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New homologous series of oxygen vacancy-ordered perovskite manganites: $Sr_NMn_NO_{3N-2}$

Leopoldo Suescun

Neutron and X-ray Scattering Group - Materials Science Division
Argonne National Laboratory, Argonne, IL, USA

Materials Science Lab. – Physics Department
Northern Illinois University, DeKalb, IL, USA

&

Cryssmat-Lab/DETEMA – Facultad de Química
Universidad de la República – Montevideo – Uruguay.

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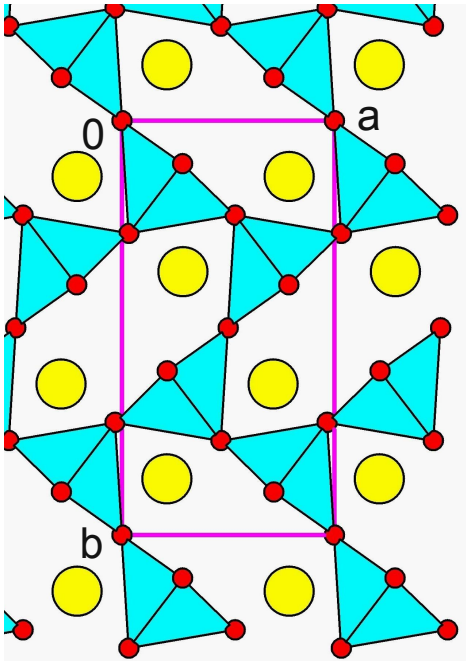
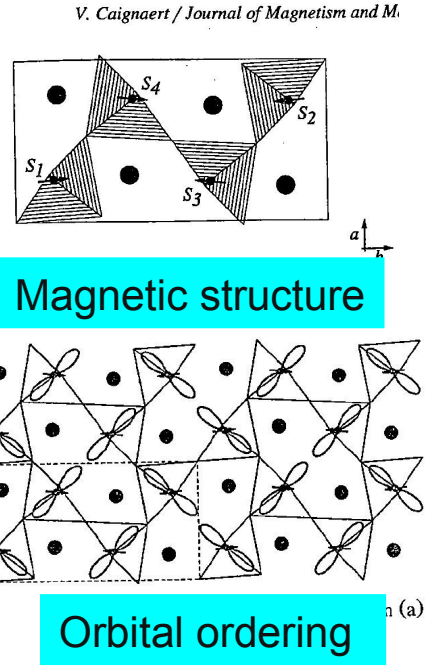
Overview

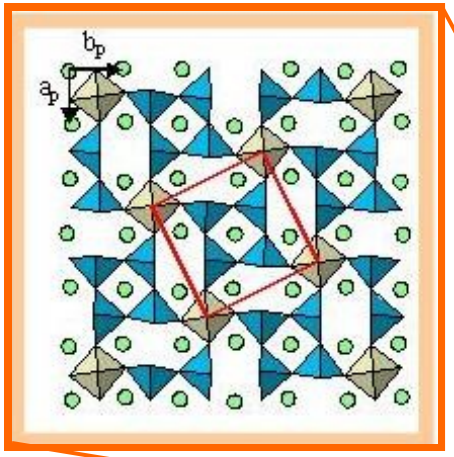
- Background, vacancy-ordered perovskite phases in the $SrMnO_x$ system
- Oxygen-vacancy, charge and orbital ordering in $Sr_2Mn_2O_5$, $Sr_5Mn_5O_{13}$ and $Sr_7Mn_7O_{19}$
- A new homologous series $Sr_NMn_NO_{3N-2}$
- Other systems showing $A_NB_NO_{3N-2}$-type ordering
- Conclusions

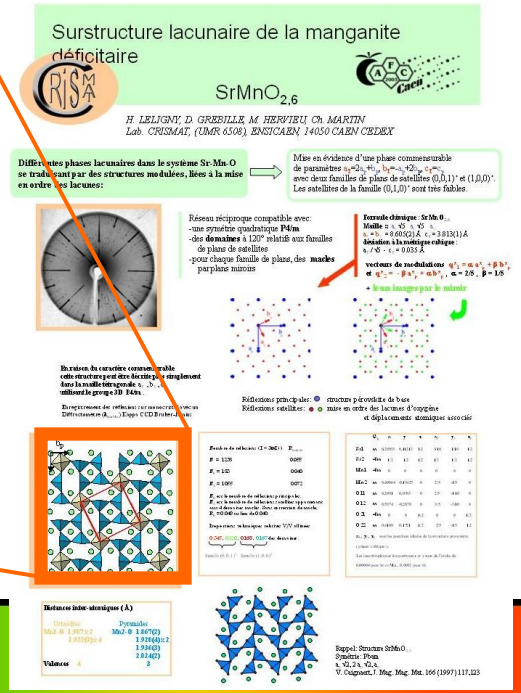
Background

- $Sr_2Mn_2O_5$
  - 1985: Preparation and structural refinement (X-rays) Mn^{3+} in square-pyramidal coordination ($Ca_2Mn_2O_5$ type phase)
  - 1997: Magnetic and nuclear structure from neutron data. Orbital ordering in Mn^{3+} cations also proposed.
- $Sr_5Mn_5O_{13}$
  - 2003: conference report on phase $Sr_5Mn_5O_{13}$ with $BaLa_4Cu_5O_{13}$ tetragonal structure.
  - Charge ordering of Mn^{3+}/Mn^{4+} proposed, however, no paper followed.





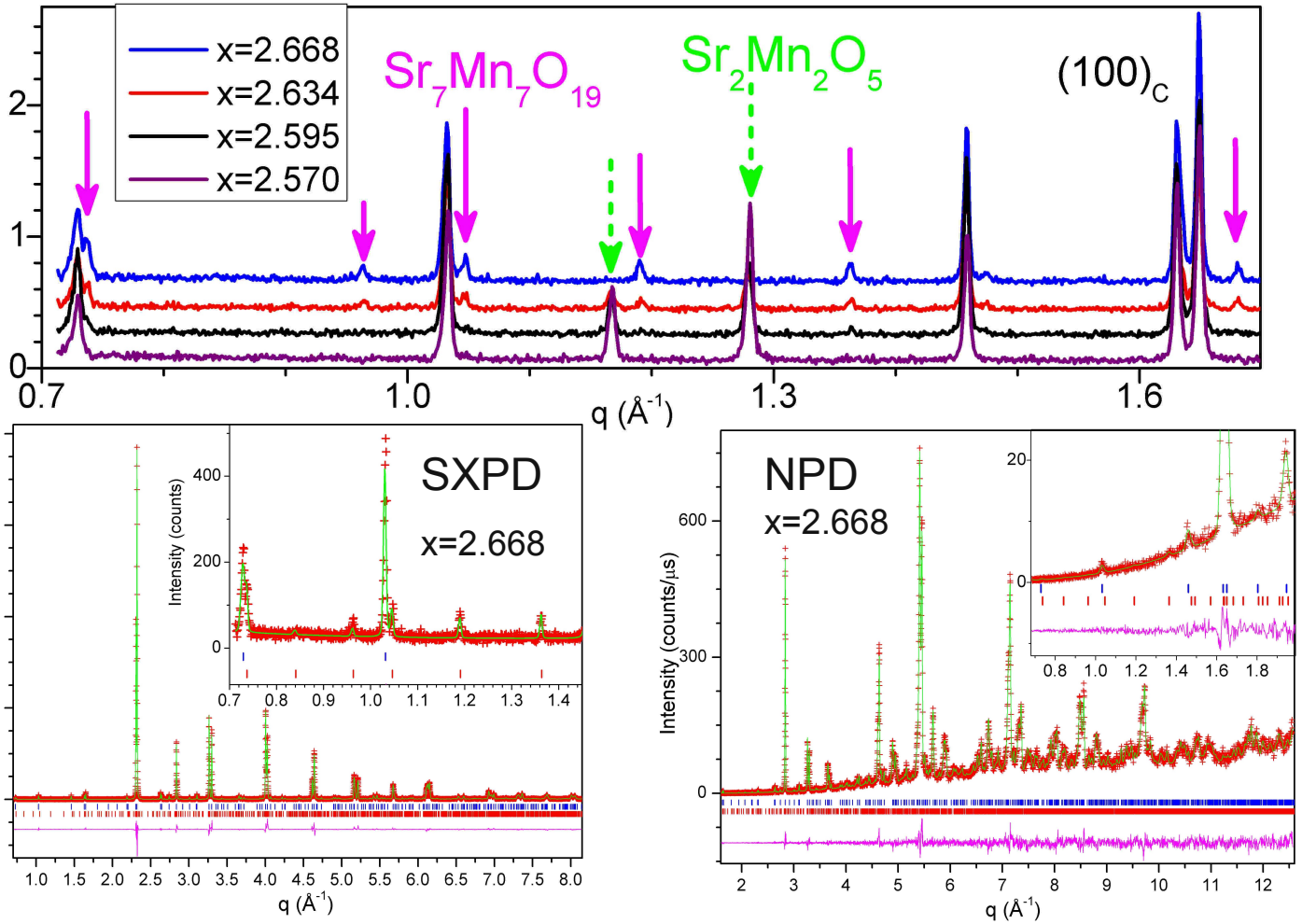




Caignaert V. et al, Mat. Res. Bull. 20 (1985) 479-484.
V. Caignaert, J. Magn. Magn. Mater. 166 (1997) 117-123.
Leligny et al (2003) Association Française de Cristallographie Meeting

Background:

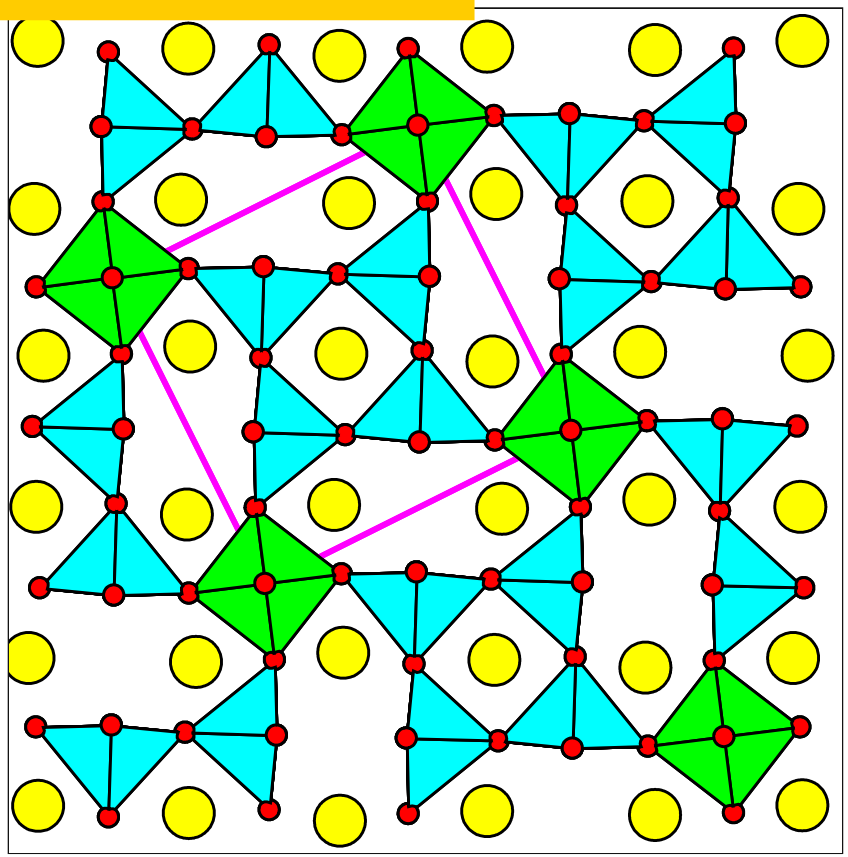
- Structures of $Sr_5Mn_5O_{13}$ ($SrMnO_{2.6}$) and the new $Sr_7Mn_7O_{19}$ ($SrMnO_{2.714}$) phases were determined using synchrotron X-rays and neutron TOF data from multi-phase $SrMnO_{\nu}$ samples.

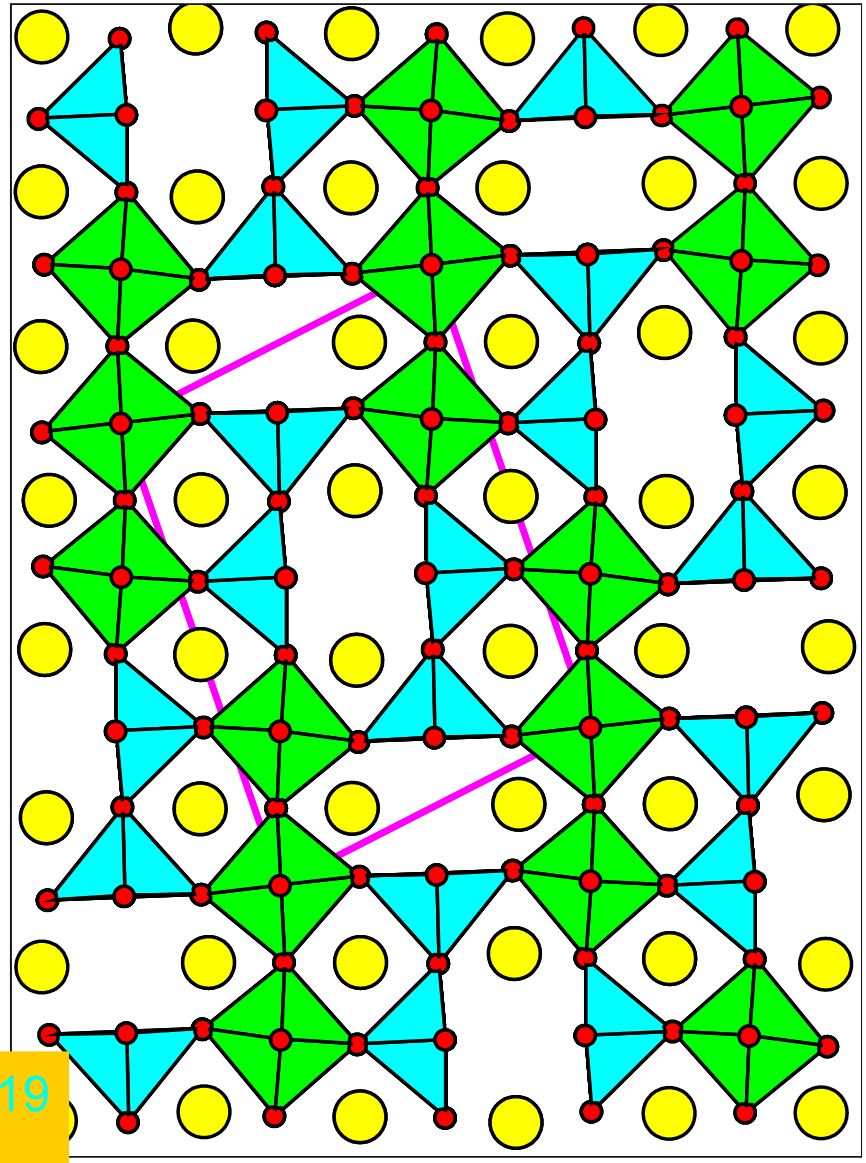


* Suescun L., Chmaissem O., Dabrowski B., Mais J. & Jorgensen J.D., J. Solid State Chem (2007) In Press.

Background: $Sr_5Mn_5O_{13}$ and $Sr_7Mn_7O_{19}$

Sr5Mn5O13





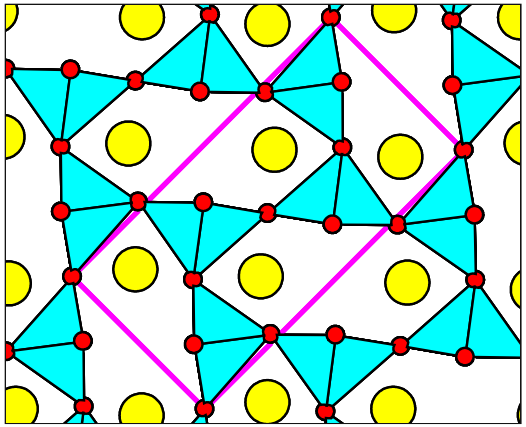
7 7 19

Sr Mn O

Charge ordering in $Sr_5Mn_5O_{13}$ and $Sr_7Mn_7O_{19}$

$Sr_2(Mn^{3+})_2O_5$

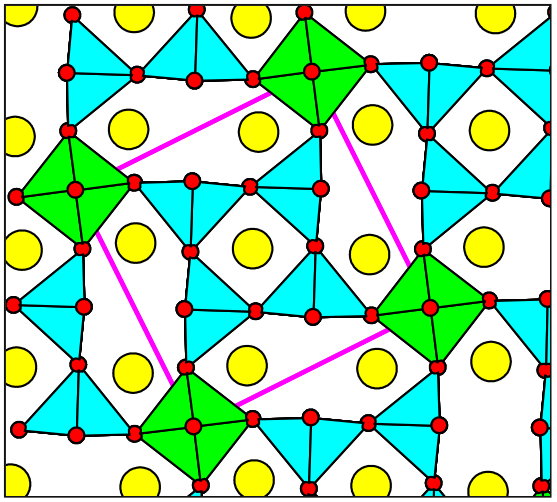
Mn^{3+} pyramids



BV sum
Mn1 3.08 (P)

Sr5(Mn3+)4Mn4+O13

4 Mn3+ pyramids (P)
1 Mn4+ octahedron (O)

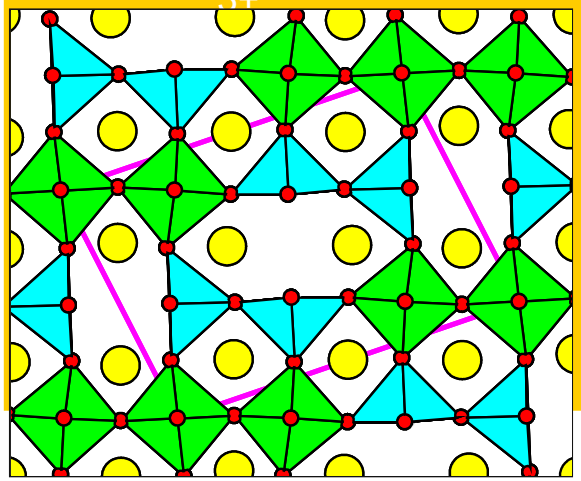


BV sum
Mn1 3.81(O)
Mn2 3.15 (P)

7 3+ 4 4+ 3 19

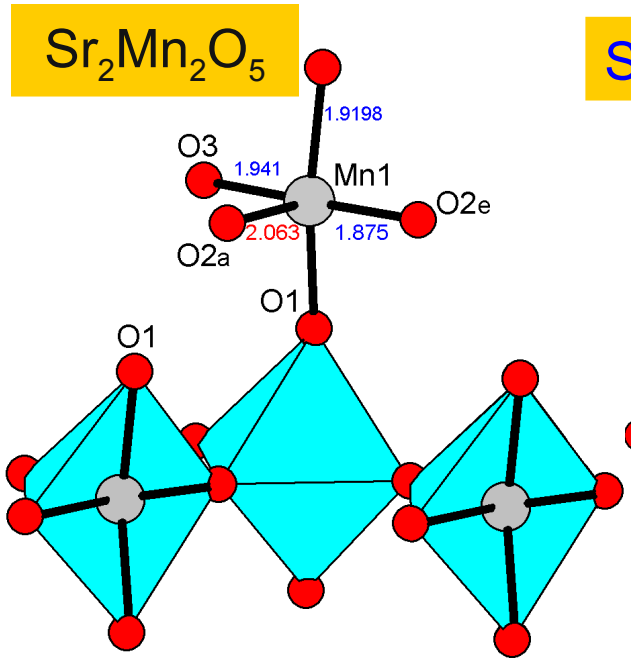
Sr (Mn) (Mn) O

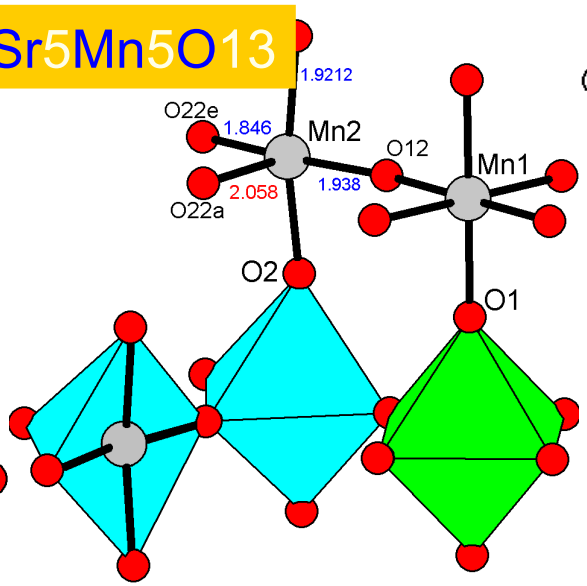
3+

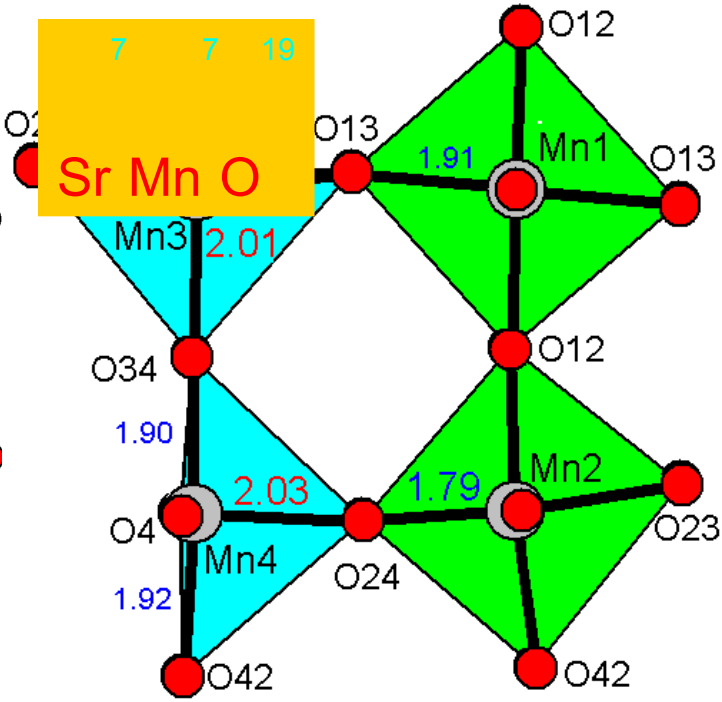


BV sum
Mn1: 3.86; Mn2: 4.04 (O)
Mn3: 3.07; Mn4: 3.12 (P)

Orbital ordering in $Sr_5Mn_5O_{13}$ and $Sr_7Mn_7O_{19}$







$Sr_2Mn_2O_5$	
Mn1	
O1 (×2)	1.9198(4)
O3	1.941(3)
O2a	2.063(3)
O2e	1.875(3)

Sr Mn O	
Mn2	
O2 (×2)	1.9212(5)
O12	1.938(5)
O22a	2.058(4)
O22e	1.846(4)

Sr Mn O			
Mn3		Mn4	
O3 (×2)	1.923(3)	O4 (×2)	1.922(2)
O23	1.97(3)	O42	1.92(2)
O24	2.03(3)		
O13	1.89(3)	O34	1.90(2)

d^4 Mn^{3+} with occupied d_{z^2} orbital in elongated square pyramids

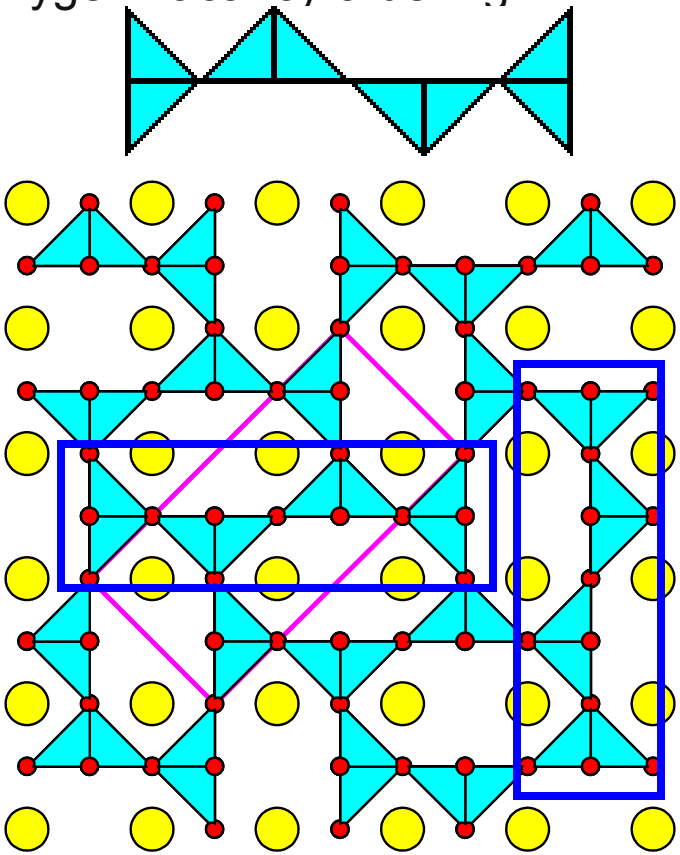
d^3 Mn^{4+} in slightly distorted octahedra

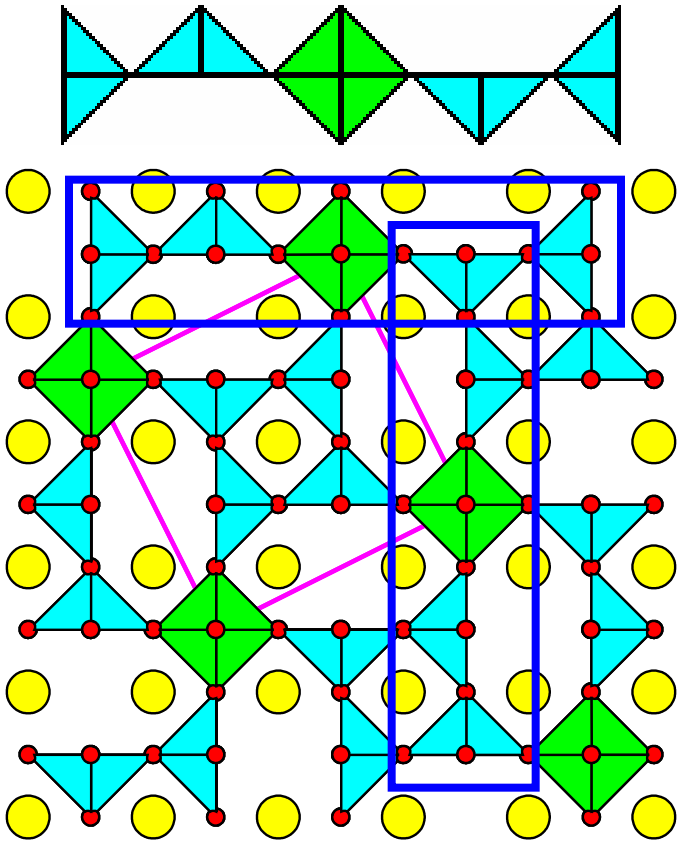
New homologous series $Sr_NMn_NO_{3N-2}$

- Chemical formula $Sr_2Mn_2O_5$ should be re-written $Sr_4Mn_4O_{10}$.
- $Sr_4Mn_4O_{10}$, $Sr_5Mn_5O_{13}$ and $Sr_7Mn_7O_{19}$ comply with the notation $Sr_NMn_NO_{3N-2}$ with *N=4*, *5,* and *7,* respectively, for structures formed by *4* Mn^{3+} pyramids and *N-4* Mn^{4+} octahedra.
- Is this a new homologous series? What are building rules?
- Phases in the $SrMnO_x$ series should have oxygen contents x related to N by x=3-2/N:
  N=4 ⇒ x=2.5, N=5 ⇒ x=2.6, N=6 ⇒ x=2.667, N=7 ⇒ x=2.714, N=8 ⇒ x=2.75
- Is there other series of oxygen deficient perovskites (ABO_x) displaying the same structural features?

New homologous series $Sr_NMn_NO_{3N-2}$

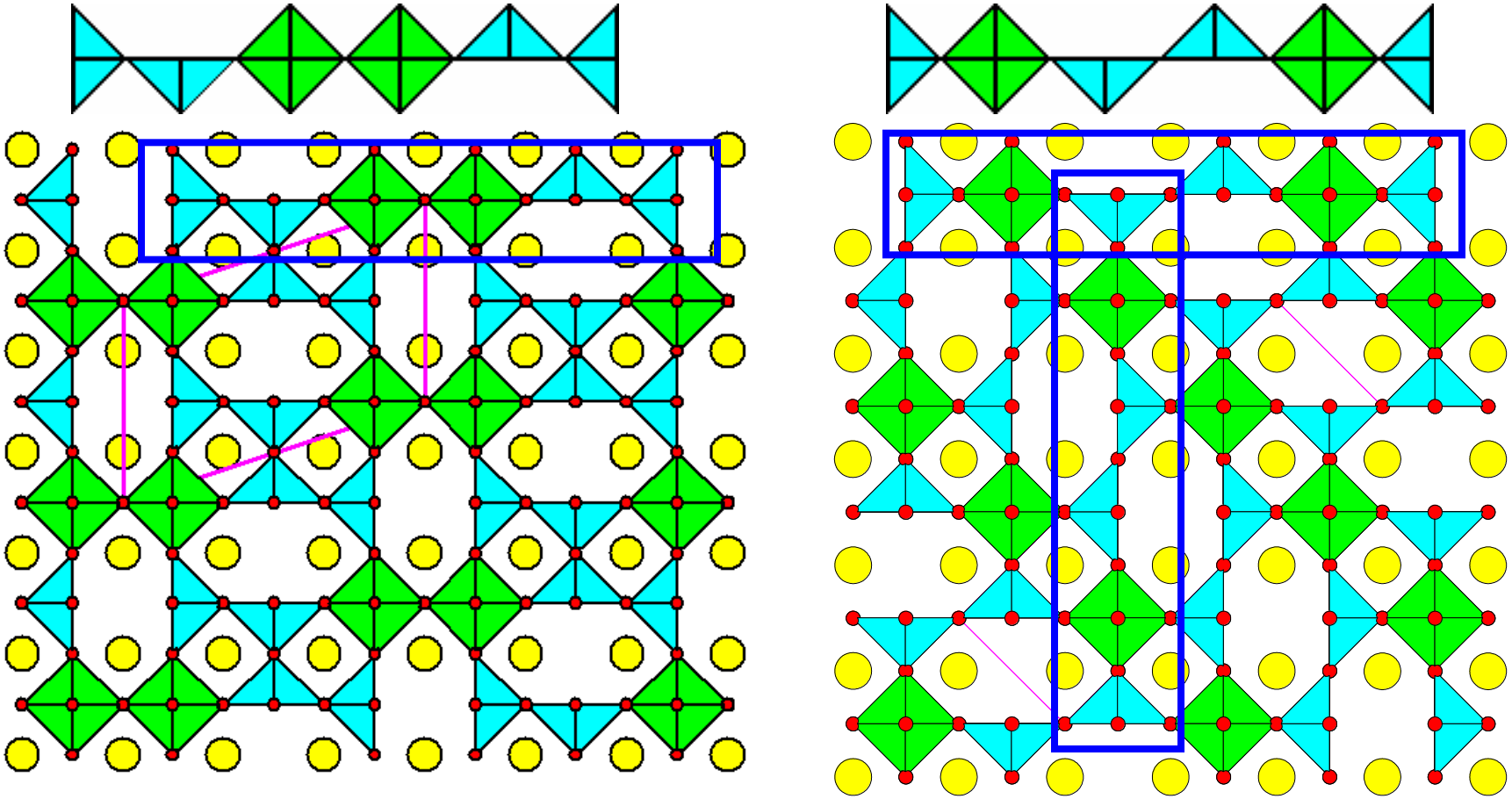
- Models of $Sr_4Mn_4O_{10}$ and $Sr_5Mn_5O_{13}$ can be built by joining *N=4* and *N=5* building blocks formed by *4* pyramids and *N-4* octahedra with 2/m symmetry.
- Building blocks allow for charge and orbital ordering associated with the oxygen vacancy ordering.





New homologous series $Sr_NMn_NO_{3N-2}$

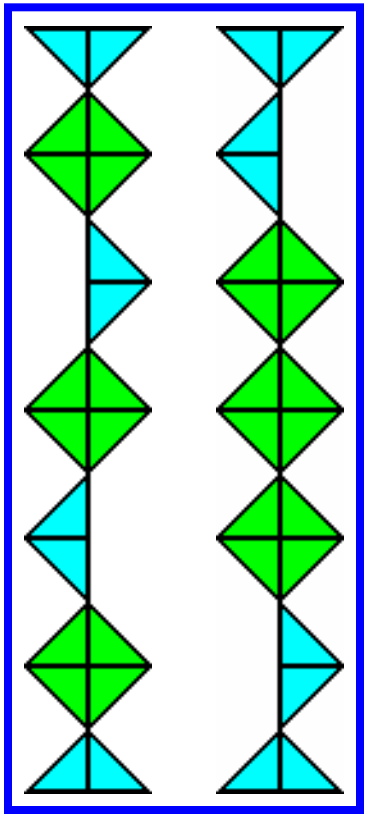
- Two different blocks of *4* pyramids and *N-4=2* octahedra with 2/m symmetry can generate the hypothetical compounds $Sr_6Mn_6O_{16}$.

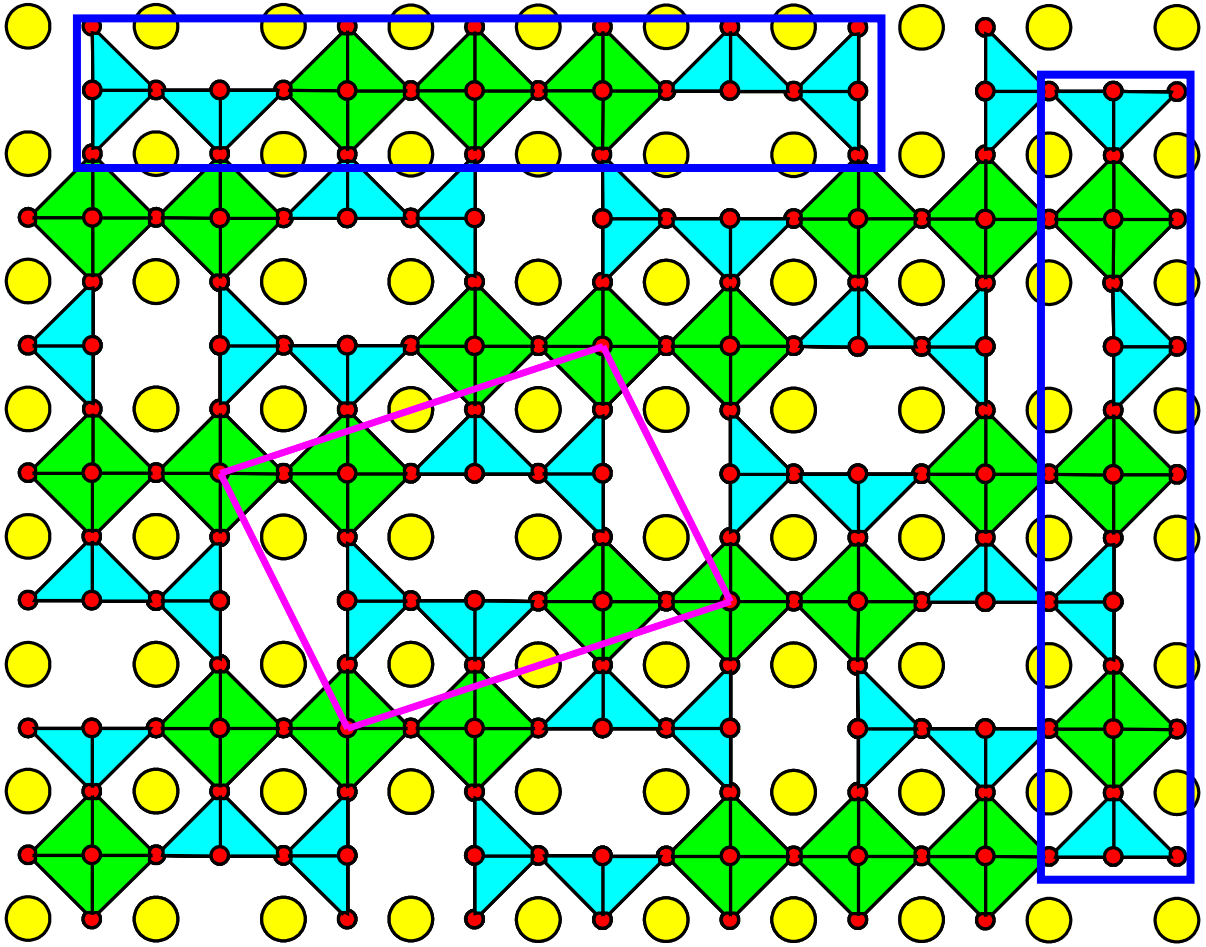


Two possible structures associated with N=6 blocks, not observed

New homologous series $Sr_NMn_NO_{3N-2}$

- Two blocks of *4* pyramids and *N-4=3* octahedra with 2/m symmetry can generate compound $Sr_7Mn_7O_{19}$.

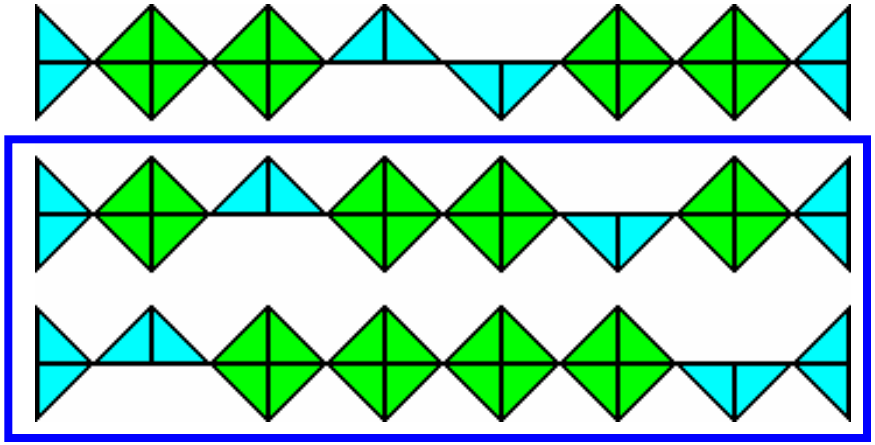




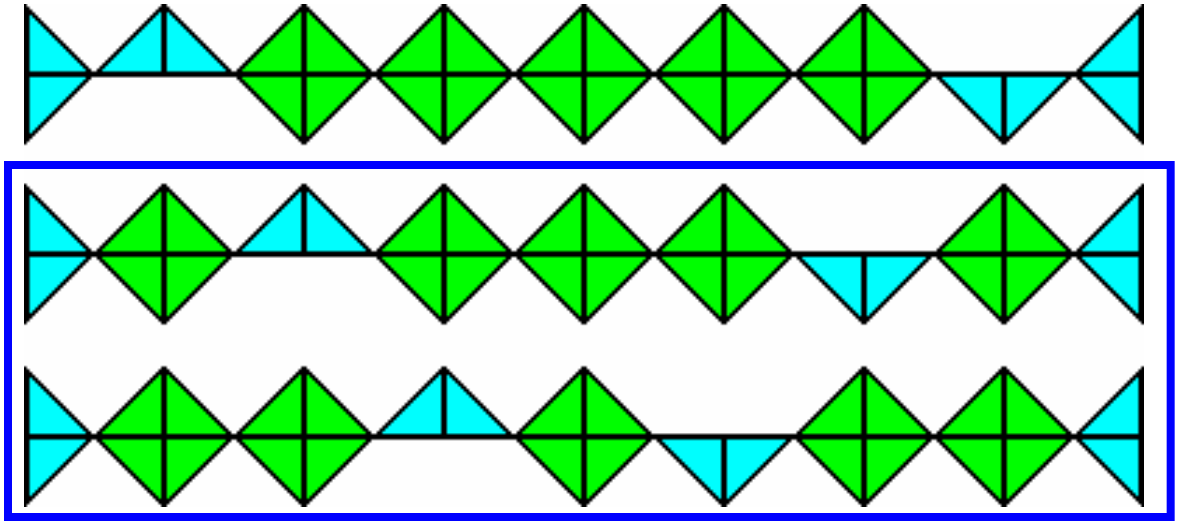
Only one structural pattern is formed from both blocks

New homologous series $Sr_NMn_NO_{3N-2}$

- For N>7 three or more blocks lead to two or more $Sr_NMn_NO_{3N-2}$ compounds



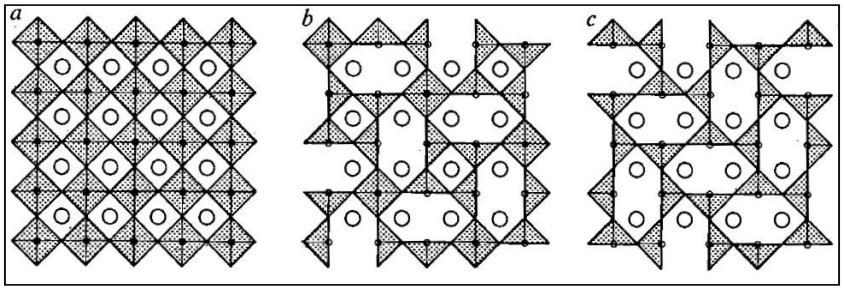
N=8, 3 blocks form 2 different structural arrangements.



N=9, 3 blocks form 2 different structural arrangements.

Other systems showing $A_NB_NO_{3N-2}$-type ordering:

LaCuOx & NdCuOx systems



- N=4 observed for d^9 Cu^{2+} (pyramids)
- N=5 observed for d^9 Cu^{2+} and d^8 Cu^{3+} (octahedra). Large monoclinic distortion observed
- No phases with N>5 observed

Bringley et al, *Letters to Nature* (1990) 347, 263-265
Chen et al, *Inorg Chem.* (1995) 34, 2077-2083.

CaMnOx system

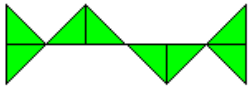
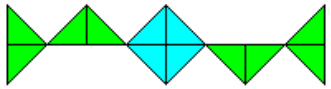
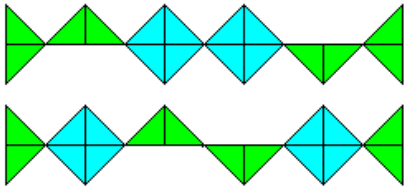
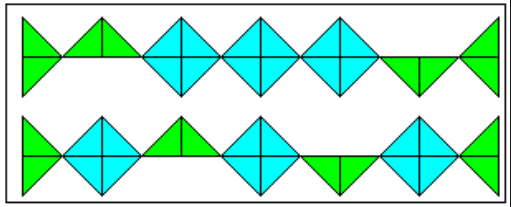
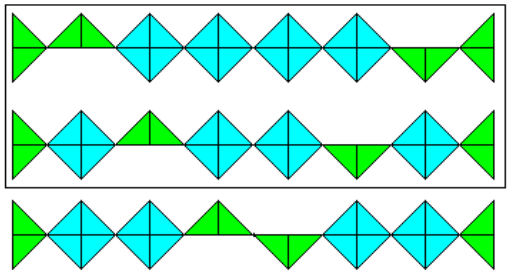
- $Ca_2Mn_2O_5$ (N=4) structure has been determined
- HREM and ED studies of $CaMnO_{2.667}$ and $CaMnO_{2.75}$ have shown formation of local structures with unit cells compatible with those proposed for N=6 ($Ca_6Mn_6O_{16}$) and N=8 ($Ca_8Mn_8O_{22}$) members of the series respectively
- A neutron powder diffraction of $CaMnO_{2.75}$ was inconclusive possibly due to the coexistence of multiple ordering arrangements

Poeppelmeier et al *J. Solid State Chem.* (1982) 45, 79-79.
Reller et al *Proc. R. Soc. Lond. A* (1984) 349, 223-241.
Chiang & Poeppelmeier, *Mater Lett.* (1991) 12, 102-108.

Size and charge of A-site cation appears to play a key role in the stabilization of different structural patterns.

Summary of observed phases $A_NB_NO_{3N-2}$

- Blocks formed by *4* pyramids and *N-4* octahedra with 2/m symmetry give rise to a series of compounds that could display orbital and charge ordering associated with the oxygen vacancy-ordering.

Building blocks	N	Cell setting, S.G.	Latt. param. (a, b, γ≠90)	Observed
	4	Orthorhombic, Pbam	$\sqrt{2}a_P, 2\sqrt{2}a_P$	(Sr/Ca) Mn O (La/Nd/Sr) Cu O
	5	Tetragonal, P4/m	$\sqrt{5}a_P, \sqrt{5}a_P$	Sr Mn O (La/Nd) Cu O (P2/m
	6	Orthorhombic, Pbmm Monoclinc, P2/m	$\sqrt{2}a_P, 3\sqrt{2}a_P$ $2a_P, \sqrt{10}a_P, 108.4^\circ$	CaMnO ?
	7	Monoclinic, P2/m	$\sqrt{5}a_P, \sqrt{10}a_P, 98.13^\circ$	Sr Mn O
	8	Monoclinc, P2/m Orthorhombic, Pbam	$2\sqrt{2}a_P, \sqrt{10}a_P, 116.6^\circ$ $\sqrt{2}a_P, 4\sqrt{2}a_P$	CaMnO ?

Conclusions & Outlook

- New homologous series $Sr_NMn_NO_{3N-2}$ where Jahn-Teller orbital-ordered d^4 Mn^{3+} pyramids coexist with d^3 Mn^{4+} octahedra has been described by simple model of building blocks formed by 4 pyramids and N-4 octahedra.

  ⇒ Single-phase samples are under preparation to study magnetic and transport properties.

- *N=4* and possibly *N=6* and *8* phases observed in $Ca_NMn_NO_{3N-2}$ system.

  ⇒ Extension of the model to include asymmetric building blocks may explain multiphase behavior of CaMnO$_x$ system.

- *N=4* and *N=5* phases observed in the $LaCuO_x$ and $NdCuO_x$ systems show analogous charge and orbital order of d^9 Cu^{2+} pyramids and d^8 Cu^{3+} octahedra.

  ⇒ Better understanding of electronic configuration relations among *d* and *d* manganates and cuprates could possibly be established.

- A-site cationic charge and size play a key role in the stabilization and distortion of various members of the series.

  ⇒ Theoretical calculations are performed to understand the A-site effect.

Collaborators

- Bogdan Dabrowski & J.D. Jorgensen/Ray Osborn (supervisors)
- At Materials Science Lab. – Physics Department - NIU:
  - Omar Chmaissem (also at ANL)
  - Jim Mais & Steve Remsen (synthesis, transport)
  - Stan Kolesnik (magnetism)
- At IPNS
  - Joe Fieramosca, Ryoji Kiyanagi, Bob von Dreele (SEPD)
  - Evan Maxey, Jim Richardson (GPPD)
- At APS
  - Yang Ren (11 ID-C)
- At Cryssmat-Lab. – Facultad de Química – Universidad de la República
  - Álvaro W. Mombrú & Ricardo Faccio (modelling)

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In memoriam

James D. Jorgensen, 1948 - 2006