STRIPING OF ORBITAL-ORDER WITH CHARGE-DISORDER IN OPTIMALLY DOPED MANGANITES

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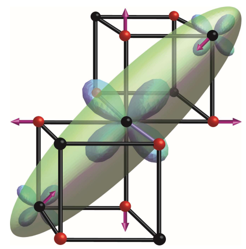
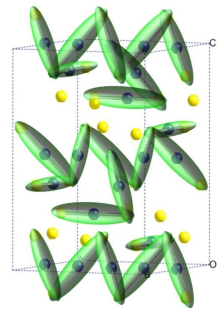
THE ROYAL SOCIETY

"Electronic Crystallography"

- Emphasis on using crystallography and symmetry analysis to study phase transitions in transition metal oxides.

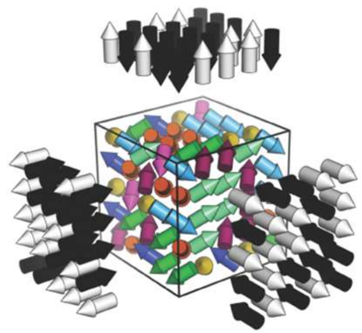
- Verwey structure of Magnetite (*Nature* **481** (2012), 173)





orbital molecules

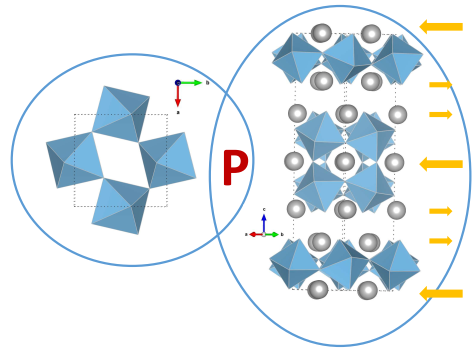
- Order-disorder pe transitions in $BaTiO_3$ (*Phys. Rev. Lett.* **116** (2016), 207602)



correlated disorder

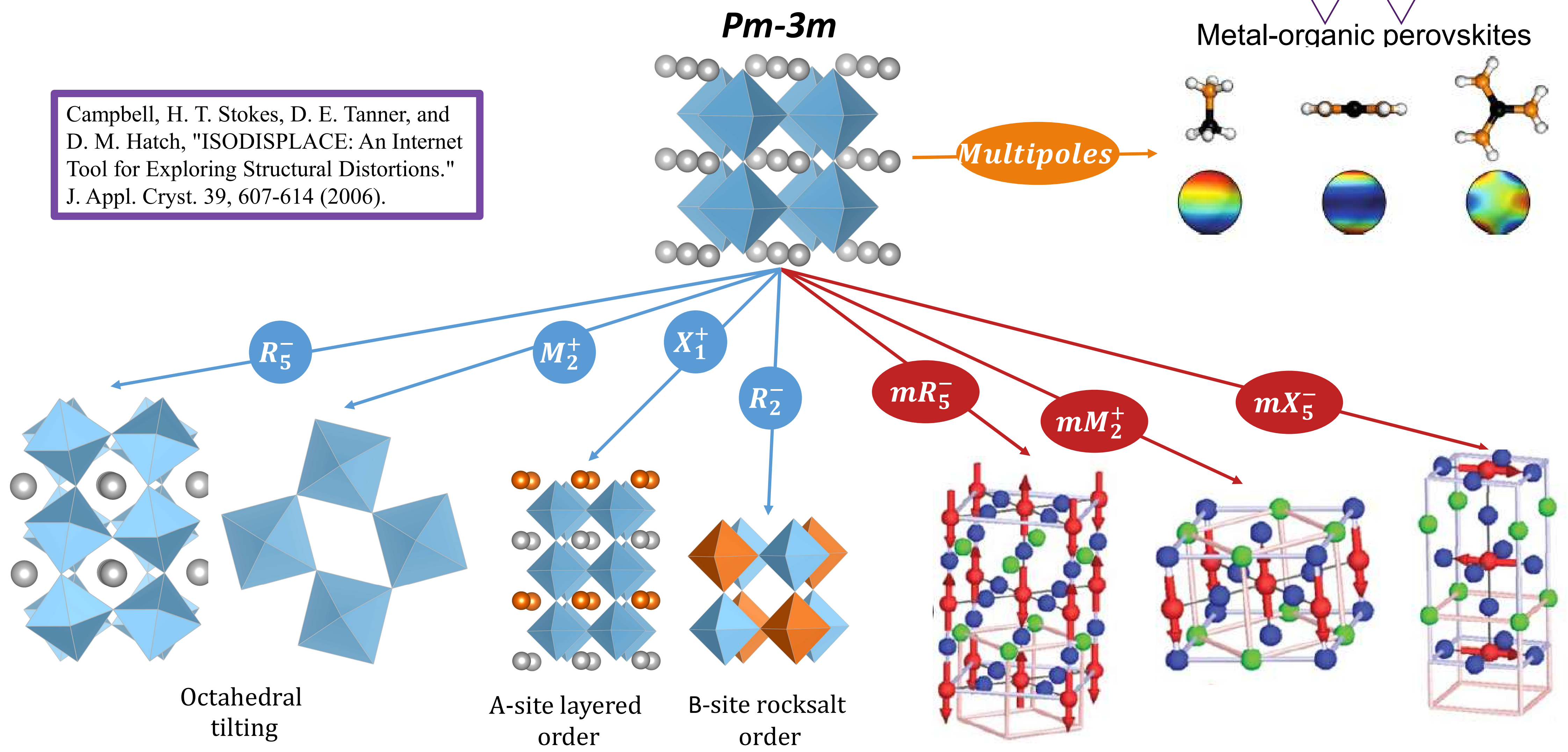
- Improper Ferroelectric mechanisms (*Phys. Rev. Lett.* **114** (2015), 035701; *Nat. Commun.* **9** (2018), 2380)

trilinear couplings



Symmetry Breaking Ingredients for Magnetoelectric Recipes

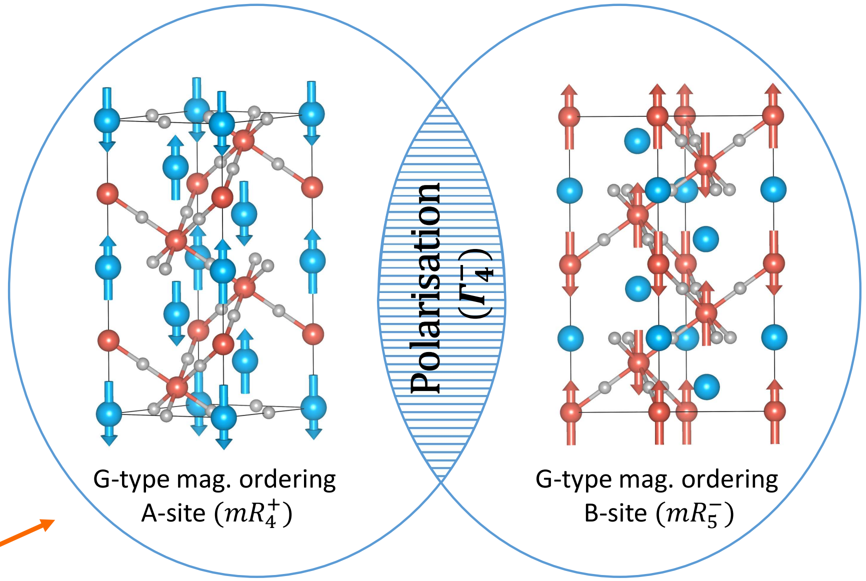
Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, "ISODISPLACE: An Internet Tool for Exploring Structural Distortions." J. Appl. Cryst. 39, 607-614 (2006).



Some Simple Recipes: Third Order Magnetoelectric Couplings

- Starting from a *Pm-3m* perovskite, magnetoelectric couplings at the third order can be shown to be limited to the following:

B-site Magnetic Order	A-site Magnetic Order		
	A-type	C-type	G-type
A-type	P	X	X
C-type	X	X	X
G-type	X	X	P



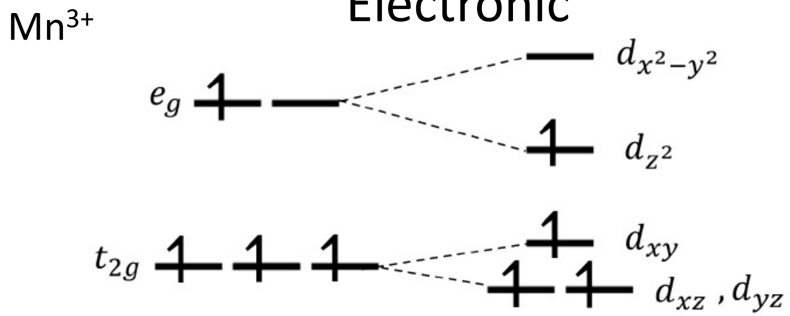
$$F = mR_4^+ mR_5^- P$$

A Group-theoretical Approach to Enumerating Magnetoelectric and Multiferroic Couplings in Perovskites, Mark S Senn, Nicholas C. Bristowe, *Acta Crystallogr. Sect. A* **74** (2018), 308 – 321

Preliminaries about $LaMnO_3$

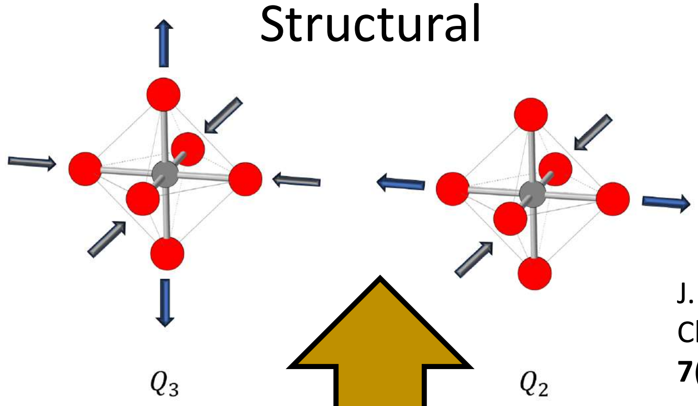
Local

Electronic

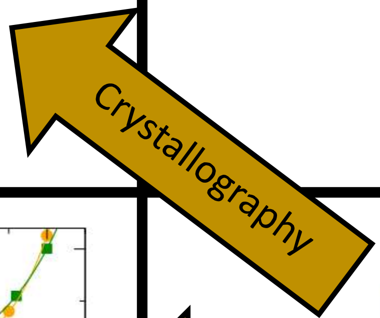


H. A. Jahn & E. Teller, Proc. Roy. Soc. **161** (1937), 220.

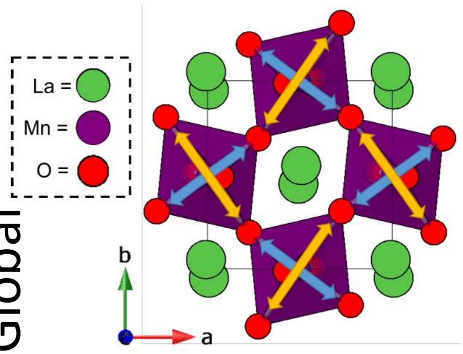
Structural



J. Van Vleck, J. Chem. Phys., **7**(1939), 72.

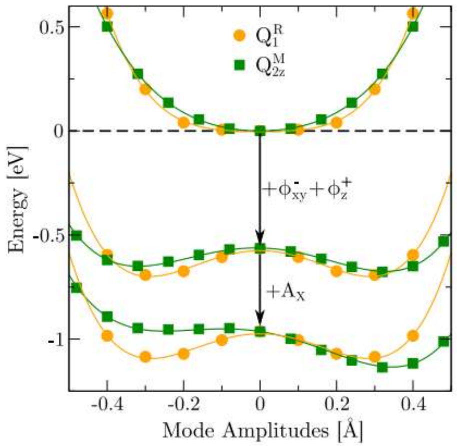


Global

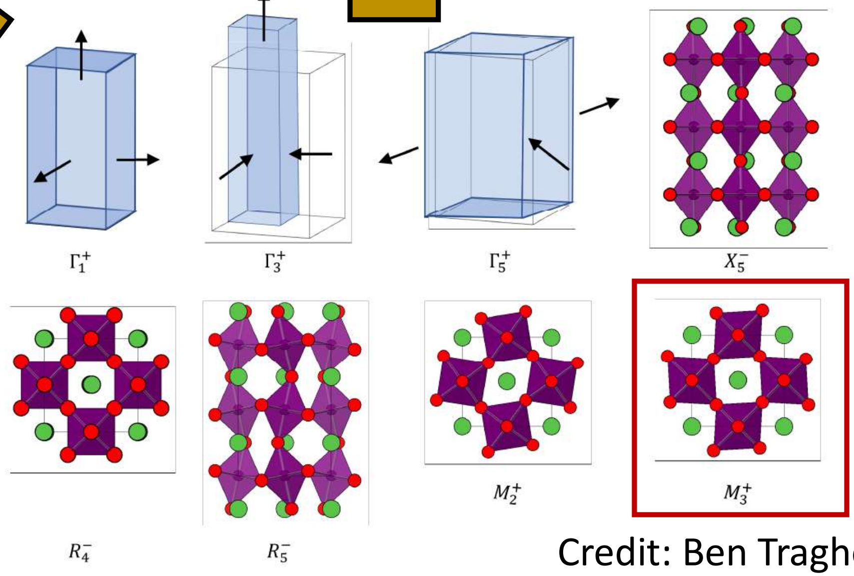


C-type orbital order

J.B. Goodenough, *Phys. Rev.* 100 (1955), 564.

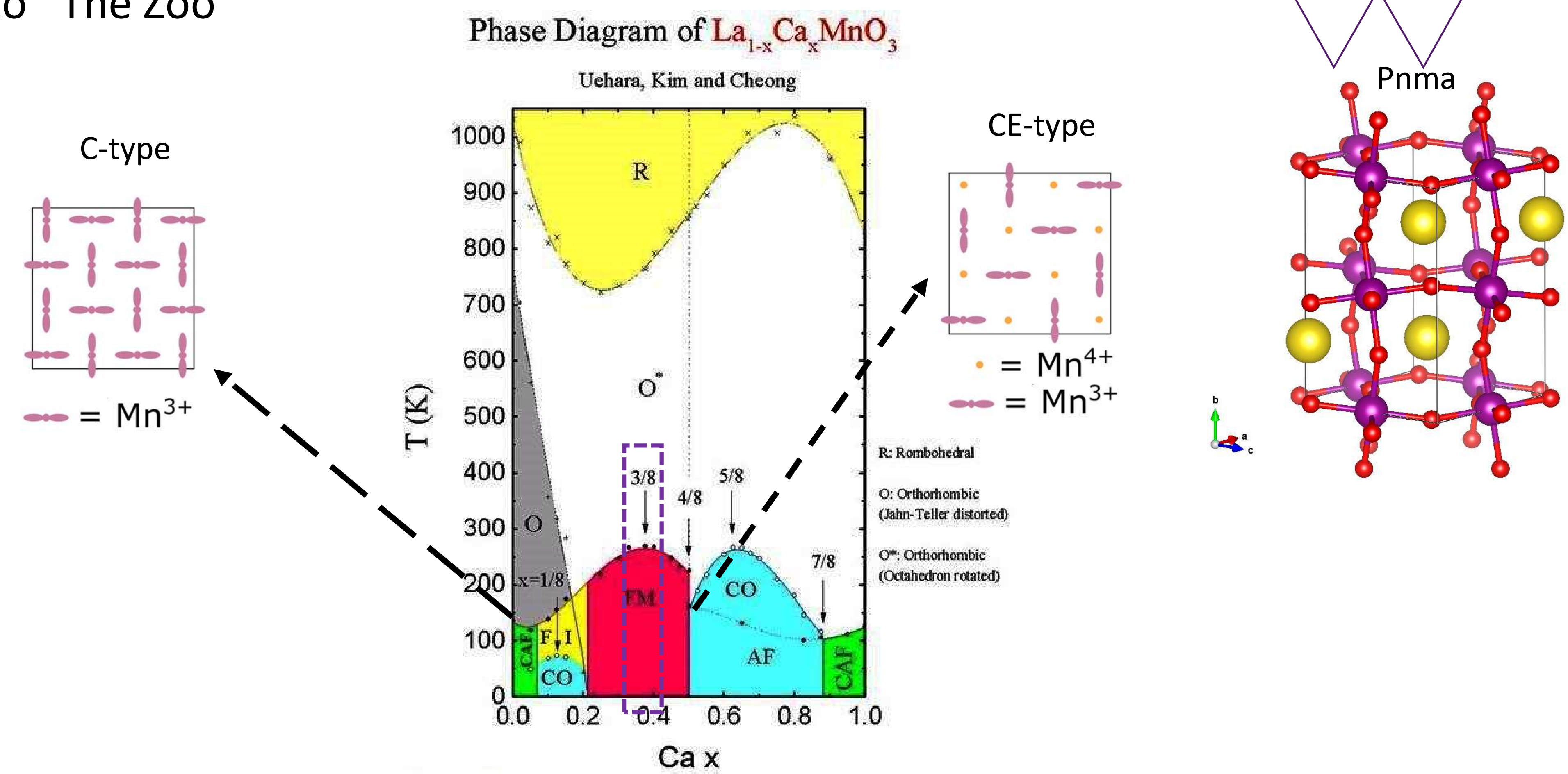


M. M. Schmitt, Y. Zhang, A. Mercy & P. Ghosez. *Phys. Rev. B* **101**(2020), 214304



Credit: Ben Tragheim

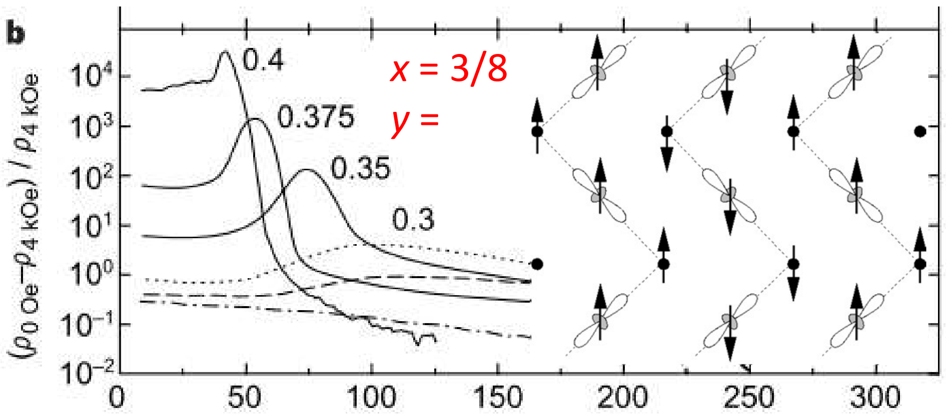
Welcome to “The Zoo”



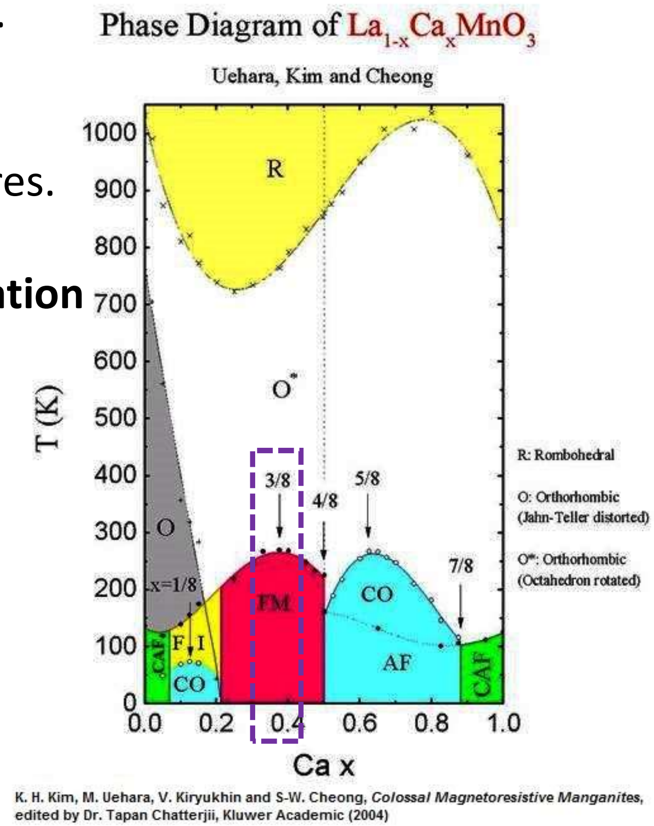
K. H. Kim, M. Uehara, V. Kiryukhin and S-W. Cheong, *Colossal Magnetoresistive Manganites*, edited by Dr. Tapan Chatterjii, Kluwer Academic (2004)

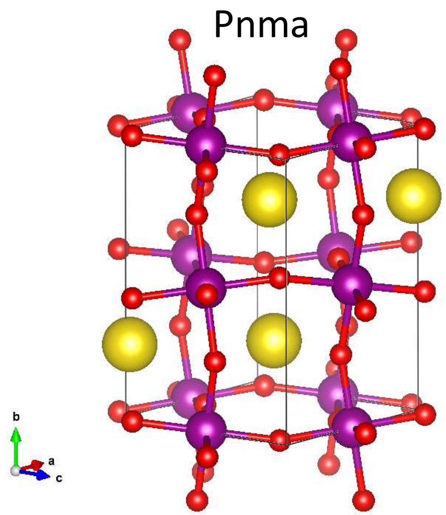
Colossal Magnetoresistance in $La_{1-x}A^{2+}_{x}Mn^{3+x}O_3$ doped systems

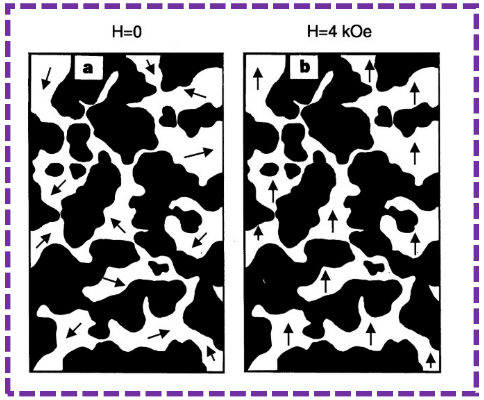
- Ferromagnetic conducting state competes with insulating AFM charge and orbital ordered phase.
- Canonical $La_{5/8-y}Pr_yCa_{\mathbf{3/8}}MnO_3$, (LPCMO***, x* = 3/8**) shows maximum MR response at low temperatures.
- Understood to be due to **Electronic Phase Separation** on the ~200 nm length scale.
- OO at 3/8[th] assumed to be similar to x =1/2.



Cox, D., Radaelli, P., Marezio, M. & Cheong, S. W. *Phys. Rev. B* **57**(1998), 3305–3314.



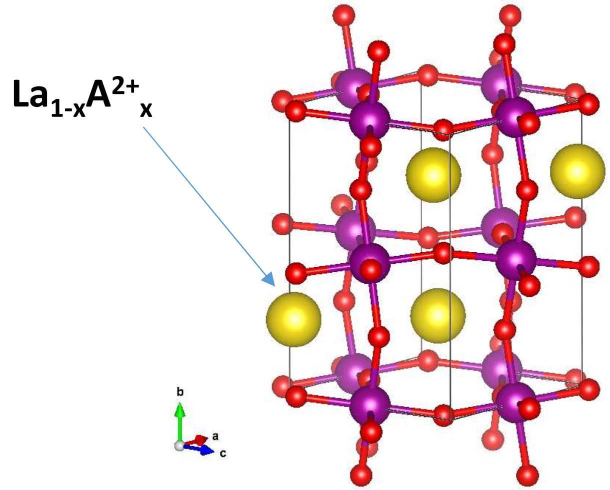




Percolative phase separation underlies colossal magnetoresistance in mixed-valent manganites. M. Uehara, S. Mori, C. H. Chen, & S. W. Cheong, *Nature* **399** (1999), 560.

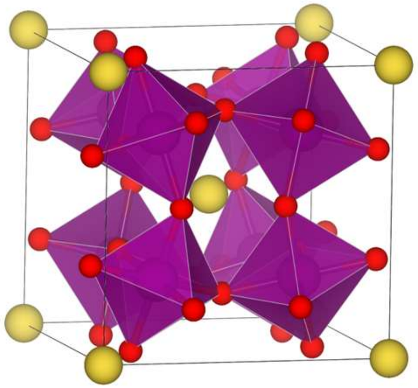
Problems with Vegetables

- Divalent substitutions in $La_{1-x}A^{2+}_xMn^{3+x}O_3$ with A^{2+} 'vegetables' change more than just the nominal valence at the Mn site:
  - Average ionic radii (both A and B-site)
  - Variance
  - Octahedral tilting (band narrowing?)
  - Phase coexistence

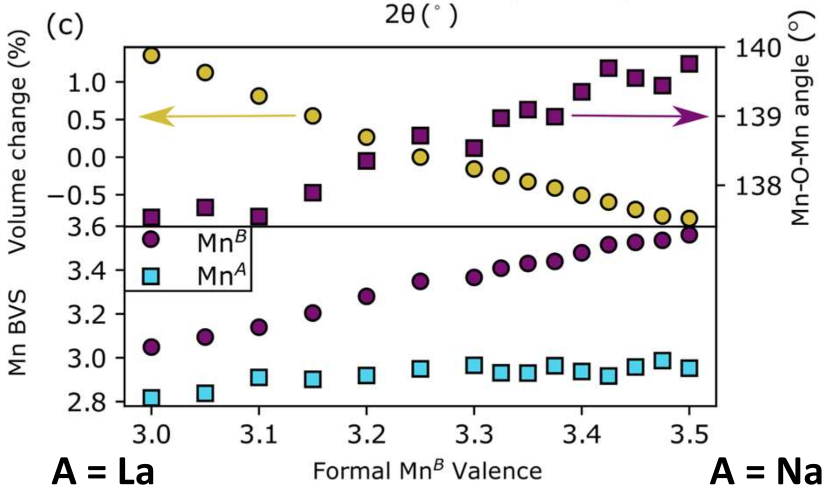


- *Pnma* (*Pbnm*) perovskites have their own problems:
  - Lattice symmetry already orthorhombic, prior to orbital ordering.
  - Lattice degrees of freedom conspire to give a pseudo-cubic metric.
  - Normal modes that describe C-type OO already allowed by symmetry.
  - Single crystals highly twinned.

Prototype system: 134-type perovskite $AMn_3^{A'}Mn^{B}_4O_{12}$

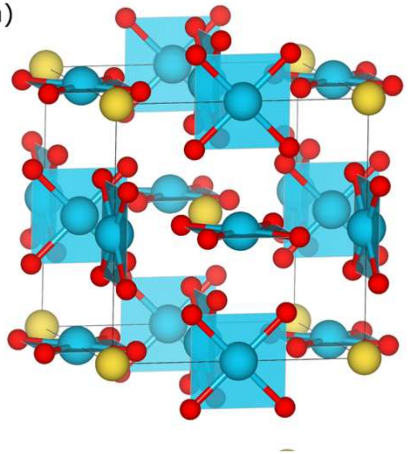


- Cubic *Im-3* aristotype based on $2a_p$ x $2a_p$ x $2a_p$ w.r.t. perovskite Pm-3m.
- Tilt system ($a^+a^+a^+$) is independent of A-site.
- A = $[La_{1-x}Ca_x]$ and $[Na_{1-x}Ca_x]$ may be used to hole dope on Mn^B from 3+ to 3.5+.

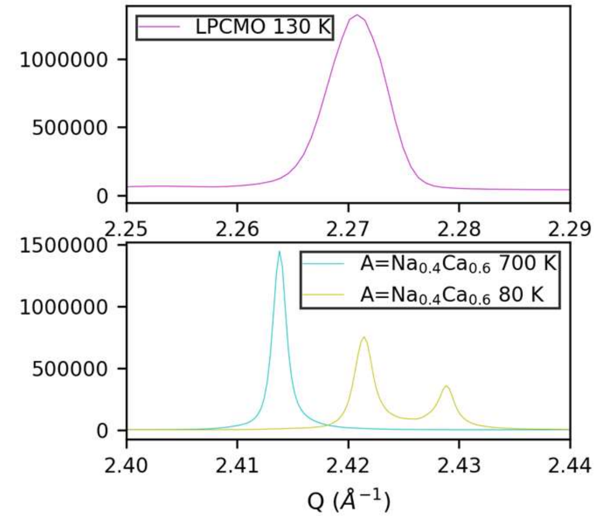


A = La **A = Na**

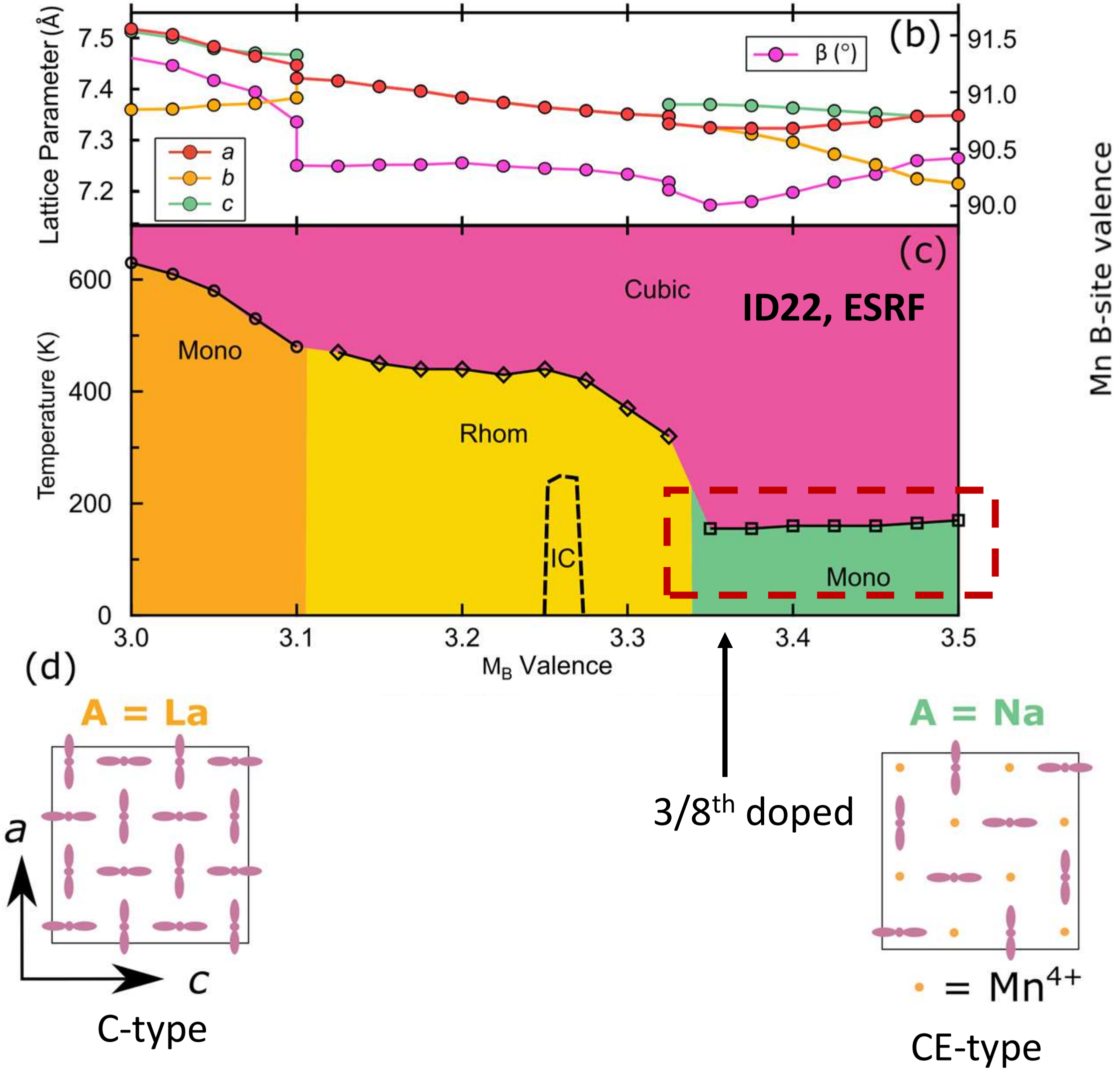
(a)

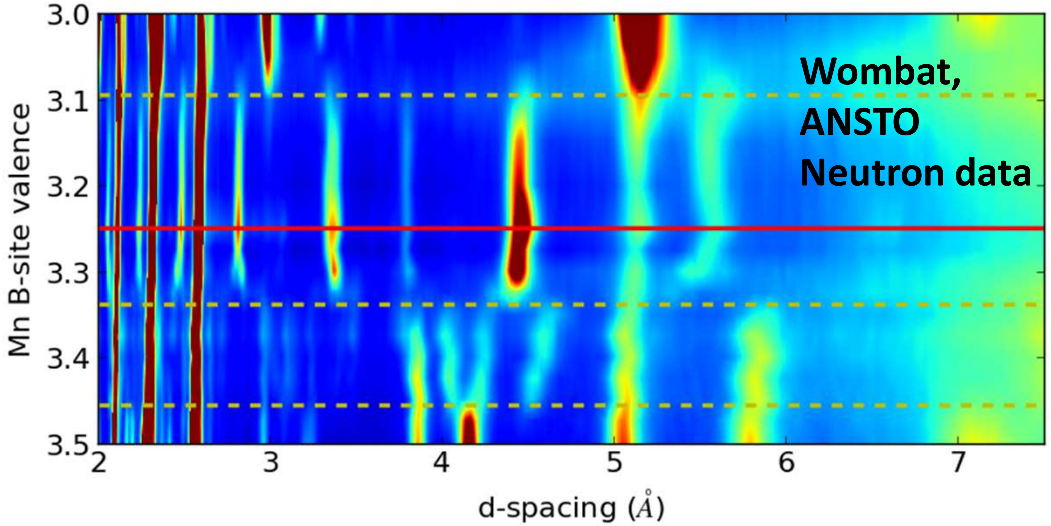


- A-site variance reduced w.r.t "classic" perovskite.
- This and other factor contribute to greatly enhancecrystallinity (low microstrain) of the prototype system
- Crucially **no EPS** is observed.



Prototype phase diagram from 0 – ½ doping level

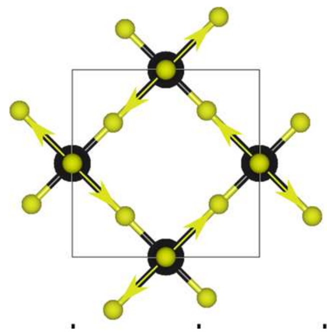




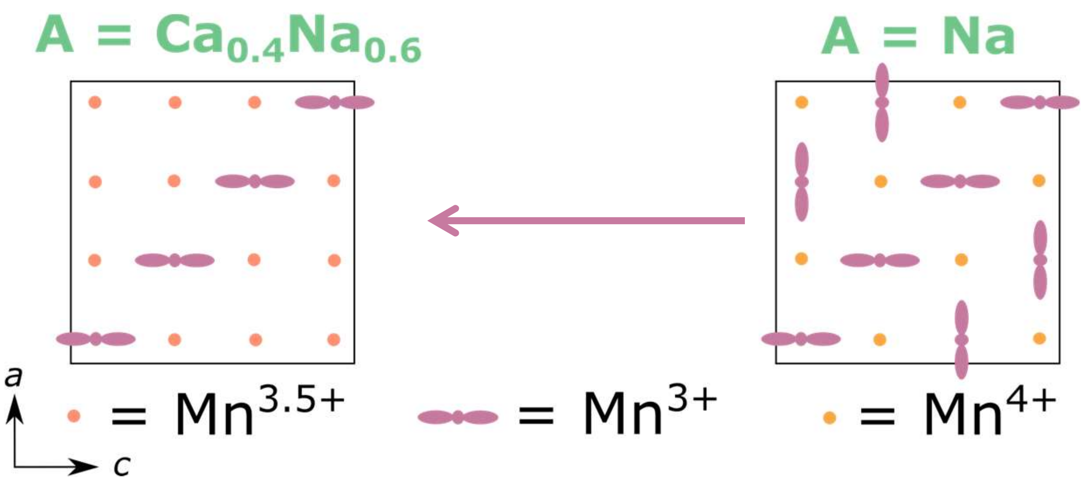
Dr Wei-tin Chen

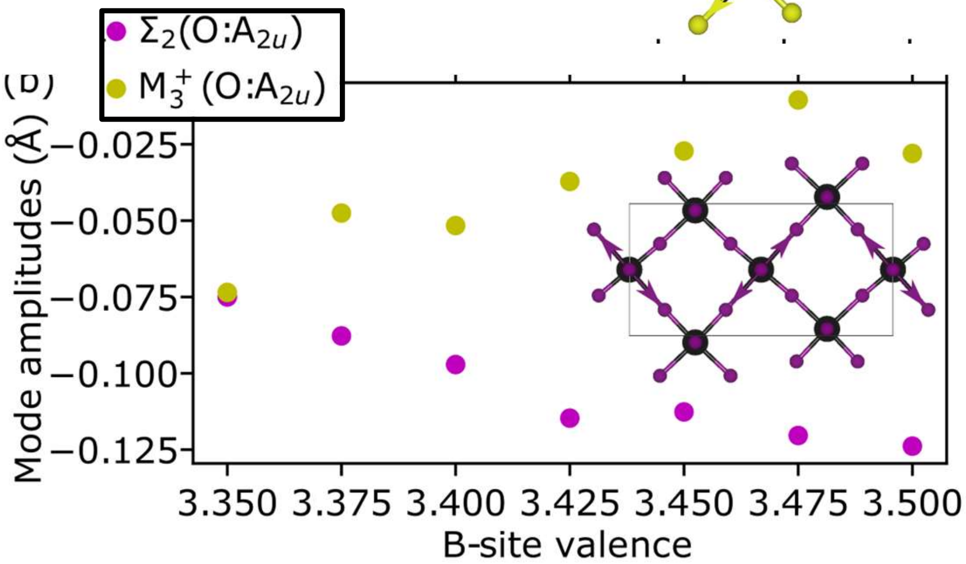
Orbital Order and Charge Disorder at the 3/8th doping level

- ‘C-type’ M_3^+ (k = ½ ½ 0) and ‘CE-type’ Σ_2 (k = ¼ ¼ 0) mode amplitudes evolve continuously from half to 3/8th doping level.

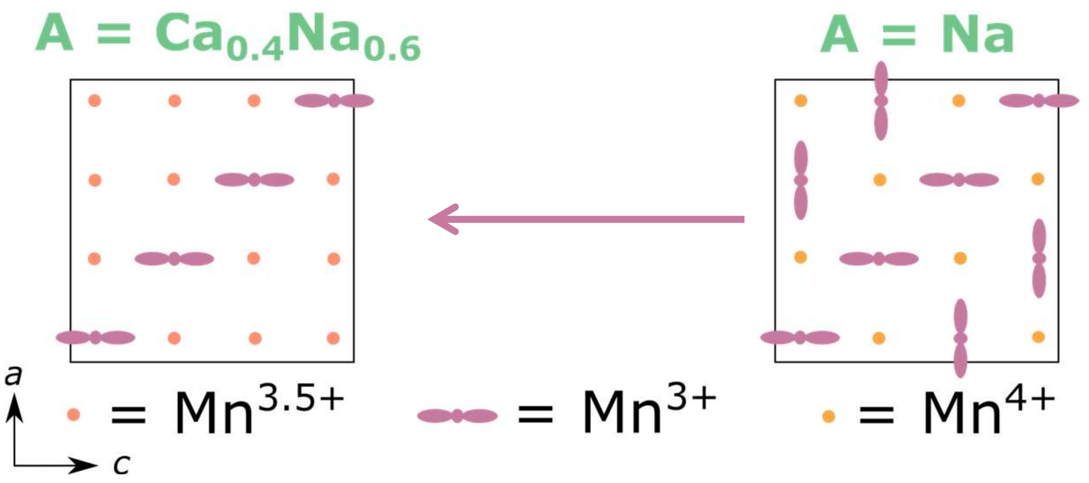


- modes approach equality at 3/8th doping level leading to cancellation of JT type distortions in half of the stripes



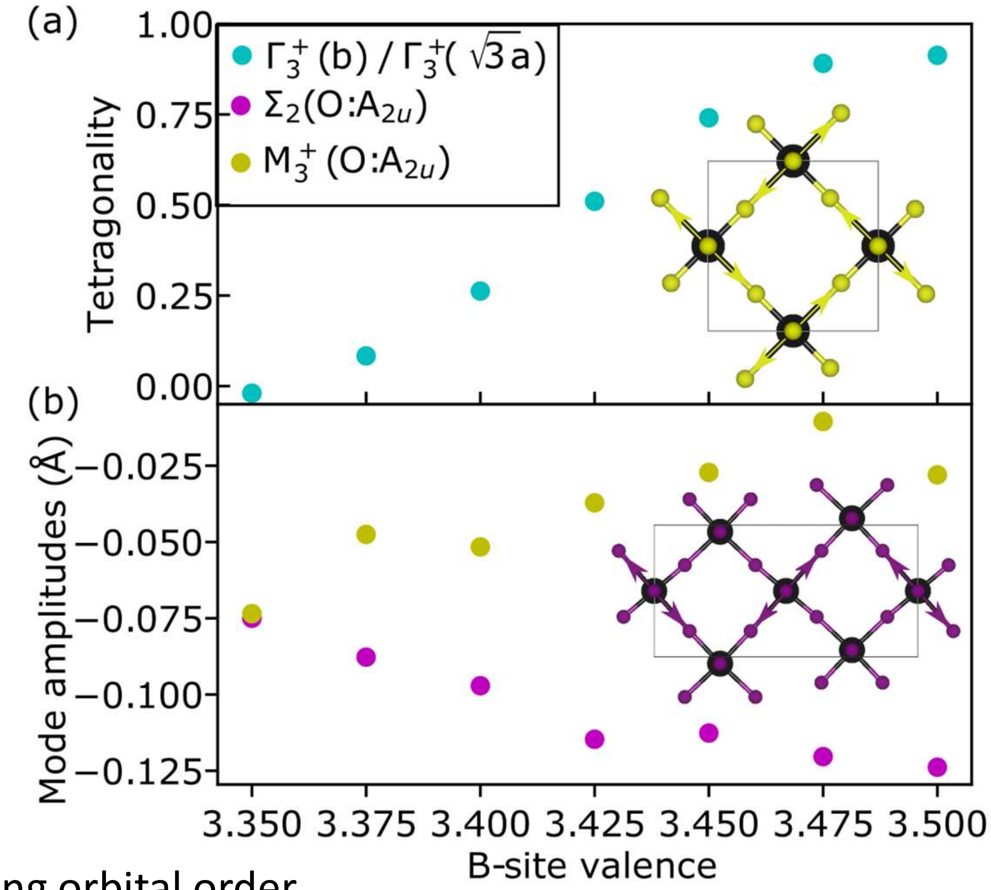


Pseudo-tetragonal metric symmetry at the 3/8th doping level



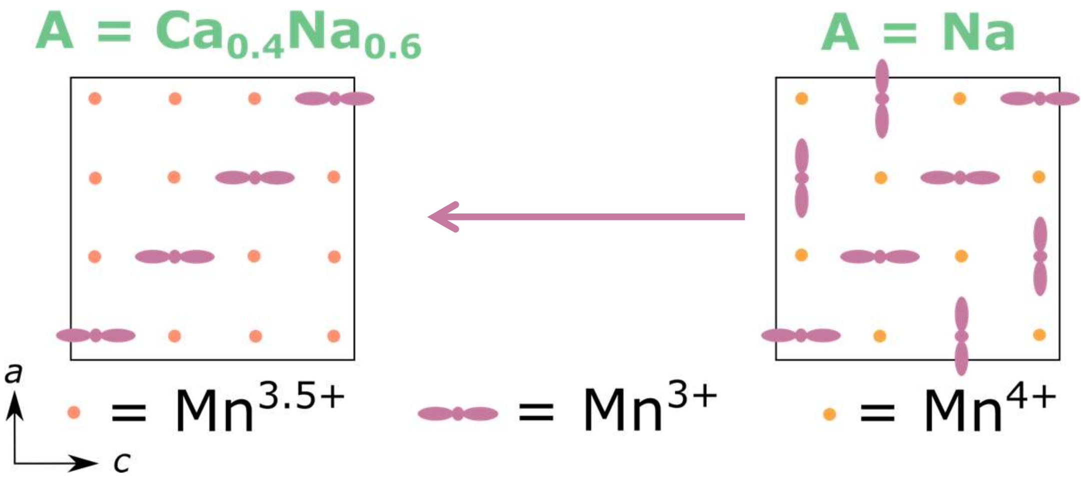
Lattice distortion is of type 1 long 2 short (Tetragonality = 0)

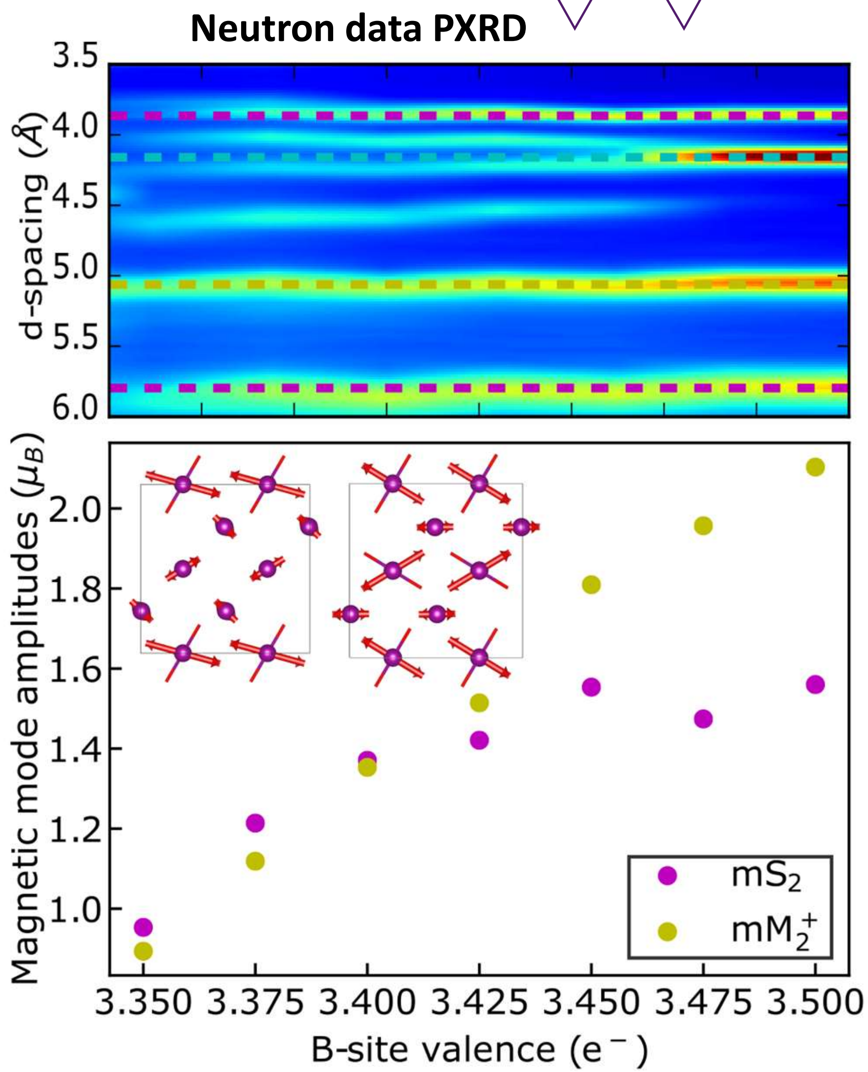
Lattice distortion is of type 2 long 1 short (Tetragonality = 1)



- The tetragonal pseudo symmetry is a hallmark of underlying orbital order
- This trend is likely obfuscated in the Pnma manganite perovskites
- **Melting of OO as e^- doped in to the x = ½ state is a very striking feature of the transitions**

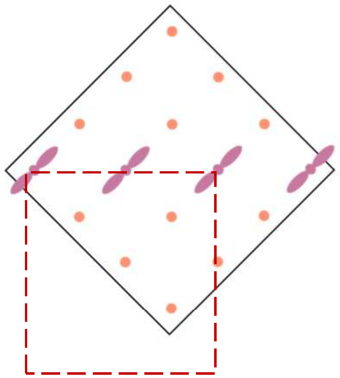
Orbital order and Charge Disorder at the 3/8th doping level



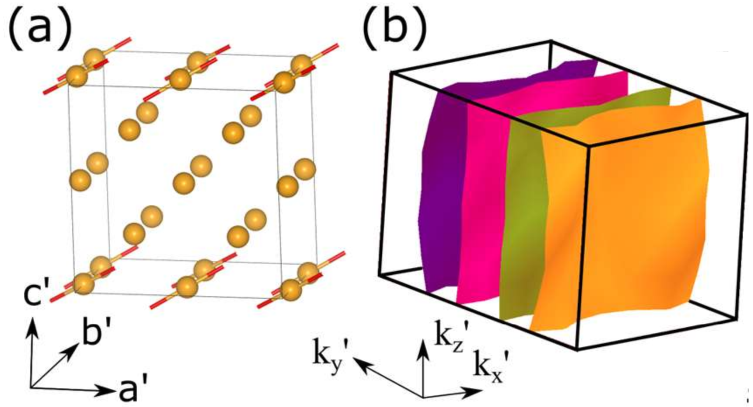


- ➢ Commensurate (CE) part of the magnetic structure evolves continuously
- ➢ Consistent with melting of order in half of the OO stripes

OO-CD model stable to relaxation under DFT + U

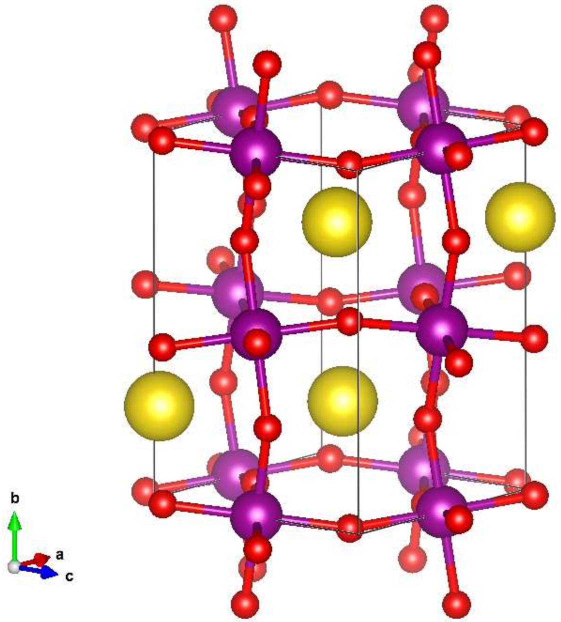


DFT unit cell

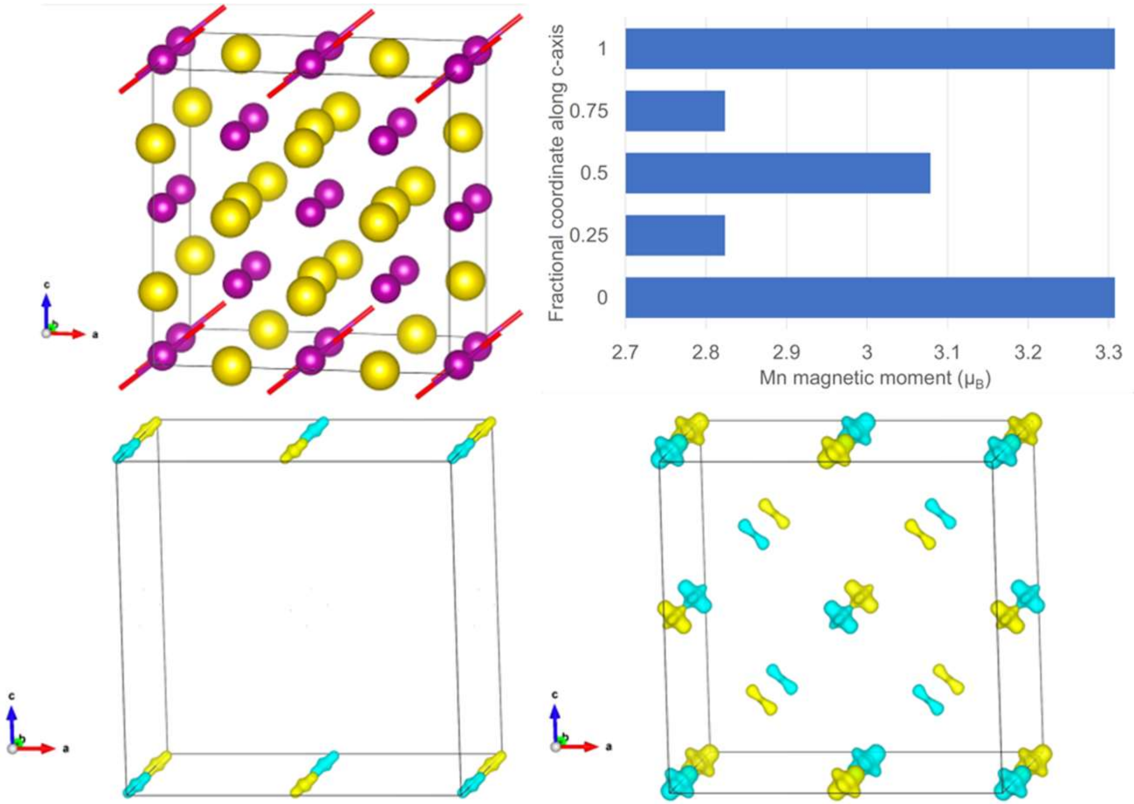


Dr Nicholas C. Bristowe

OO CD model stable in 3/8th hole-doped $LaMnO_3$ under DFT+U

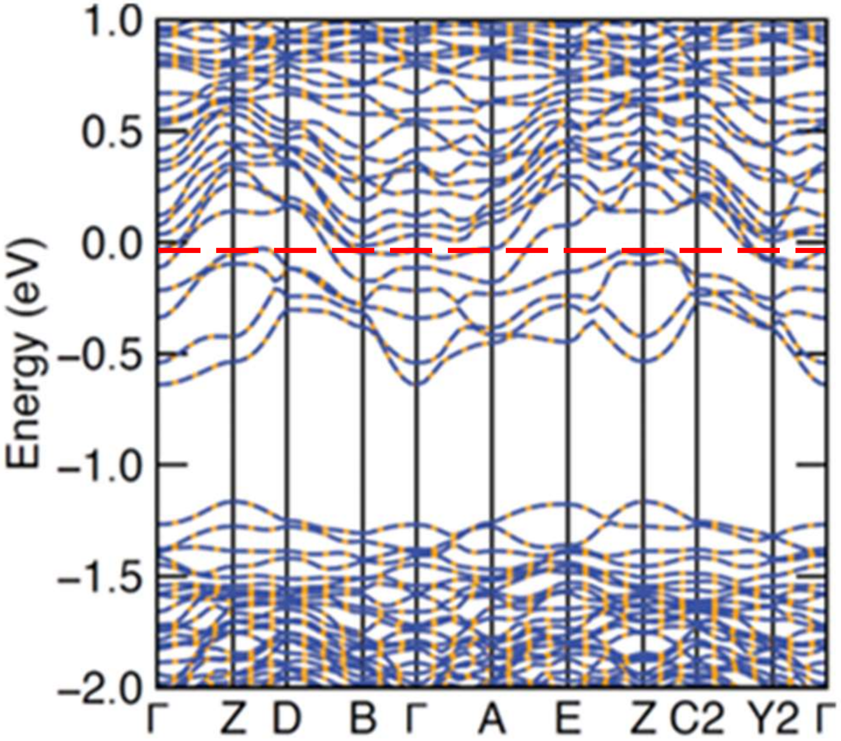


Pnma perovskite

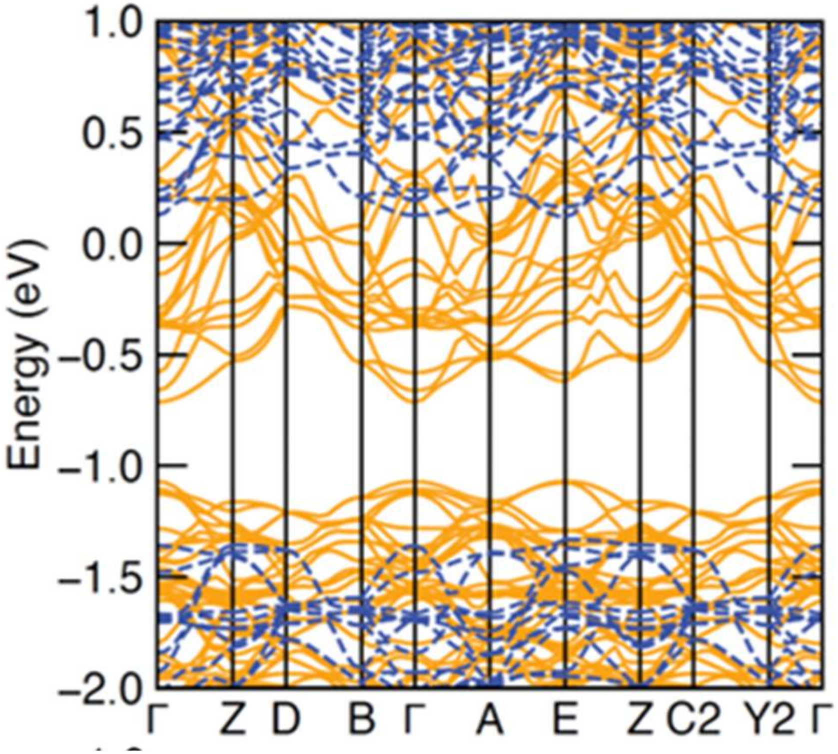


Coupling between OO with CD state and magnetic ordering

DFT+U experimental **AFM**



DFT+U forced **FM**



Striping of orbital-order with charge-disorder in optimally doped manganites. Wei-Tin Chen, Chin-Wei Wang, Ching-Chia Cheng, Yu-Chun Chuang, Arkadiy Simonov, Nicholas C. Bristowe & Mark S. Senn. *Nat Commun* **12** (2021)**,** 6319.

Conclusions

- A novel orbital-order with charge disorder (OO-CD) state has been observed in a prototype system at the optimal doping level for CMR in the manganite perovskites.
- The structure at the 3/8th doping level is described by a superposition of two lattice modes corresponding with the C-type (undoped) and CE-type (half-doped) OO structures.
- The gradual melting of the OO in half of the layers of the half-doped CE state is supported by the evolution of the lattice strain and magnetic modes.
- The OO-CD state is found to be stable with respect to relaxation under DFT +U.
- Instability of the OO-CD with respect to FM order is demonstrated theoretically.
- **EPS is likely a very general phenomena of electronic phase transitions and further understanding is required.**

Acknowledgements

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ISODISTORT:
http://stokes.byu.edu/iso/isodistort.php; B. J. Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, "ISODISPLACE: An Internet Tool for Exploring Structural Distortions." J. Appl. Cryst. 39, 607-614 (2006).