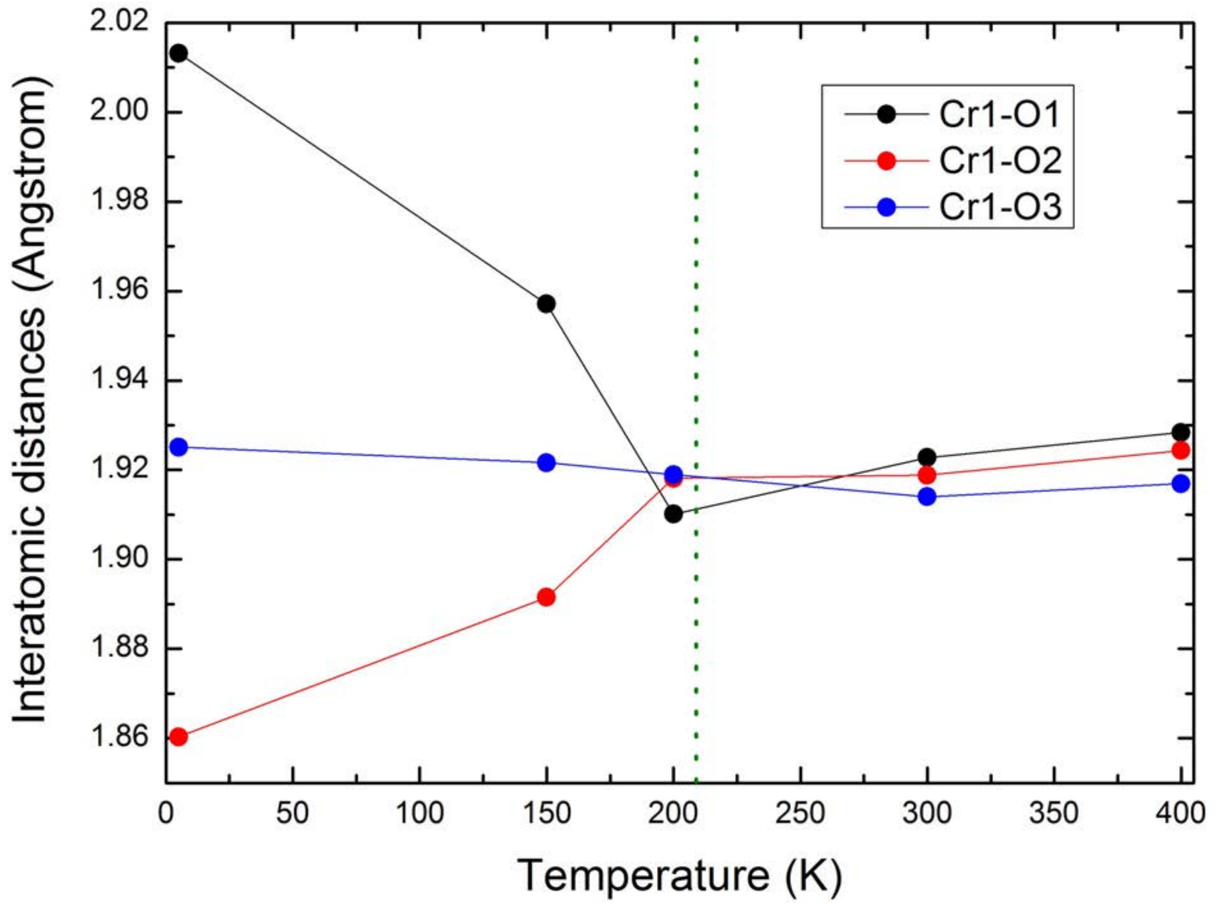
ILL, D1B & D2B instruments

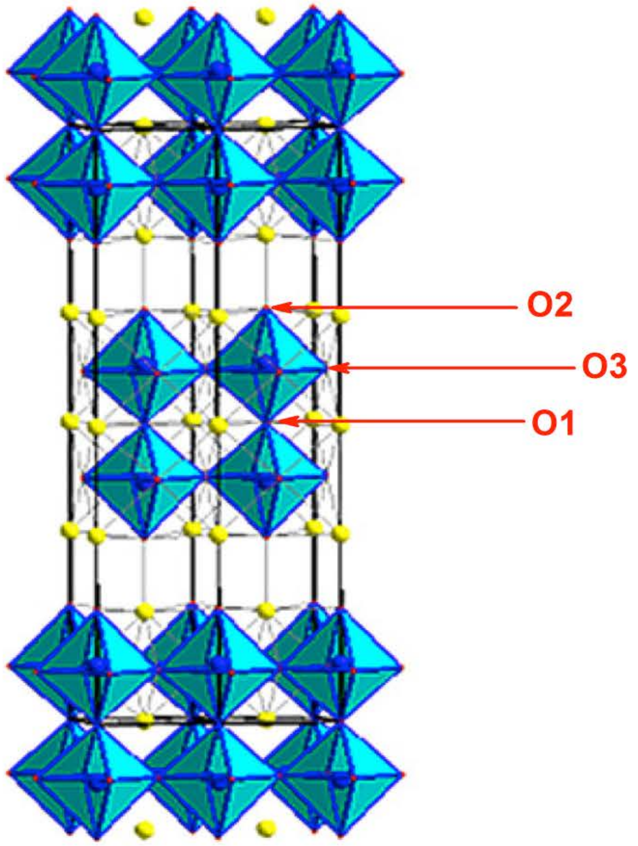


$Sr_3Cr_2O_7$

Neutron Powder diffraction

ILL, D1B & D2B instruments





$Sr_3Cr_2O_7$

Neutron Powder diffraction

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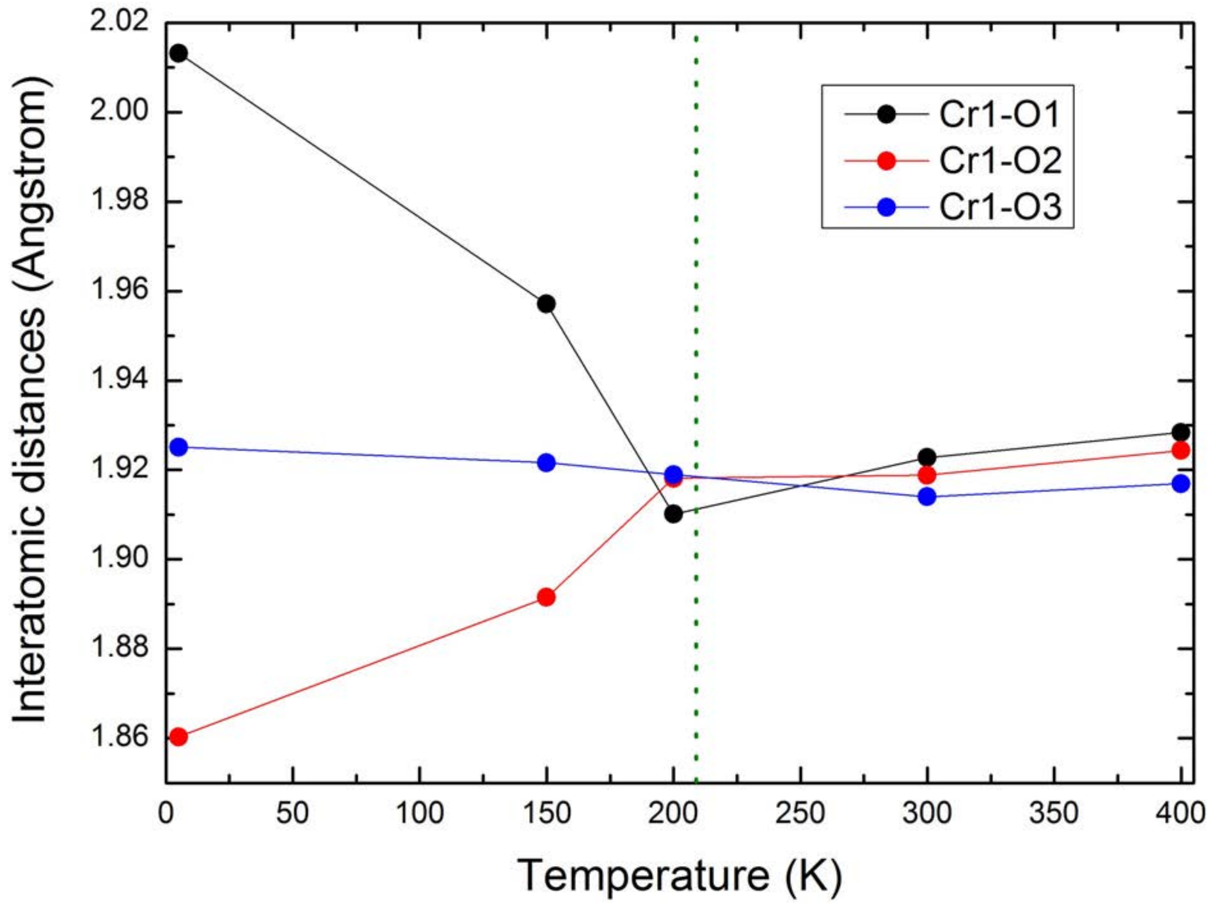
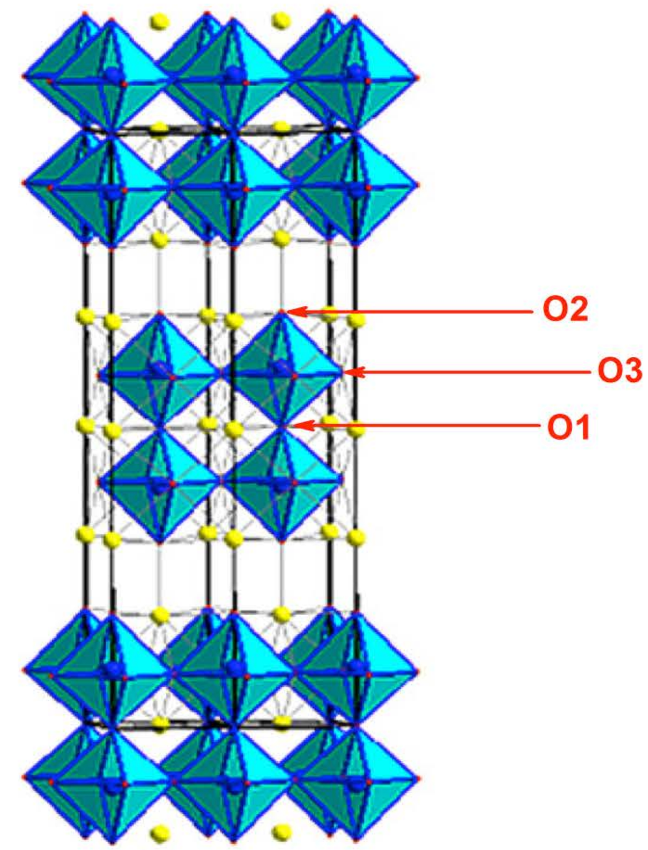
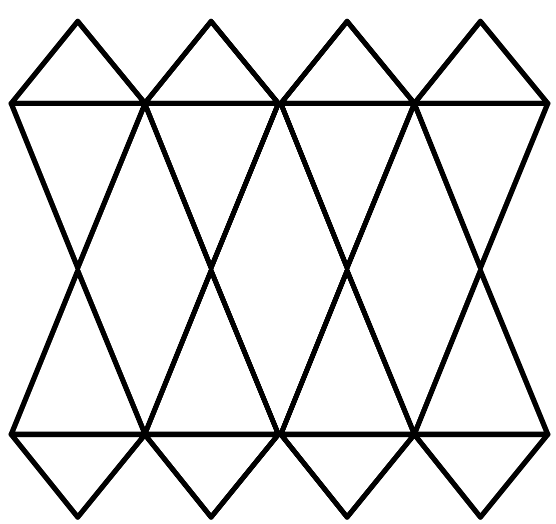
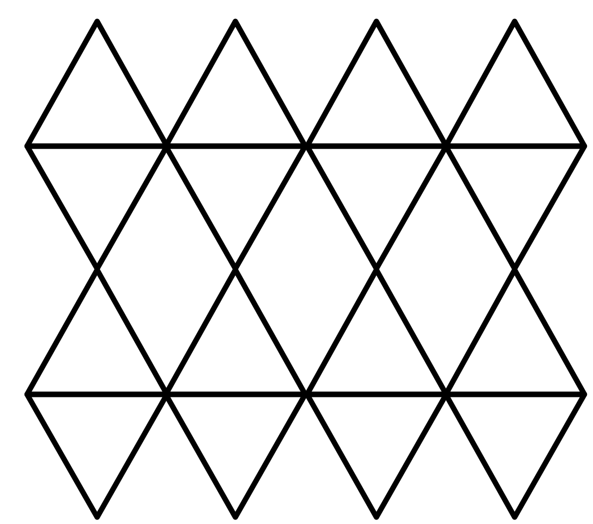






non symmetric
CrO_6 octahedron distortion

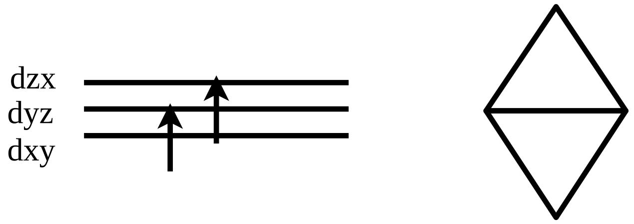
210K
AF order



Low temperature

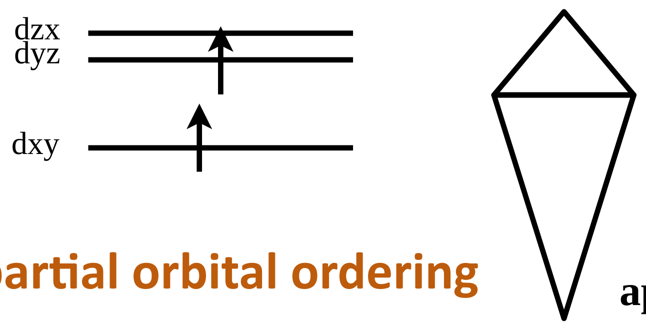
High temperature

Orbital model



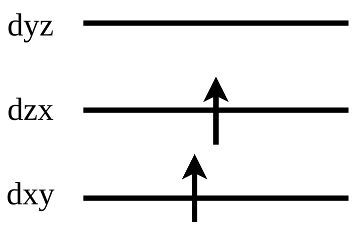
orbital degenerescence

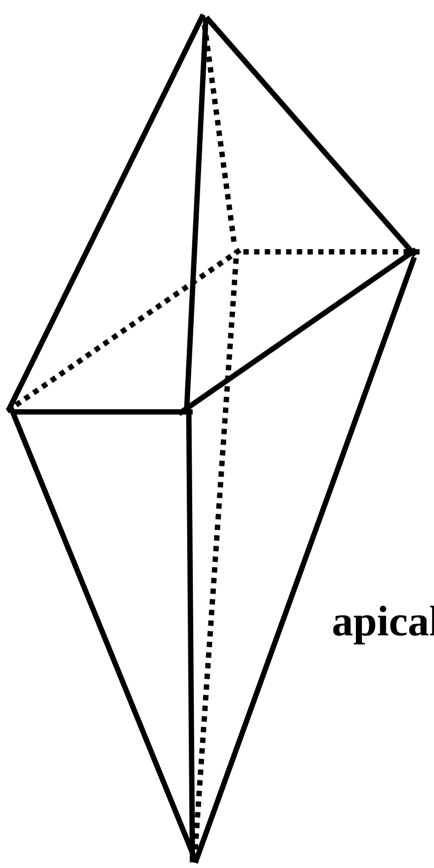
regular octahedra



partial orbital ordering

apical distortion

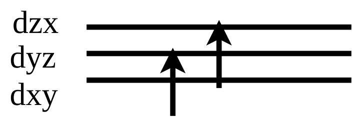


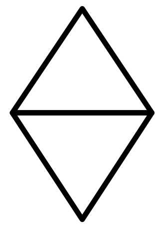


total orbital ordering

apical & in-plane distortion

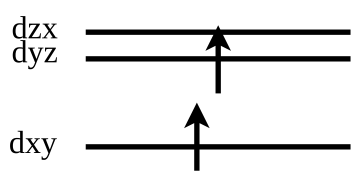
Orbital model

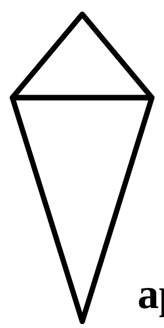




orbital degenerescence

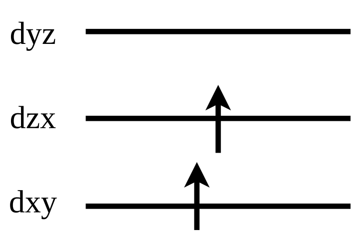
regular octahedra

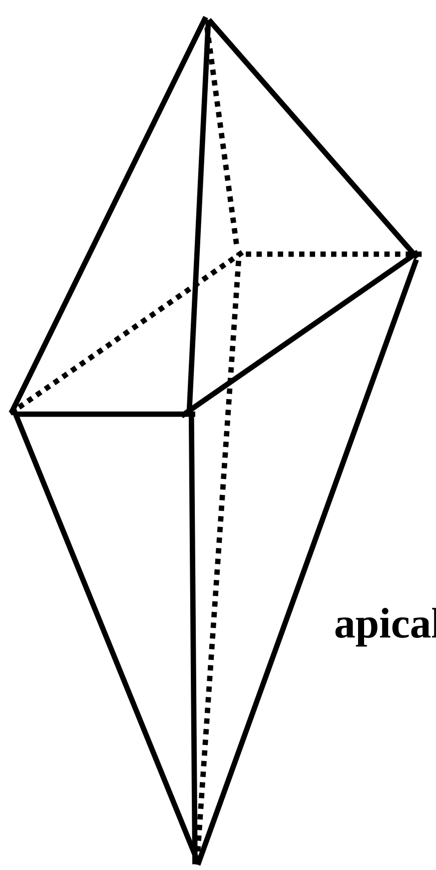




partial orbital ordering

apical distortion

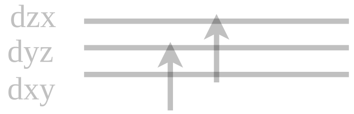


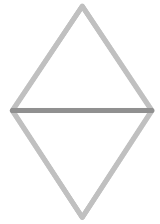


total orbital ordering

apical & in-plane distortion → **ESRF & lab XRD : no in-plane distortion observed**

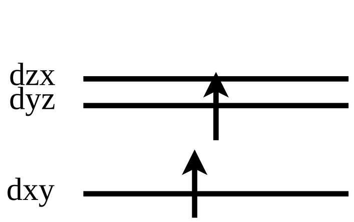
Orbital model

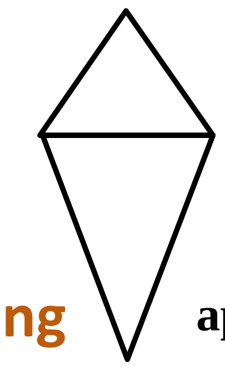




orbital degenerescence

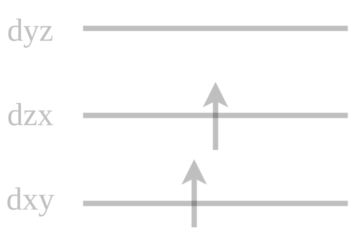
regular octahedra

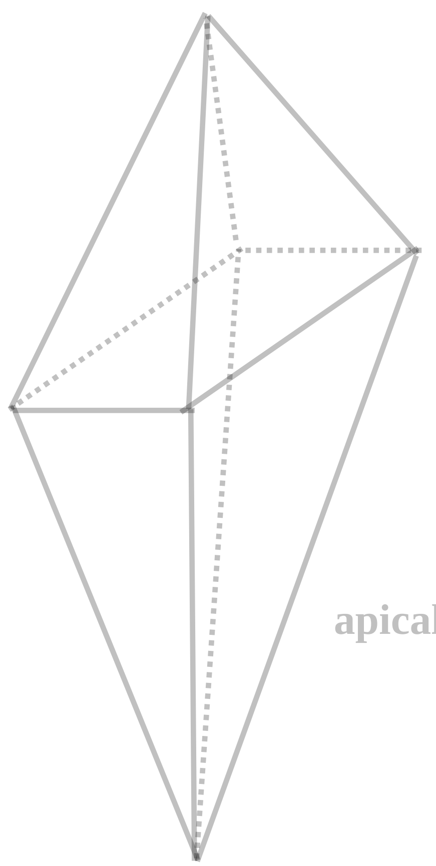




partial orbital ordering

apical distortion



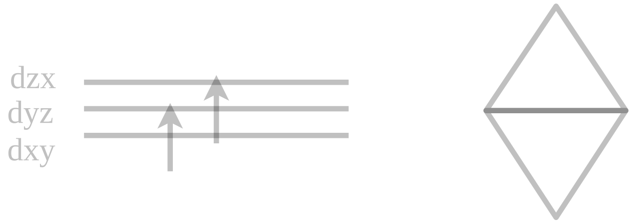


total orbital ordering

apical & in-plane distortion

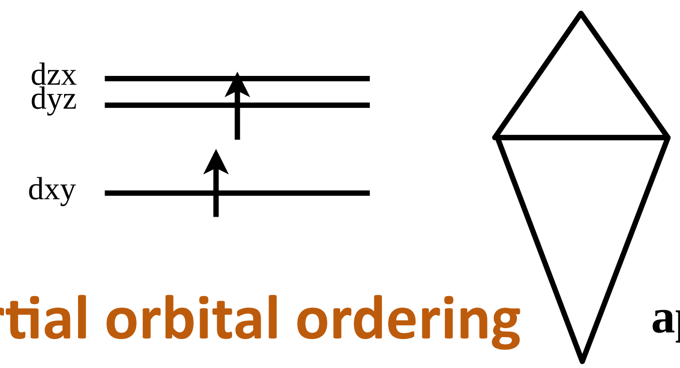
ESRF & lab XRD : no in-plane distortion observed

Orbital model



orbital degenerescence

regular octahedra



partial orbital ordering

apical distortion

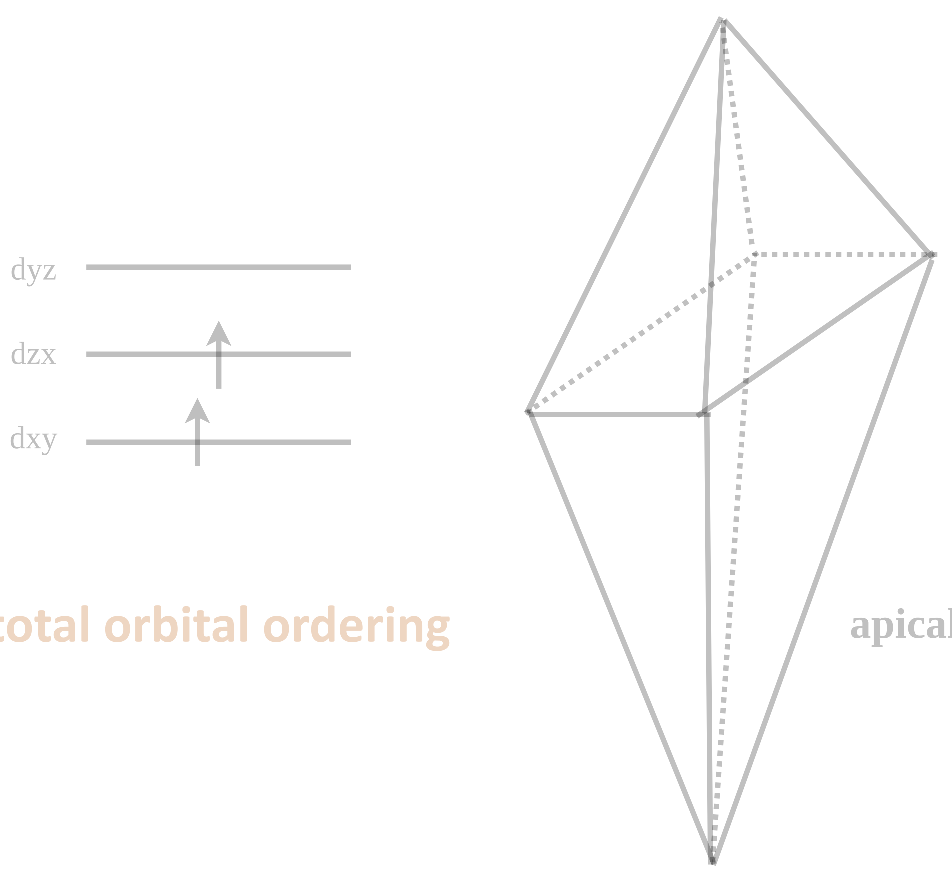
Clément Février
Claudine Lacroix
Arnaud Ralko

Armando A. Aligia

Kugel-Khomski Hamiltonian

$$\mathbf{H}_{\mathrm{eff}} = \mathbf{S}_{i}.\mathbf{S}_{j} \; \mathrm{x} \; f(\boldsymbol{\tau}_{i};\boldsymbol{\tau}_{j}) + g$$

spin **pseudo-spin**



total orbital ordering

apical & in-plane distortion

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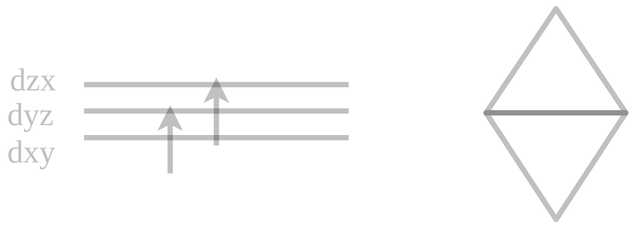
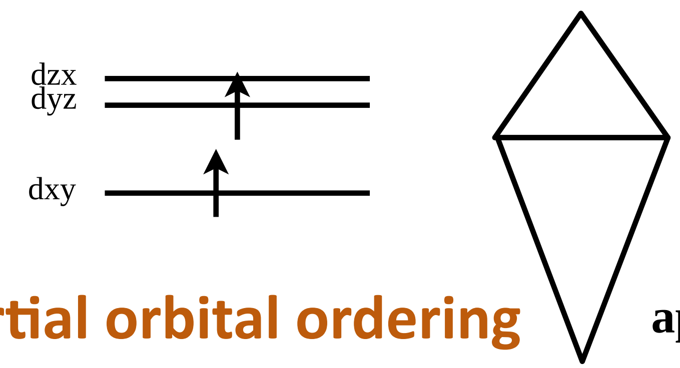
Orbital model



orbital degenerescence

regular octahedra



partial orbital ordering

apical distortion

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Kugel-Khomski Hamiltonian

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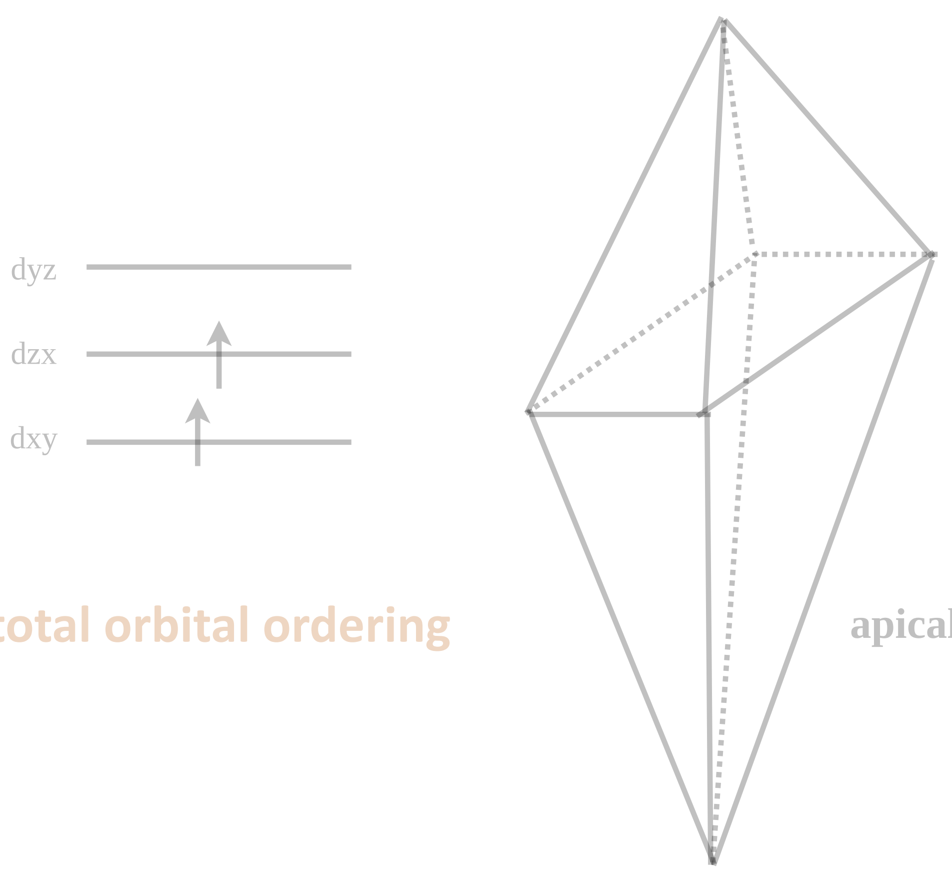
spin **pseudo-spin**

Total orbital ordering
AF in-plane and between adjacent Cr planes



total orbital ordering

apical & in-plane distortion

ESRF & lab XRD : no in-plane distortion observed

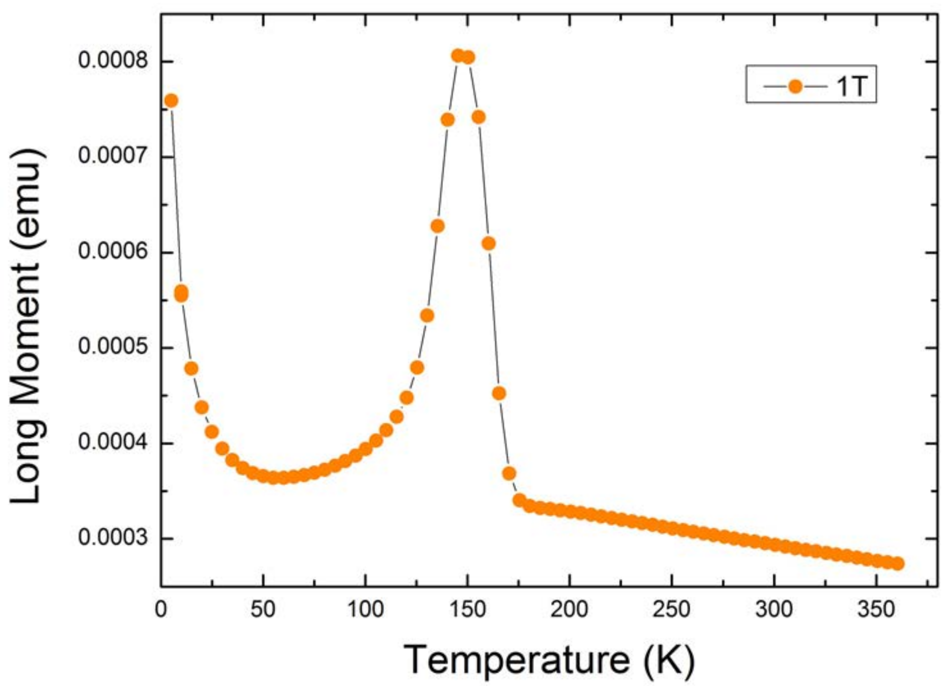
New Ca-based phases

$Ca_3Cr_2O_7$

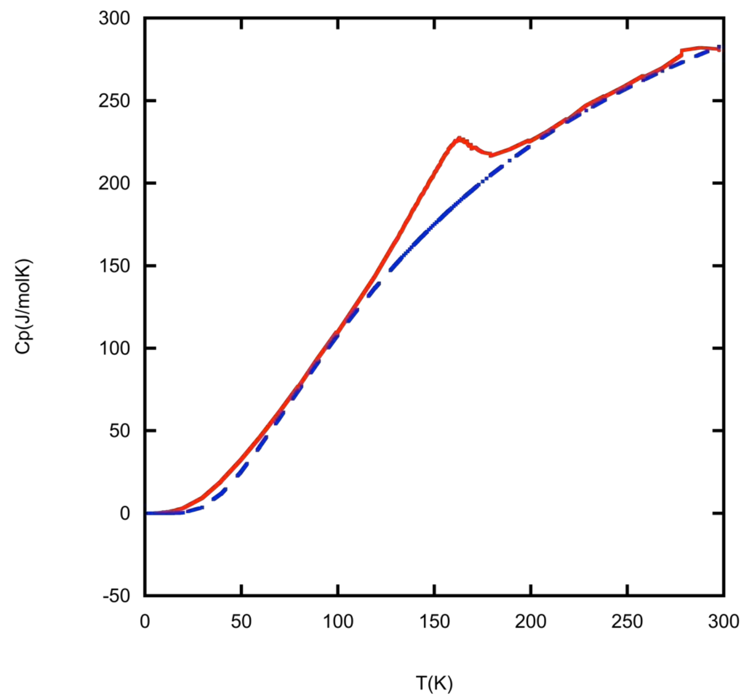
New Ca-based phases

$Ca_3Cr_2O_7$

Magnetic measurement



Specific heat measurement



$T_{Néel\ (Ca327)}$ = 150K

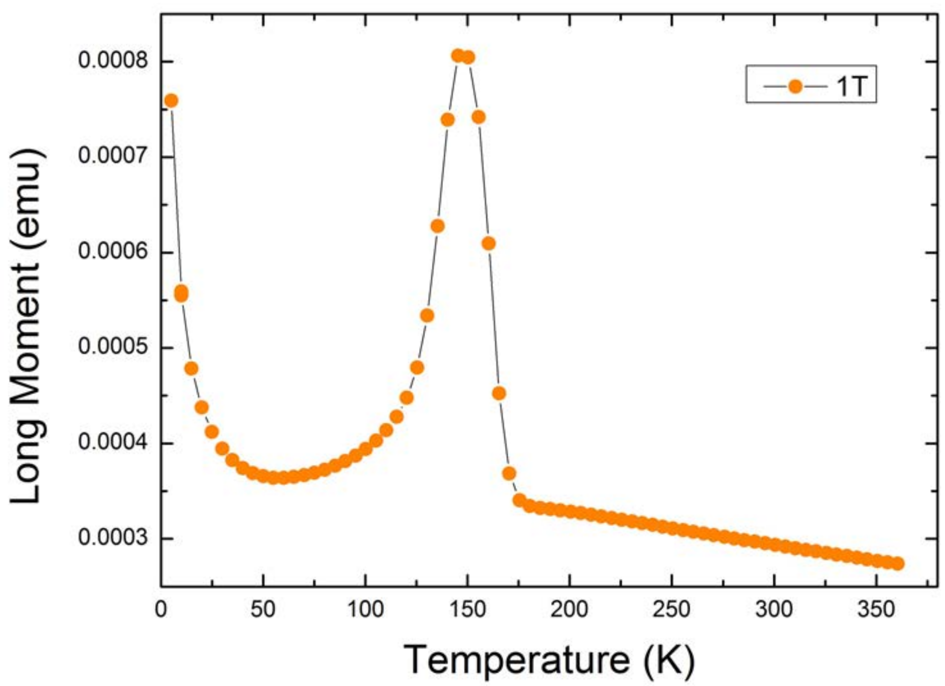
<

$T_{Néel(Sr327)}$ = 210K

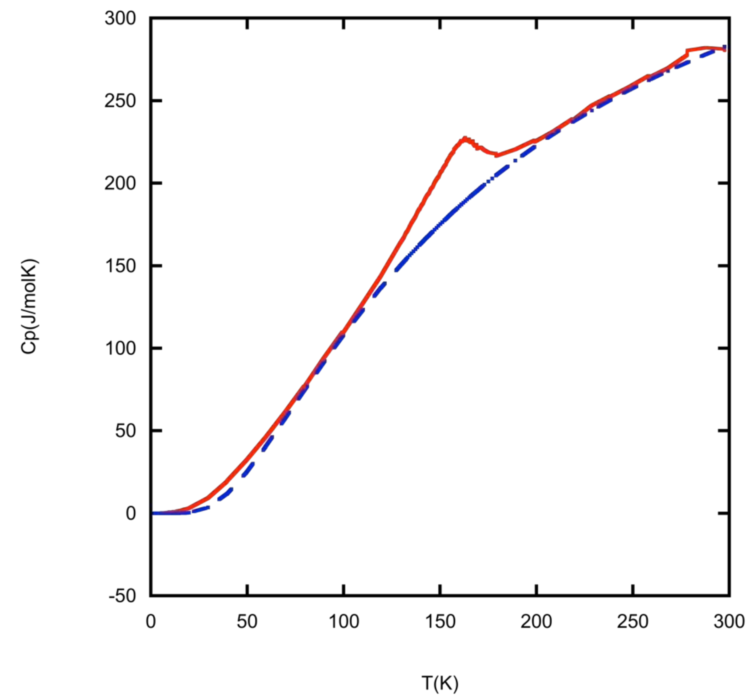
New Ca-based phases

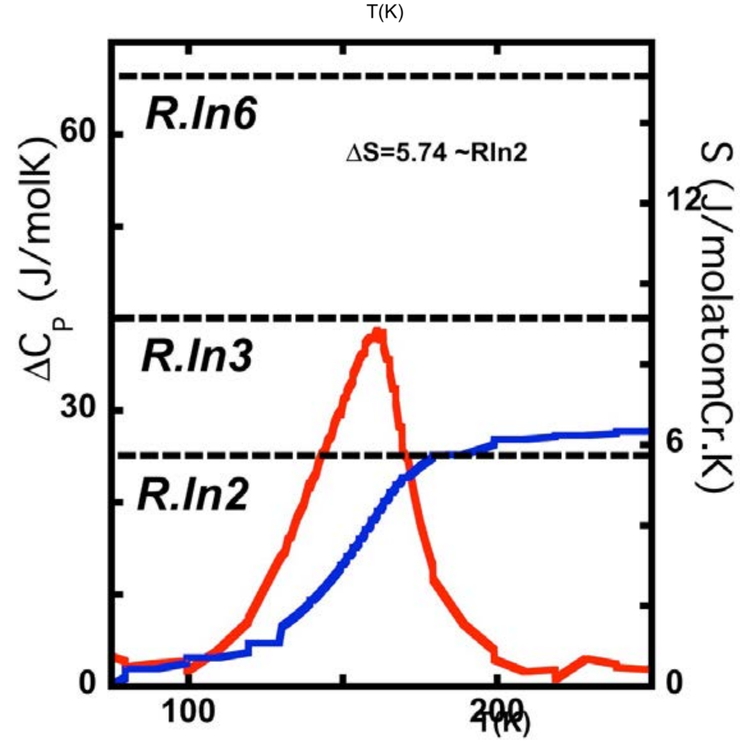
$Ca_3Cr_2O_7$

Magnetic measurement



Specific heat measurement





$T_{\text{Néel (Ca327)}}$ = 150K

<

$T_{\text{Néel(Sr327)}}$ = 210K

$S_{(Ca327)}$ = Rln2

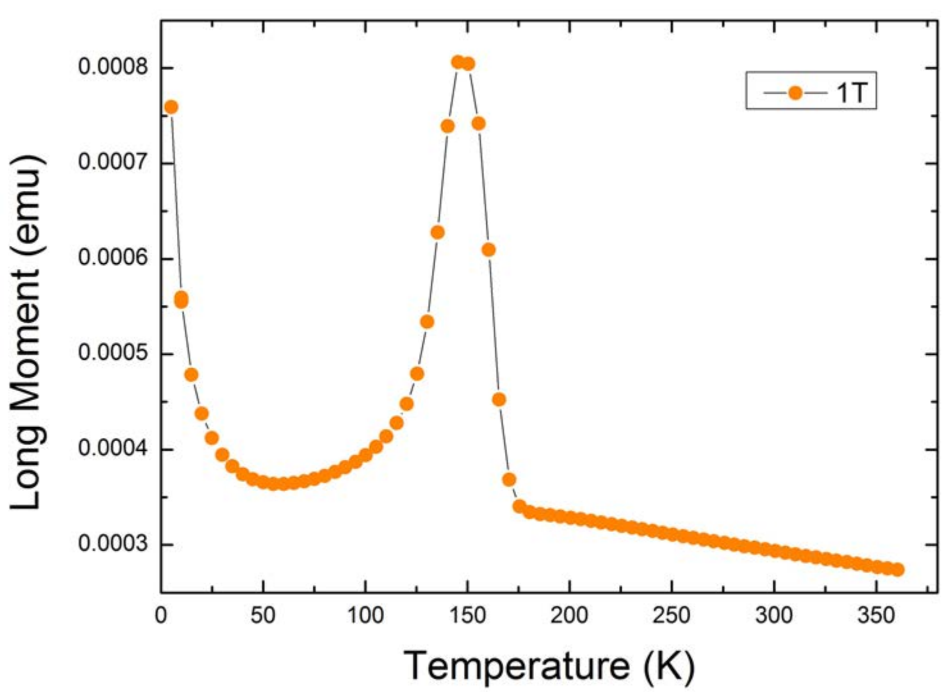
<

$S_{(Sr327)}$ = Rln6

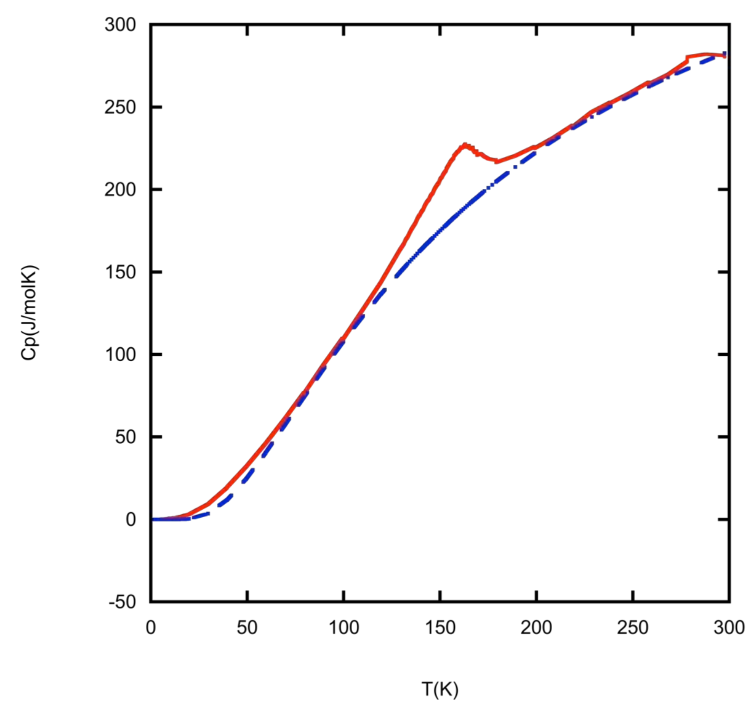
New Ca-based phases

$Ca_3Cr_2O_7$

Magnetic measurement



Specific heat measurement



$T_{Néel\ (Ca327)}$ = 150K

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$S_{(Ca327)}$ = Rln2

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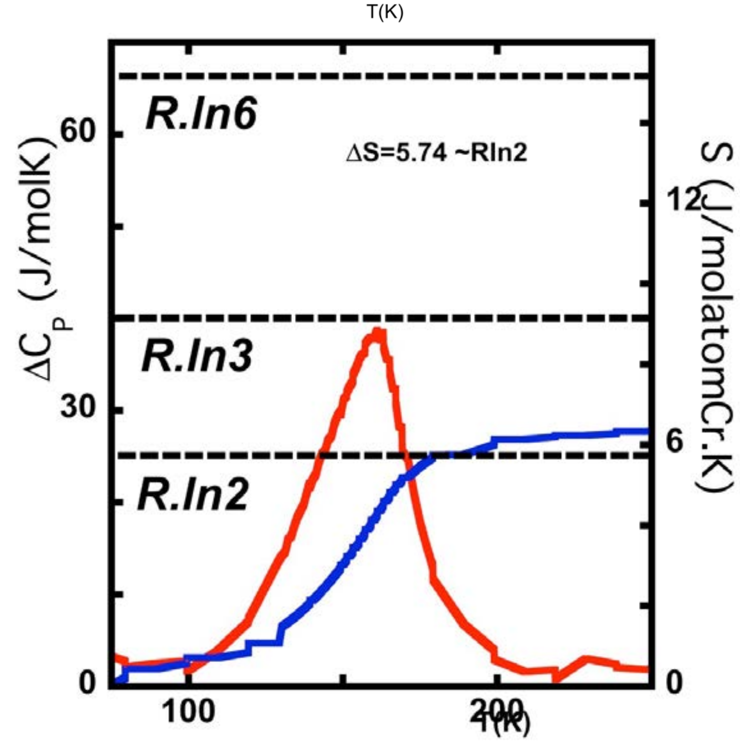
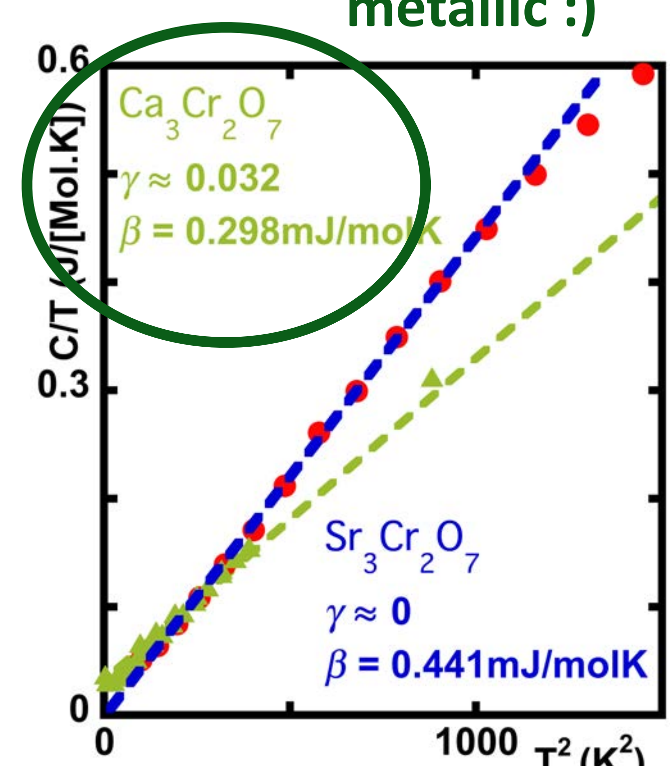


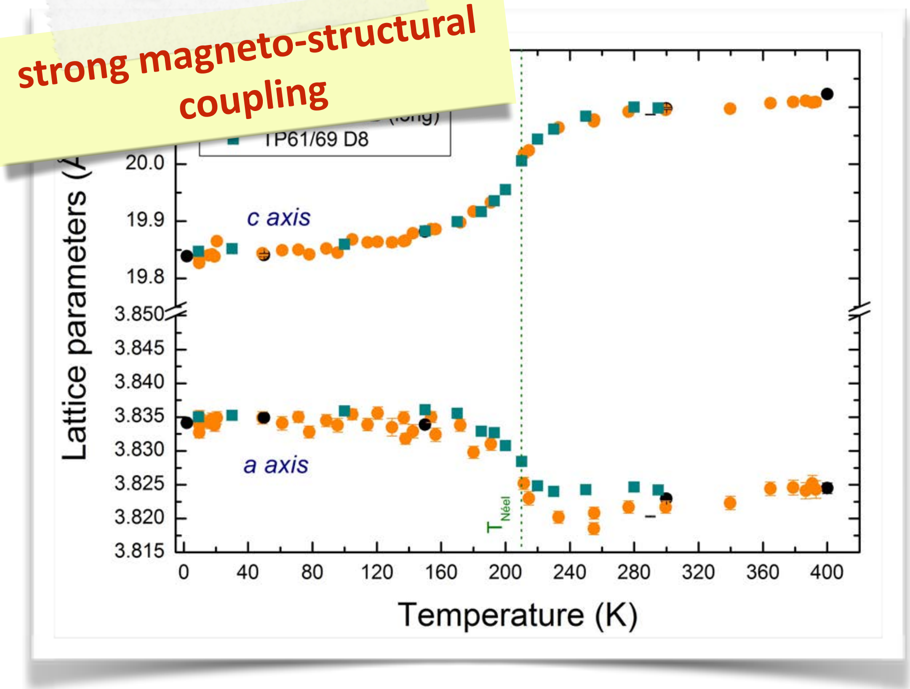
metallic :)



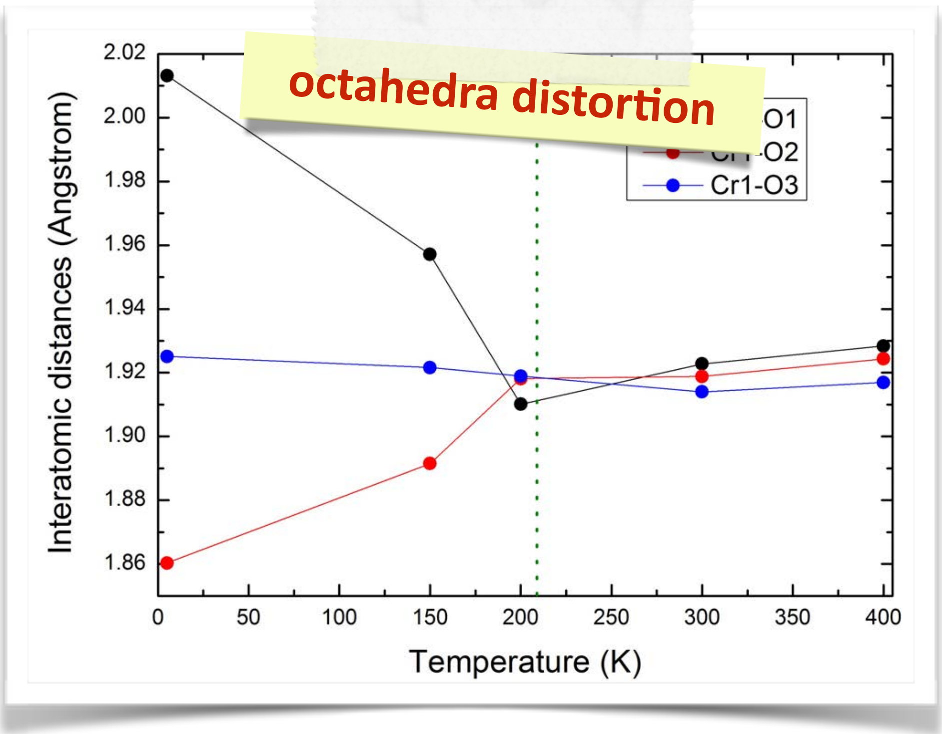
Conclusion

$Sr_3Cr_2O_7$

strong magneto-structural coupling



octahedra distortion



AFM structure determined

Orbital ordering..

Big thank to..

Pierre Bouvier
Frédéric Gay
Gaétan Giriat
Céline Goujon
Claudine Lacroix
Christophe Lepoittevin
Murielle Legendre
Olivier Leynaud
José-Emilio Lorenzo-Diaz
Gyorgy Remenyi
Pierre Rodiere
Denis Testemale
Pierre Strobel
André Sulpice
Ruben Weht

D1B
Claire Collin
Vivan Nassif
D2B
Emmanuelle Suard

and you!

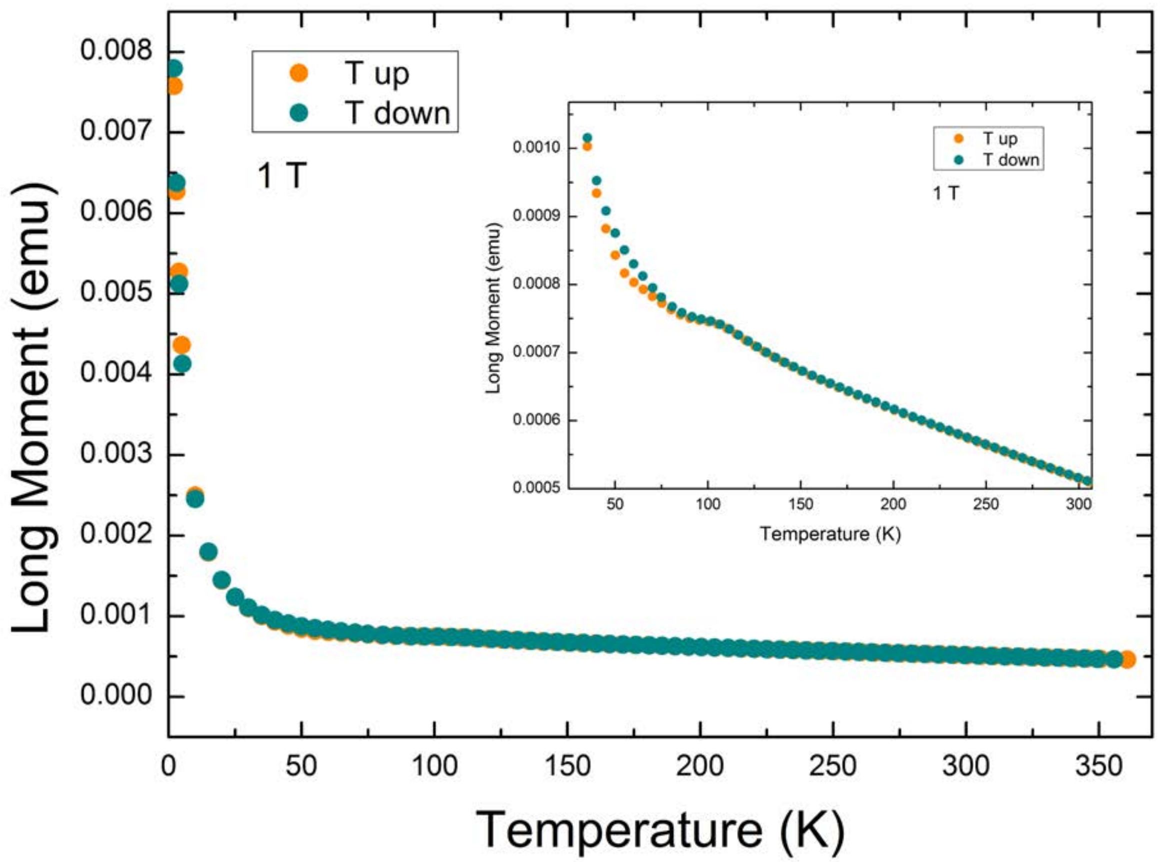
New Ca-based phases

Ca_2CrO_4

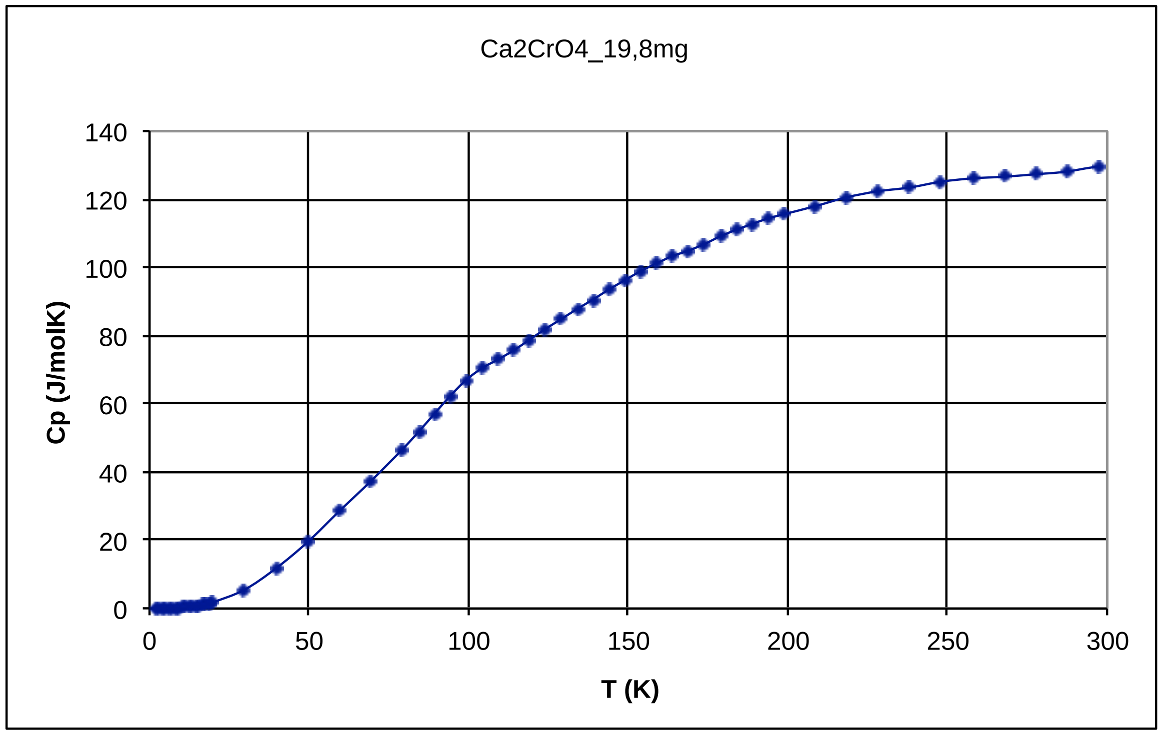
New Ca-based phases

Ca_2CrO_4

Magnetic measurement



Specific heat measurement

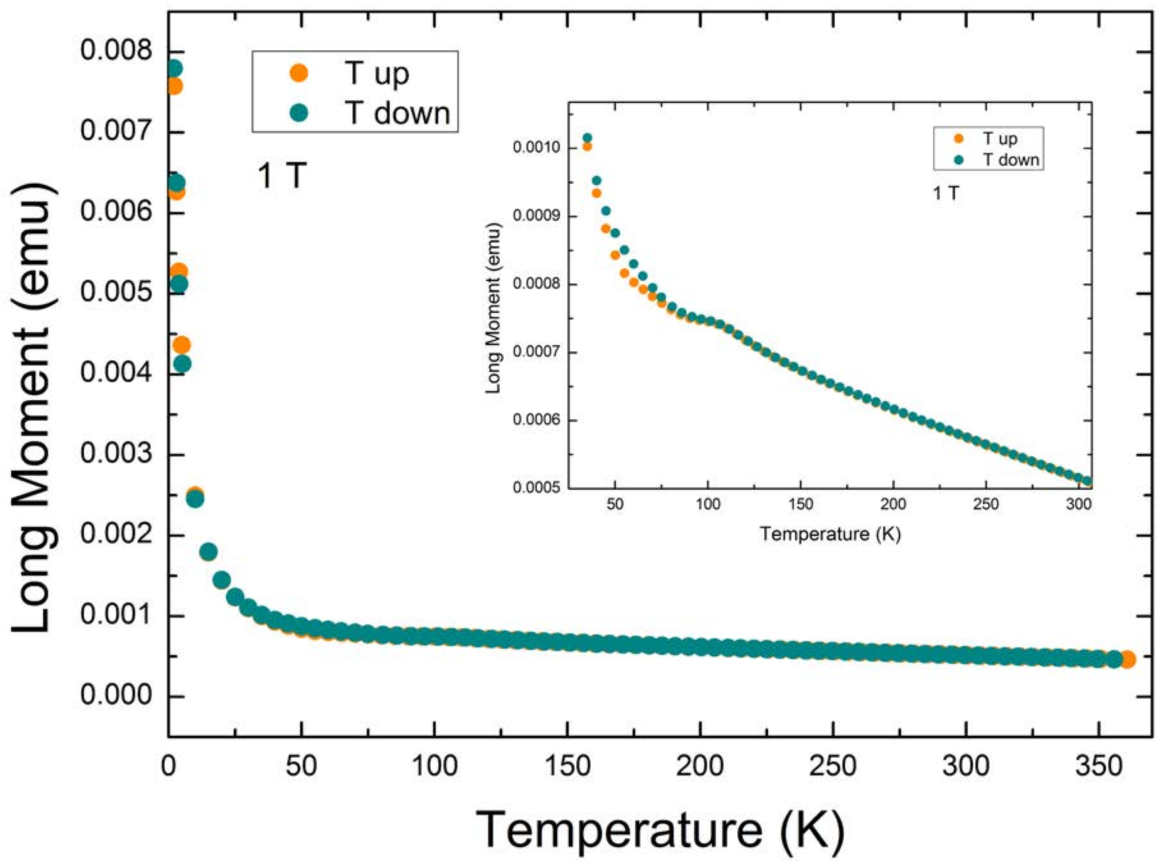


- **No AFM anomaly at high temperature (Sr-based:T_N=305 K)**
- **Weak AFM anomaly on magnetic measurement and specific heat around 100 K**

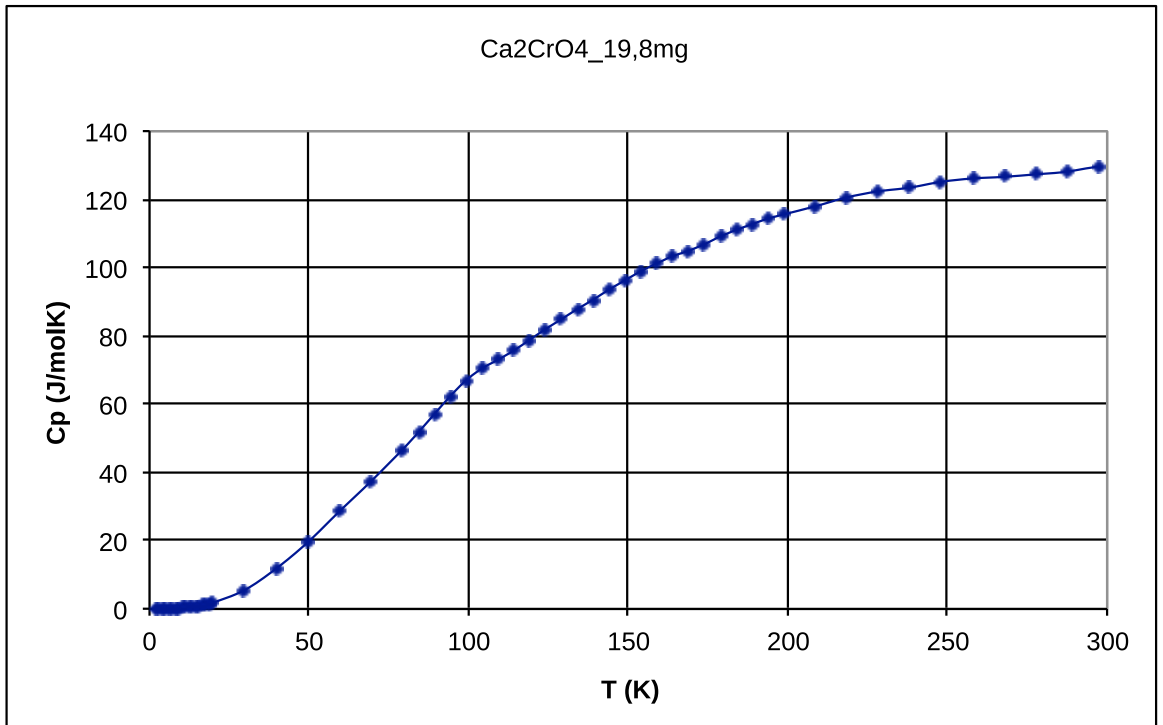
New Ca-based phases

Ca_2CrO_4

Magnetic measurement

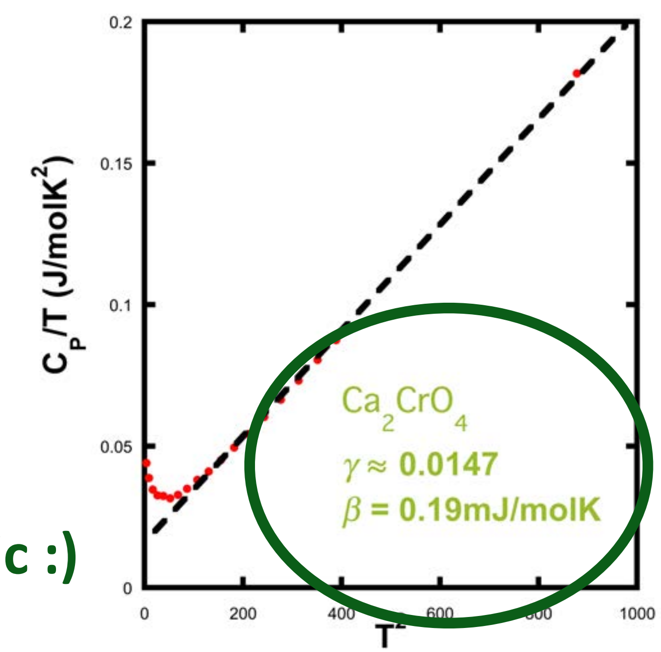


Specific heat measurement



- No AFM anomaly at high temperature (Sr-based:T_N=305 K)
- Weak AFM anomaly on magnetic measurement and specific heat around 100 K

metallic :)

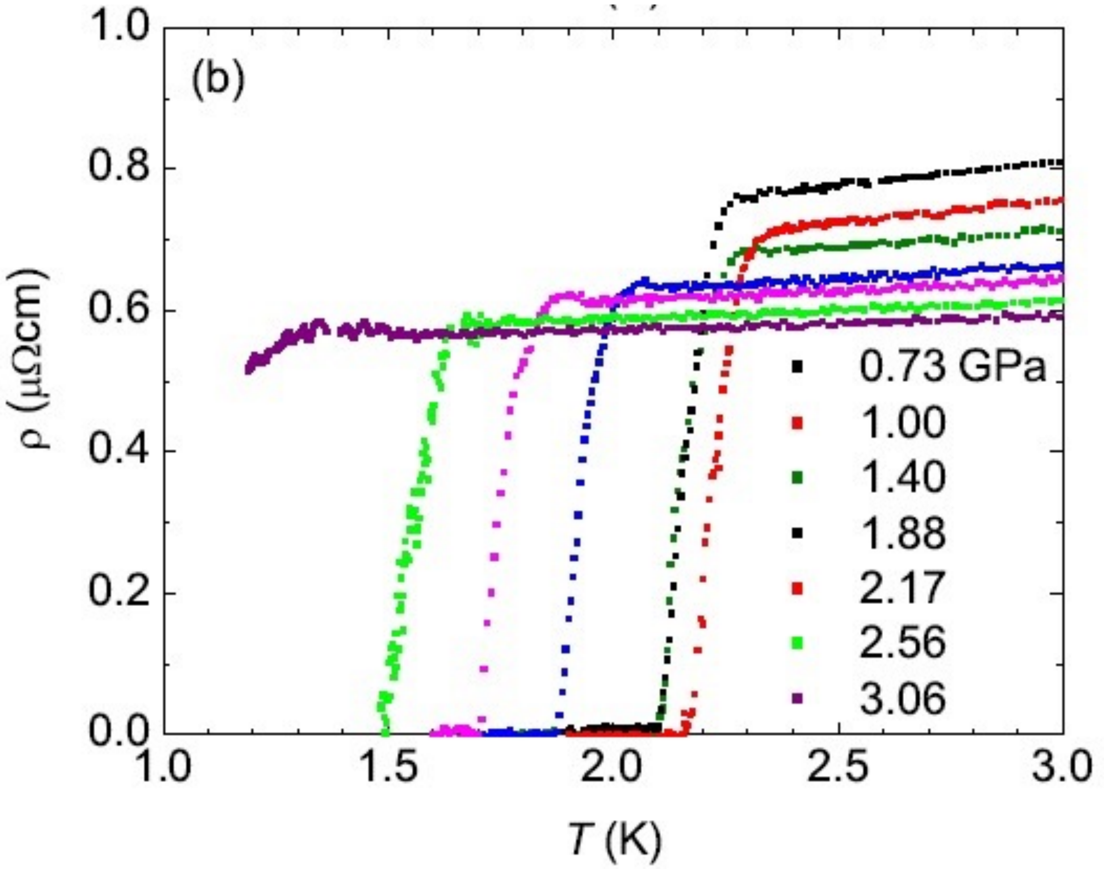


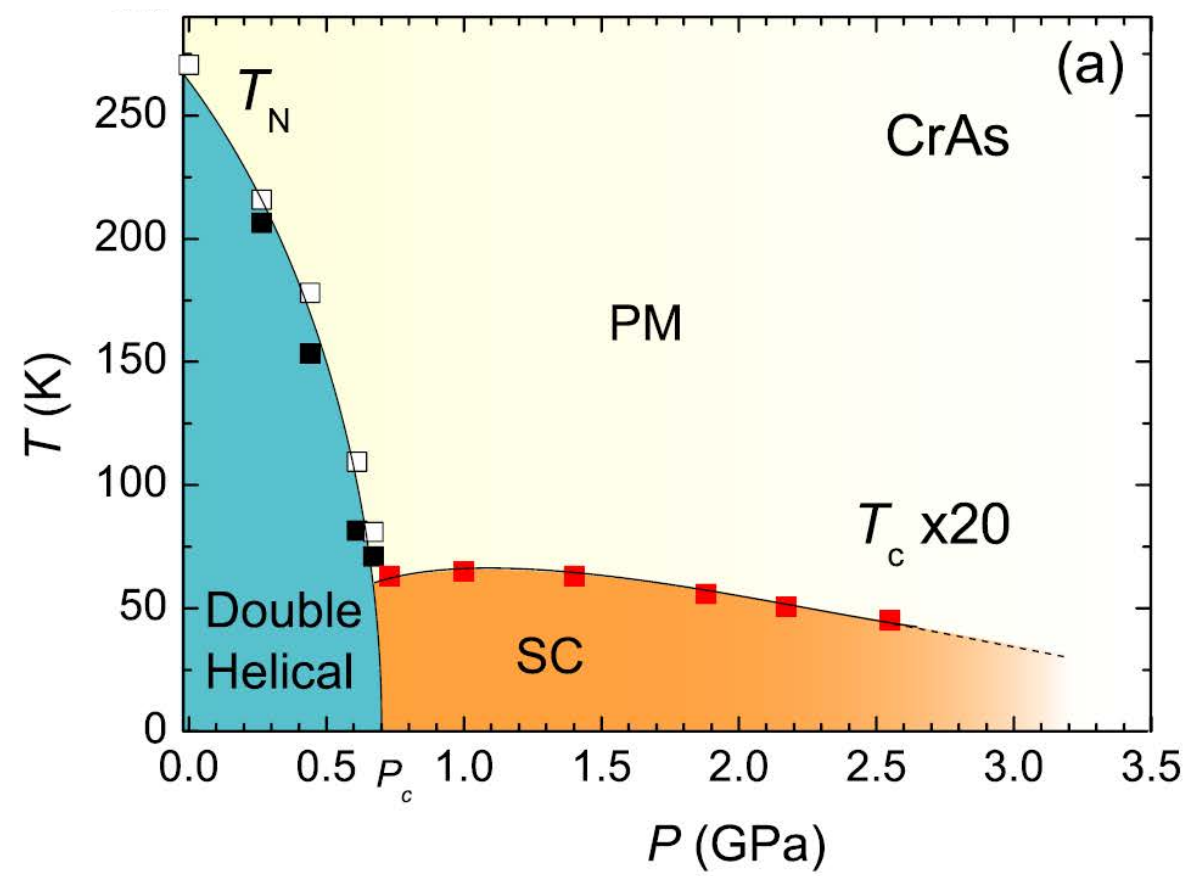
$CrSb_2$

CrAs motivation

CrSb$_2$

CrAs motivation





3D compound : orthorhombic (MnP-type structure)

double helical magnetic structure (Cr moment = 1.7 μb)

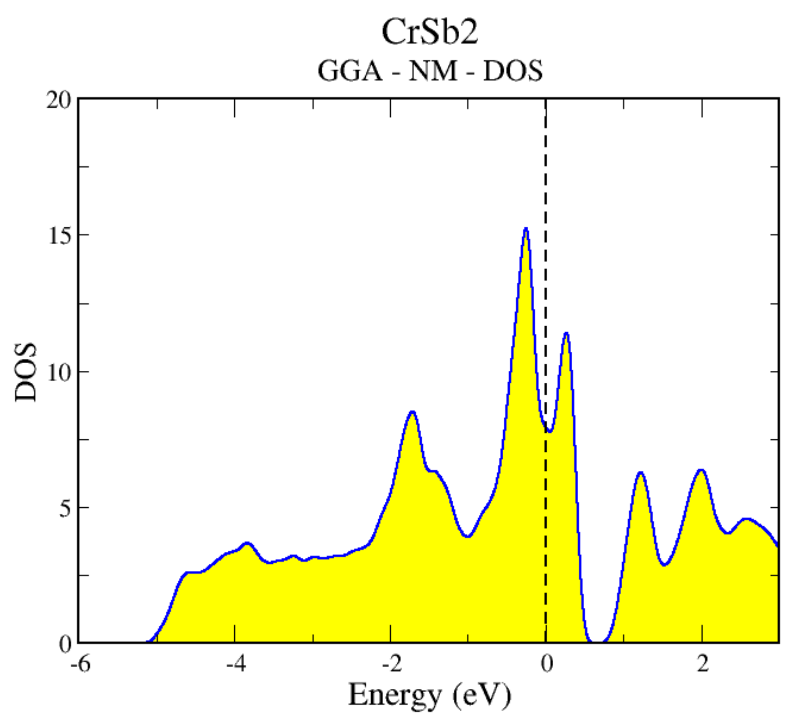
T_N = 265K

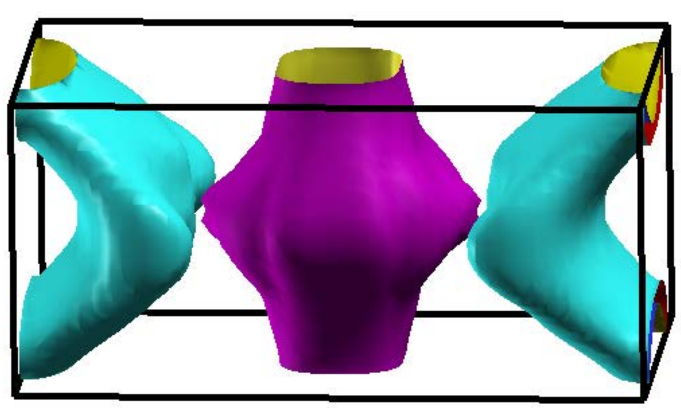
T_c = 2K (at 0.7 GPa)

CrSb$_2$

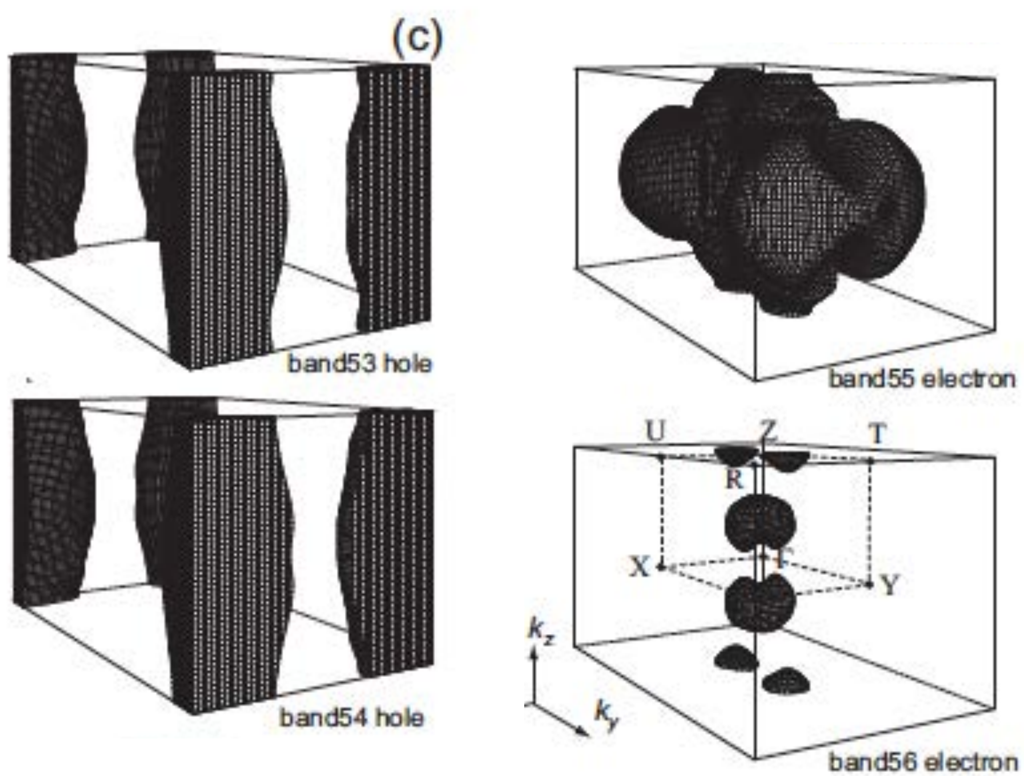
CrAs motivation

CrSb2



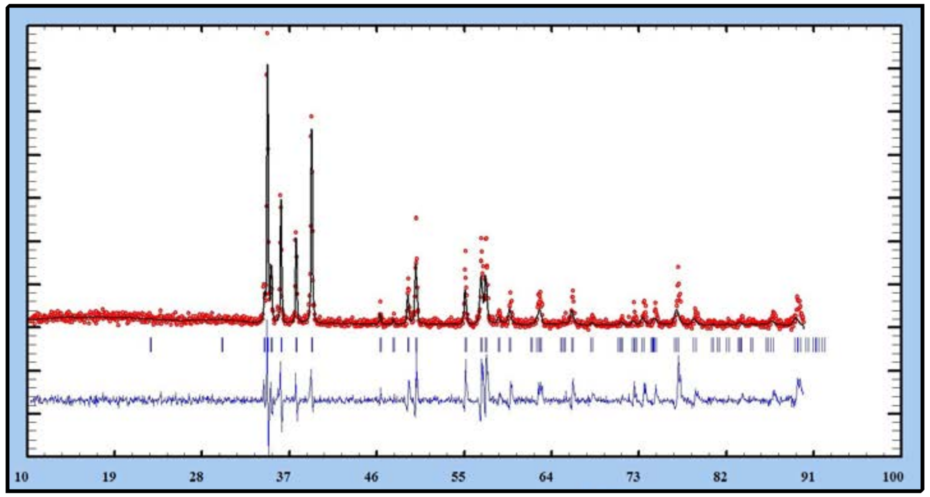


CrAs



3D compounds but quasi-2D band

$CrSb_2$



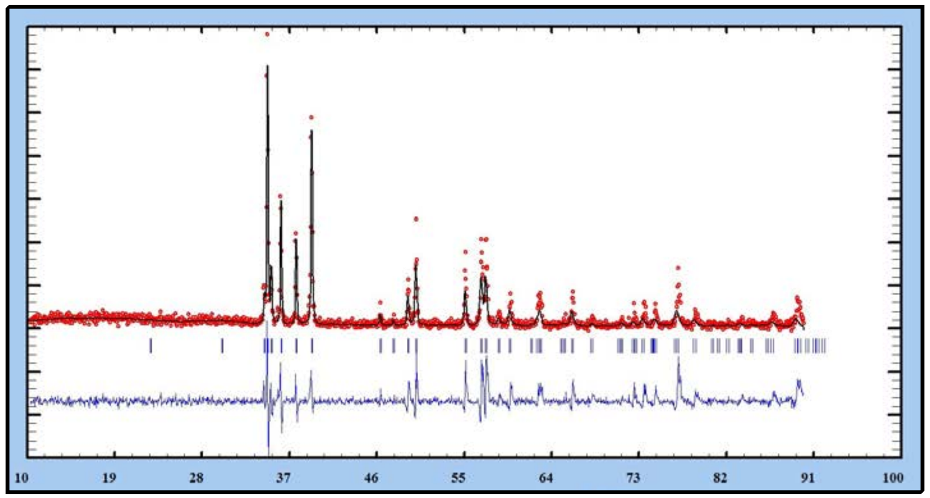
Marcasite-type structure
(space group Pnnm)

a = 6.04 Æ
b = 6.89 Æ
c = 3.28 Æ

$T_{Néel}$ = 273 K

Pure polycrystal & singlecrystal synthesis

$CrSb_2$



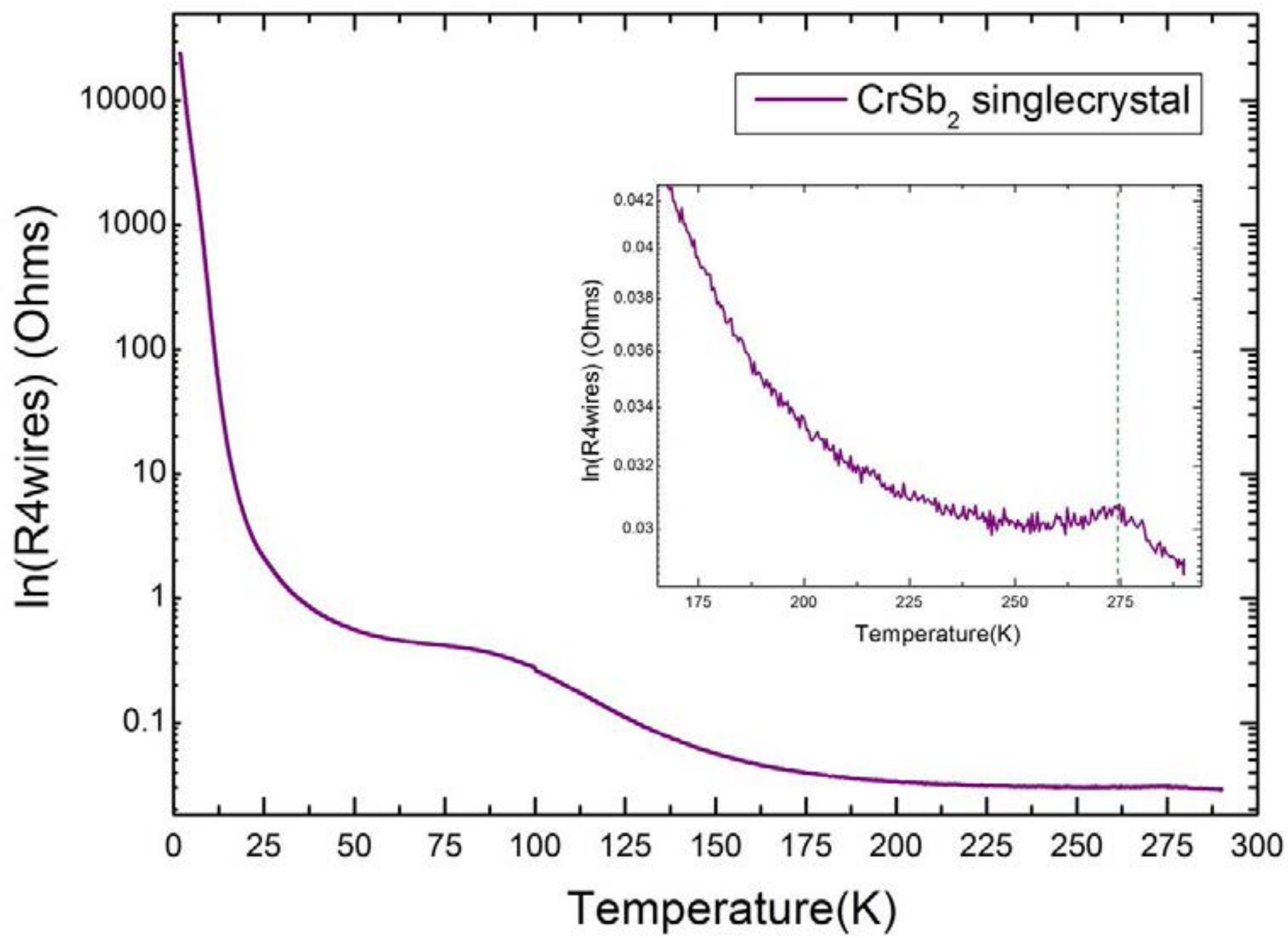
Marcasite-type structure
(space group Pnnm)

a = 6.04 Æ
b = 6.89 Æ
c = 3.28 Æ

$T_{Néel}$ = 273 K

Pure polycrystal & singlecrystal synthesis

Transport measurement (ambiant pressure)

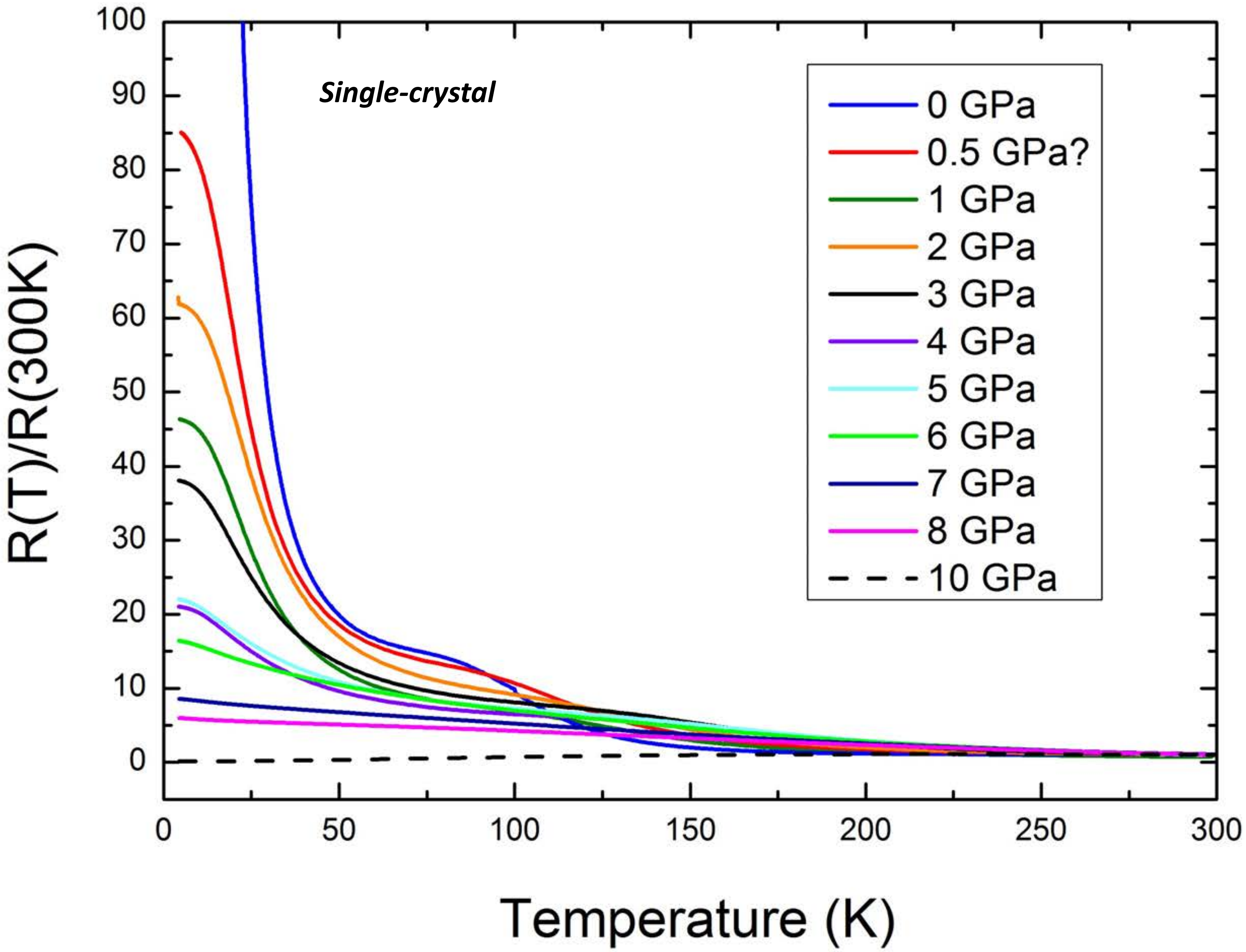


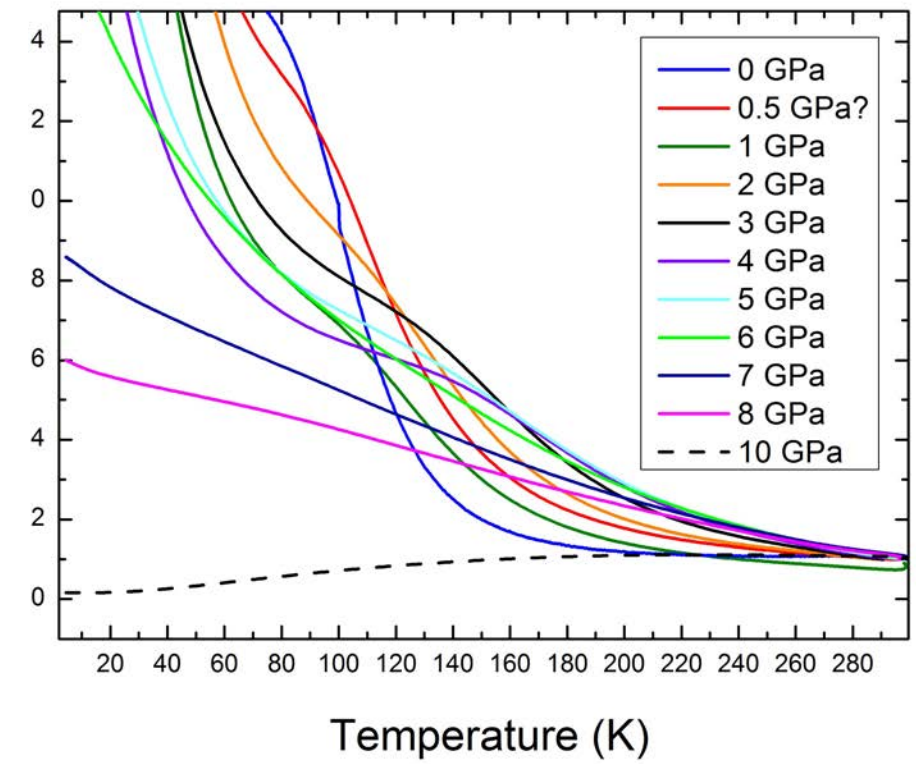
$CrSb_2$

High pressure transport measurement

$CrSb_2$

High pressure transport measurement



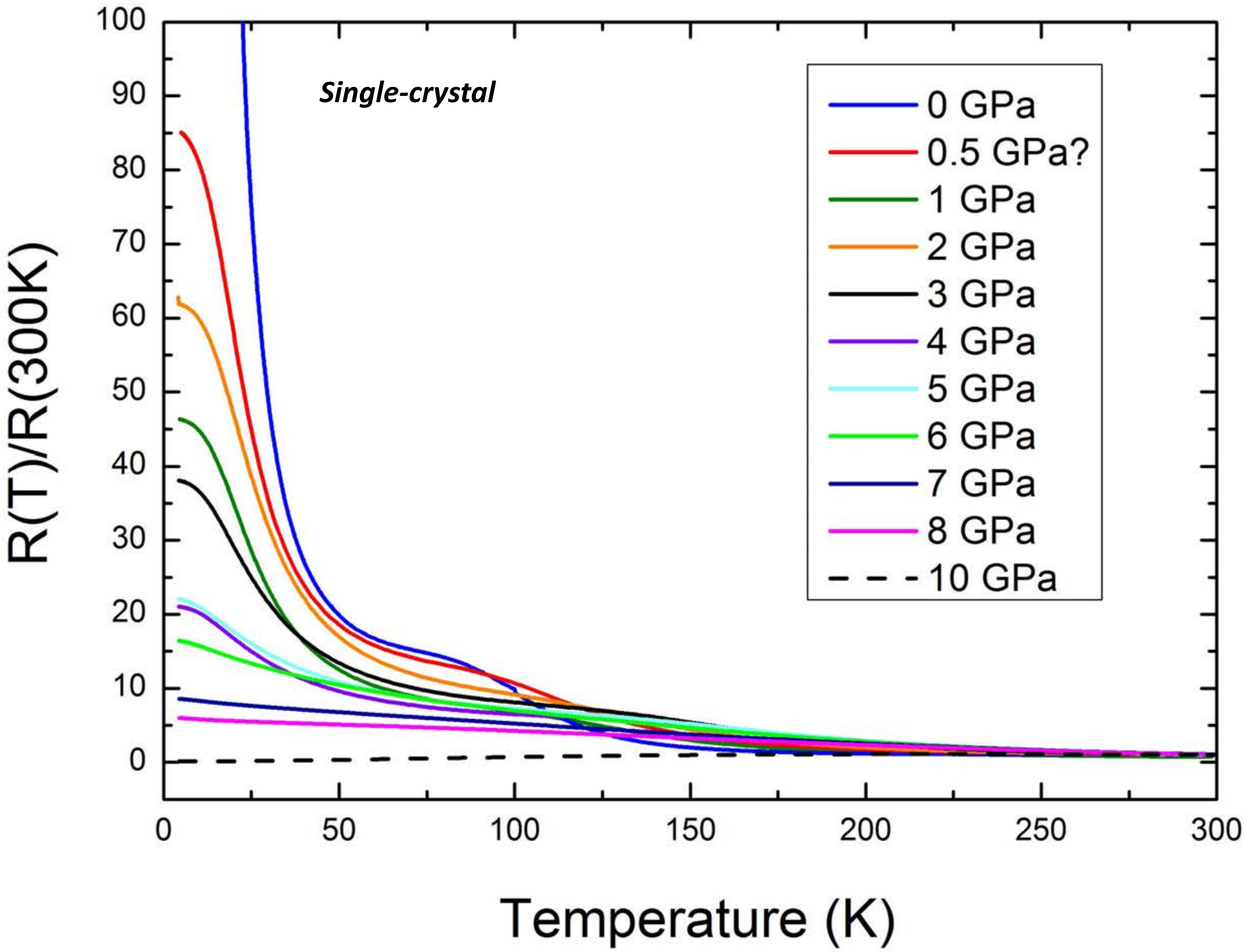


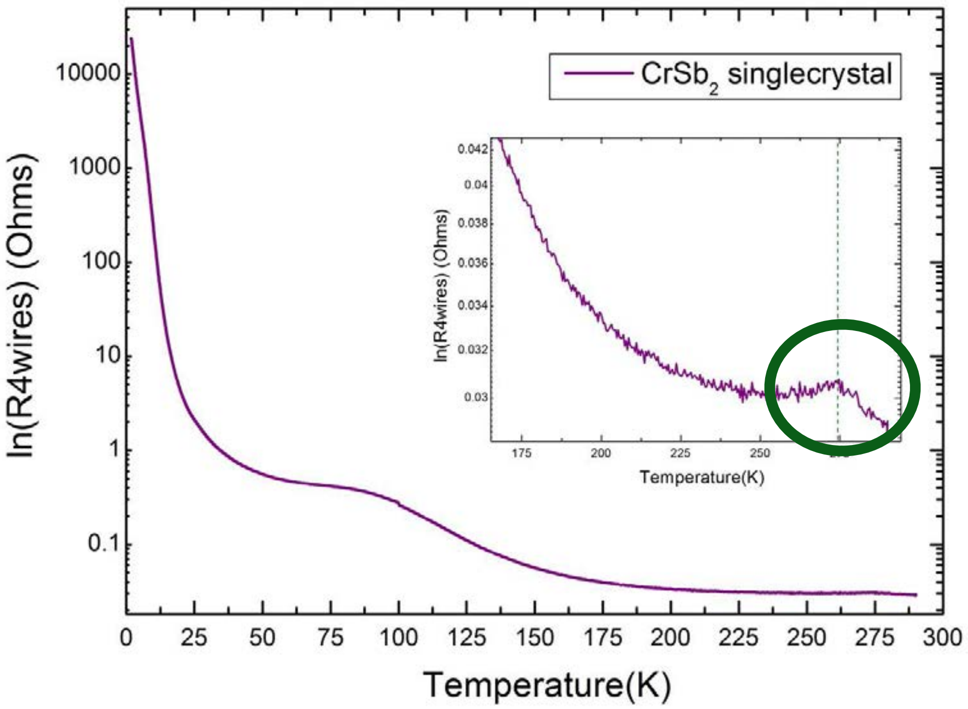
Transition metal-insulator at 10 GPa

No SC up to 20 GPa and down to 2k

CrSb$_2$

High pressure transport measurement





Transition metal-insulator at 10 GPa

No SC up to 20 GPa and down to 2k

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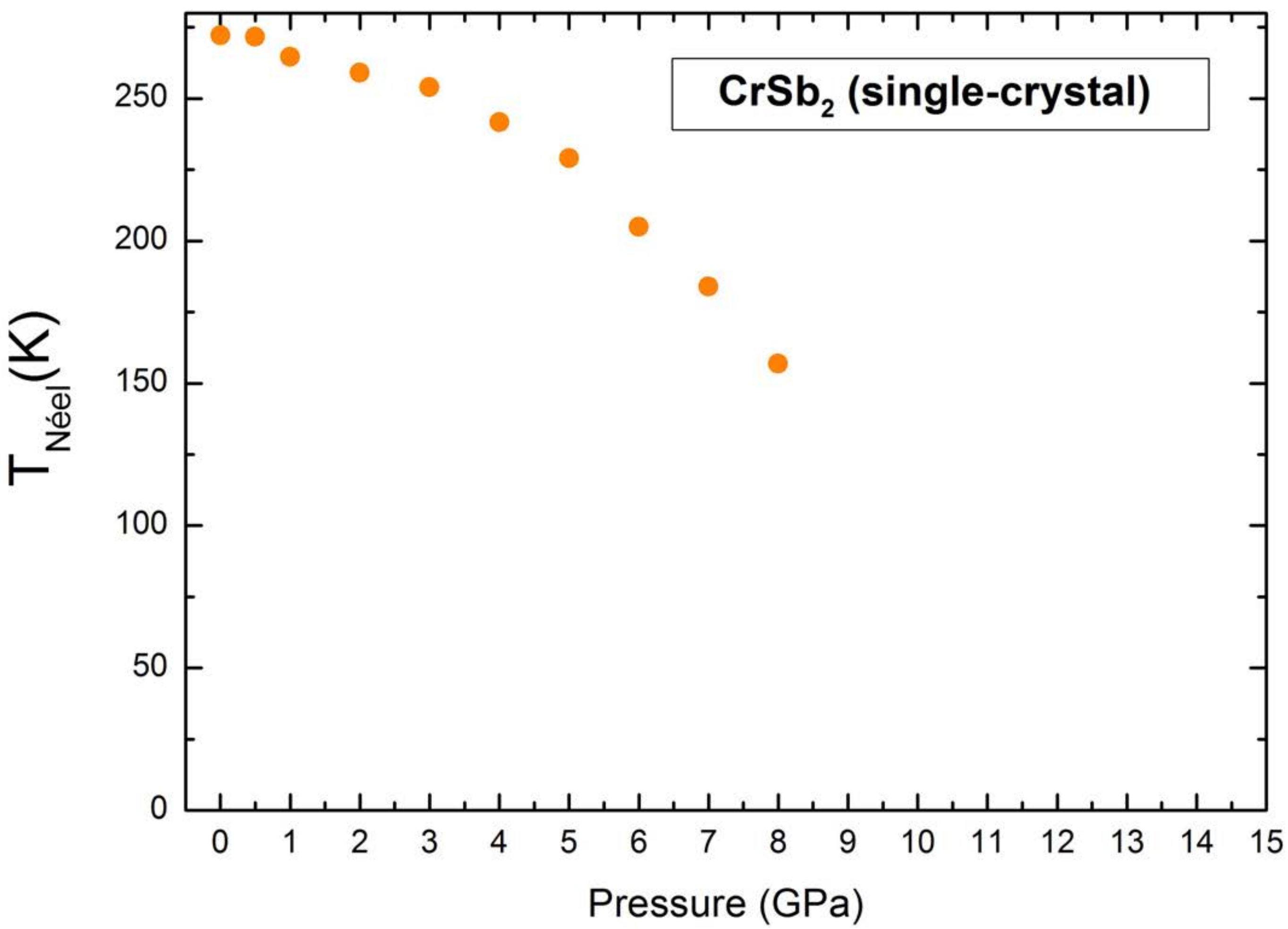
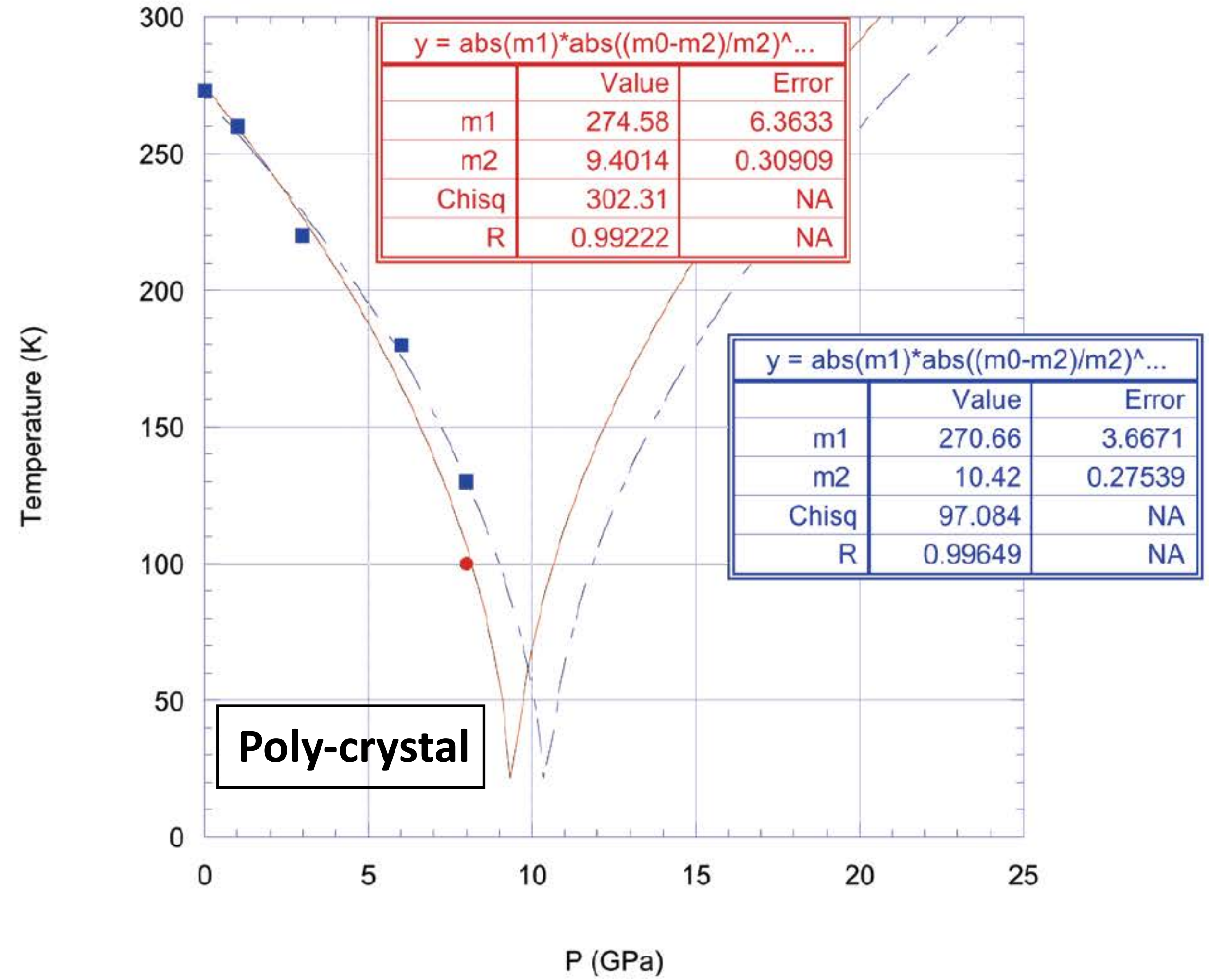
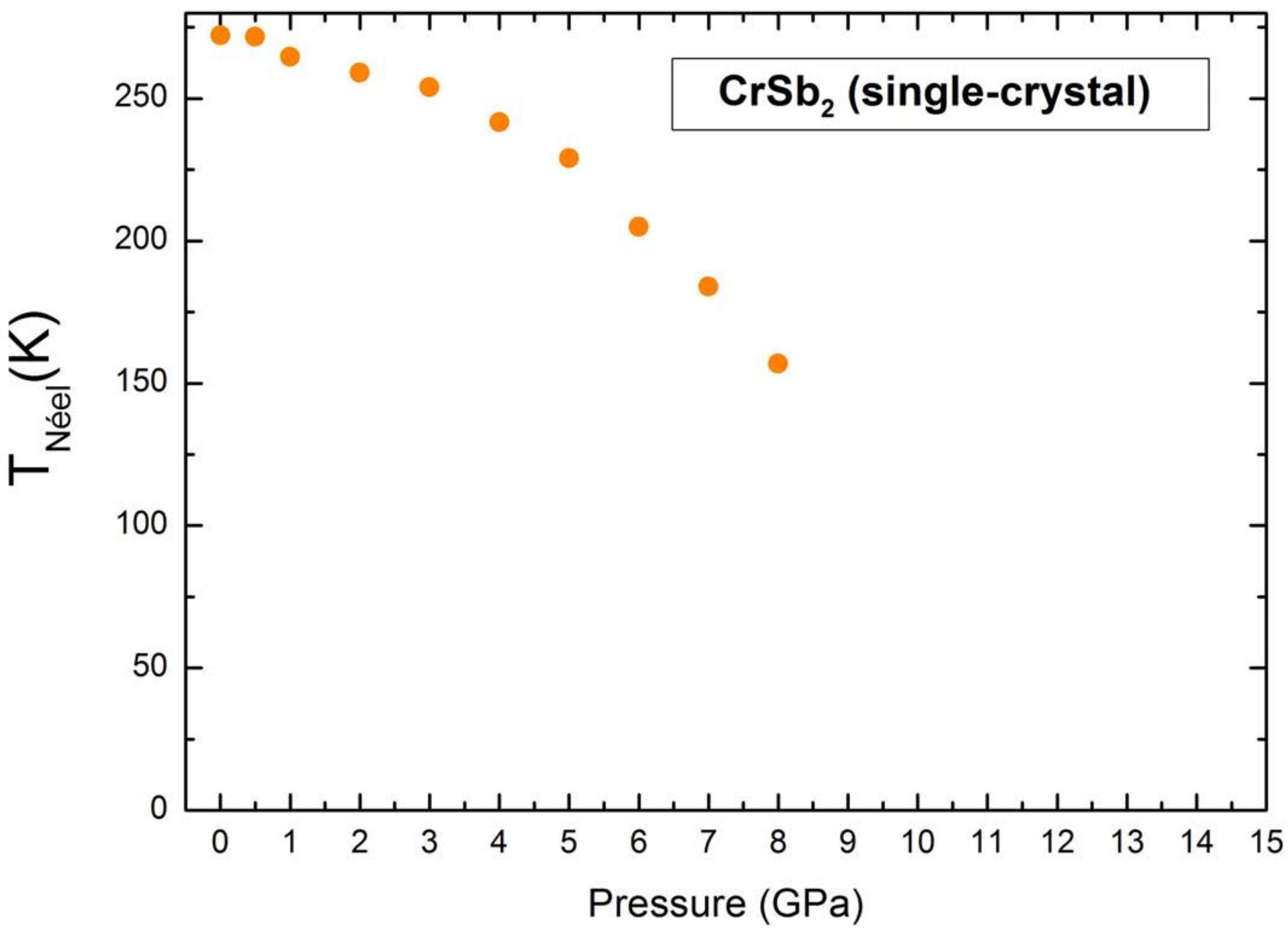
High pressure transport measurement

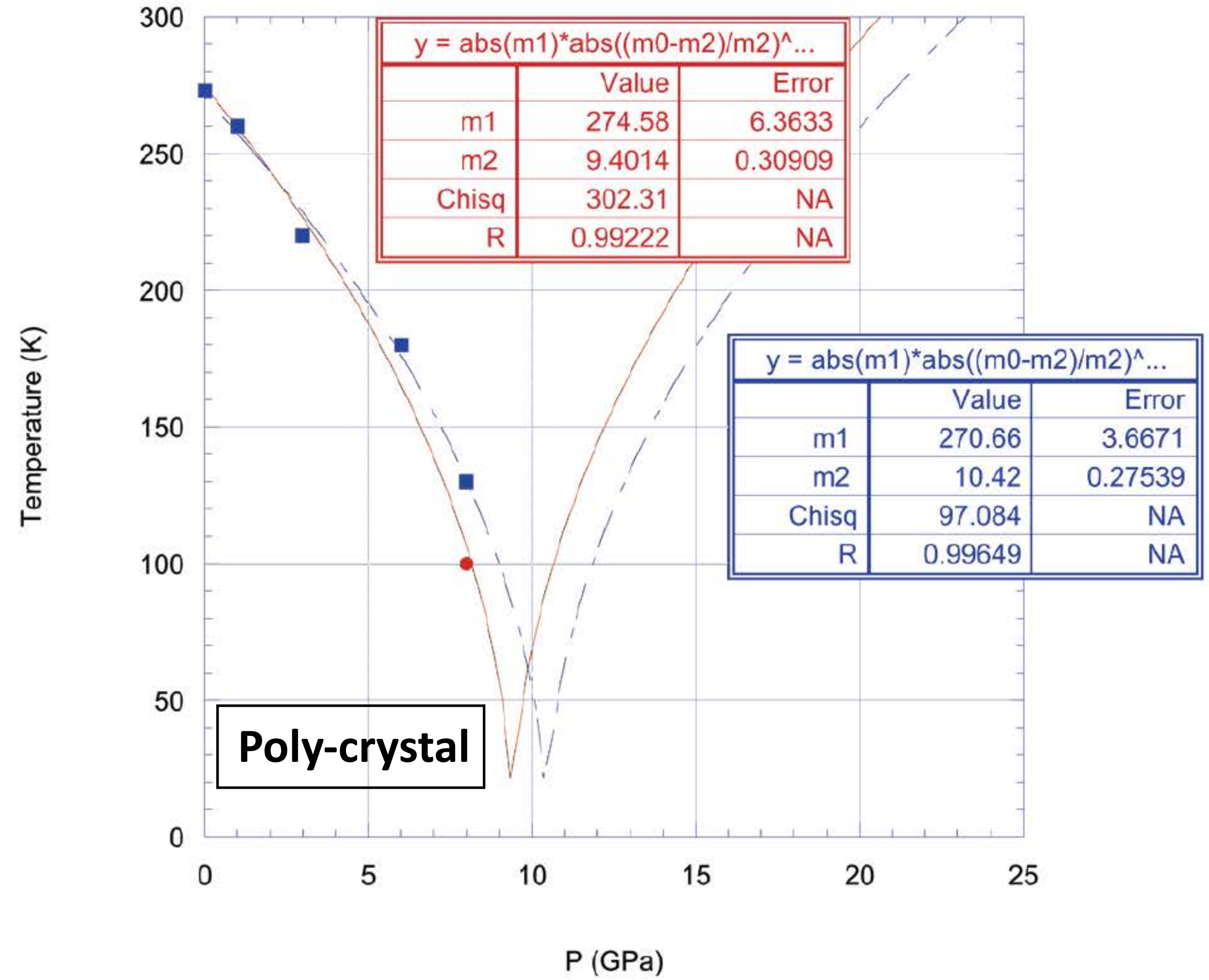




$CrSb_2$

High pressure transport measurement





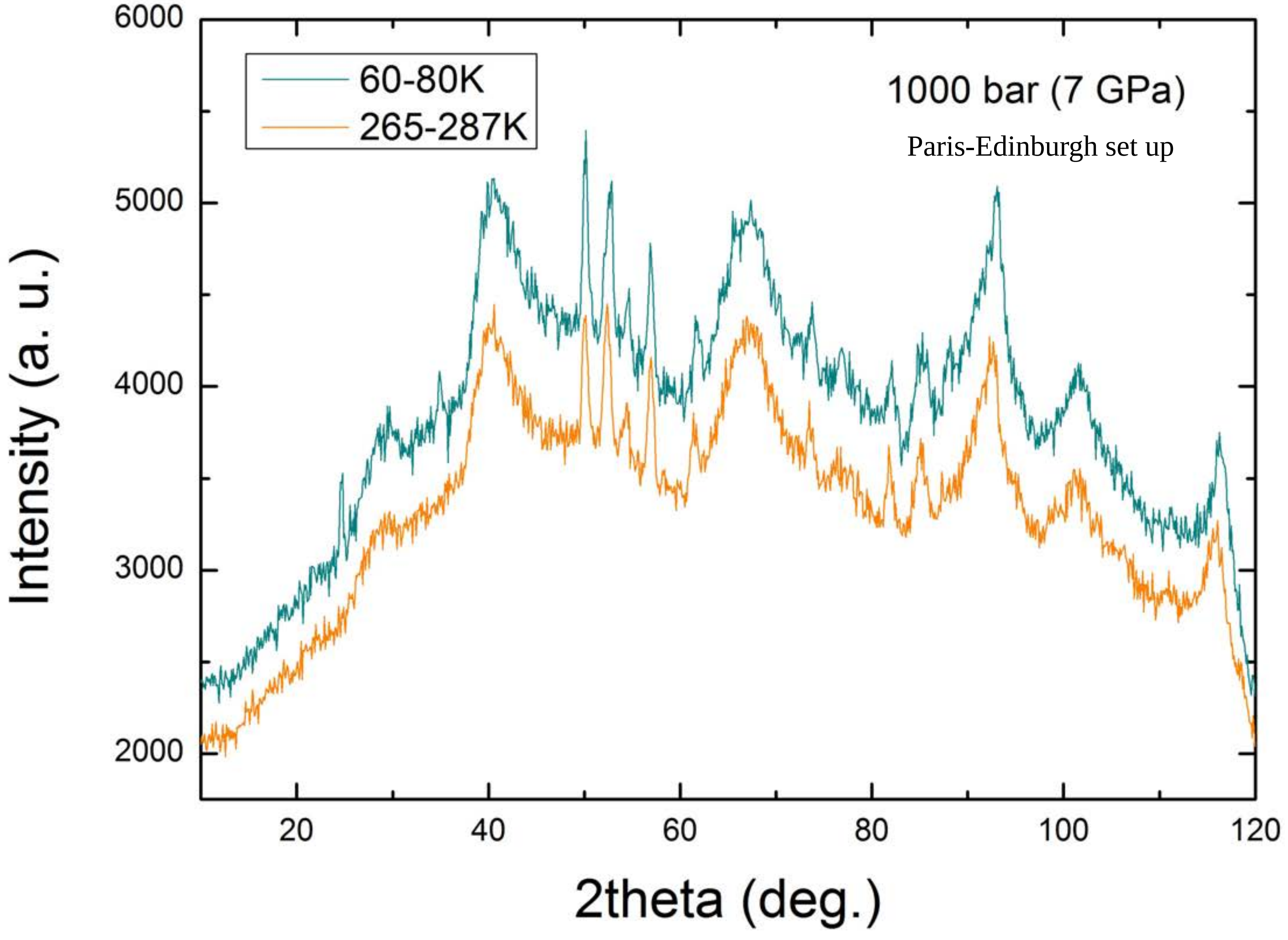
AFM should be destroyed around 10 GPa according to HP transport measurements : OK with metal-insulator pressure transition

$CrSb_2$

Neutron Powder Diffraction under pressure (D1B instrument)

$CrSb_2$

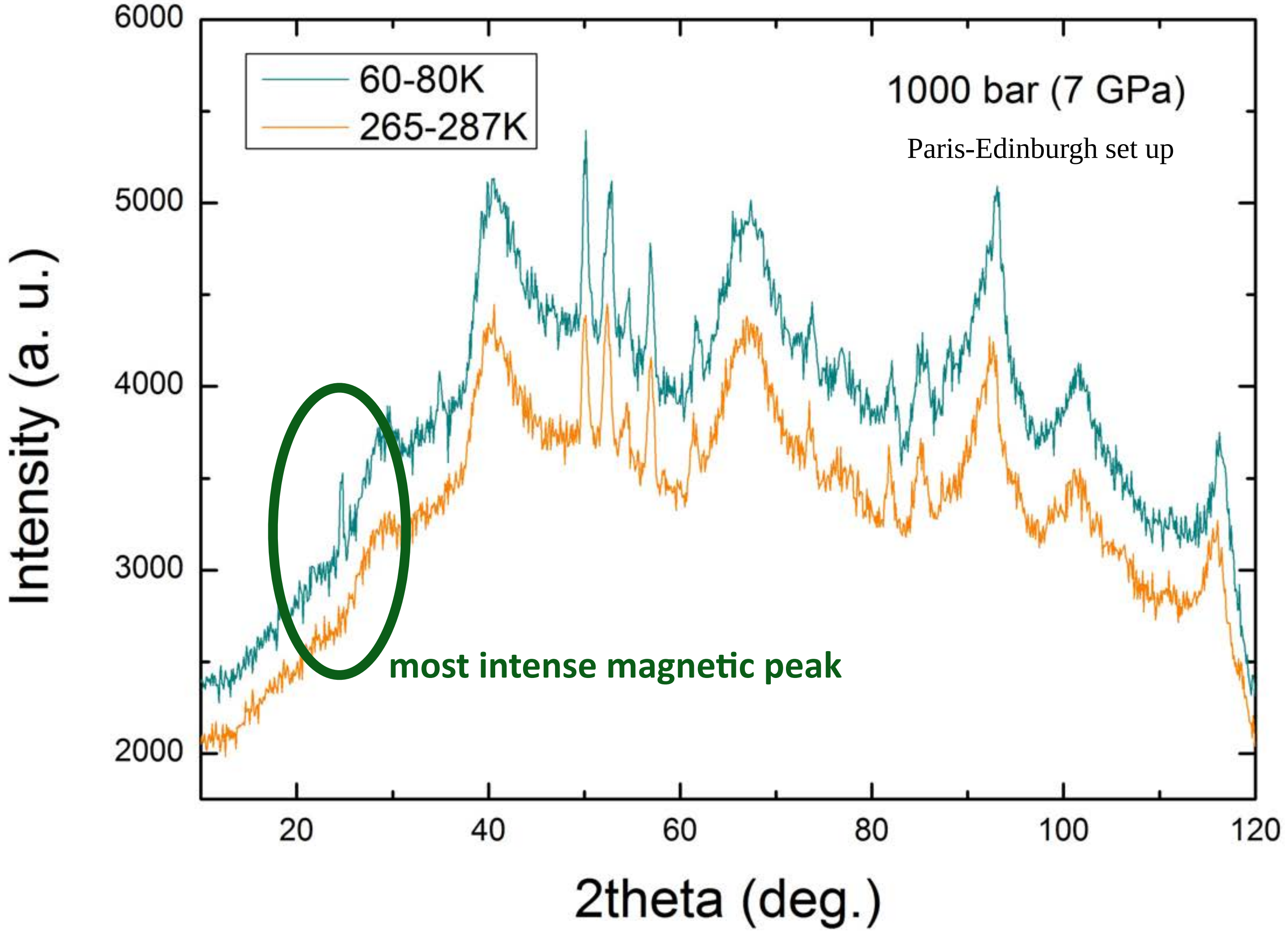
Neutron Powder Diffraction under pressure (D1B instrument)



No phase transition observed until 10 GPa (limit of PE press)

CrSb$_2$

Neutron Powder Diffraction under pressure (D1B instrument)

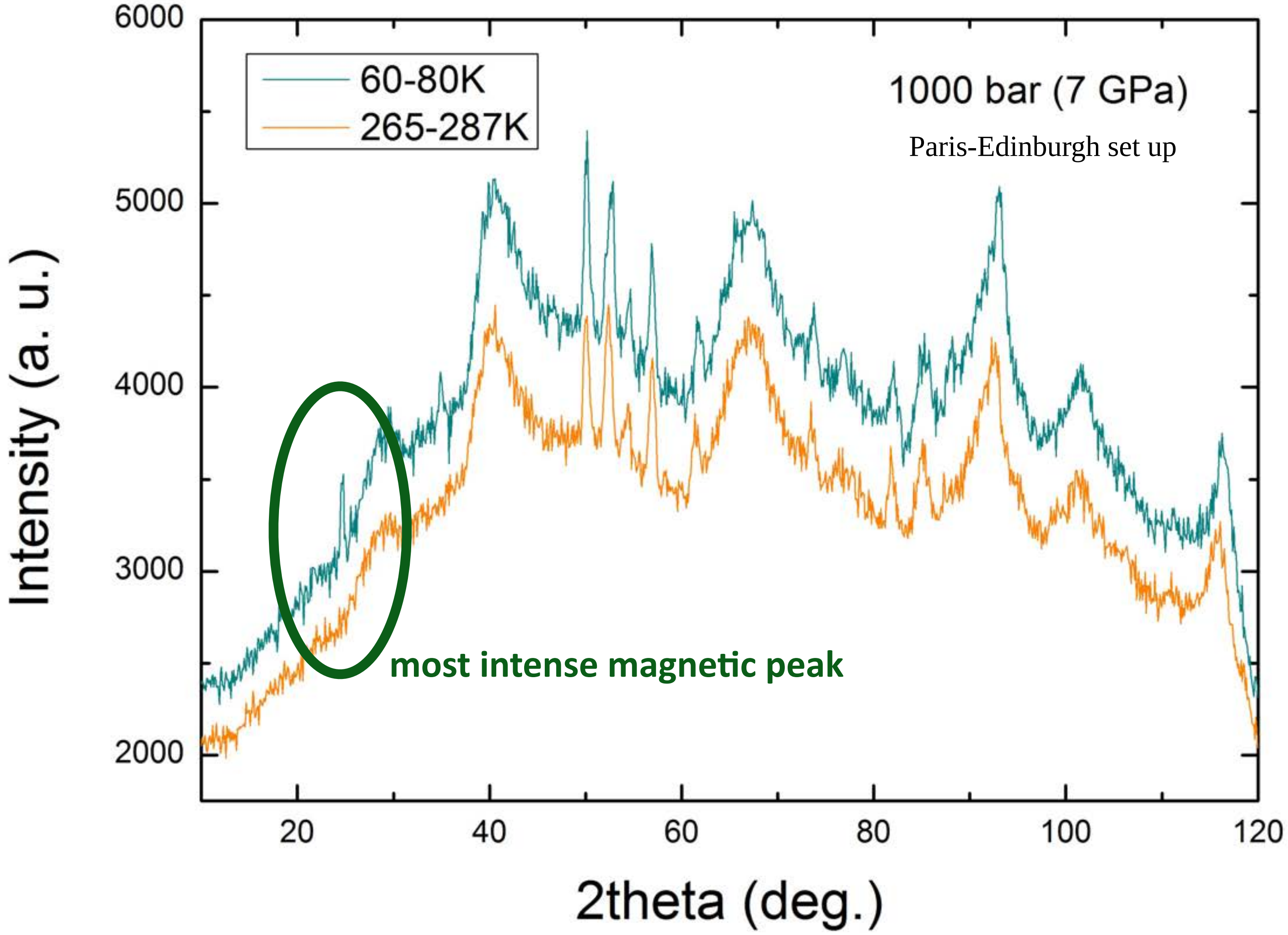


No phase transition observed until 10 GPa (limit of PE press)

Following the AFM order under pressure

$CrSb_2$

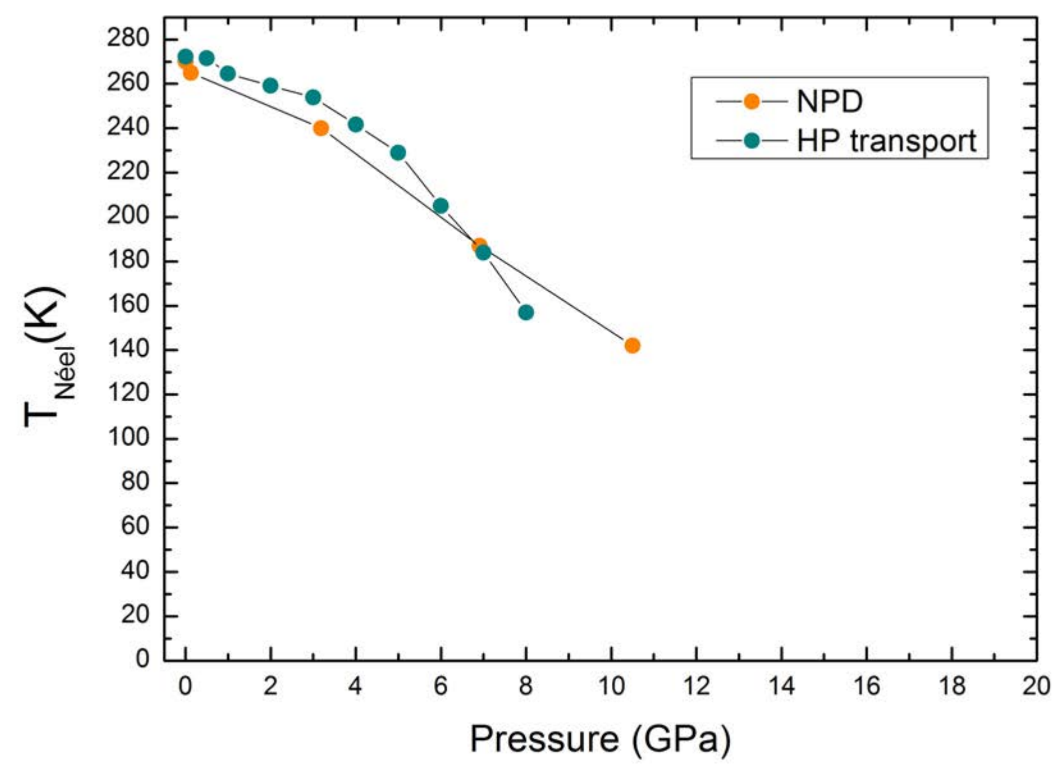
Neutron Powder Diffraction under pressure (D1B instrument)



No phase transition observed until 10 GPa (limit of PE press)

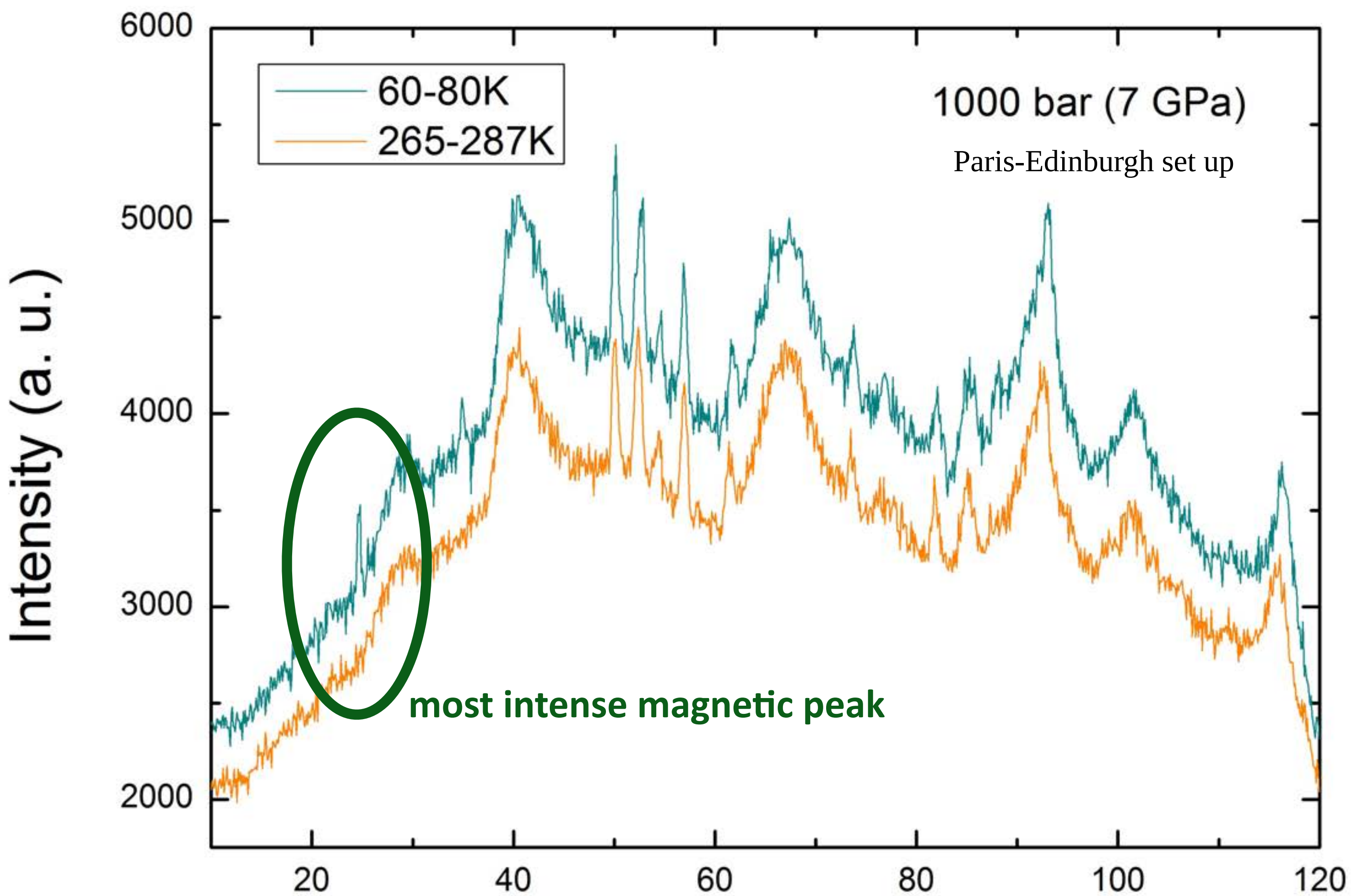
Following the AFM order under pressure

—> seems much difficult to kill (more pressure needed)



$CrSb_2$

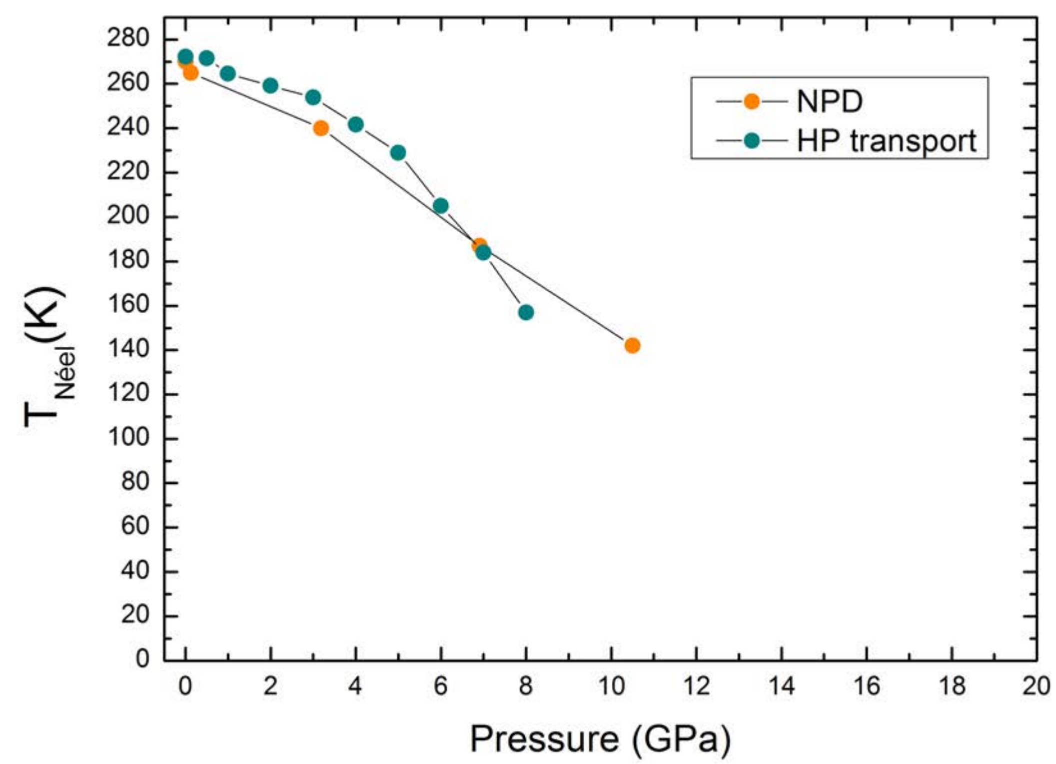
Neutron Powder Diffraction under pressure (D1B instrument)



No phase transition observed until 10 GPa (limit of PE press)

Following the AFM order under pressure

—> seems much difficult to kill (more pressure needed)



CrSb2, AF most stable solution (DFT Ruben W.)
—> strong AFM order

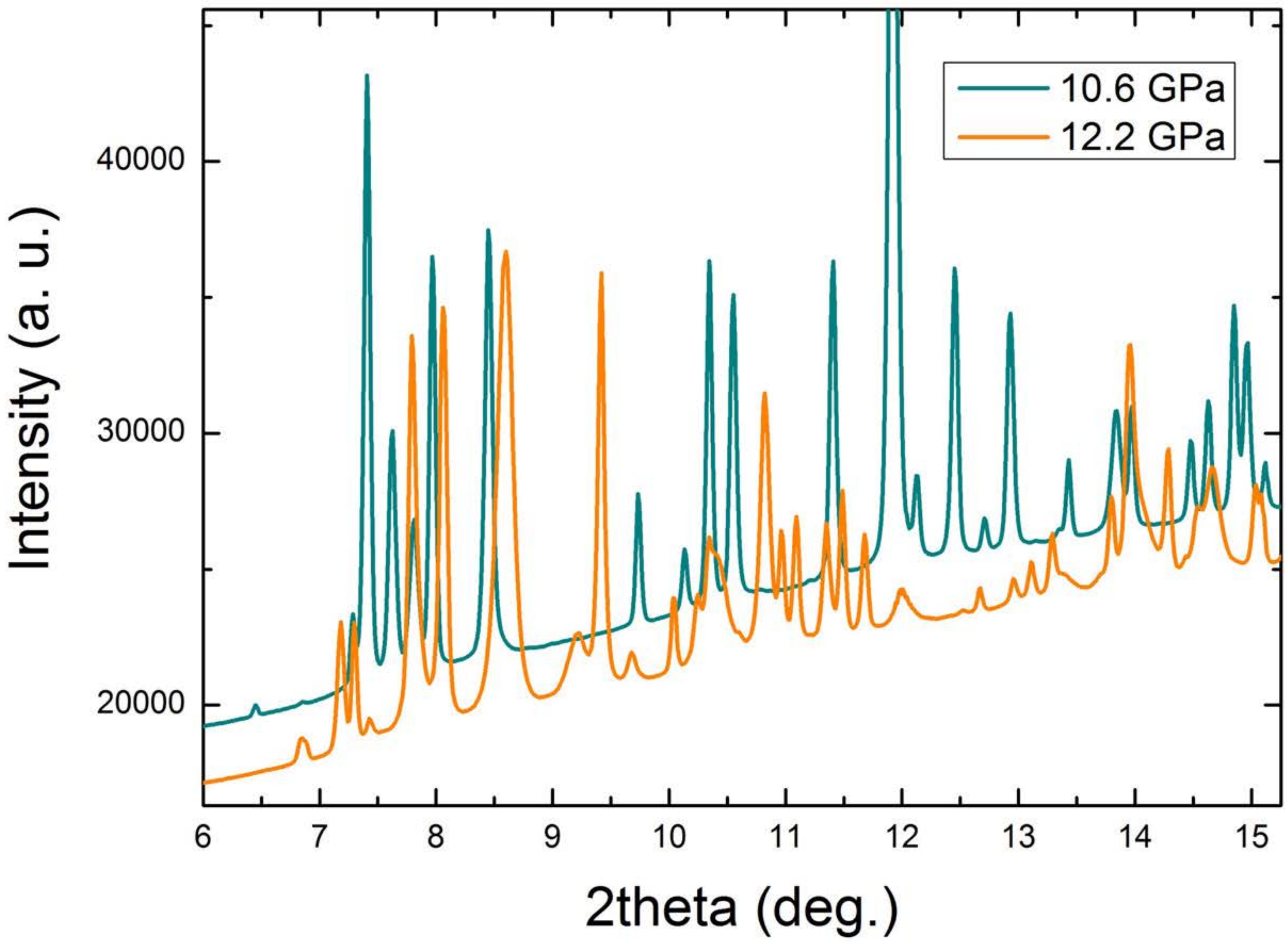
CrAs, AF and FM orders almost degenerated (DFT Ruben W.)
—> helicoidal order

$CrSb_2$

XRD /HP at RT (ESRF, id27)

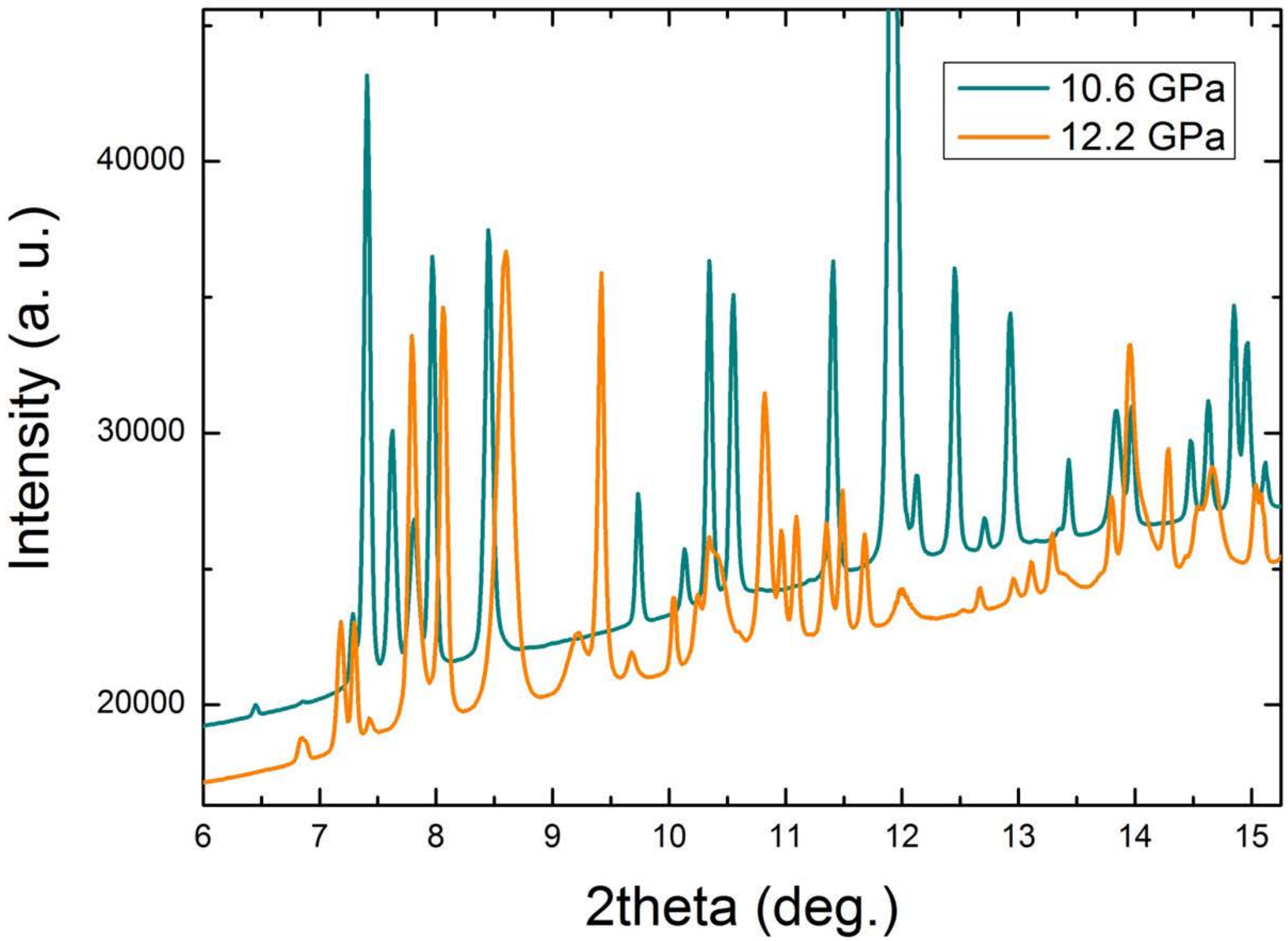
$CrSb_2$

XRD /HP at RT (ESRF, id27)



$CrSb_2$

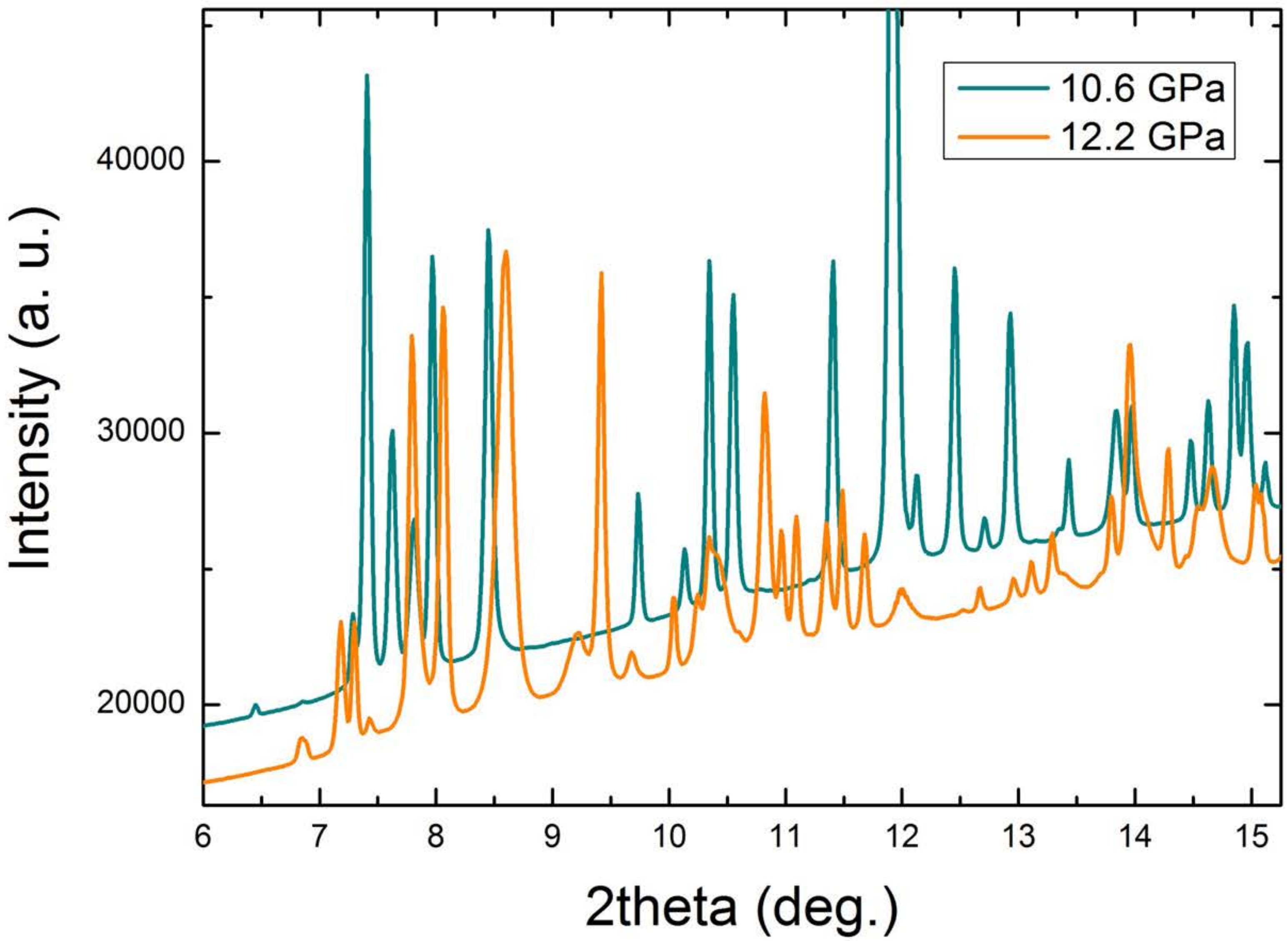
XRD /HP at RT (ESRF, id27)



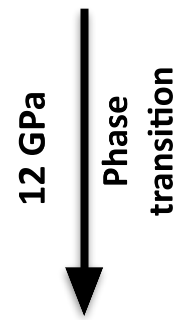
CrSb2 marcasite-type structure

$CrSb_2$

XRD /HP at RT (ESRF, id27)



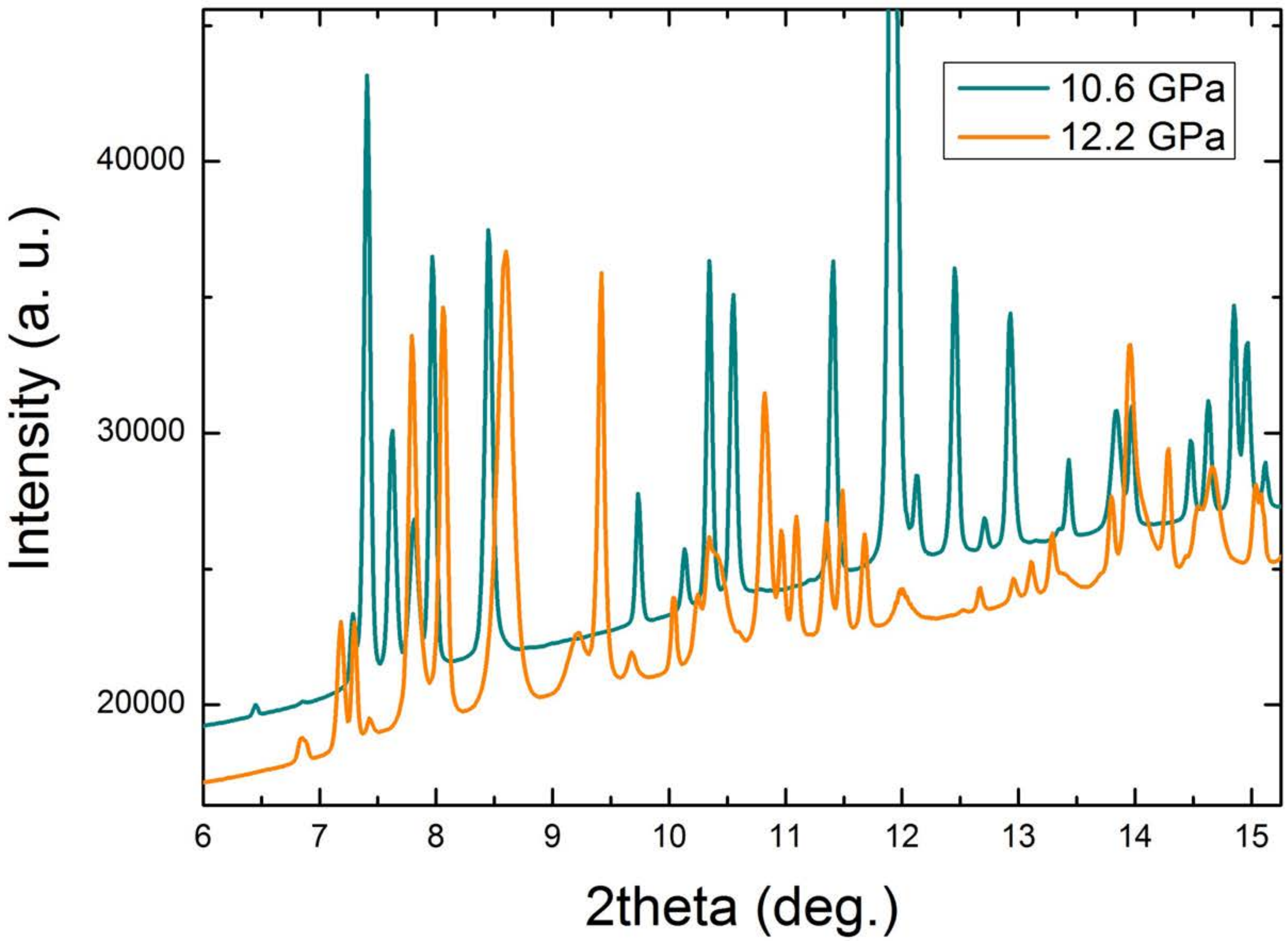
CrSb2 marcasite-type structure



??

$CrSb_2$

XRD /HP at RT (ESRF, id27)

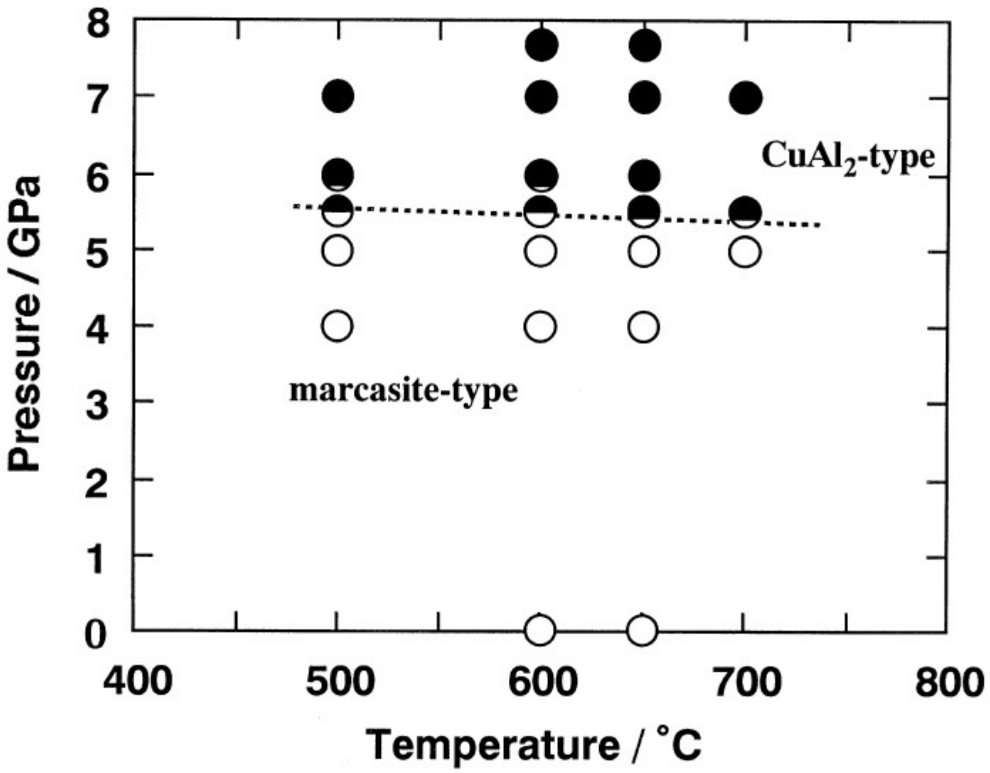


CrSb2 marcasite-type structure

12 GPa

Phase transition

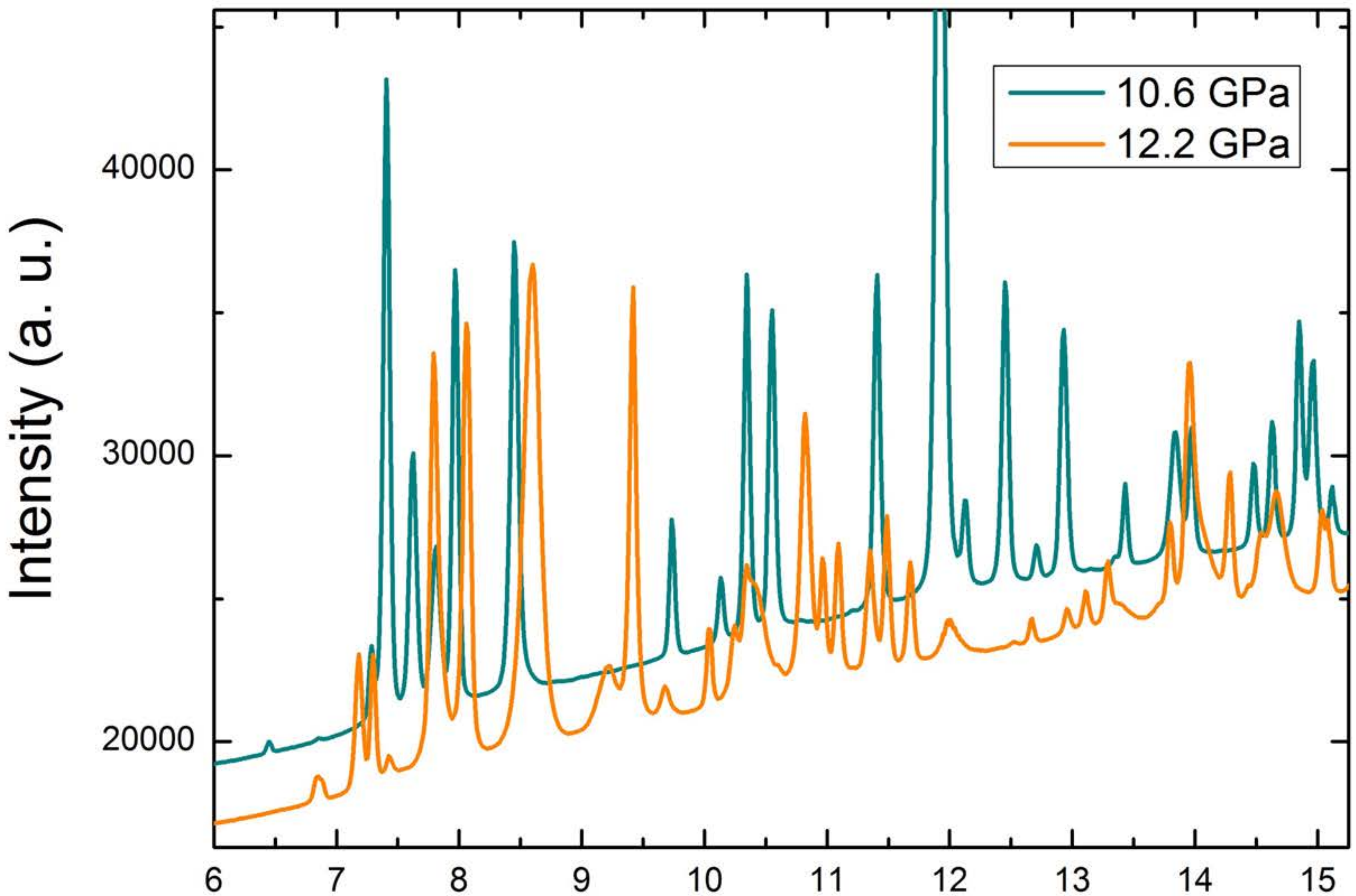
??



auteurs

$CrSb_2$

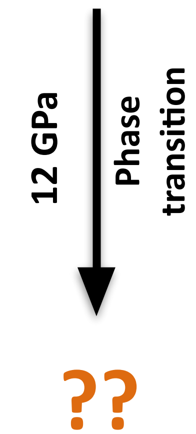
XRD /HP at RT (ESRF, id27)

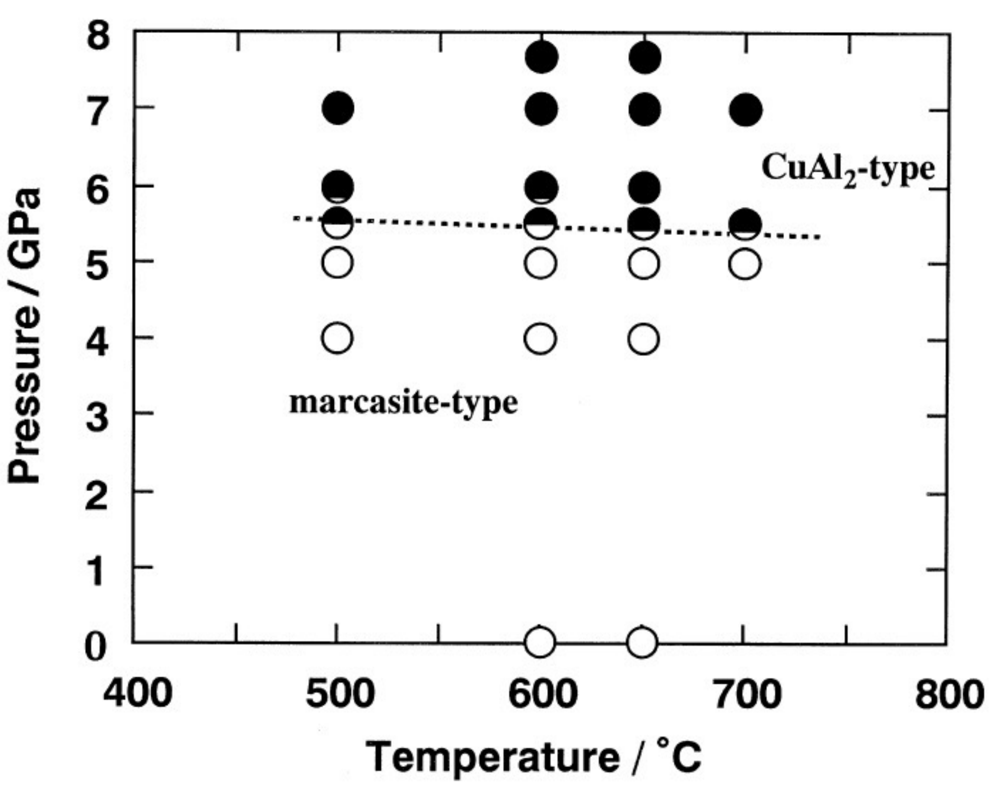


<u>First refinement tried with :</u>

CuAl2-type + deformed Marcasite-type = not bad but needs other(s) phase(s)

CrSb2 marcasite-type structure

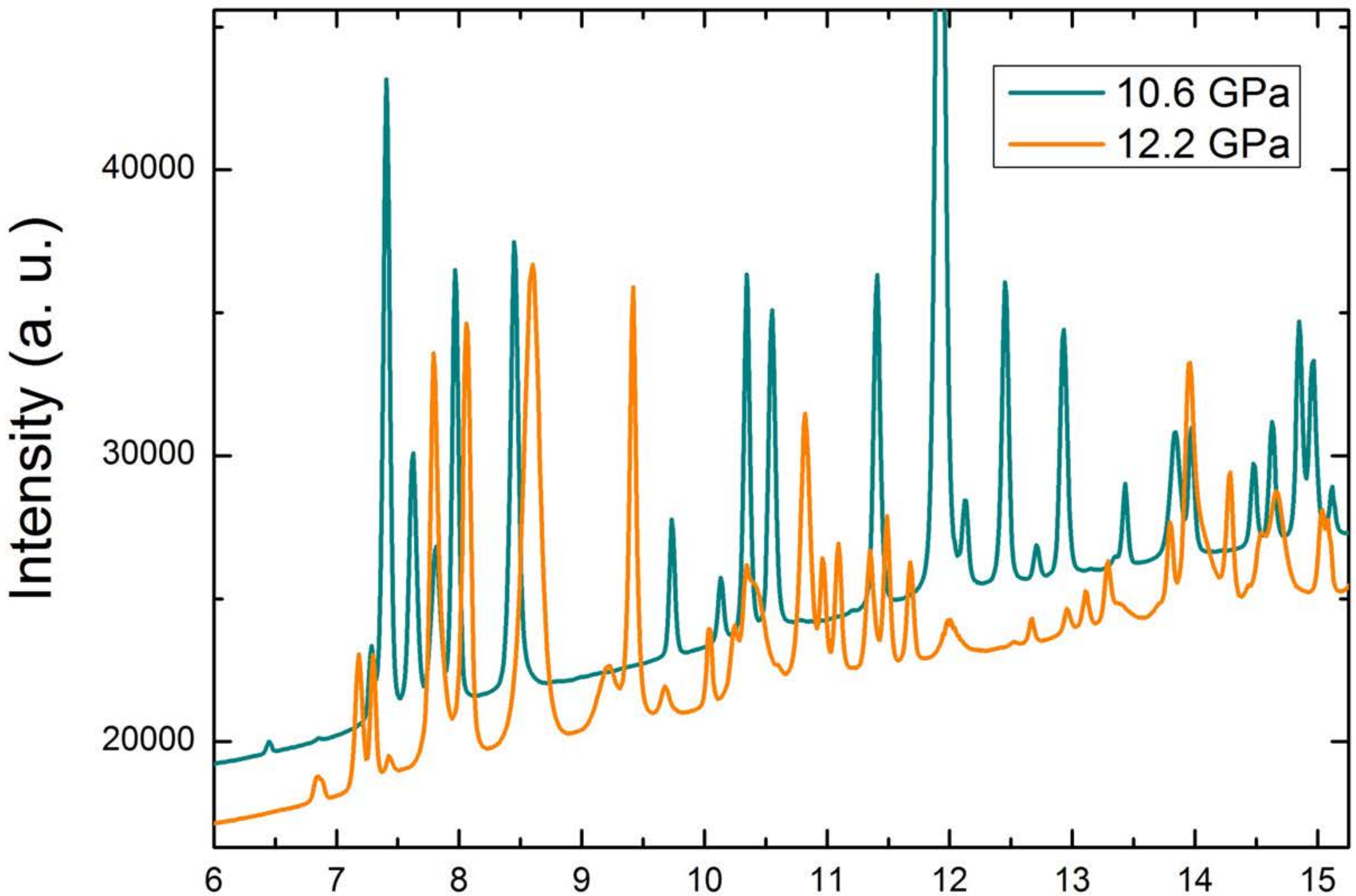




auteurs

$CrSb_2$

XRD /HP at RT (ESRF, id27)

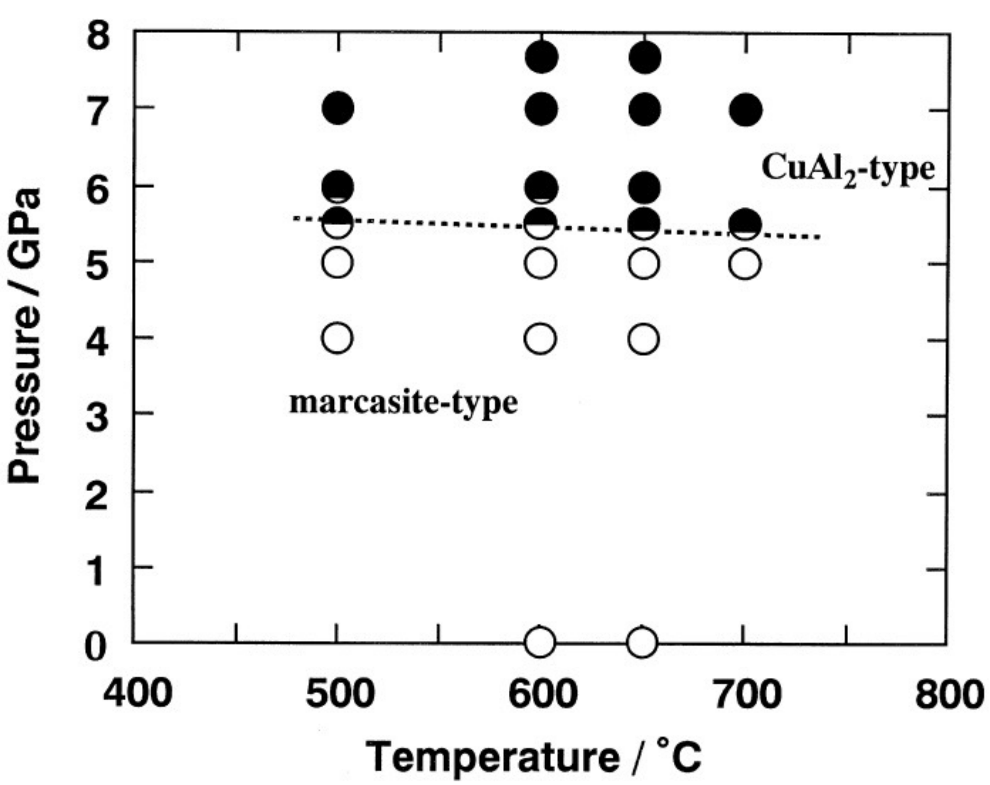


CrSb2 marcasite-type structure

12 GPa

Phase transition

??



<u>First refinement tried with :</u>

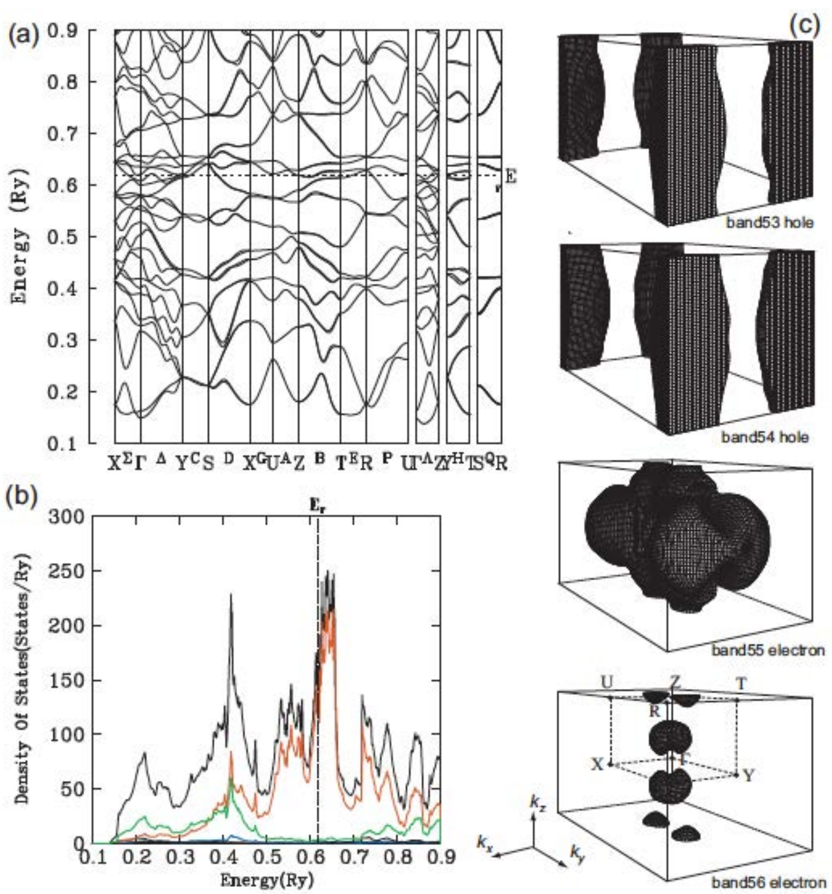
CuAl2-type + deformed Marcasite-type = not bad but needs other(s) phase(s)

Metallic and FM

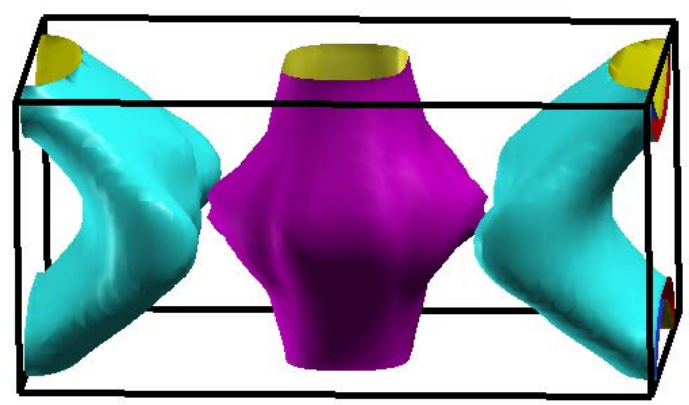
auteurs

$CrSb_2$

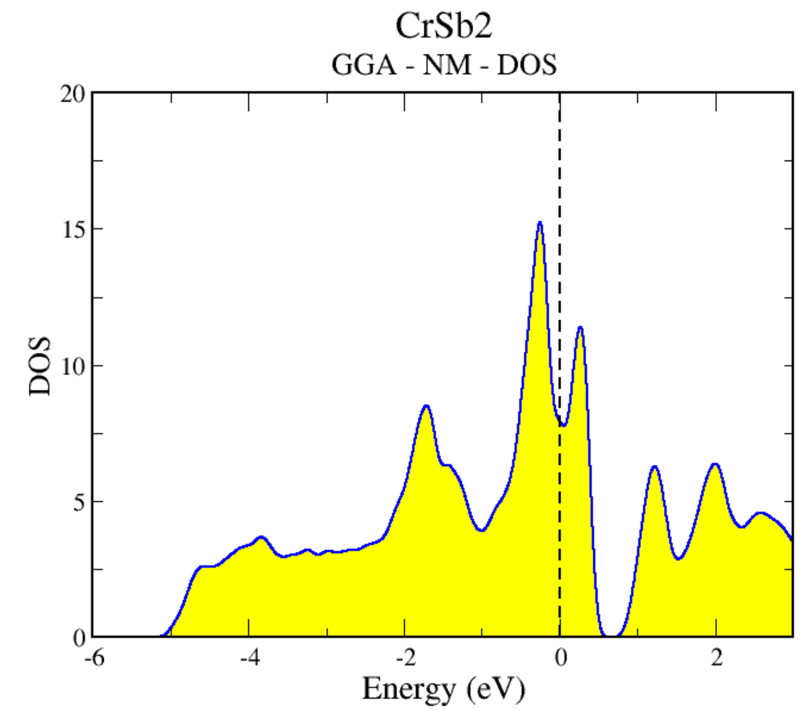
CrAs motivation



CrAs

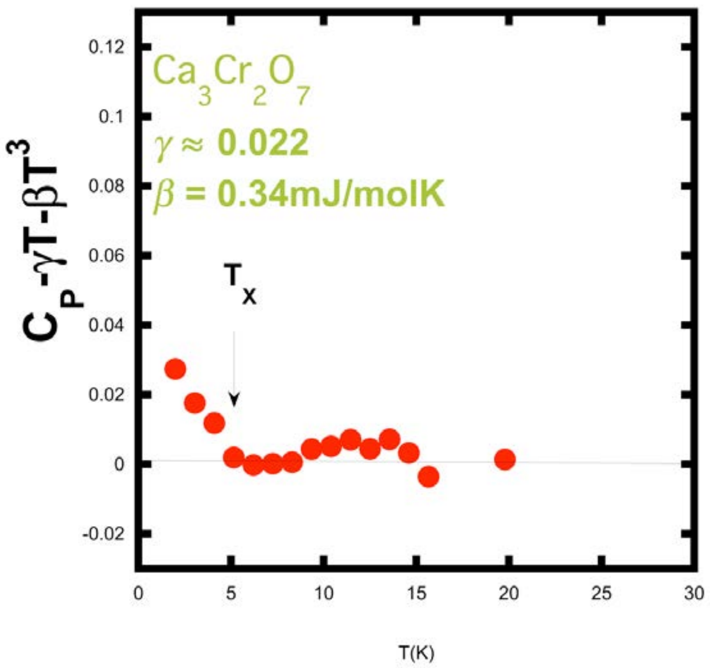


CrSb2

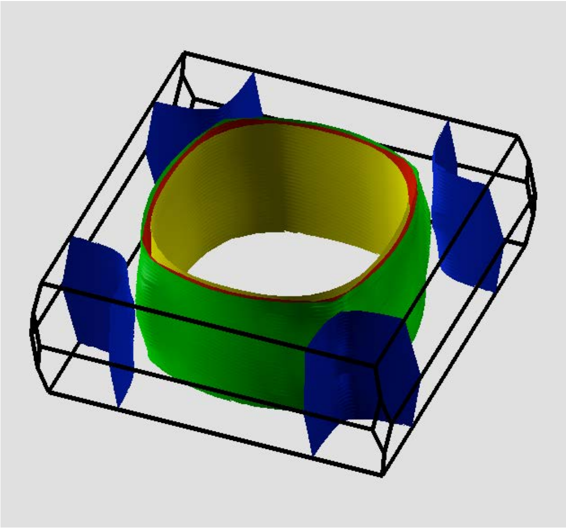


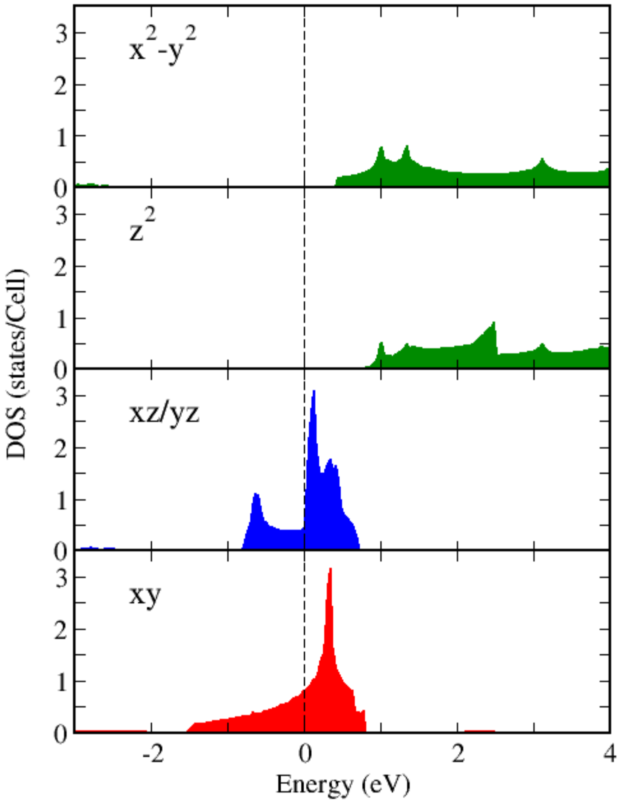
DIAPO QUESTION

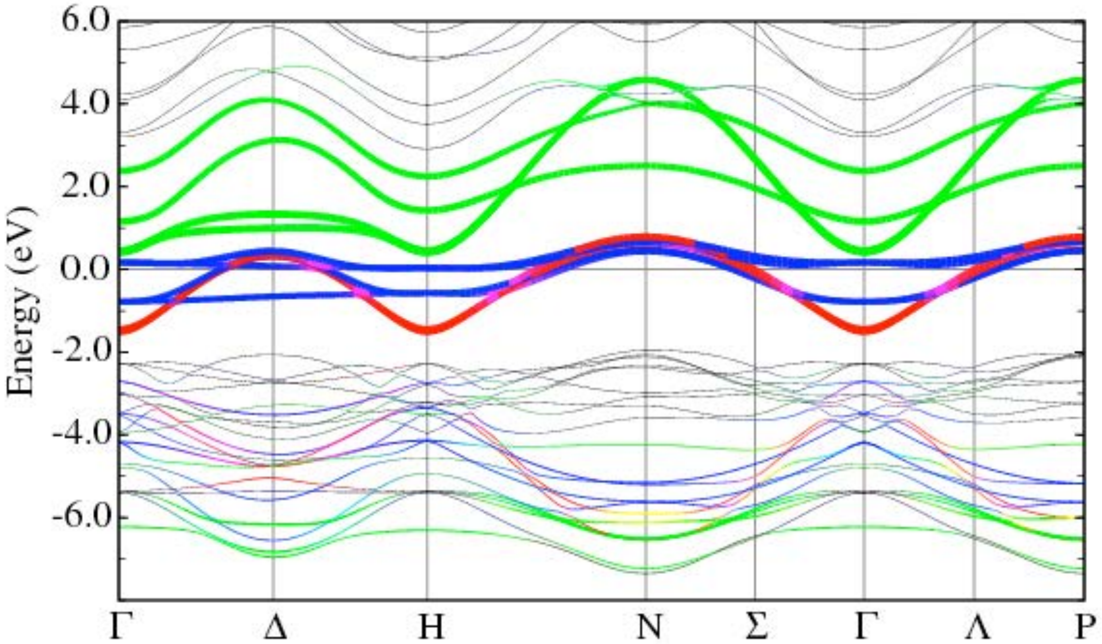
AJOUTER MAG-CURIE POUR VOIR CE PIC À BASSE T

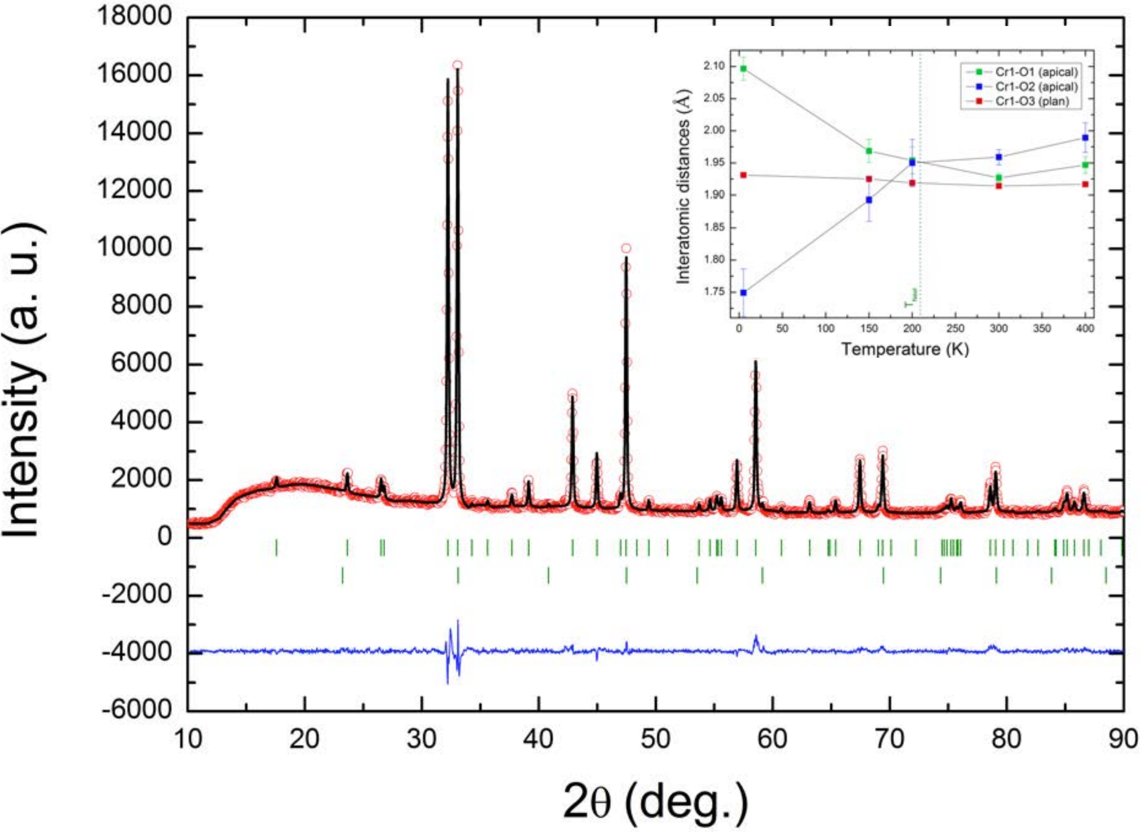


Sr3Cr2O7-2K-Non Magnetic

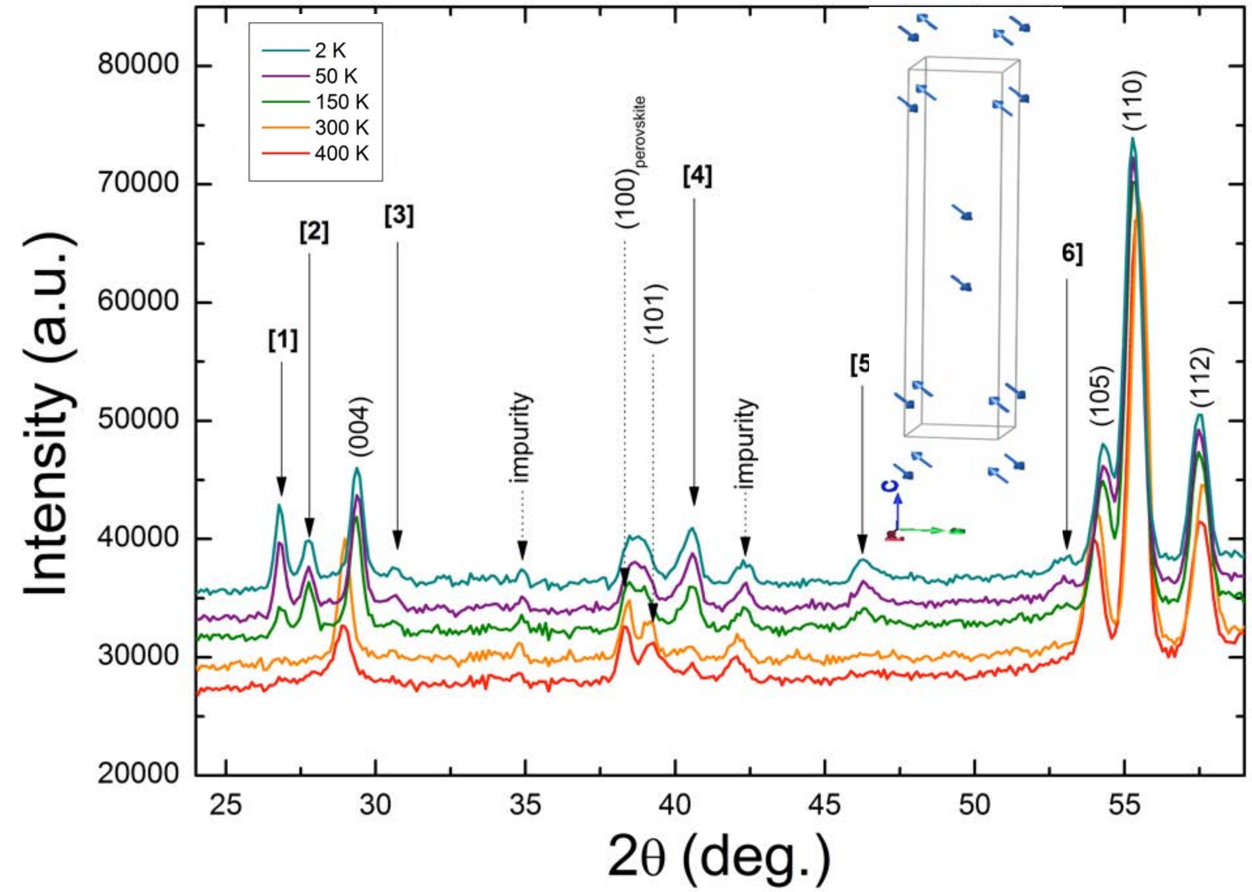




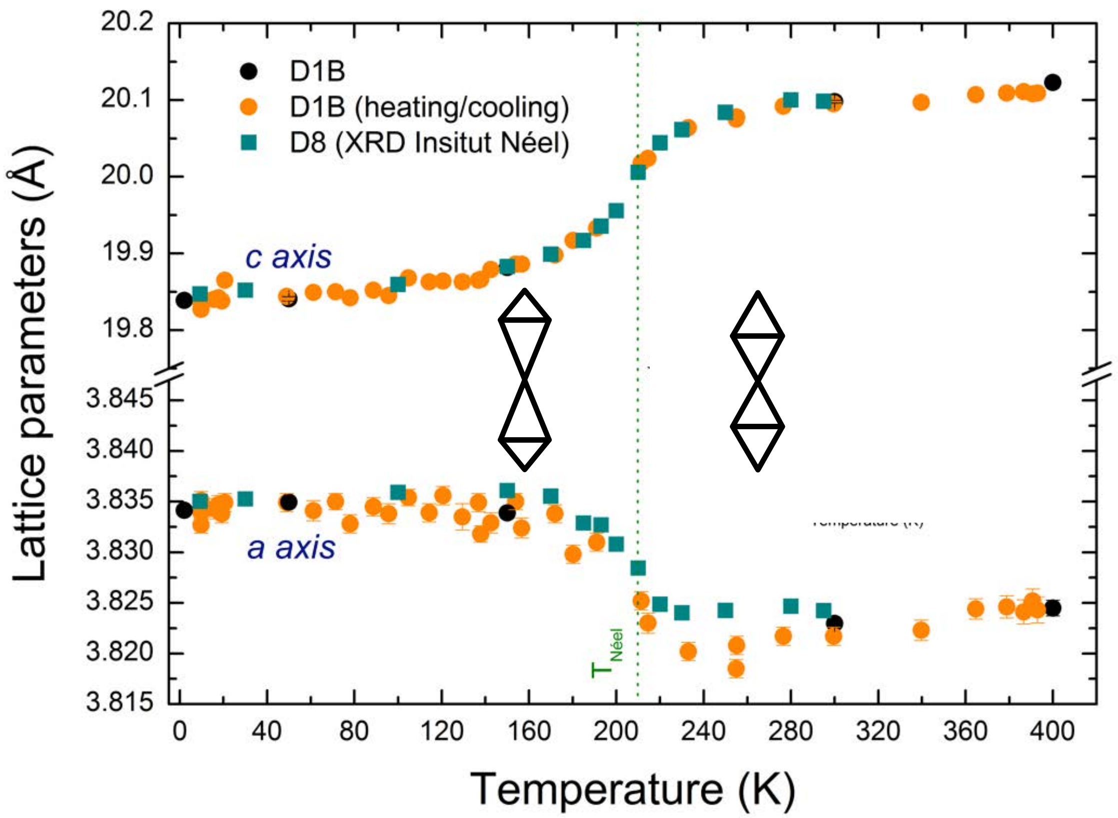




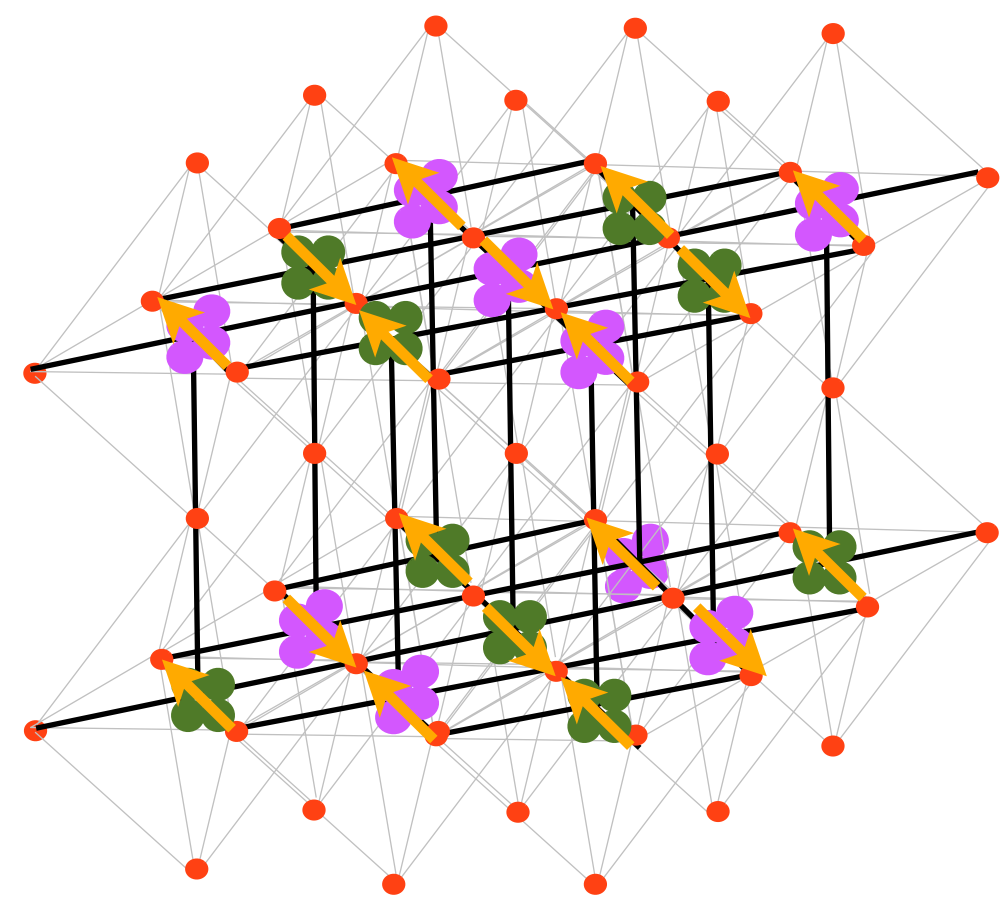
Intensity (a. u.)
2θ (deg.)
Interatomic distances (Å)
Temperature (K)
Cr1-O1 (apical)
Cr1-O2 (apical)
Cr1-O3 (plan)



Intensity (a.u.)
2θ (deg.)
2 K
50 K
150 K
300 K
400 K
[1]
[2]
[3]
[4]
[5
6]
(004)
impurity
(100)perovskite
(101)
impurity
(105)
(110)
(112)
c



Lattice parameters (Å)
Temperature (K)
D1B
D1B (heating/cooling)
D8 (XRD Insitut Néel)
c axis
a axis
T Néel



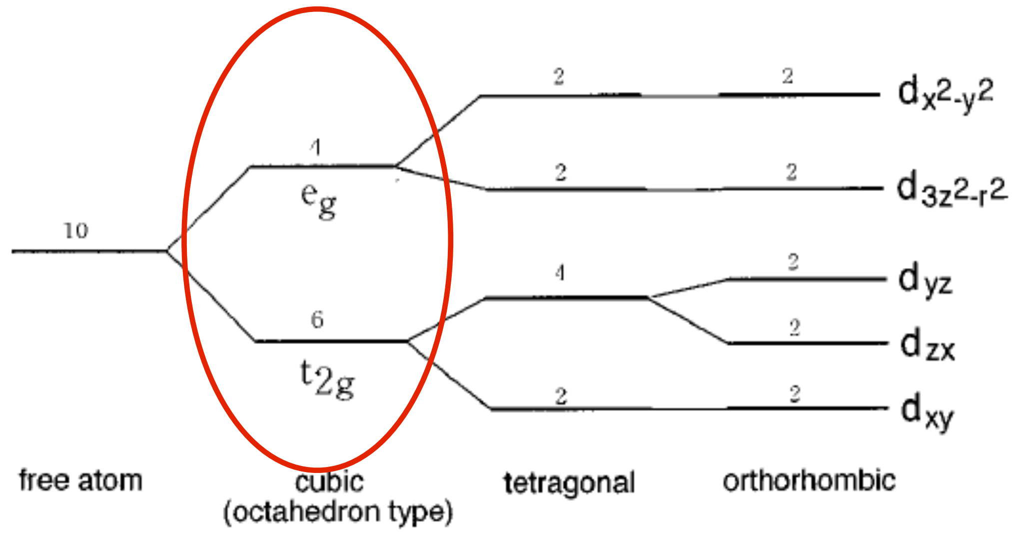
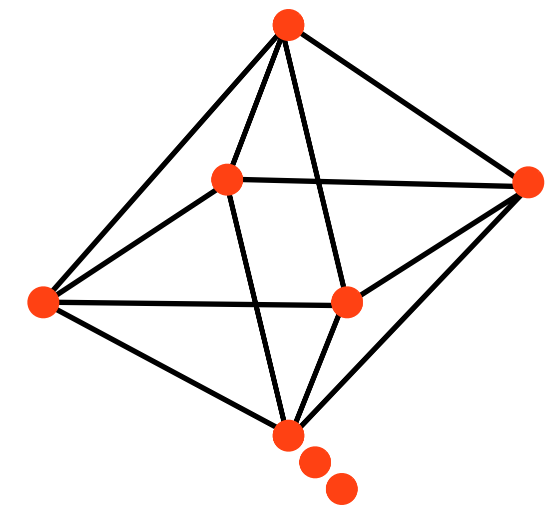
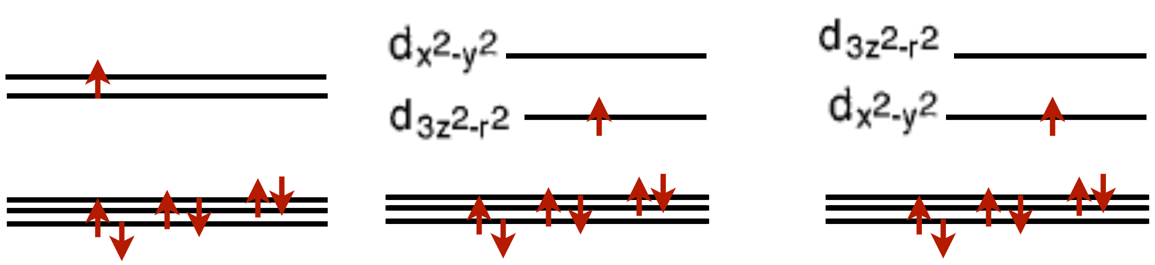
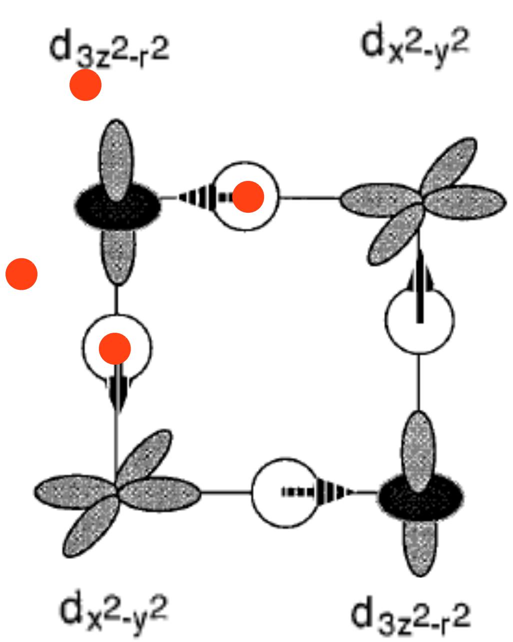


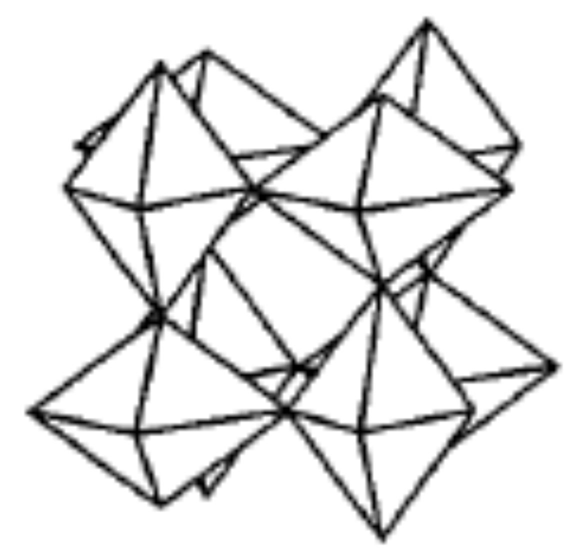
FIG. 2. Crystal-field splitting of 3*d* orbitals under cubic, tetragonal, and orthorhombic symmetries. The numbers cited near the levels are the degeneracy including spins.

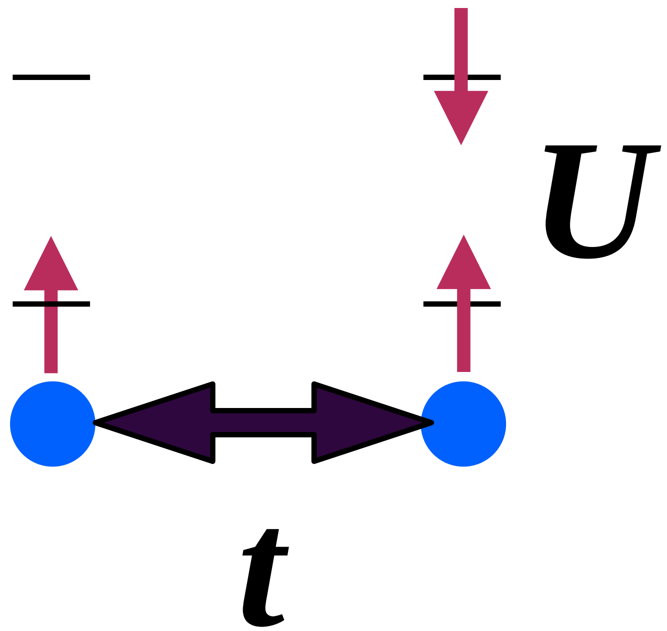


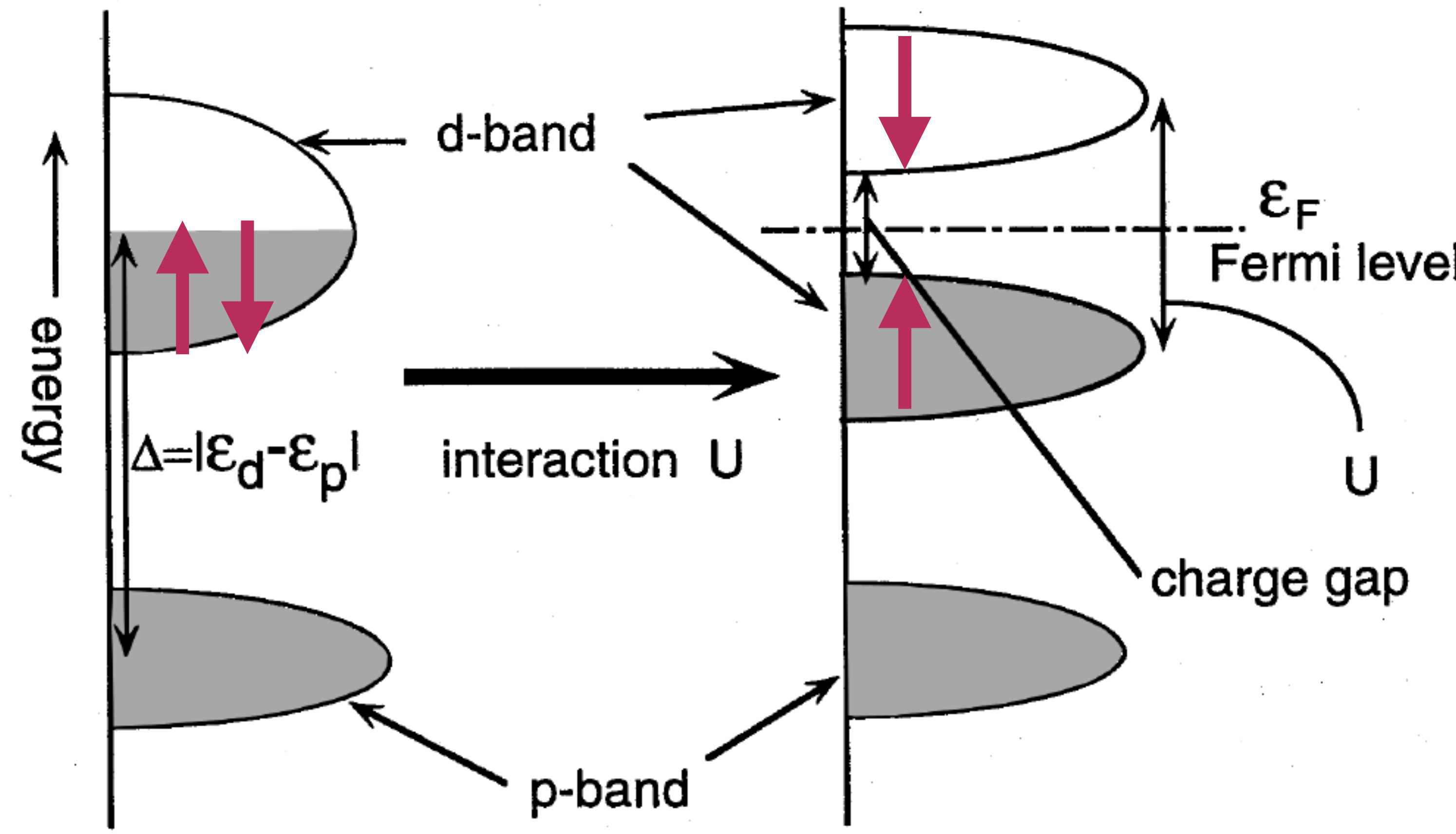
***d*⁷**











(a) Mott-Hubbard Insulator

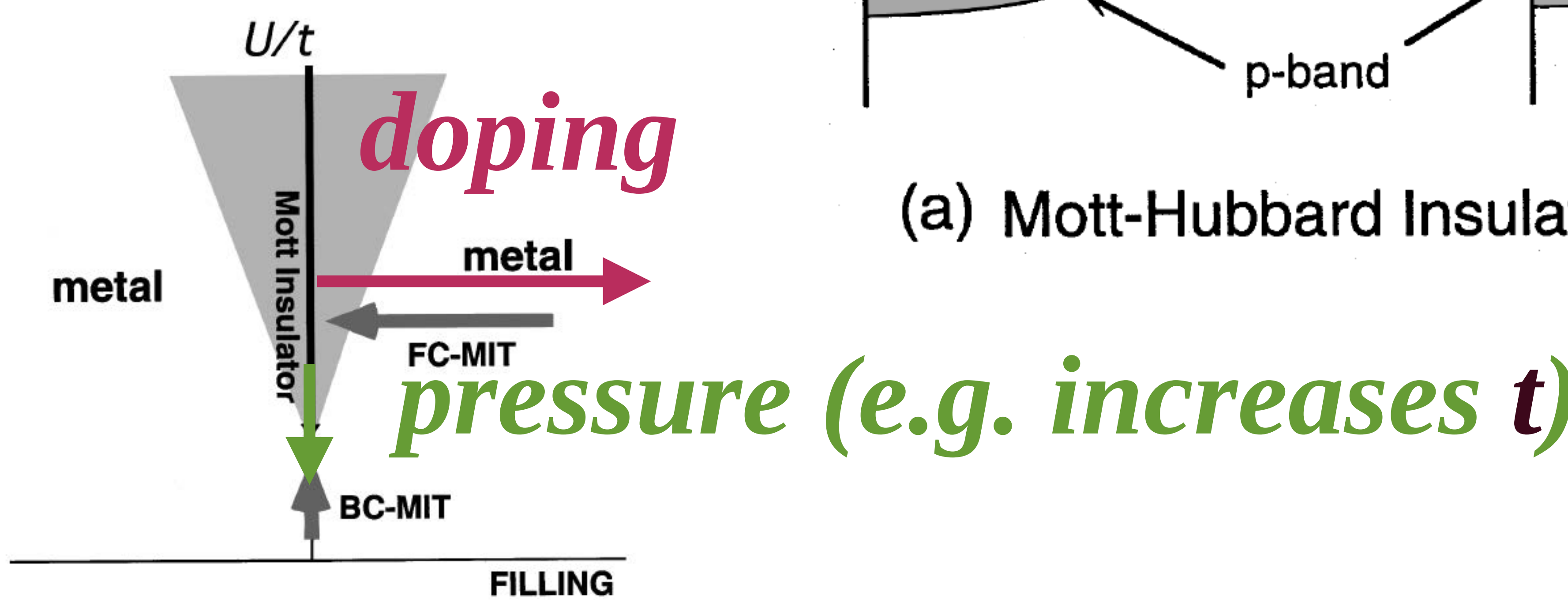


FIG. 1. Metal-insulator phase diagram based on the Hubbard model in the plane of U/t and filling n. The shaded area is in principle metallic but under the strong influence of the metal-insulator transition, in which carriers are easily localized by extrinsic forces such as randomness and electron-lattice coupling. Two routes for the MIT (metal-insulator transition) are shown: the FC-MIT (filling-control MIT) and the BC-MIT (bandwidth-control MIT).

Superexchange

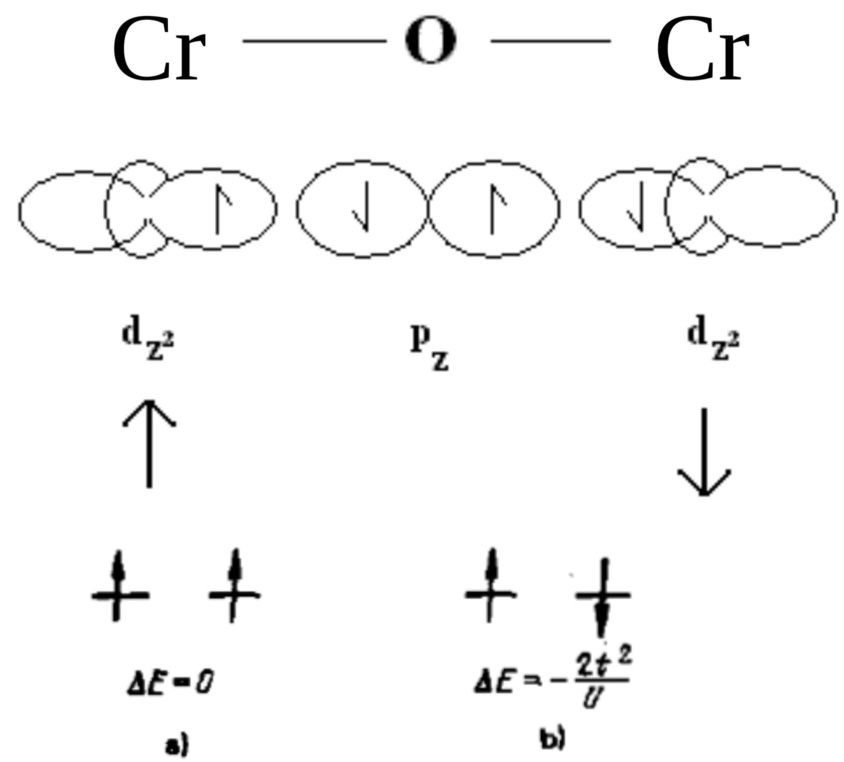


FIG. 10. Scheme for superexchange in the nondegenerate case. Shown here is the energy increase due to virtual transitions of an electron to a neighboring center. An antiparallel orientation of the spins is seen to be preferred from the energy standpoint.

Same orbitals

Different orbitals

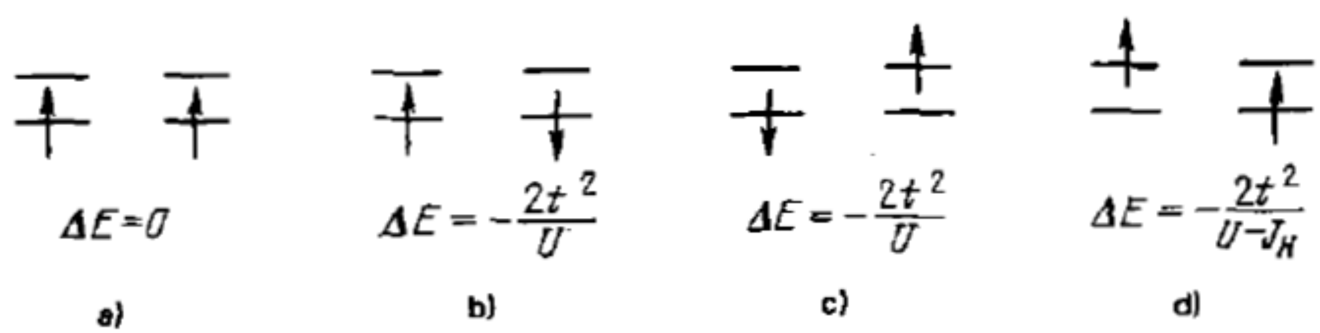
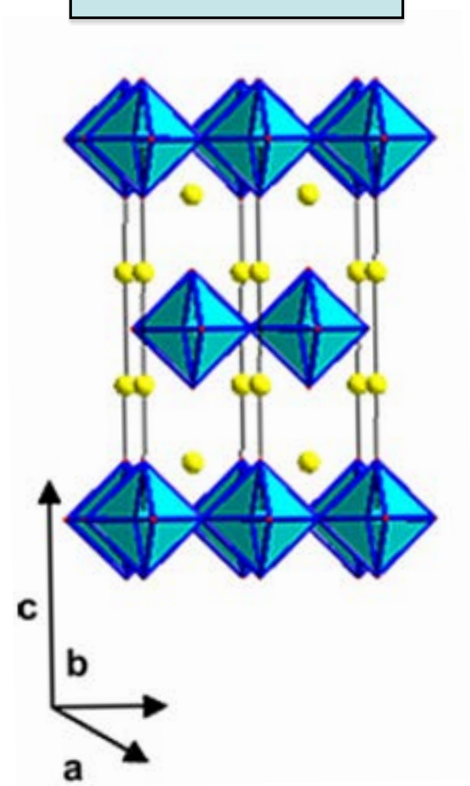


FIG. 12. Superexchange in the case of twofold-degenerate orbitals. Shown here is the energy increase if only diagonal transitions are possible ($t_{11} = t_{22} + t$, $t_{12} = 0$). Intraatomic (Hund) exchange is also taken into account.

Sr_2CrO_4

Sr214
I4/mmm

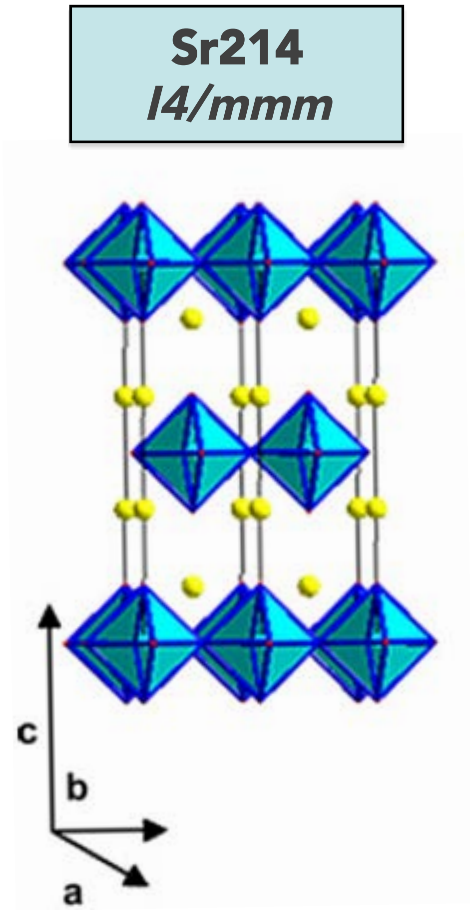


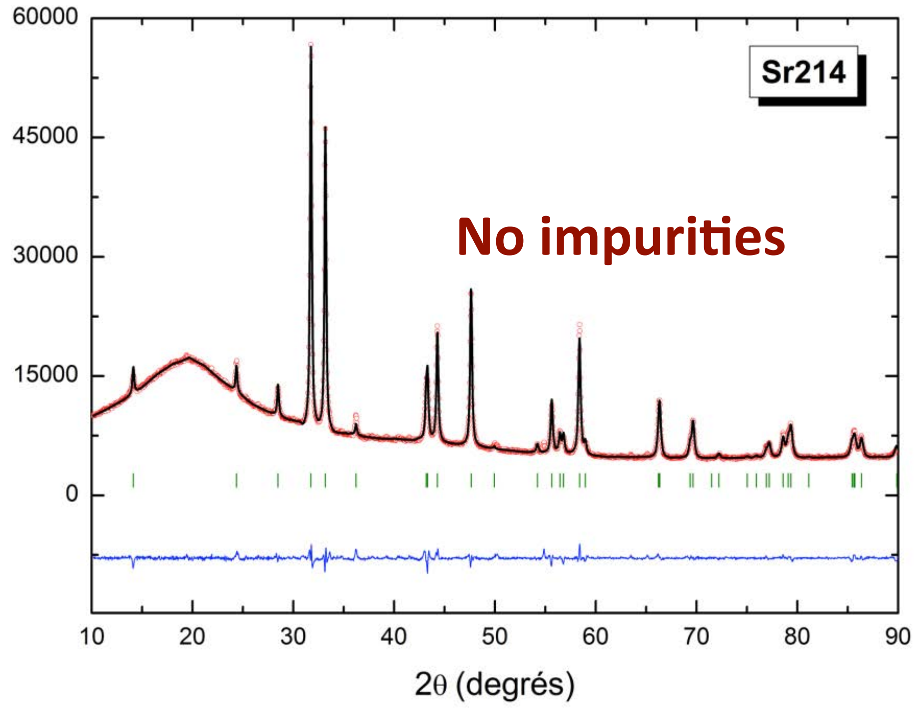
a ~ 3.81 Å

c ~ 12.52 Å

Sr_2CrO_4

X-ray diffraction



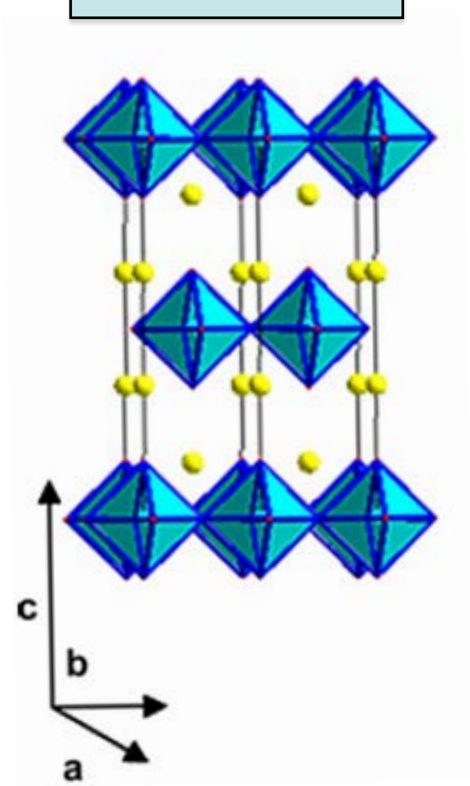


a ~ 3.81 Å

c ~ 12.52 Å

Sr_2CrO_4

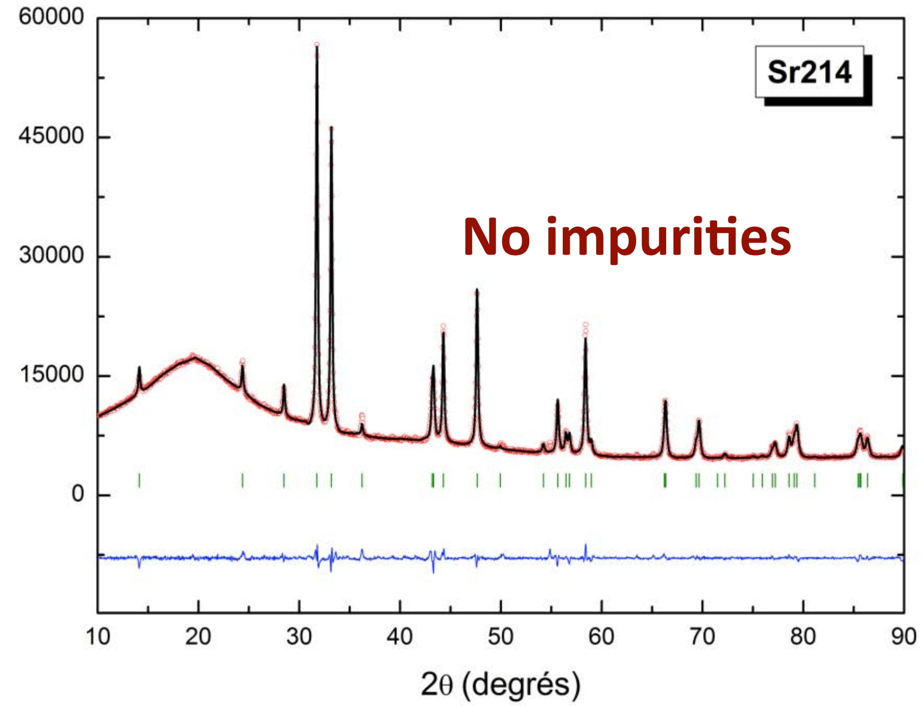
Sr214
I4/mmm



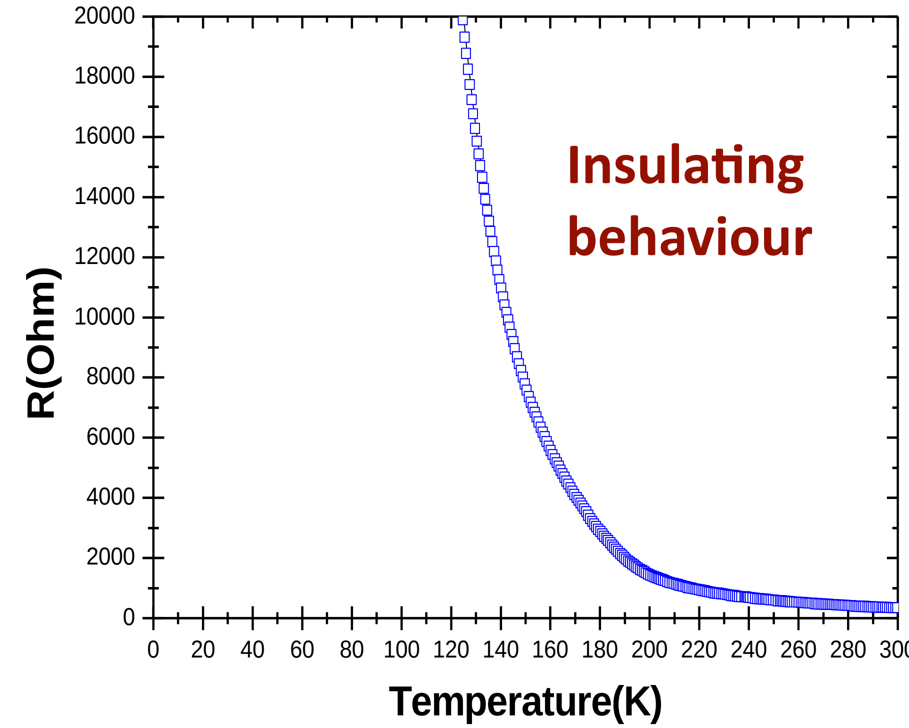
a ~ 3.81 Å

c ~ 12.52 Å

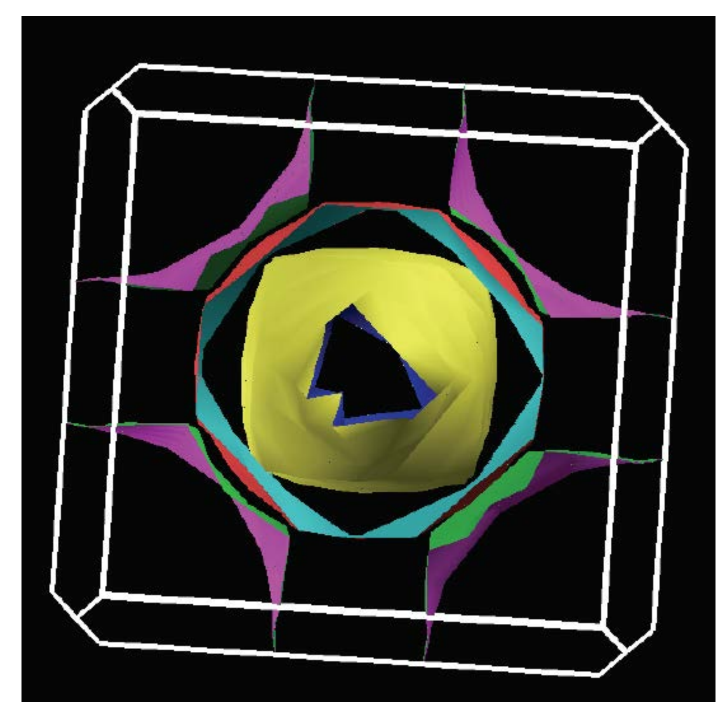
X-ray diffraction



Transport measurement

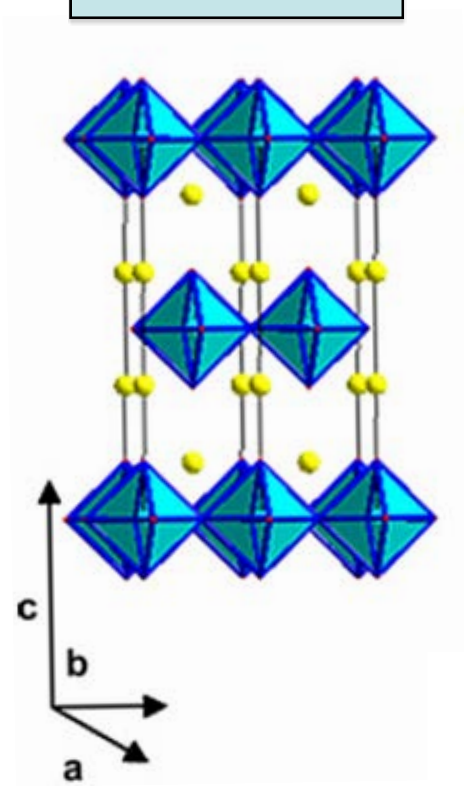


Calculations give metallic (without magnetism & U)



Sr_2CrO_4

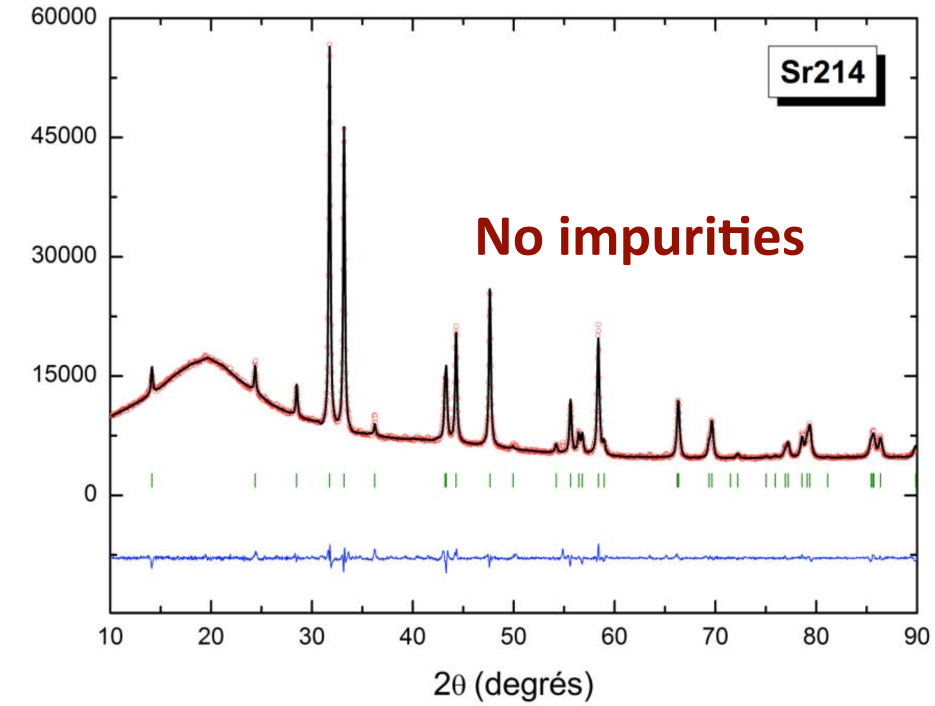
Sr214
I4/mmm



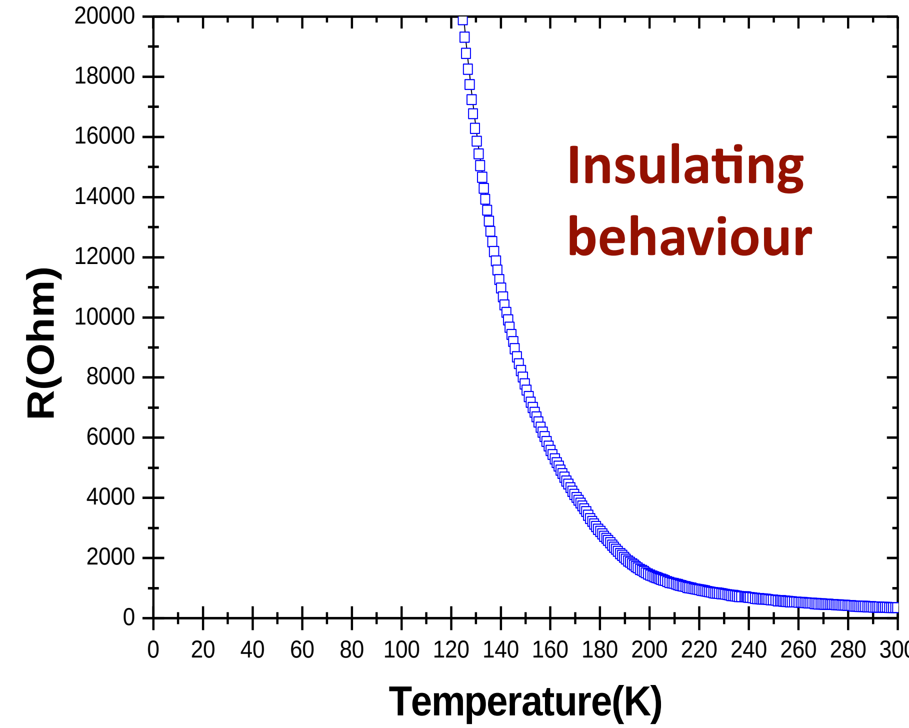
a ~ 3.81 Å

c ~ 12.52 Å

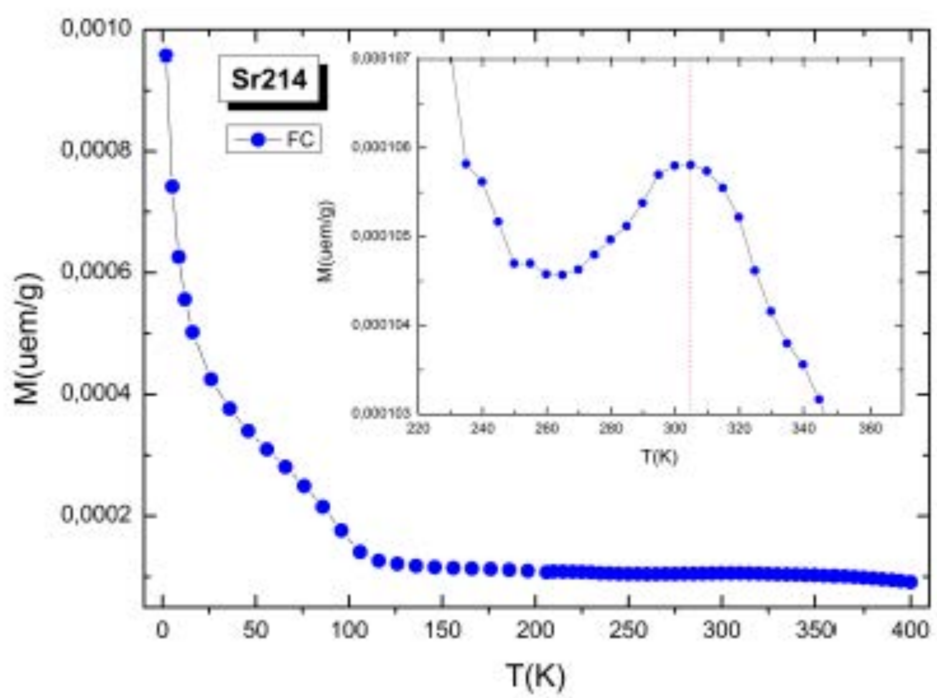
X-ray diffraction



Transport measurement



Magnetic measurement



AFM

T_N = 305 K

Sr_2CrO_4

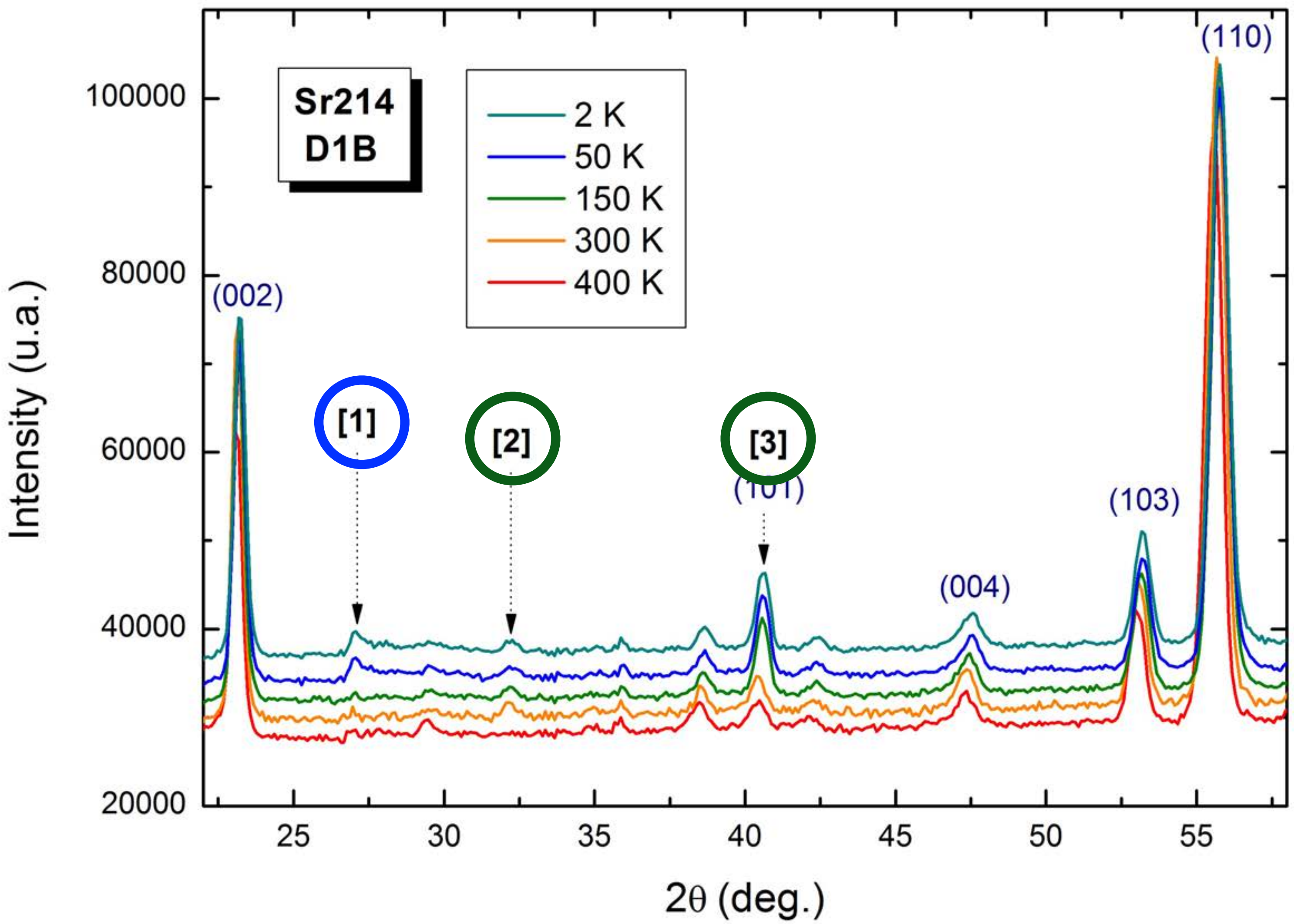
Neutron Powder diffraction

ILL, D1B & D2B instruments

Sr_2CrO_4

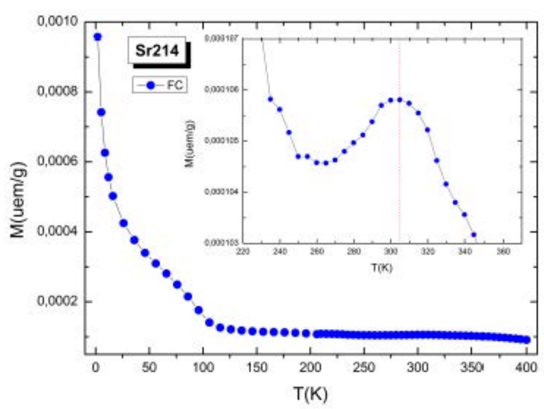
Neutron Powder diffraction

ILL, D1B & D2B instruments



Magnetic peaks appearance

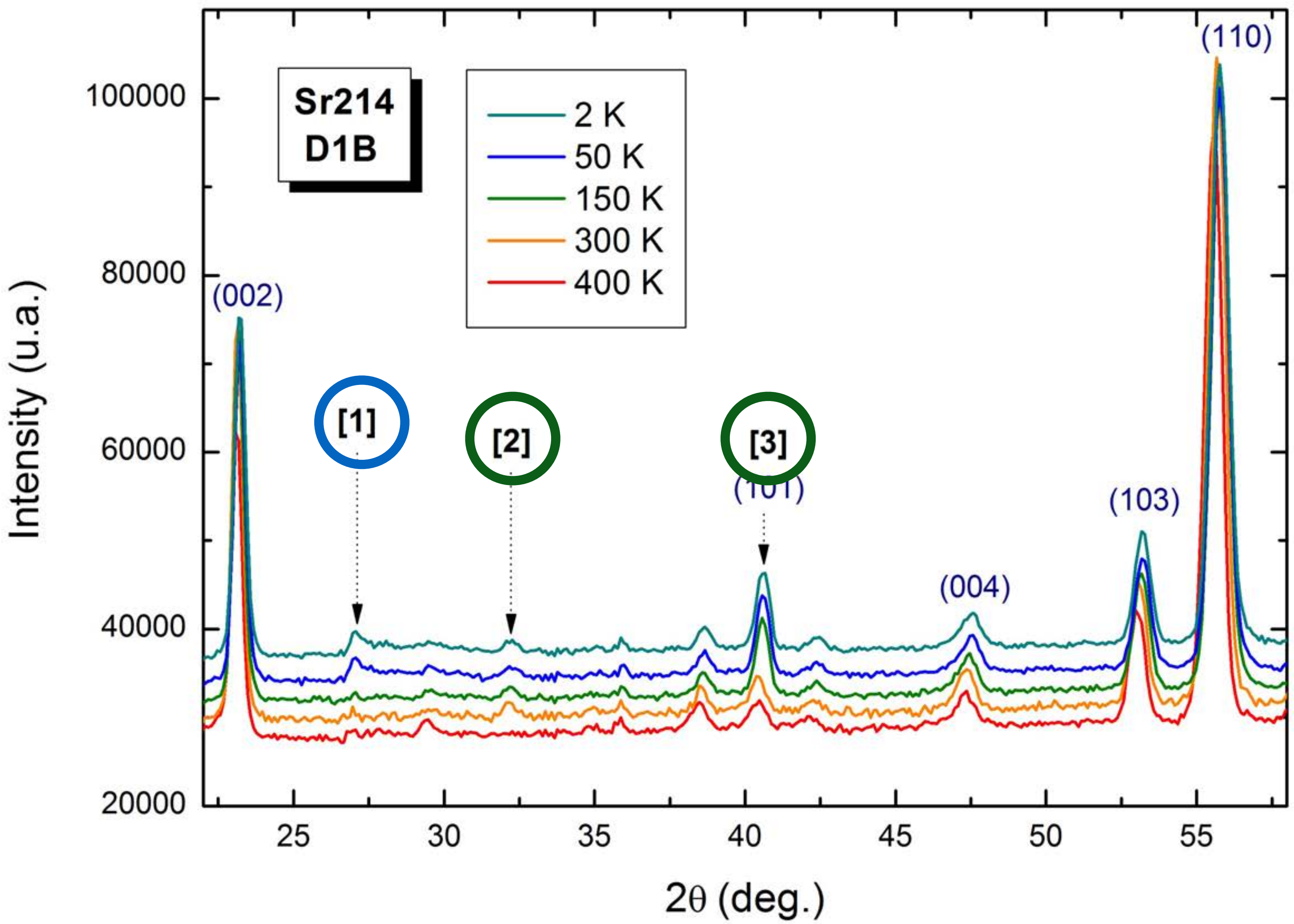
- **Number [2] and [3] : OK with T_N = 305 K**



Sr_2CrO_4

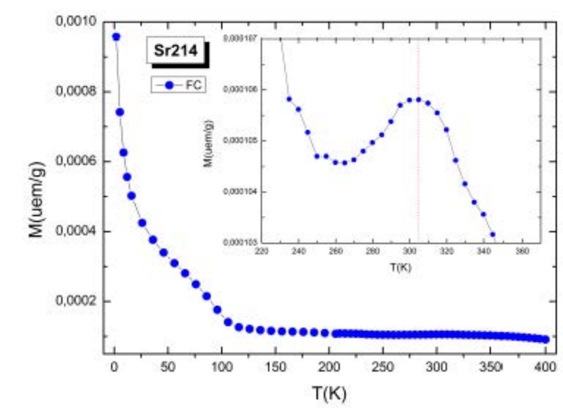
Neutron Powder diffraction

ILL, D1B & D2B instruments



Magnetic peaks appearance

- **Number [2] and [3] : OK with T_N = 305 K**



- **Number [1] : ?? Spin reorientation?**

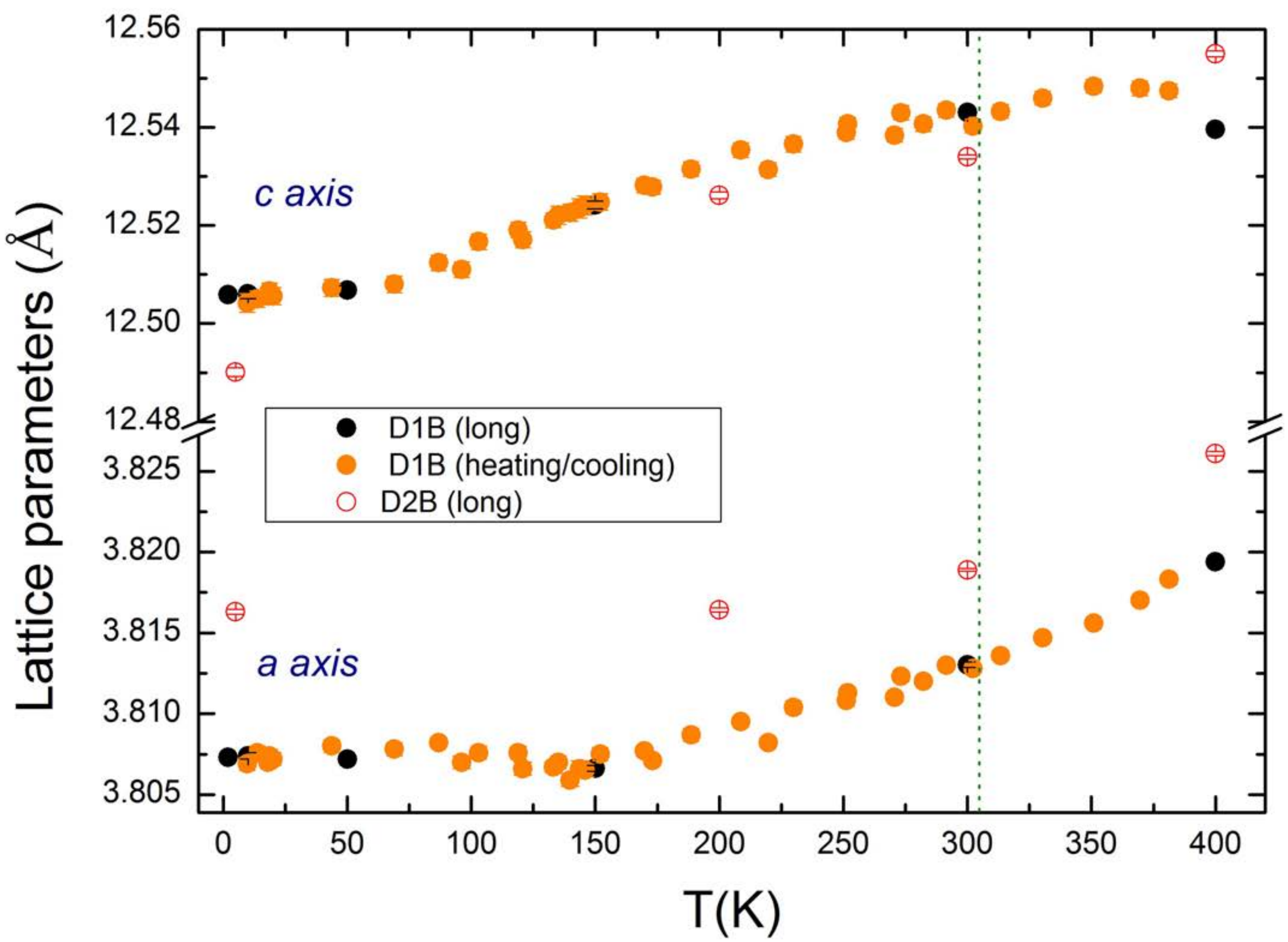
Magnetic structure difficult to determine, work in progress..

Calculs give F <-> AF —> Helicoidal structure?

Sr_2CrO_4

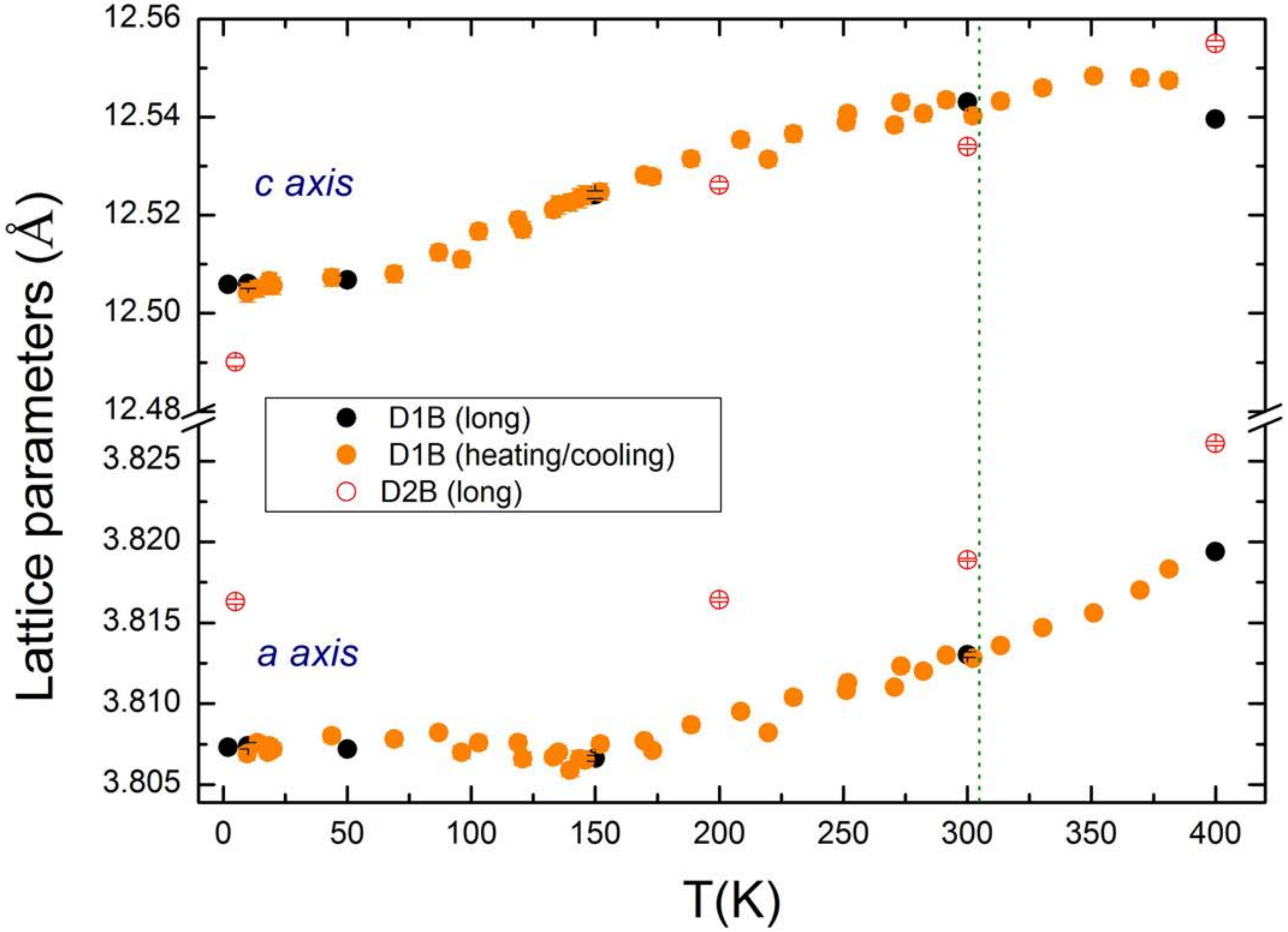
Neutron Powder diffraction

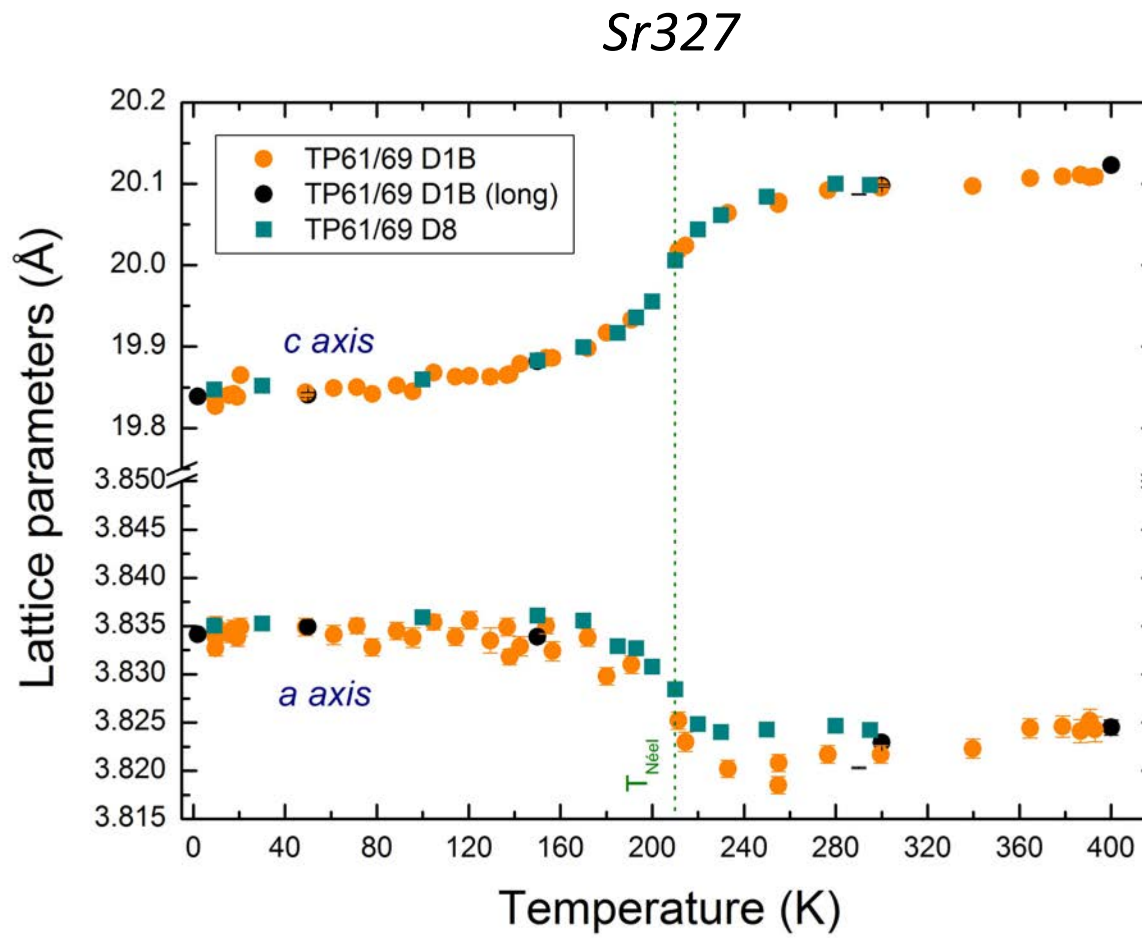
ILL, D1B & D2B instruments



Sr_2CrO_4

Neutron Powder diffraction
ILL, D1B & D2B instruments





Sr_2CrO_4

Neutron Powder diffraction

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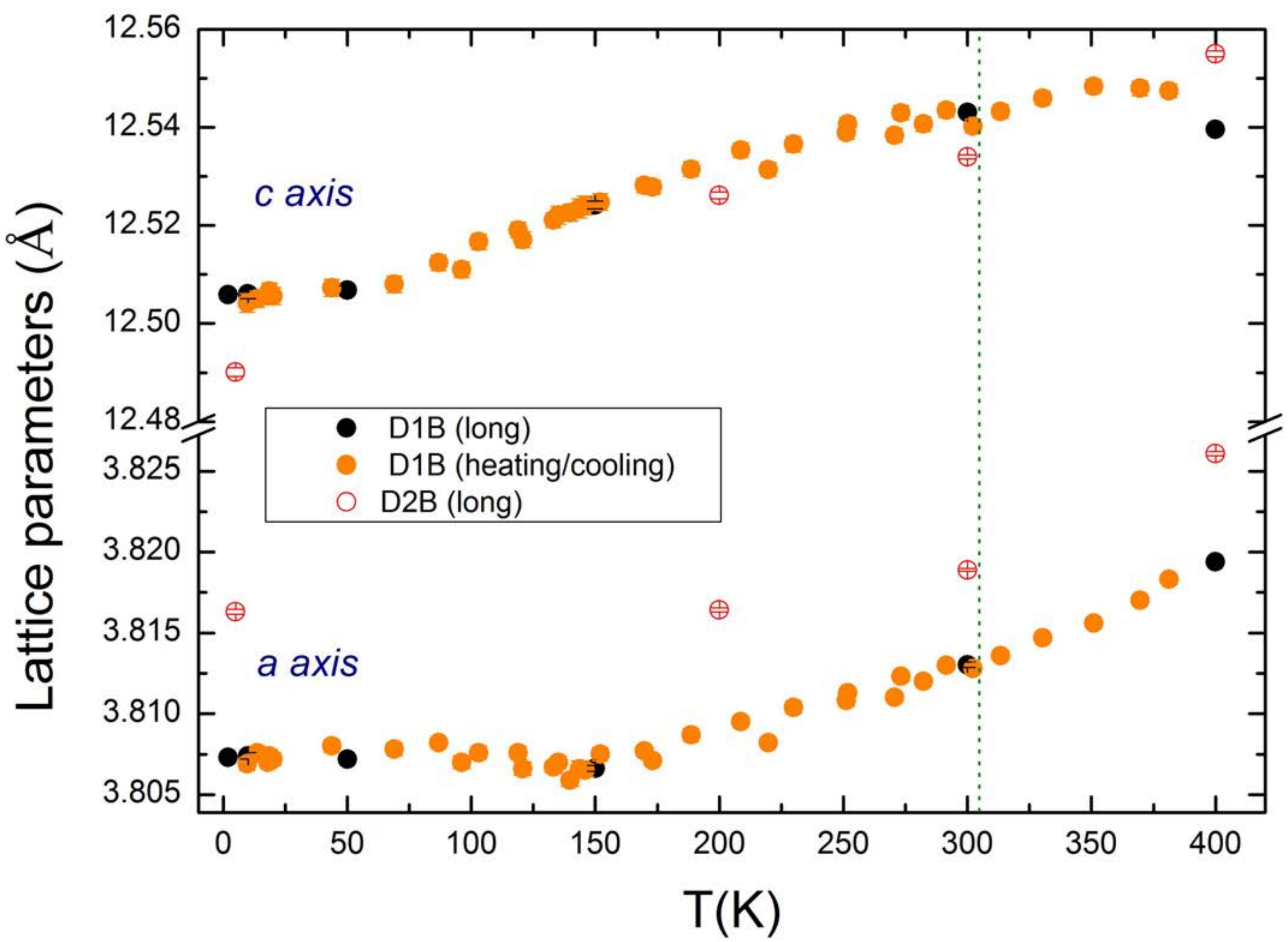

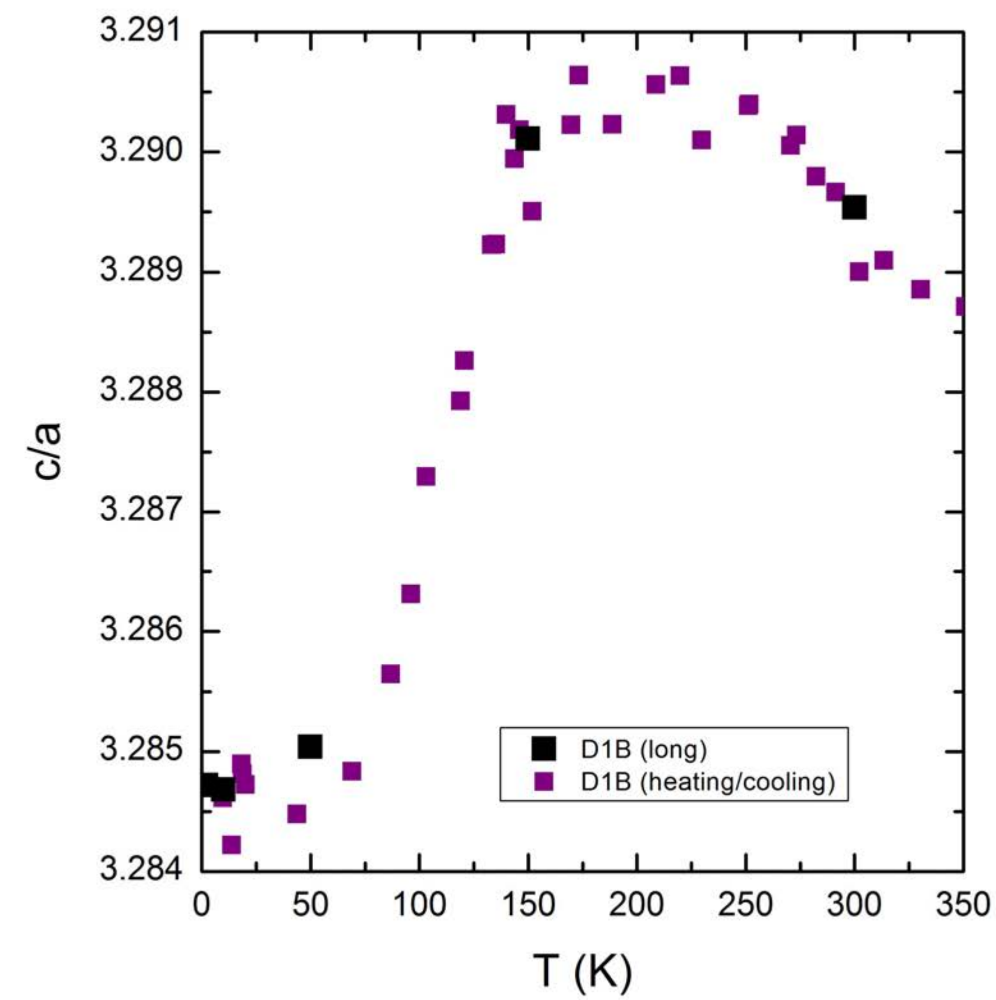

No anomaly at T_N=305K

Slight variation at 150K <—> Magnetic peak [1] ??

Sr_2CrO_4

Neutron Powder diffraction

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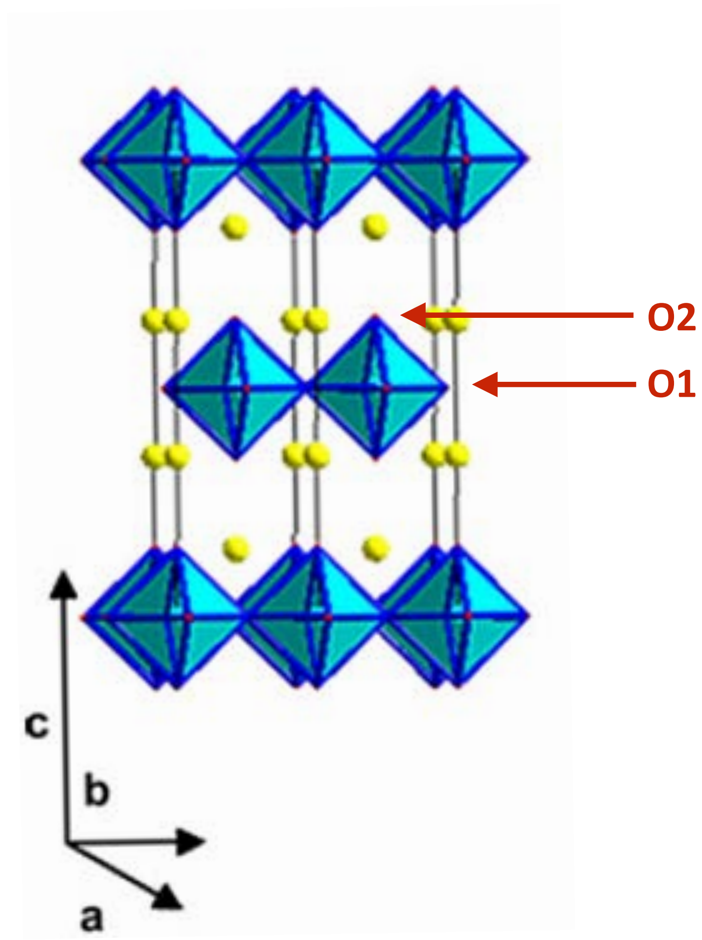
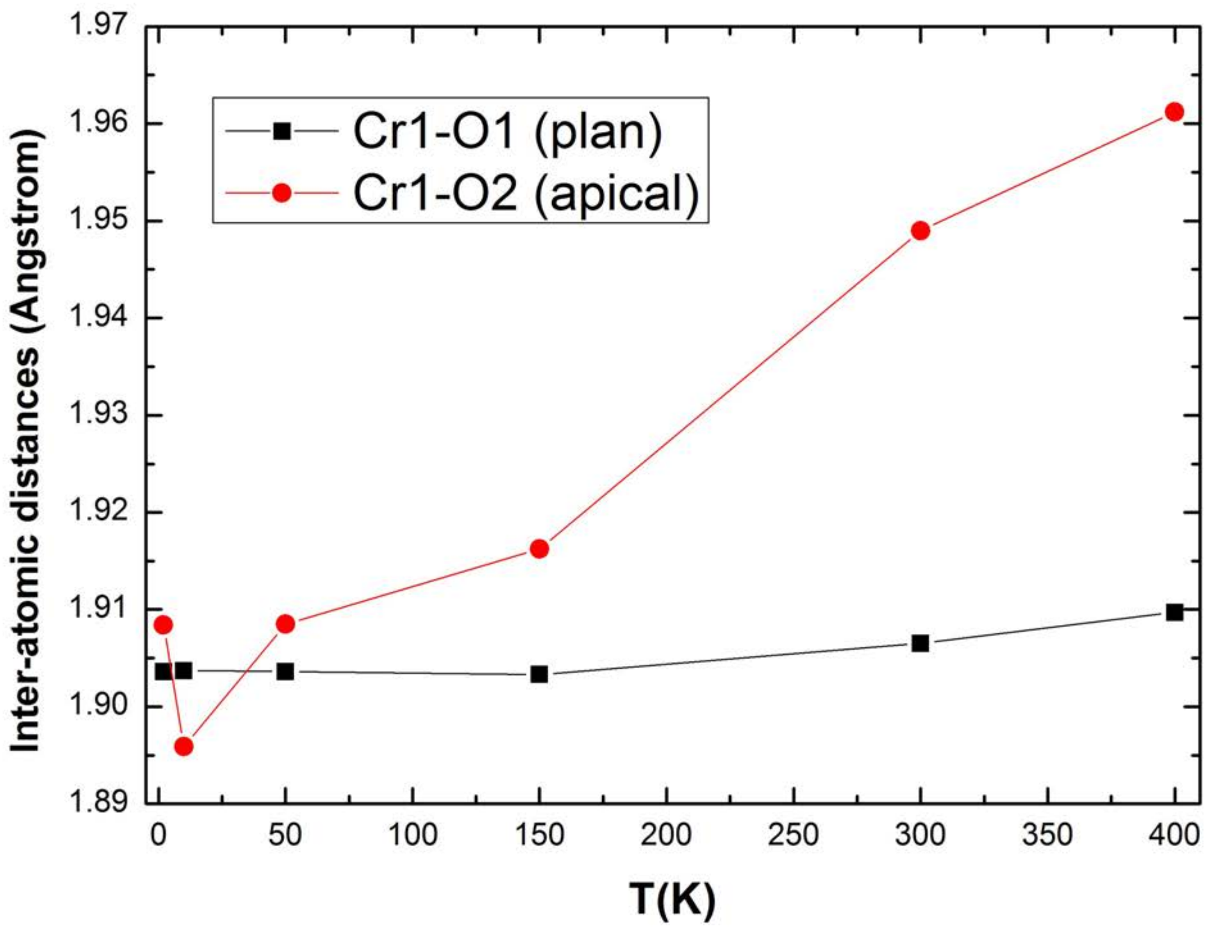
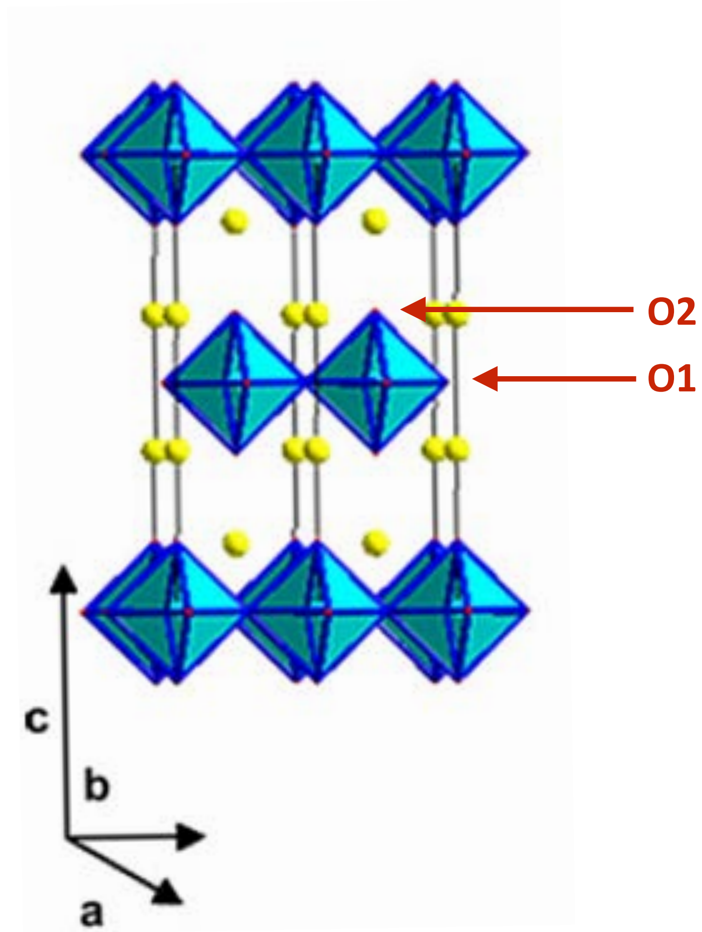


Sr_2CrO_4

Neutron Powder diffraction

ILL, D1B & D2B instruments

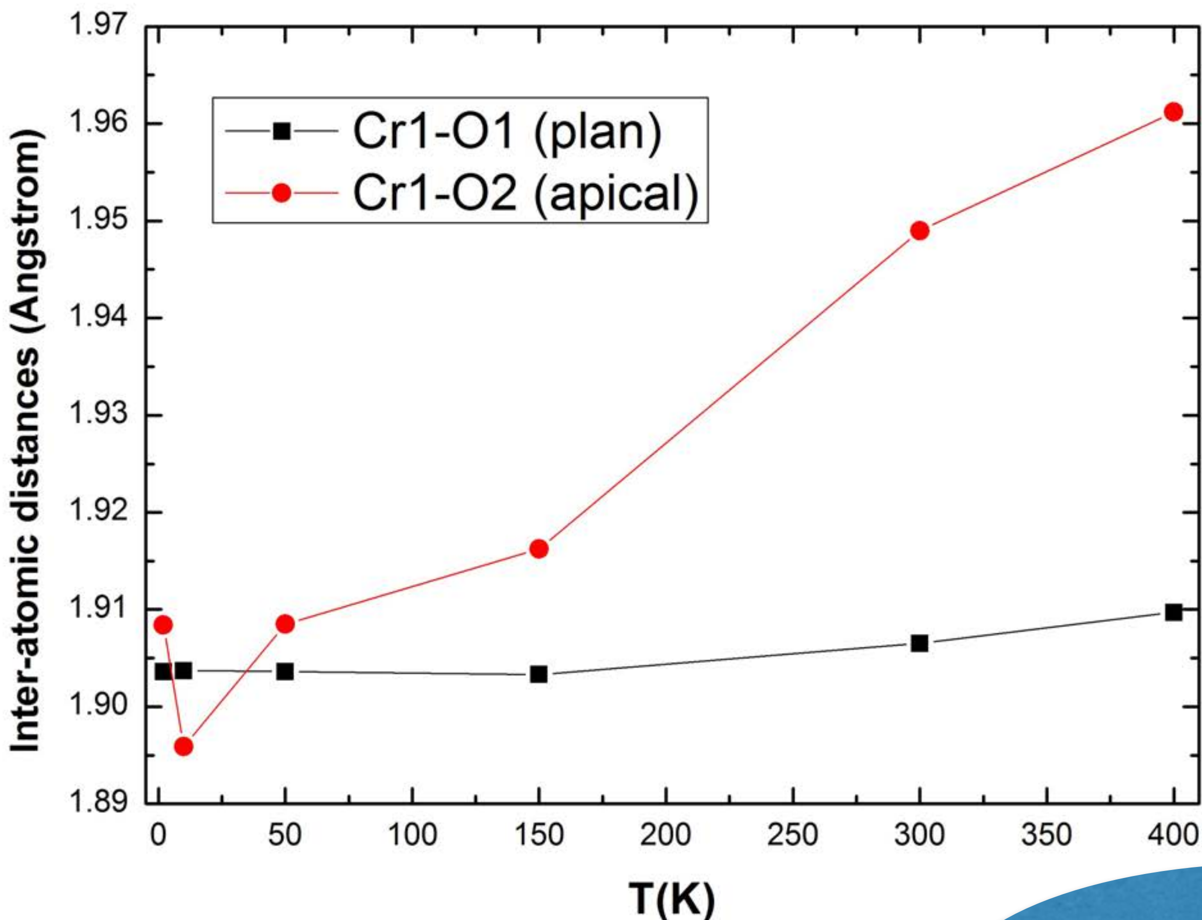


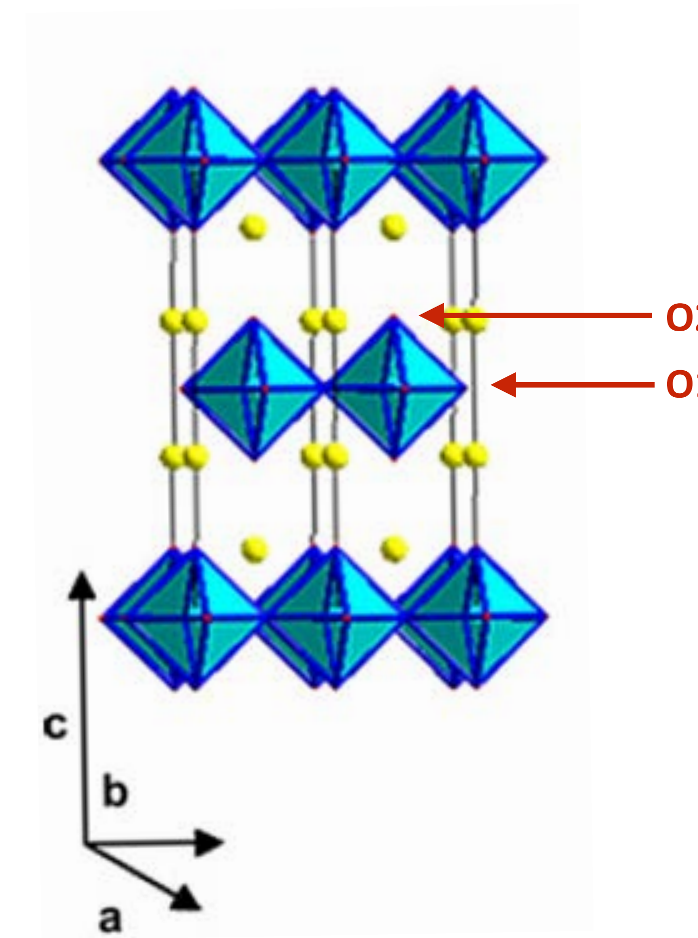


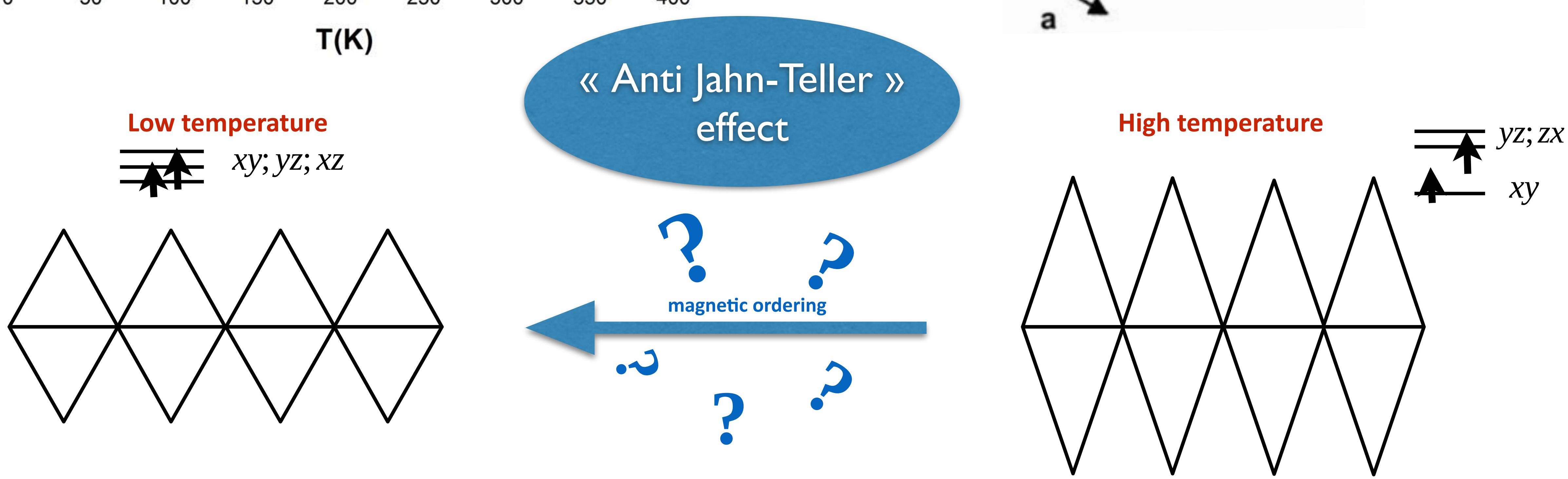
Sr_2CrO_4

Neutron Powder diffraction

ILL, D1B & D2B instruments

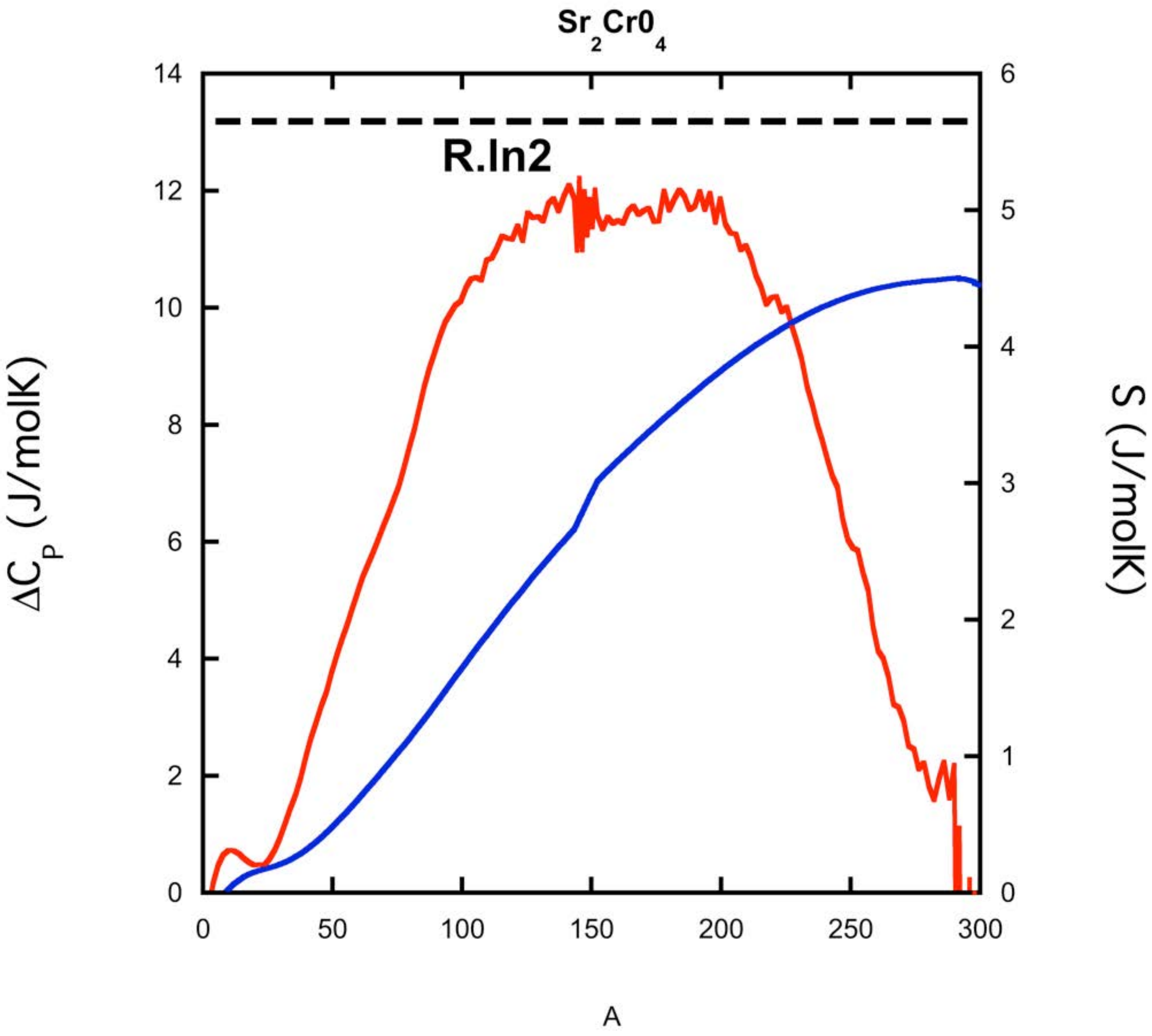






Sr$_2$CrO$_4$

Specific Heat



à refaire vendredi avec Gyorgy

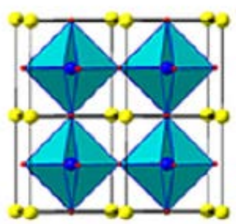
New Ca-based phases

Graphs Sr327 transport /P

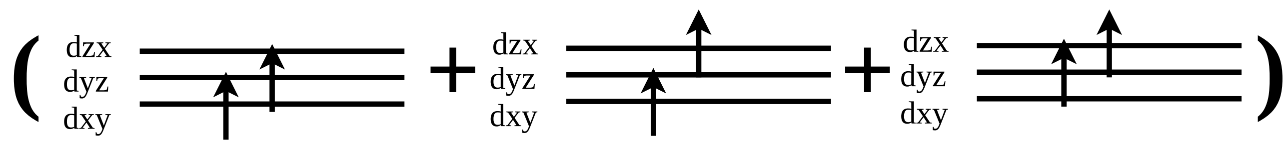
New Ca-based phases

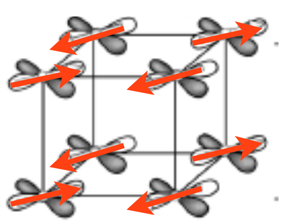
$Ca_3Cr_2O_7$

Introduction : Perovskite $SrCrO_3$

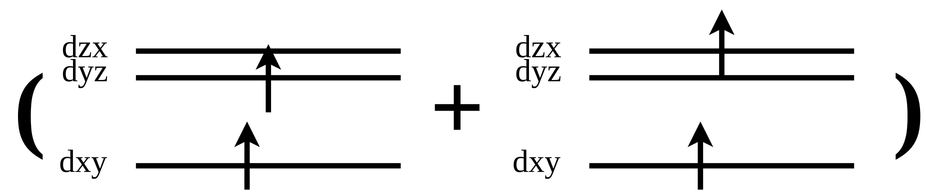


T>40K
cubic
paramagnetic
orbital degenerescence





T<40K
tetragonal c/a=0.992
antiferromagnetic order
partial orbital order



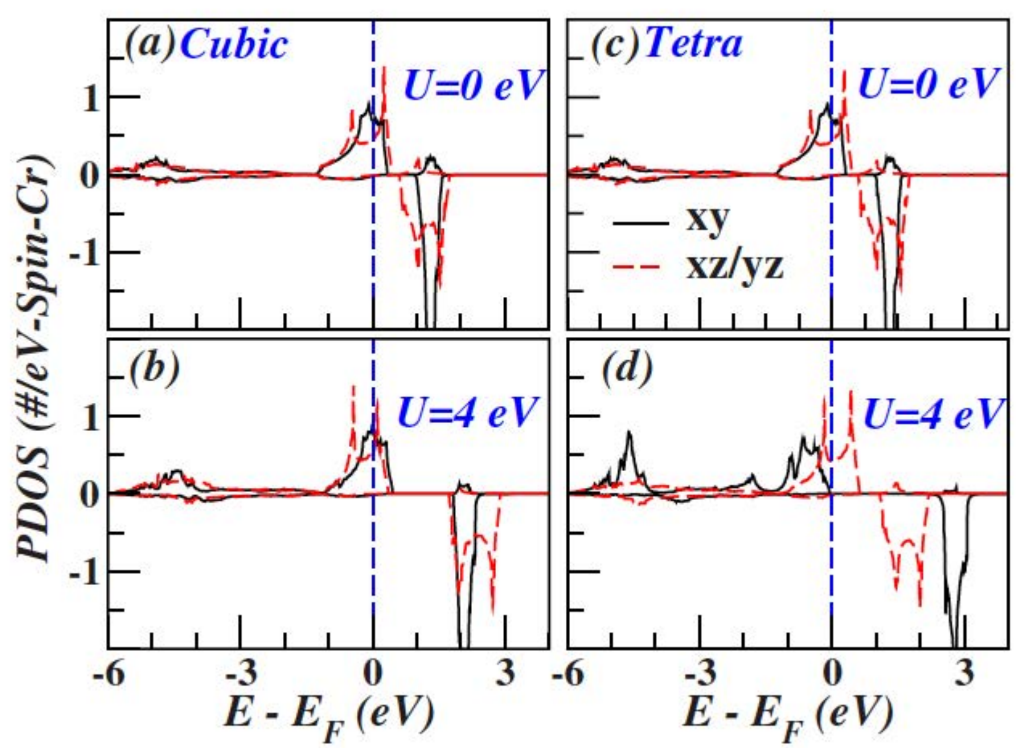


FIG. 7. (Color online) U-dependent orbital-projected densities of states of Cr t_{2g} states for (a)–(b) the cubic and (c)–(d) the tetragonal phase, at U=0 and 4 eV in C-AFM order. At U=4 eV, an orbit-ordering transition in d_{xy} orbital occurs in the tetragonal phase.

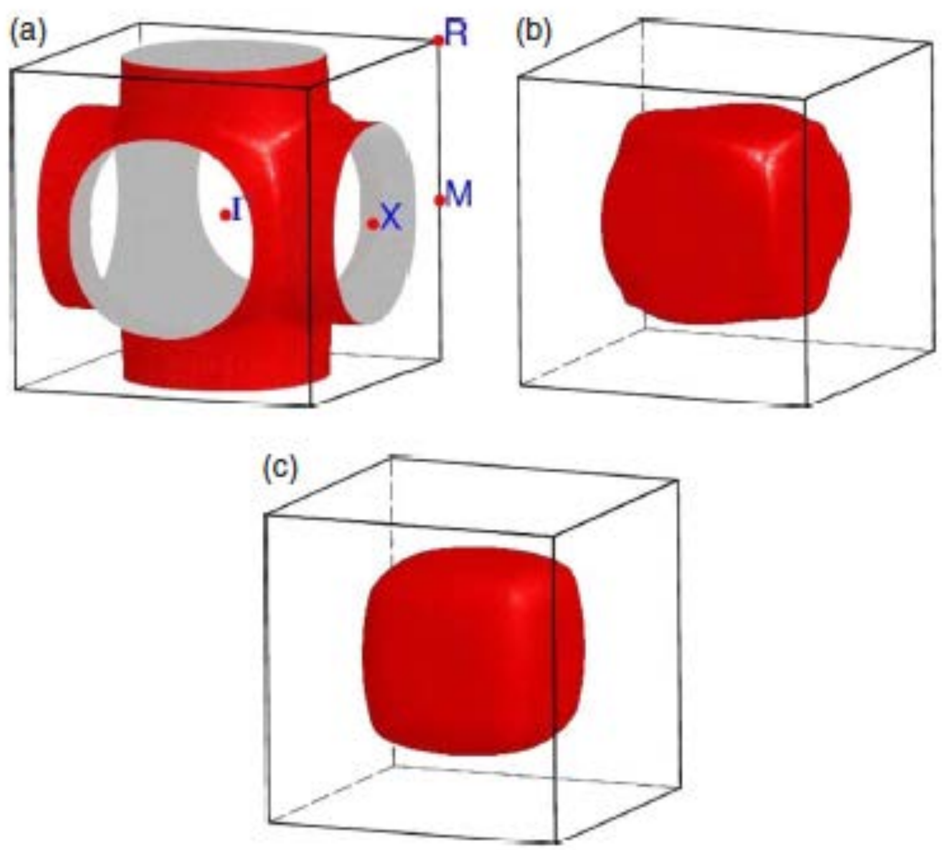
LDA+U calculations explain partial orbital ordering

Pickett *et al.*
PHYSICAL REVIEW B **80**, 125133 2009

Introduction : Perovskite $SrCrO_3$

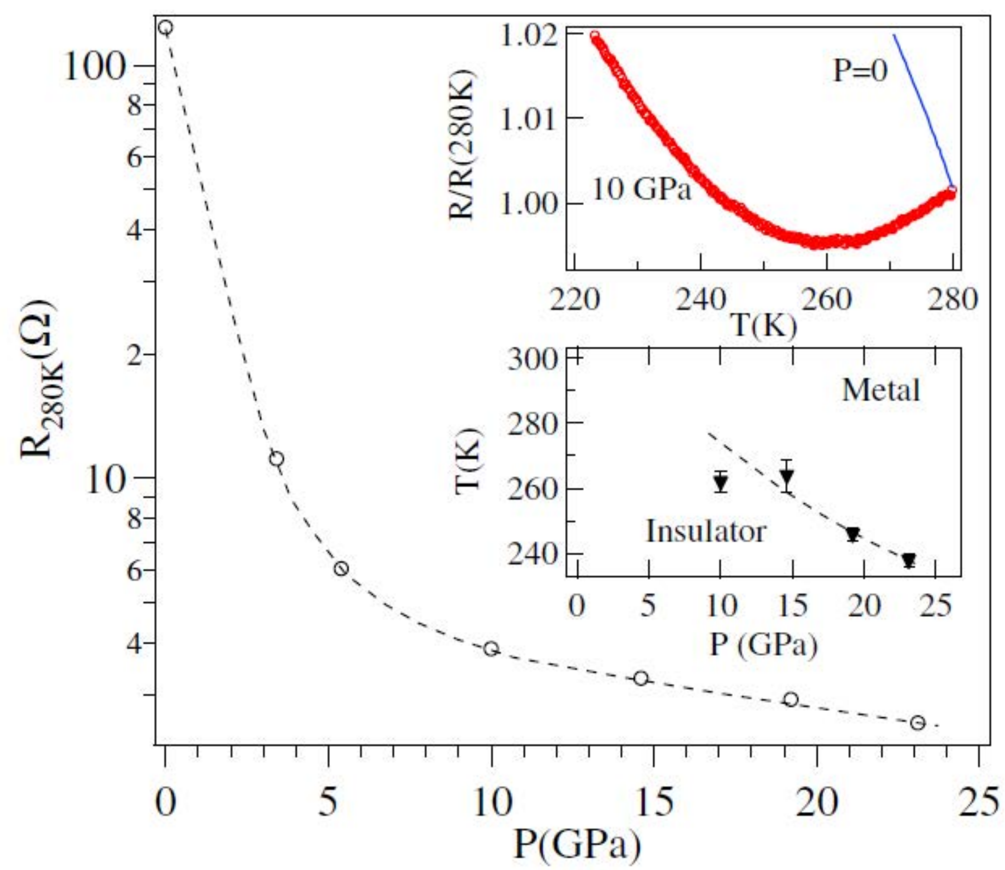
LDA calculations give Metal

Proposed Metal-Insulator transition under pressure ?



Pickett *et al.*

PHYSICAL REVIEW B **80**, 125133 2009



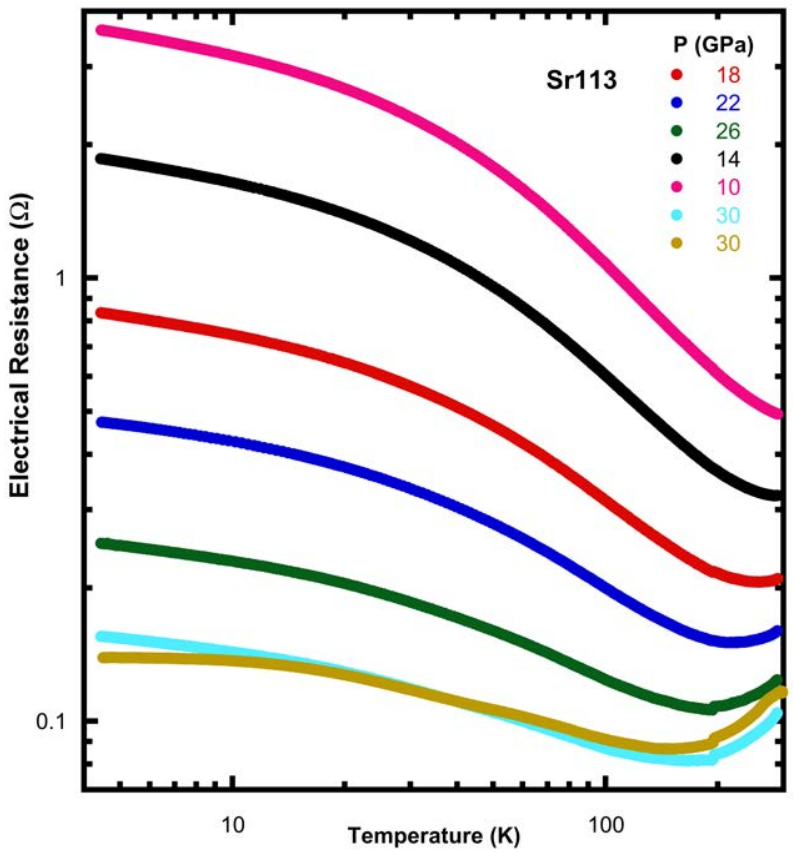
J.-S. Zhou, C.-Q. Jin, Y.-W. Long, L.X. Yang, and J. B. Goodenough, PRL ***96,*** *046408 (2006).*

Introduction : Perovskite $SrCrO_3$

4-wires transport measurement under pressure

Introduction : Perovskite $SrCrO_3$

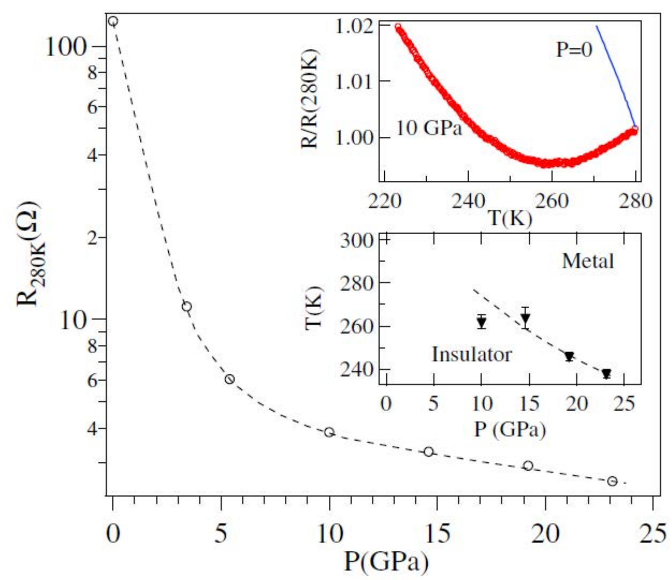
4-wires transport measurement under pressure

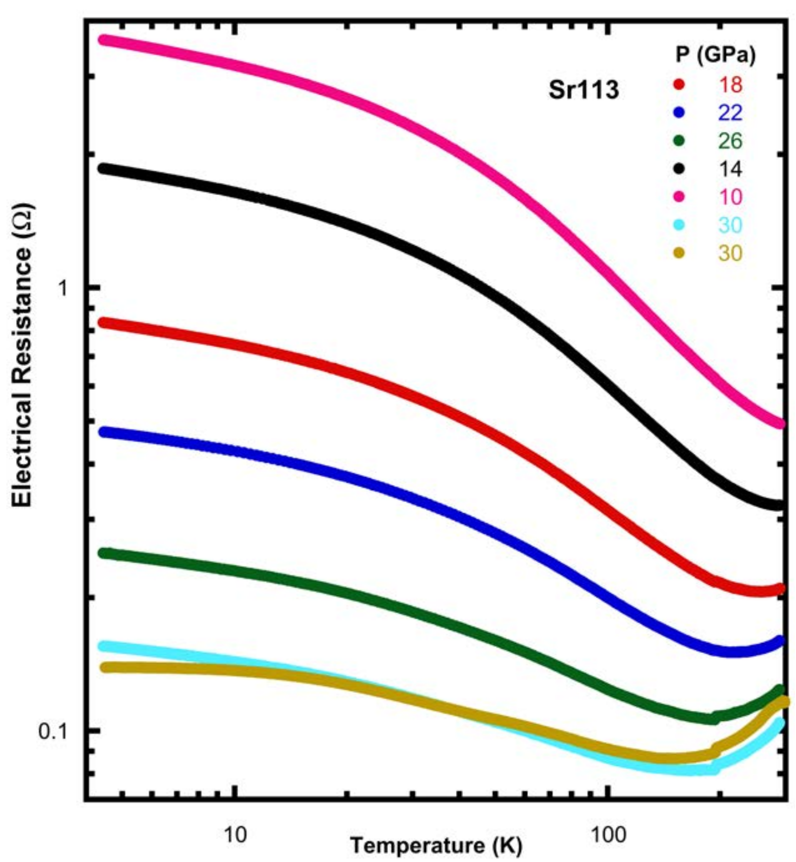


Our experiment :
Partial Metal-Insulator transition
between 14 and 18 GPa

Introduction : Perovskite $SrCrO_3$

4-wires transport measurement under pressure





?

Our experiment :
Partial Metal-Insulator transition
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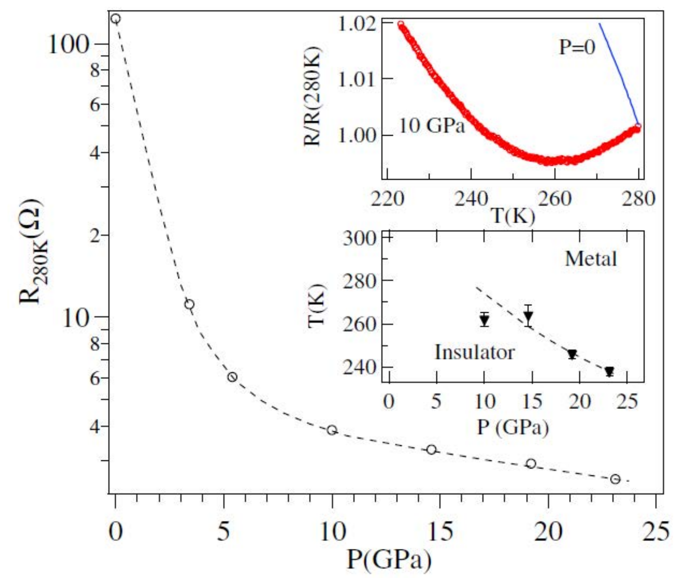
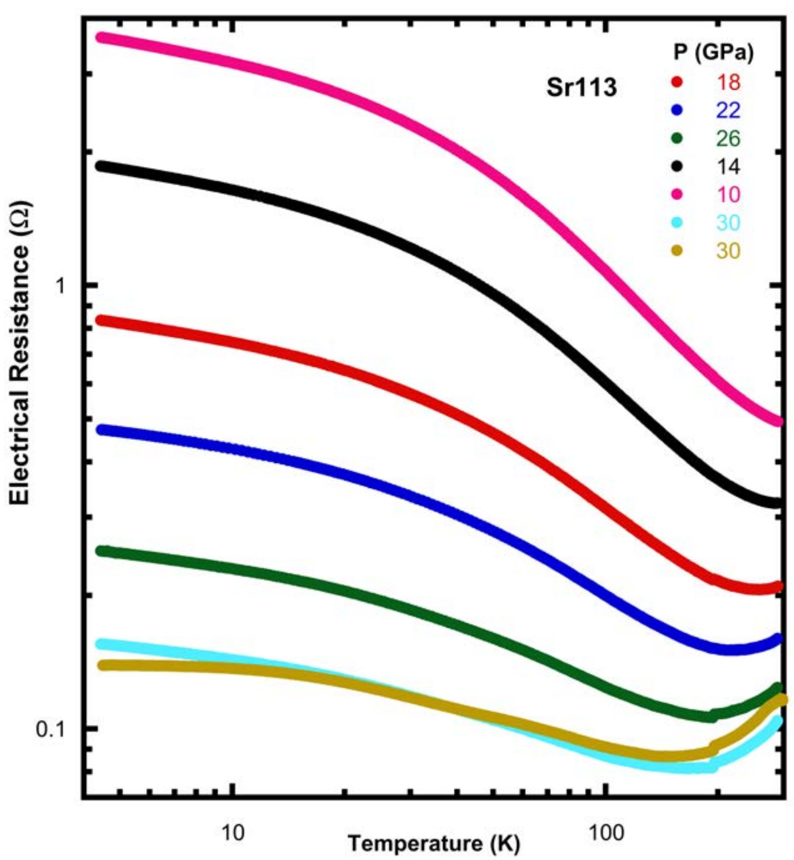
Introduction : Perovskite $SrCrO_3$

4-wires transport measurement under pressure





Our experiment :
Partial Metal-Insulator transition
between 14 and 18 GPa

Estimated Full Metal-Insulator transition around 40 GPa