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Research programs:

- **Semiconductor interfaces: band-structure engineering**

  with C. Berthod, J. Bardi, M. Peressi, and A. Baldereschi

- **Nanostructured solids and surfaces: local work functions and negative electron affinity**

  with C.J. Fall, C. Sgiarovello, and A. Baldereschi

- **Manganites: electronic, magnetic, and atomic structure**

  with G. Trimarchi, N. Stojic, and M. Altarelli

LDA+U Study of Structural and Orbital-Ordering Properties in Manganites

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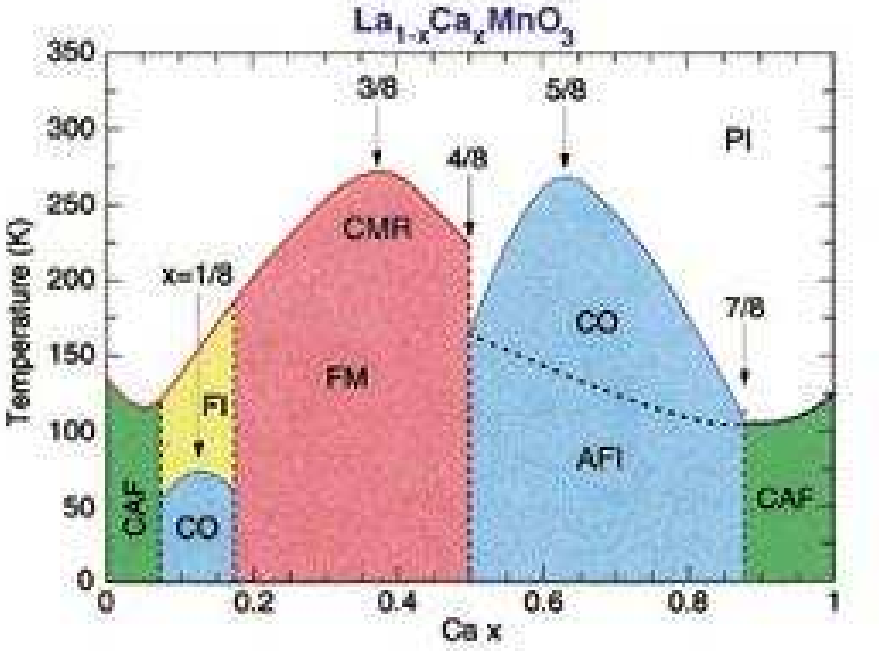
- Giancarlo Trimarchi (DEMOCRITOS)
- Natasa Stojic (ICTP)
- Massimo Altarelli (ICTP and ELETTRA)

Focus:

- **$LaMnO_3$ under pressure**
- **Mn^{+3}/Mn^{+4} charge and orbital ordering in $La_{1/2}Ca_{1/2}MnO_3$**

Interest in Manganites

- Colossal magnetoresistance, e.g., in $La_{1-x}(Ca,Sr)_xMnO_3$
- Variety of phases with remarkably different magnetic, transport, and structural properties
- Related to a complex interplay between orbital, lattice, spin, and charge degrees of freedom



Cheong and Hwang (1999)

AF: antiferromagnetism
F: ferromagnetism
P: paramagnetism
CO: charge ordering
CMR: colossal magnetoresistance

LDA/GGA *ab initio* approaches: problematic

- Fail to correctly predict the insulating ground state of $LaMnO_3$ when structural optimization is performed
- Fail to correctly predict the insulating charged-ordered ground state of doped manganites using the experimental structural parameters

ØAn alternative: LDA+U

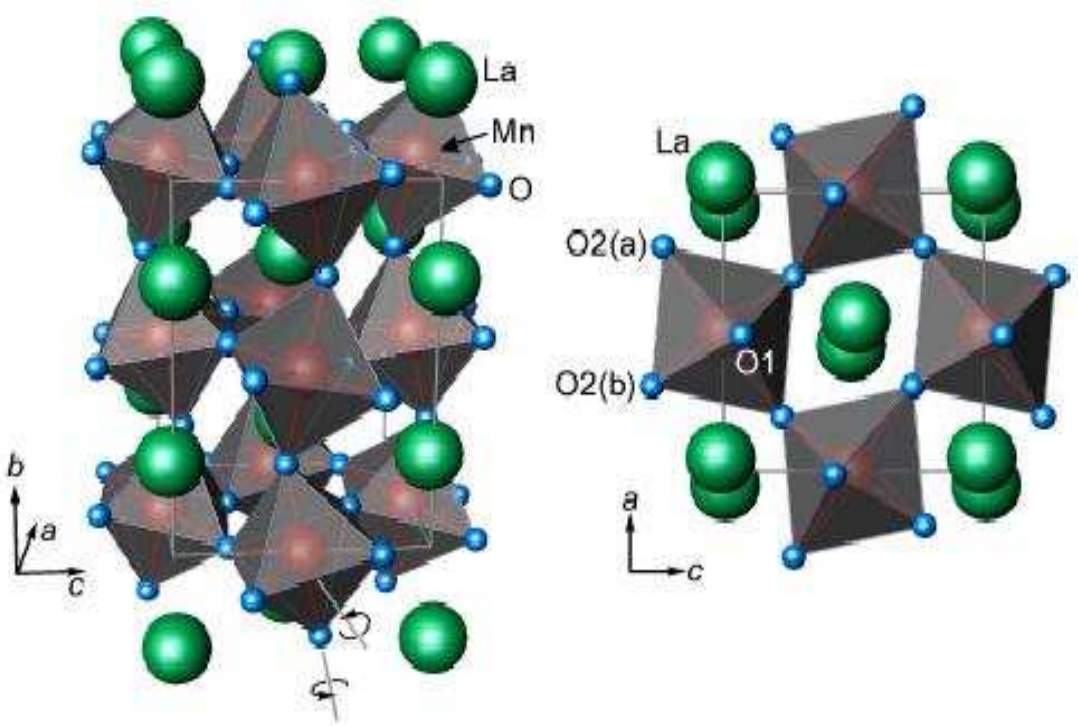
ØPredictive capability for atomic structure?

LDA + U calculations

- Energy functional:[1,2] $E_{LDA}(\rho) + (U/2)\ Tr\ [n_d\ (1-n_d)]$
- Vanderbilt ultrasoft pseudopotentials[3]
- Plane wave basis; E_{cut} = 30 Ry
- U evaluated using the LDA linear-response approach by Cococcioni and de Gironcoli[2]

[1] Sawada et al., PRB 56, 12154 (1997).
[2] Cococcioni and de Gironcoli, Cond-mat/0405160.
[3] Vanderbilt, PRB 41, 7892 (1990).

$LaMnO_3$: experimental equilibrium crystal structure



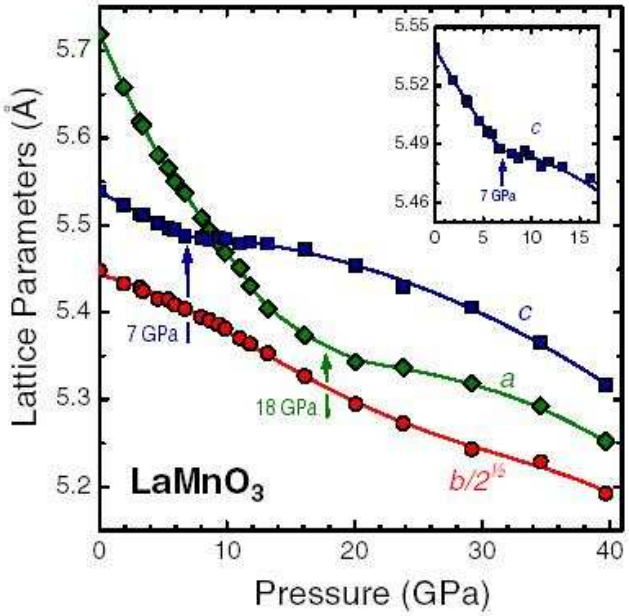
P = 0

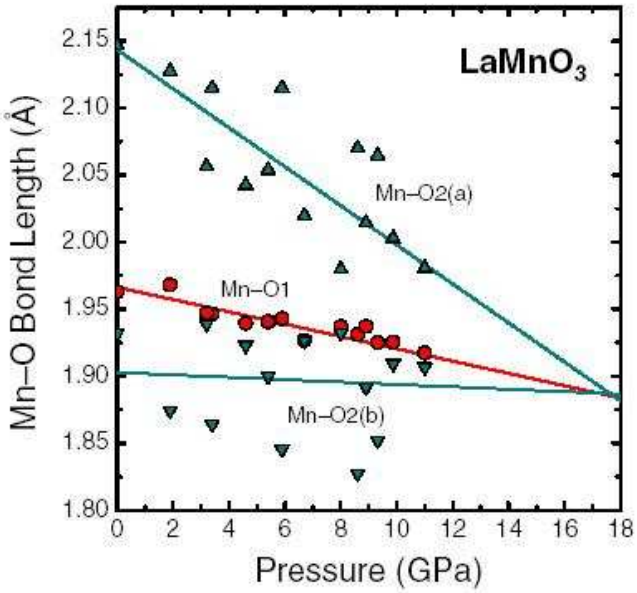
Pnma crystal structure

Cooperative Jahn-Teller (JT) distortion: alternate long and short Mn-O bonds in the ac plane

$LaMnO_3$ under pressure: experiments

- Complex structural changes[1]

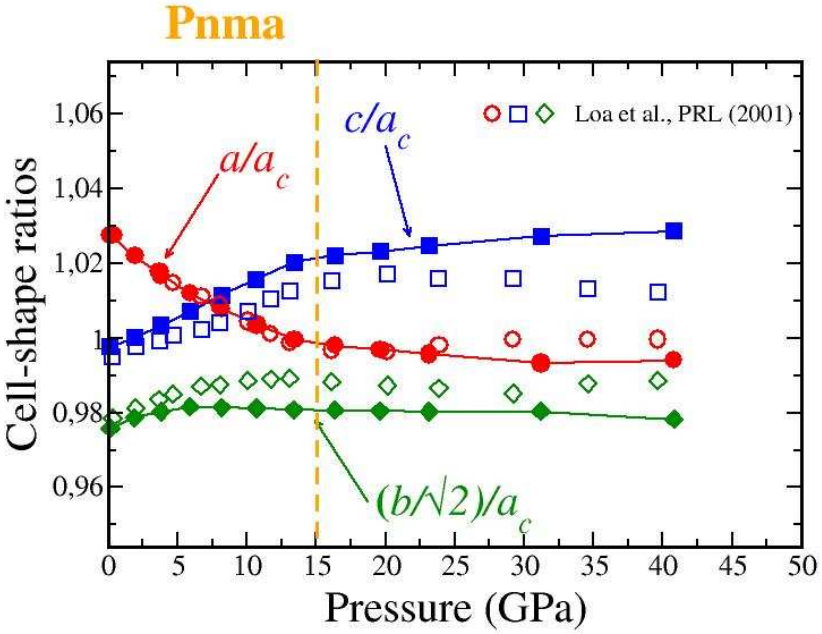


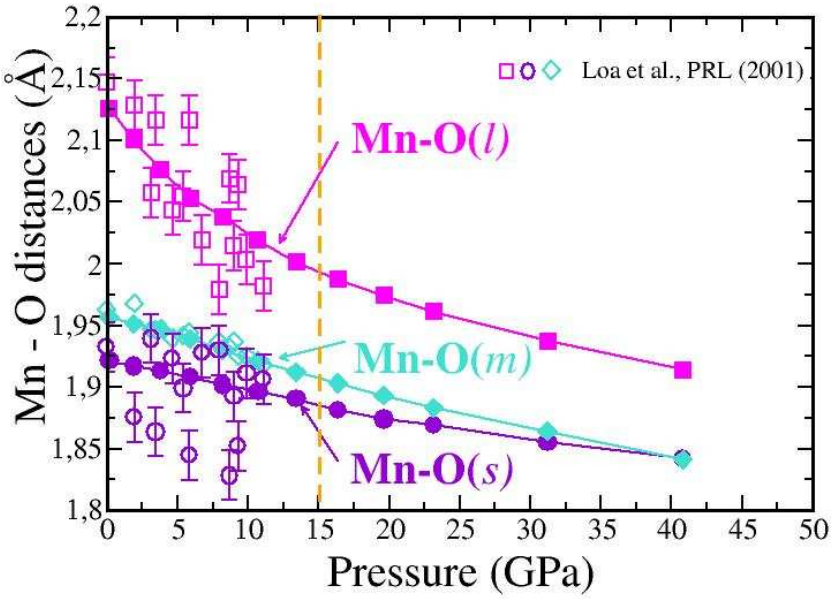


- **Structural transformation**[2] at ~15 GPa (vanishing JT?)
- **Insulator-metal transition**[1] at ~32 GPa

[1] Loa *et al.* , PRL 87, 125501 (2001).
[2] Sani *et al.* , PRB (in press).

LDA+U results: cell-shape ratios and Mn-O bonds

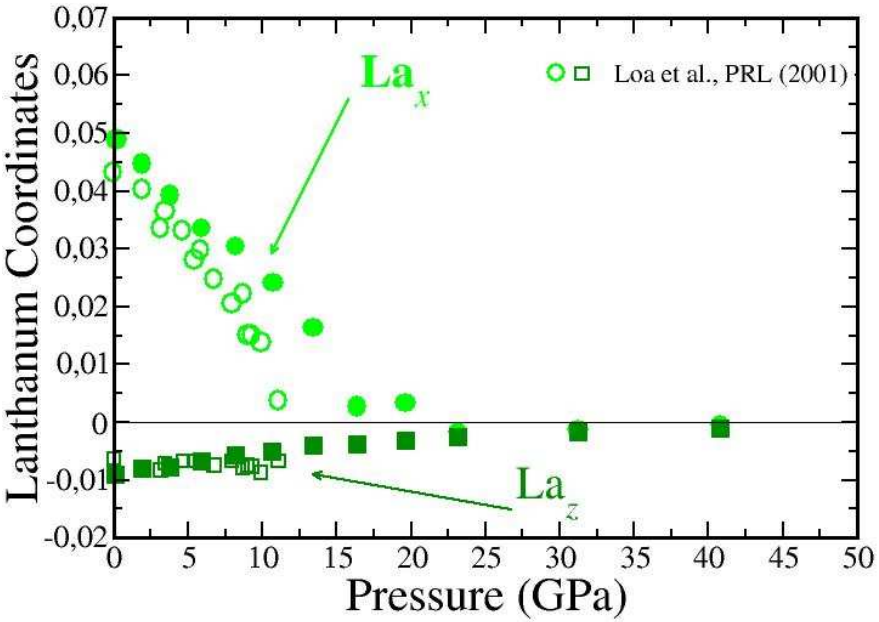


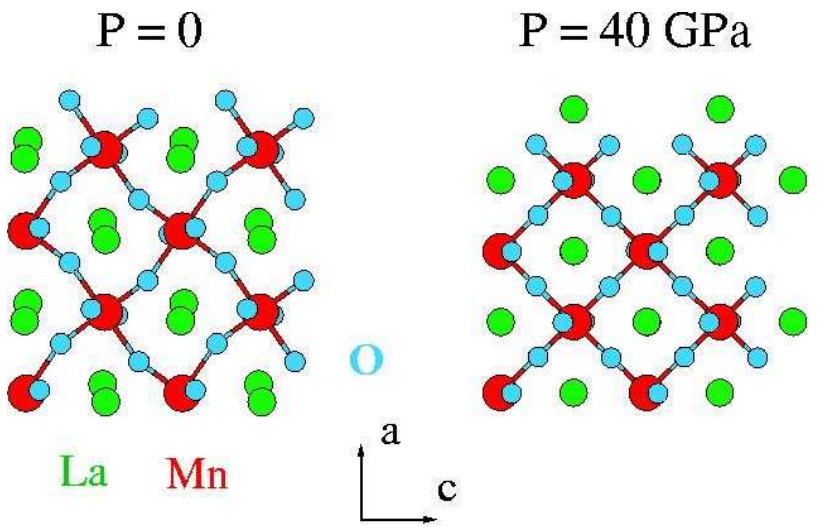


Pnma phase:

- Pressure dependence of lattice ratios and Mn-O bonds are in good agreement with experiment
- JT distortion does not vanishes up to 40 GPa (insulating up to ~40 GPa)

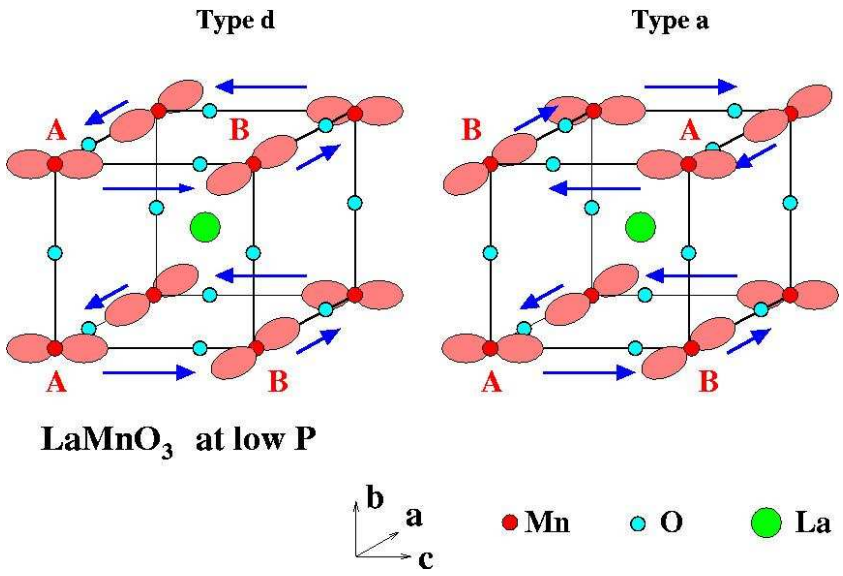
LDA+U results: La displacement

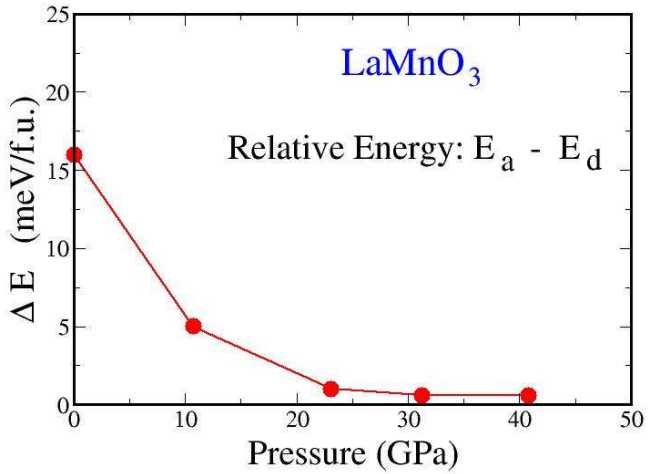




- La off-center displacement vanishes around 15 GPa, consistent with experiment
- Rotation of the octahedra around the b axis also vanishes
- O packing: close stacked oxygen (100) planes at high pressure

A- versus d-type JT distortion : possible origin of the transition





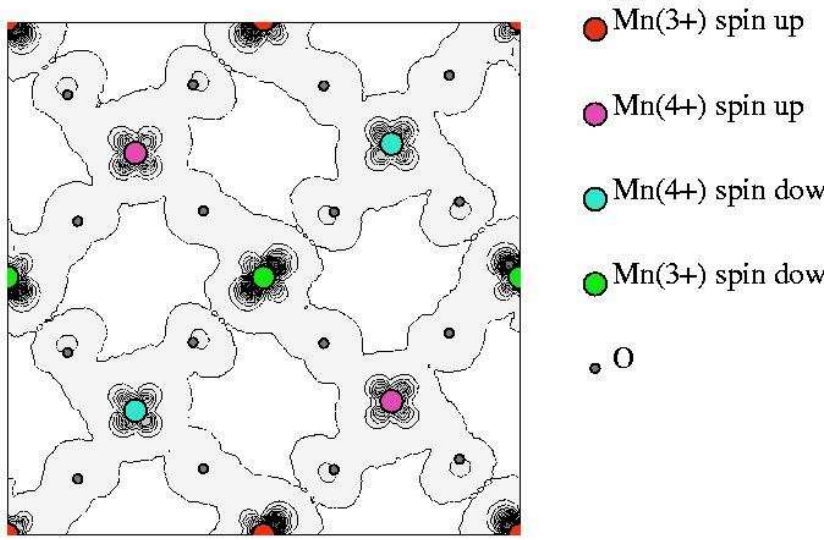
- **At ambient condition:** d-type stabilized by La off-center displacement [Mizokawa, Khomskii, Sawatzky, PRB 60, 7309 (1999)]
- **Under pressure:** we find that a-type and d-type become essentially degenerate in energy when the La shift vanishes

=> Possible origin of the transition

Doped Manganites: atomic and electronic structure

- Structural optimization of the $La_{1/2}Ca_{1/2}MnO_3$ system with $P2_1/m$ symmetry [Expt: Radaelli *et al.*, PRB 55, 3015 (1997)]
- LDA +U correctly predicts a stable "Mn^{3+}/Mn^{+4} charge" and orbital ordered insulating structure
- Difference between "Mn^{3+}" and "Mn^{+4}" sites: mostly JT distortion and orbital ordering

$La_{1/2}Ca_{1/2}MnO_3$:
e_g charge density map



Conclusions

- LDA+U describes well the complex structural change in $LaMnO_3$ under pressure
- Vanishing of the La off-center shift => degeneracy of the a- and d-type JT distortions: possible origin of the pressure-induced transformation
- LDA+U correctly predicts a stable "Mn^{+3}/Mn^{+4}" charge/orbital ordered insulating $La_{1/2}Ca_{1/2}MnO_3$ structure

Future developments

- Address the controversy about the structure of $La_{1/3}Ca_{2/3}MnO_3$
- Strain effects in $La_{1-x}Sr_xMnO_3$
- Simulation of resonant x-ray scattering to probe orbital ordering