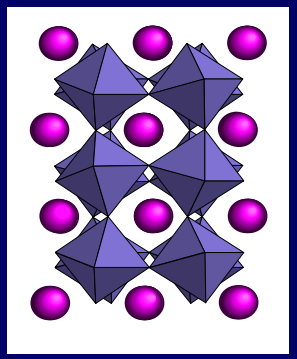
A Raman scattering investigation across the magnetic and MI transition in Rare Earth nickelate $RENiO_3$ thin films

C. Girardot [1,2], J. Kreisel [1], S. Pignard [1]

[1] Laboratoire des Matériaux et du Génie Physique (CNRS)
Minatec, Grenoble Institute of Technology , kreisel@inpg.fr

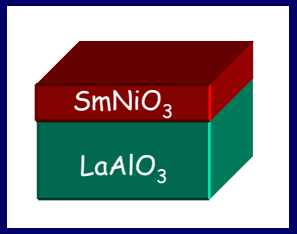
[2] Schneider Electric Industries S.A.S.
Grenoble, France

Outline

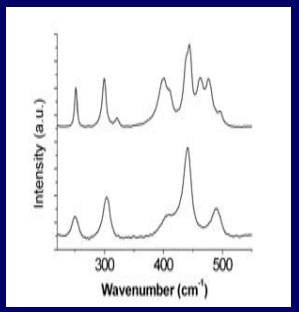


- **Rare earth nickelates: $RENiO_3$**
  - Electric phase diagram
  - Magnetic phase diagram
  - Structural phase diagram

- **Open questions**



- **Investigated samples: $Sm_{1-x}Nd_xNiO_3$ thin films**



- **Temperature-dependent Raman scattering**
  - Metal-insulator phase transition
  - Magnetic phase transition
  - The paramagnetic-insulator phase

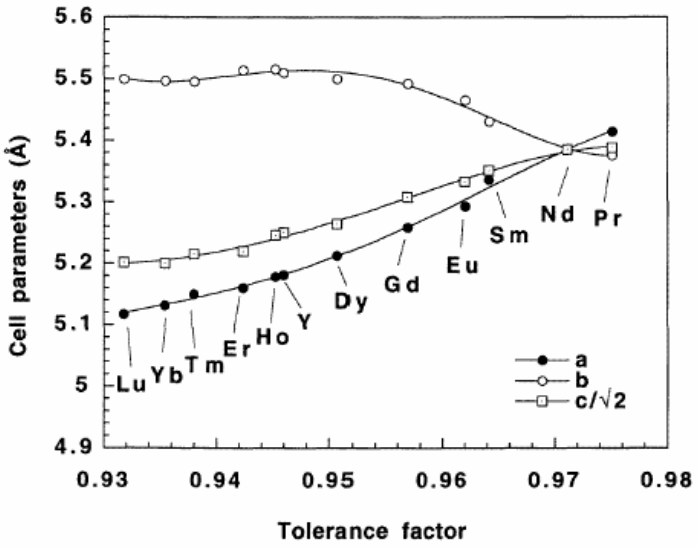
Rare earth nickelates: $RENiO_3$

Review: M.L Médarde, *J. Phys.: Condens. Mat.* **9**, 1997, 1679-1707

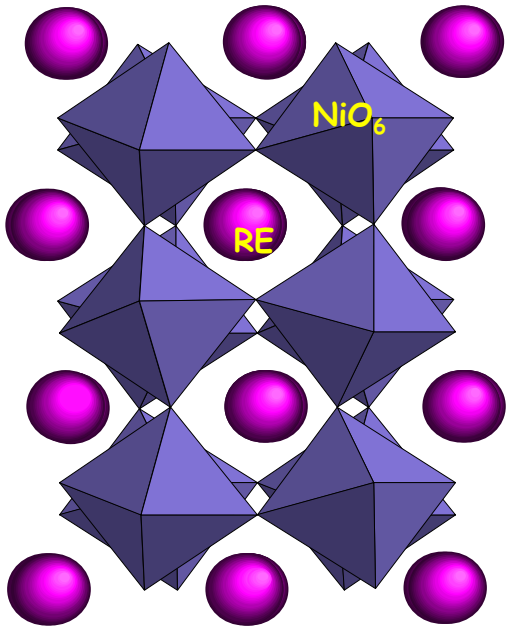
G. Demazeau, A. Marbeuf, M. Pouchard, and P. Hagenmuller, JSSC. 3, 582 (1971).

Difficult stabilization of Ni^{3+}

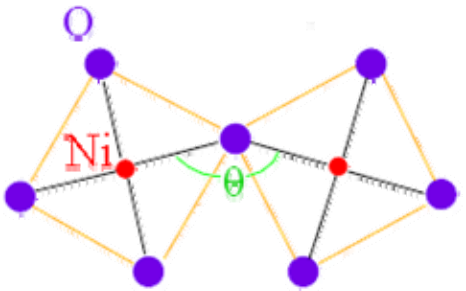
→ No single crystals available !
→ Need of high-pressure or thin film synthesis



Orthorhombic *Pbnm* ($a^-a^-c^+$ tilts)



Key parameter: Tilt angle θ

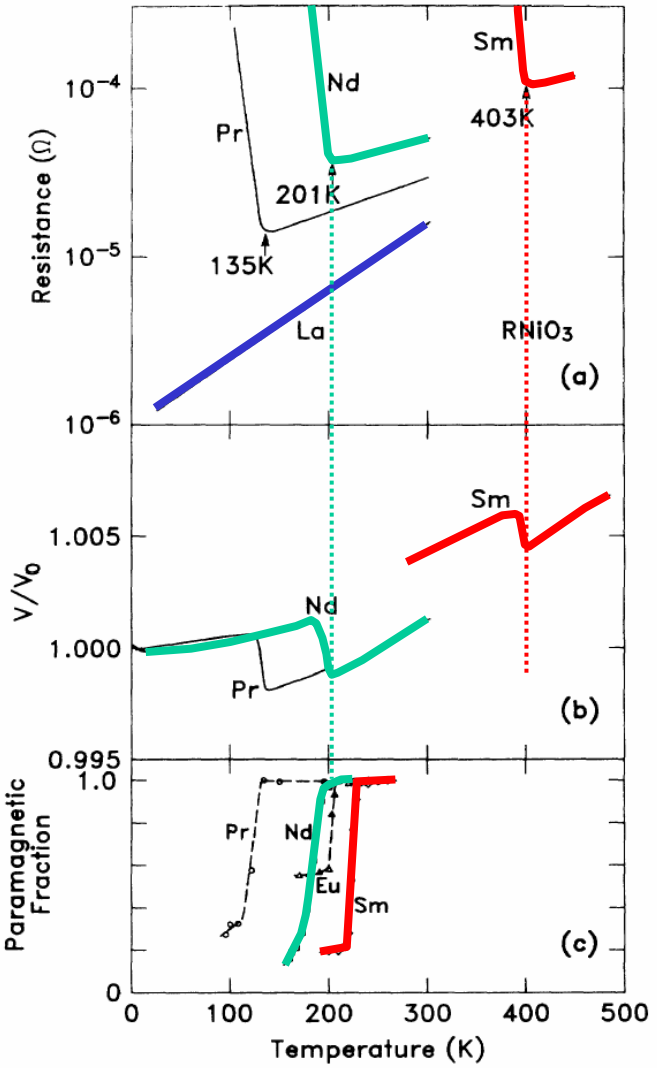


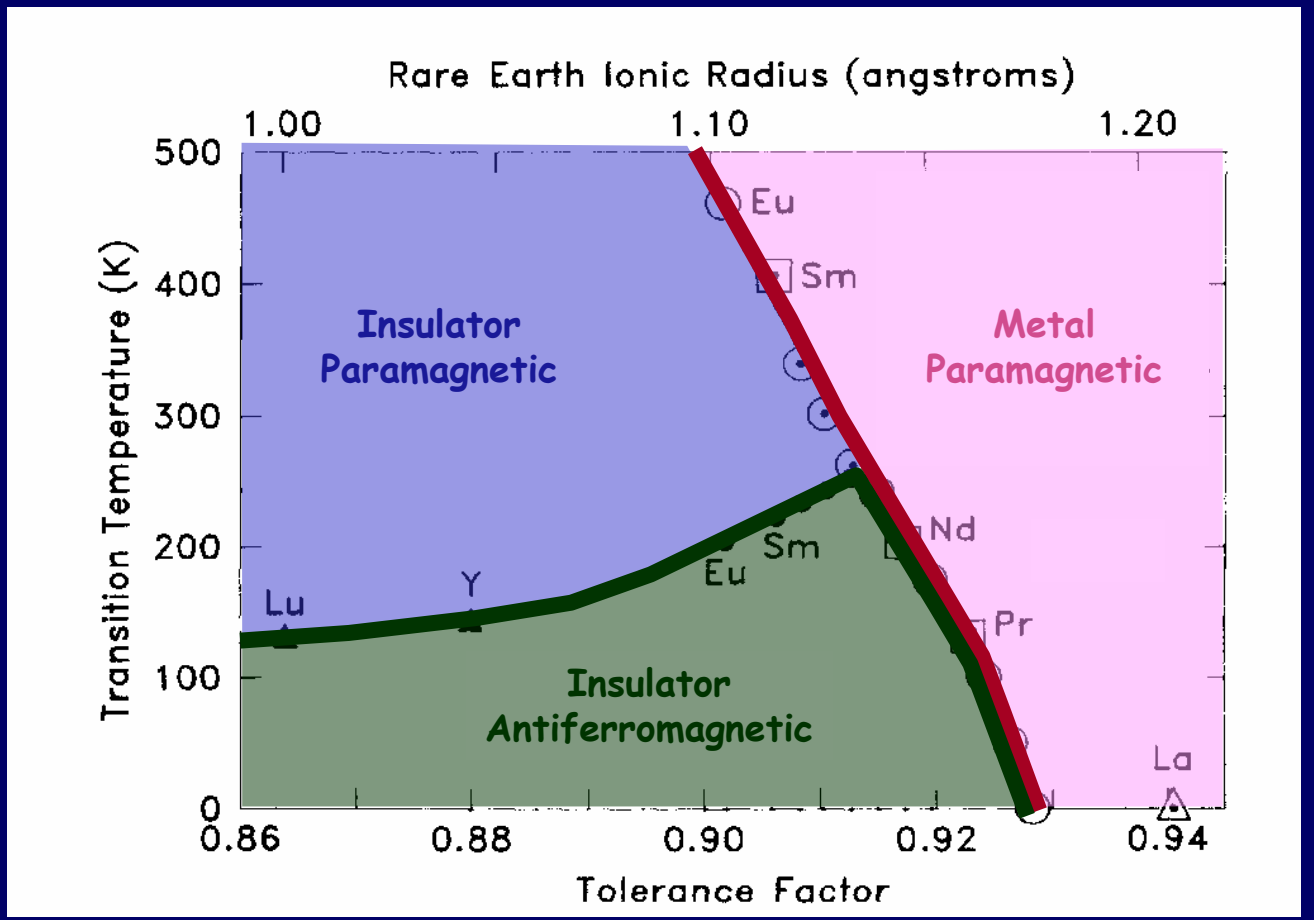
Linear decrease of tilt angle with RE^{3+} ionic size

165° ($LaNiO_3$) to 145° ($LuNiO_3$)

Electric and magnetic phase transitions in $RNiO_3$

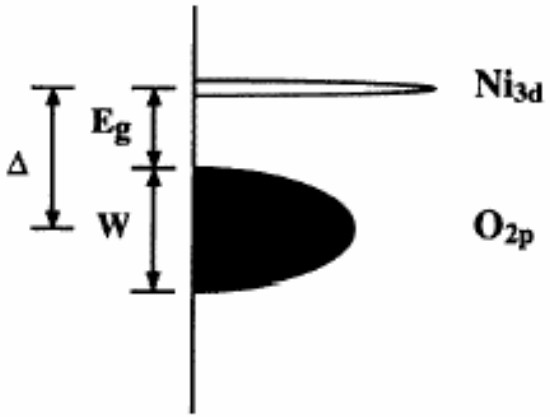
J.B. Torrance et al., Phys. Rev. B 45, 8209 (1992).

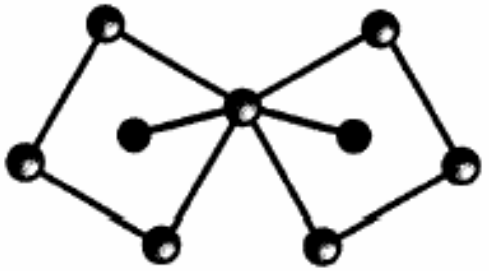




$T_{MI} = T_N$ or $T_{MI} \neq T_N$

The M-I transition in the charge-transfer scheme

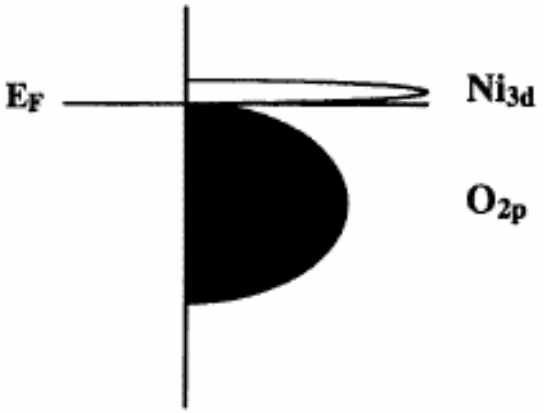


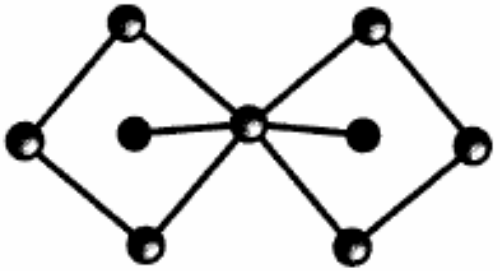


Insulator

Structure ?

Ni
O





Metal

Figure 15. The M–I transition in the charge-transfer scheme. The narrowing of the O 2p-derived valence band below T_{M-I} would take place because of the less efficient overlap of the O 2p and Ni 3d orbitals produced by the decrease of the Ni–O–Ni superexchange angle.

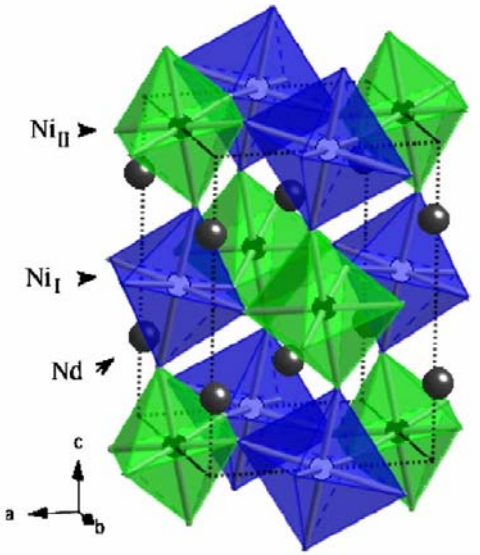
Review: M.L Médarde, *J. Phys.: Condens. Mat.* **9**, 1997, 1679

Structural phase transition at the metal-insulator transition

VOLUME 82, NUMBER 19 PHYSICAL REVIEW LETTERS 10 MAY 1999

Charge Disproportionation in RNiO$_3$ Perovskites: Simultaneous Metal-Insulator and Structural Transition in YNiO$_3$

J. A. Alonso,[1] J. L. García-Muñoz,[2] M. T. Fernández-Díaz,[3] M. A. G. Aranda,[4] M. J. Martínez-Lope,[1] and M. T. Casais[1]



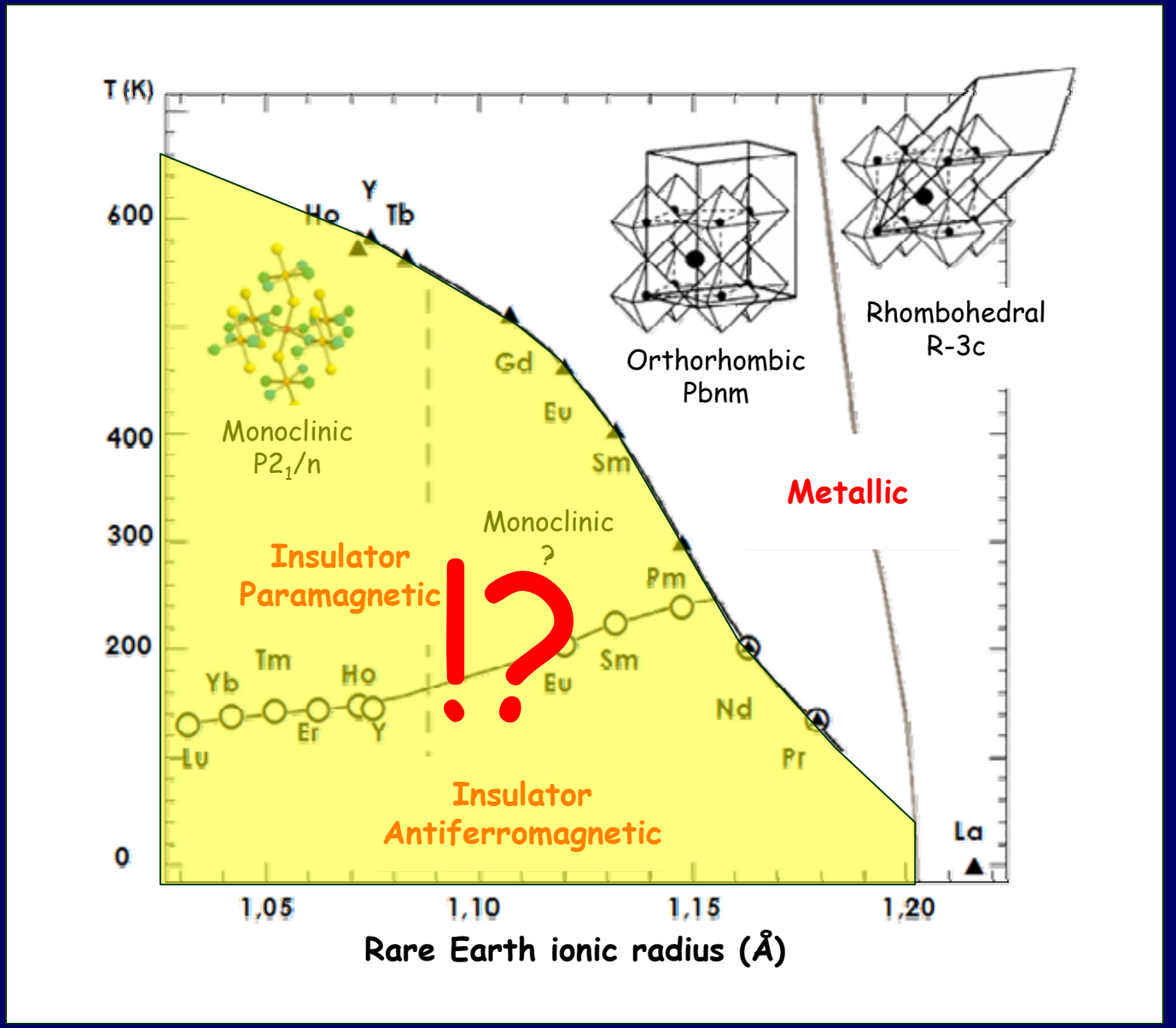
Direct evidence Structural phase transition at T_{MI} → 2 different types of octahedra

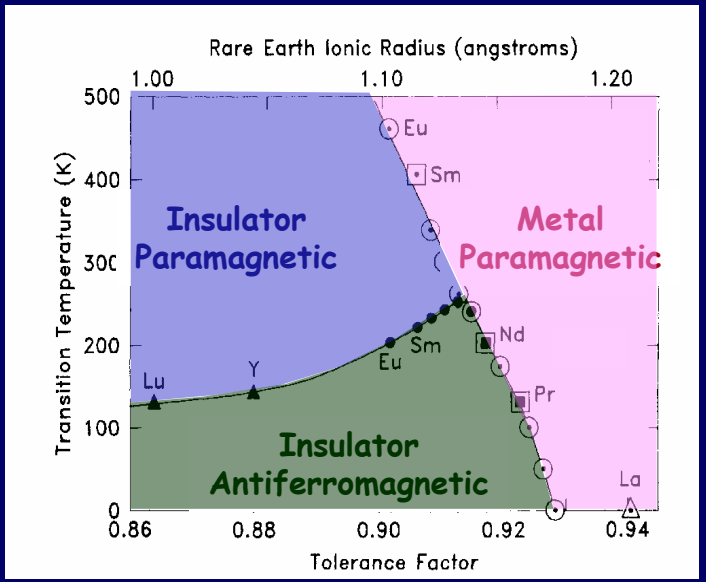
Model Long-range charge dispropornation (order)

$$2Ni^{3+} \rightarrow Ni^{(3+)+\delta} + Ni^{(3+)-\delta}$$

Proposition Universal driving force for gap opening at T_{MI} for all RENiO$_3$

Modified phase diagram





Questions

- Structural phase transition at T_{MI} for $SmNiO_3$?

  Not detected by high-resolution powder diffraction

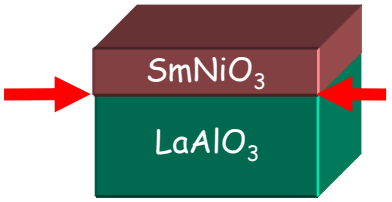
- Difference between $NdNiO_3$ and $SmNiO_3$?

  $T_{MI} = T_N \quad \leftrightarrow \quad T_{MI} \neq T_N$

- Phonon signature around magnetic and electric transition ?

N. Ihzaz et al. *Phys. Stat. Sol. (c)* **1**, 1679 (2004)
C. Girardot et al. *Surface & Coatings Techn.* **201**, 9021 (2007)
F. Conchon et al. *Appl. Phys. Lett.* **91**, 192110 (2007)

Investigated thin films (CVD synthesis)



In-plane compression

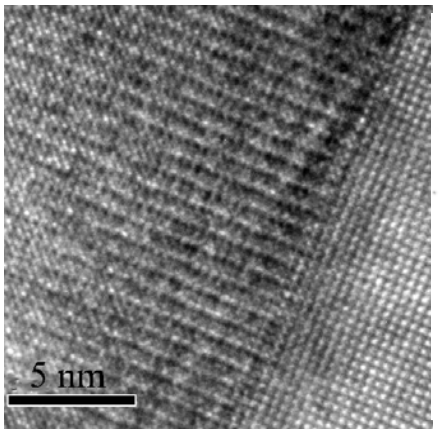
↓

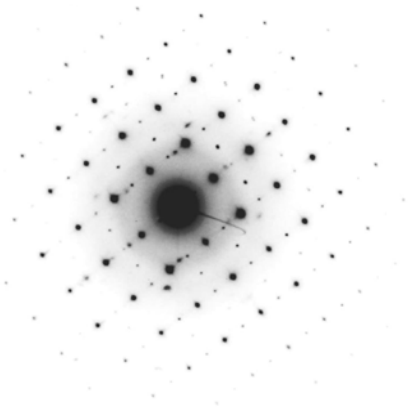
Stabilisation of Ni^{3+}

XRD: No impurities (except thick films)

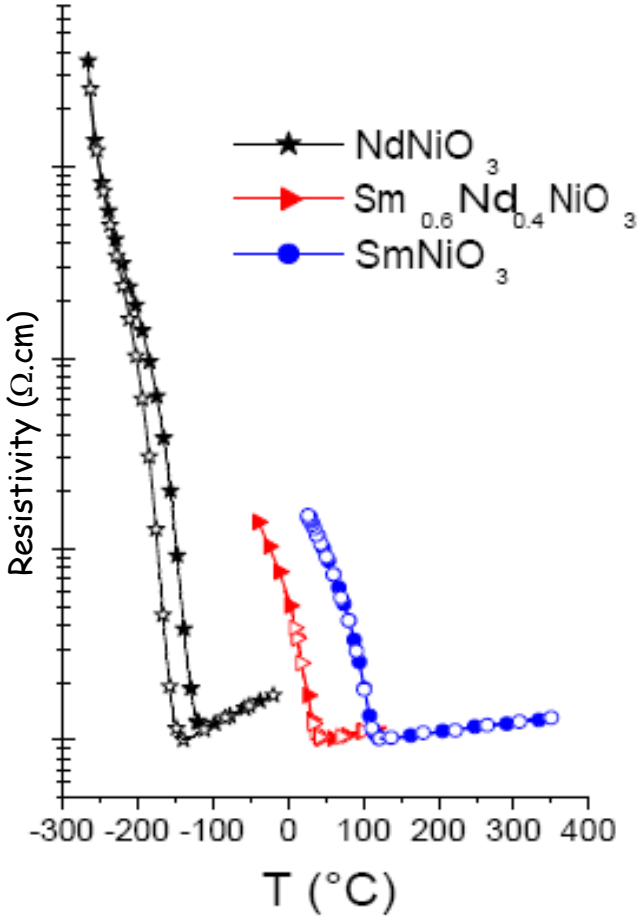
TEM: Atomically flat coherent interface for the first atomic layers

Coherent growth over whole thickness





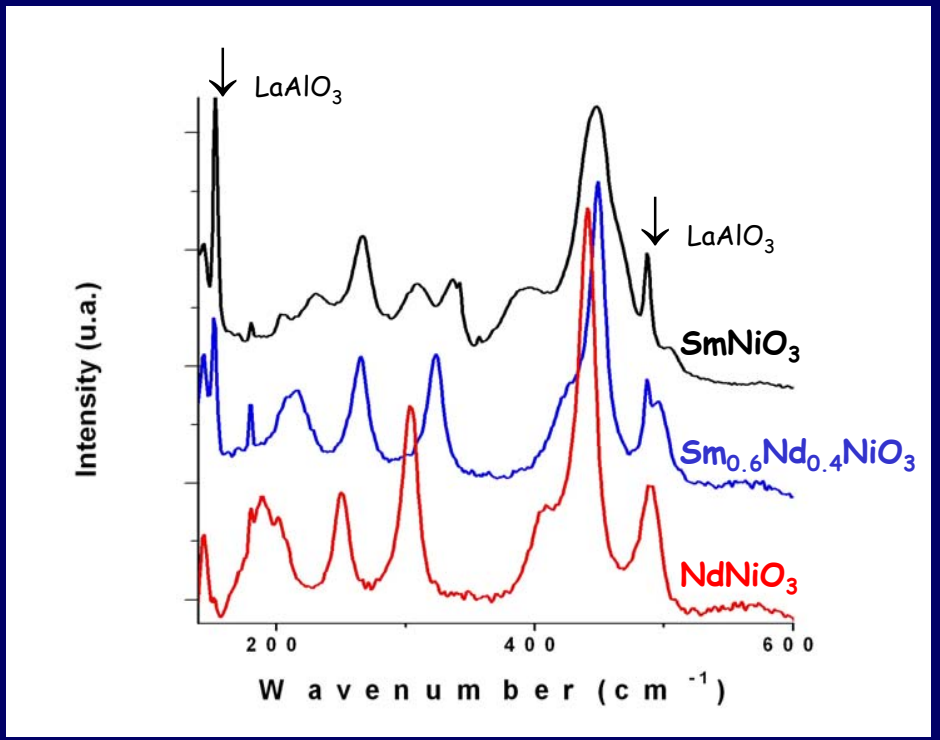
MI- Transition

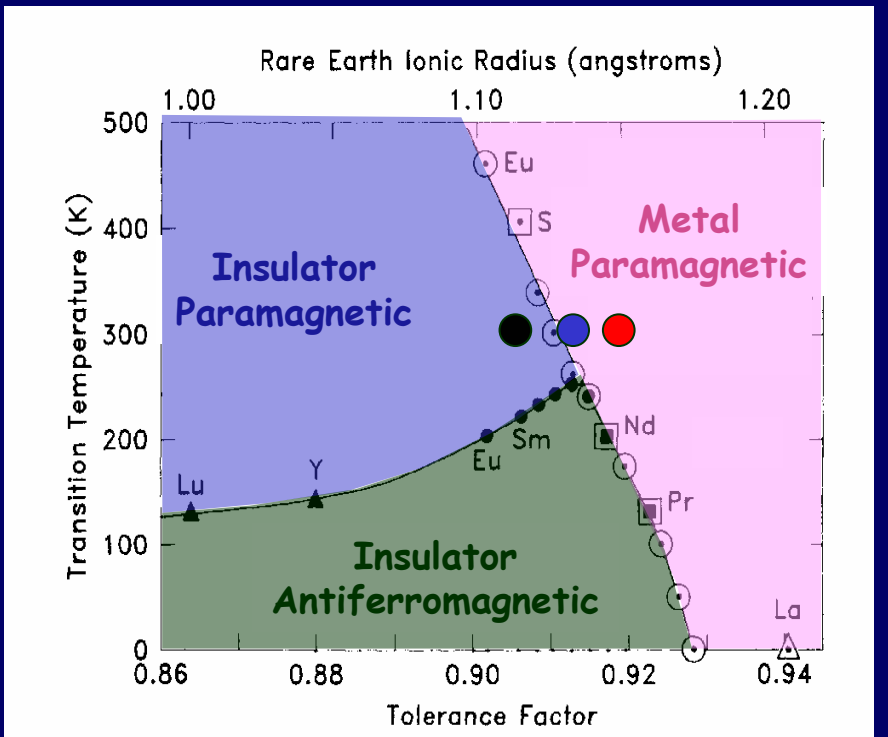


➔ T_{MI} adjustable

Room temperature Raman spectra

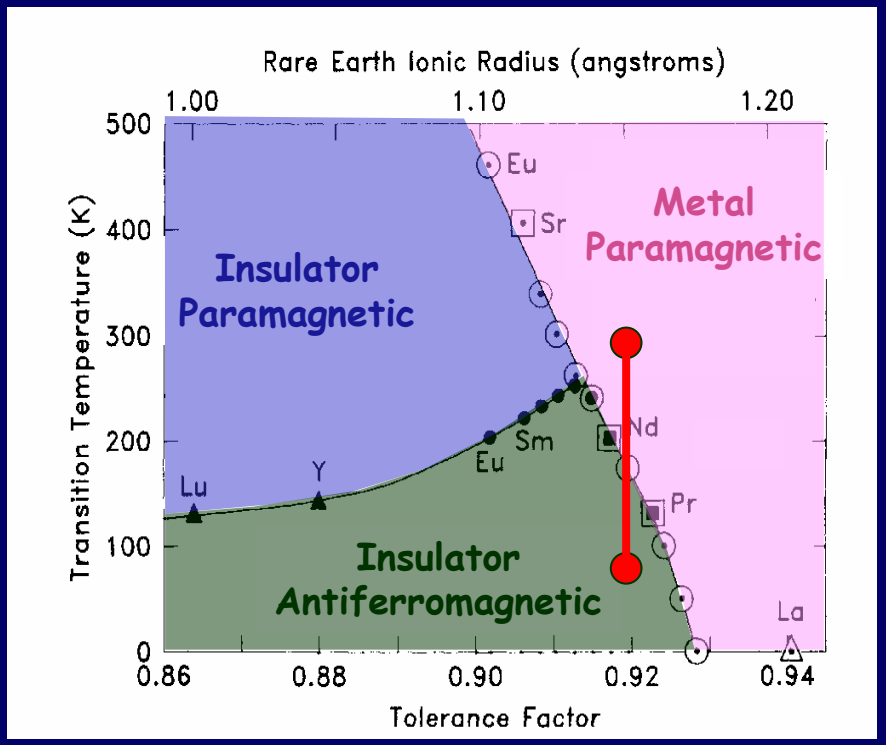
- black thin films → sensitive to laser power → long acquisition time
- with precaution: well-defined Raman spectra

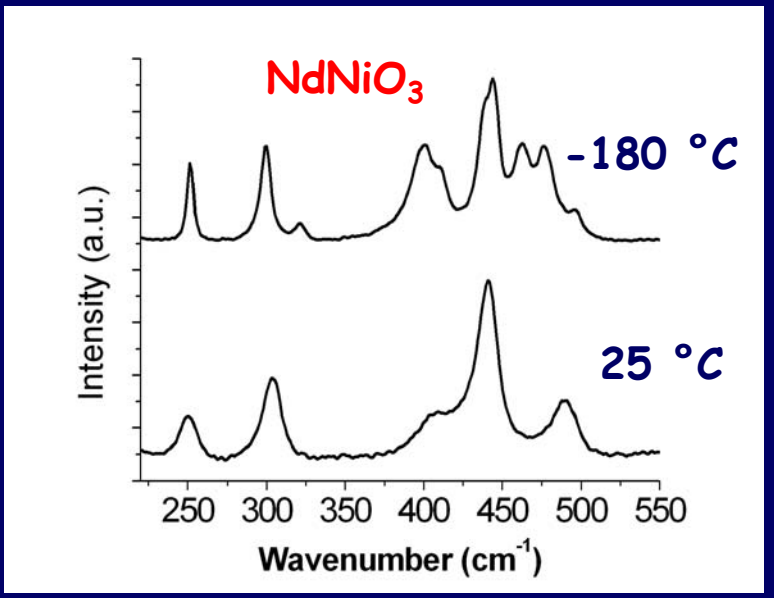


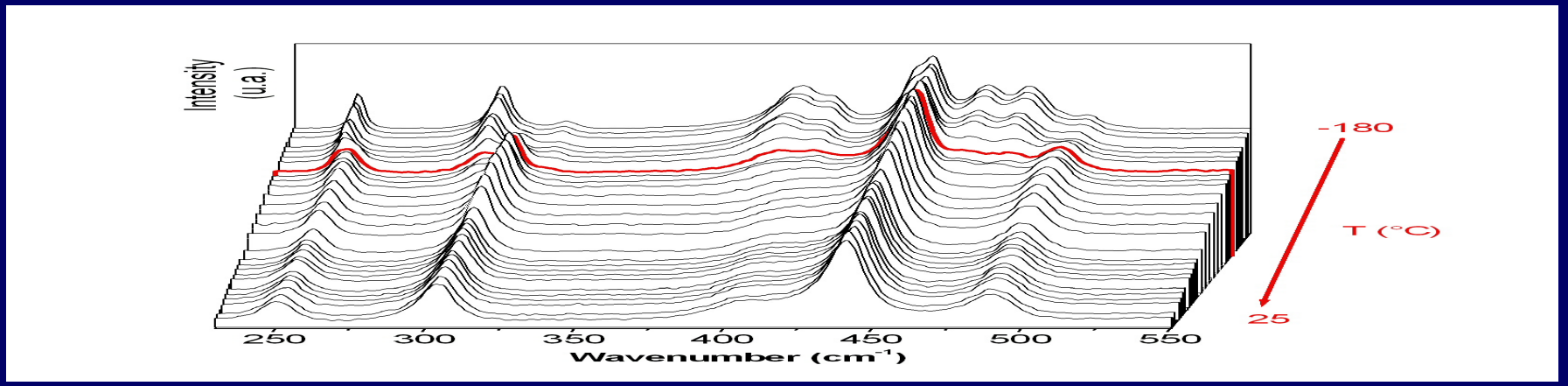


C. Girardot, J. Kreisel, S. Pignard, N. Caillault, F. Weiss *Phys. Rev. B* **78**, 104101 (2008)

Raman scattering of a $NdNiO_3$

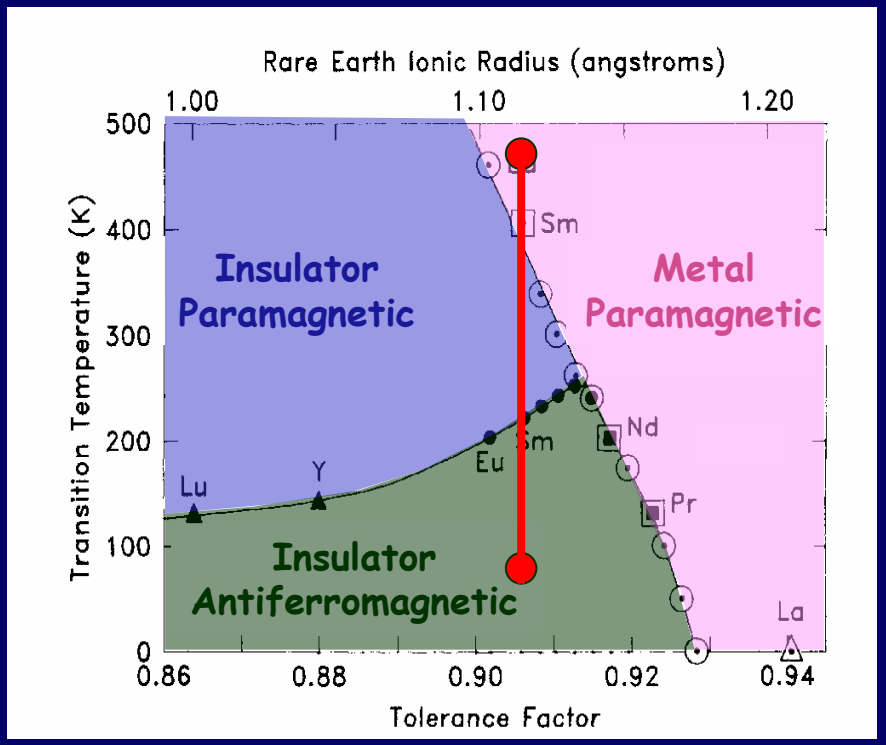


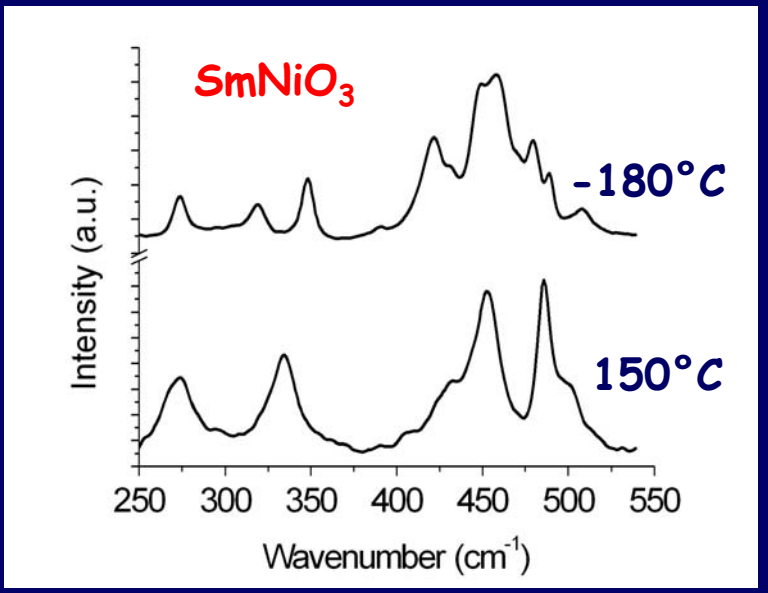


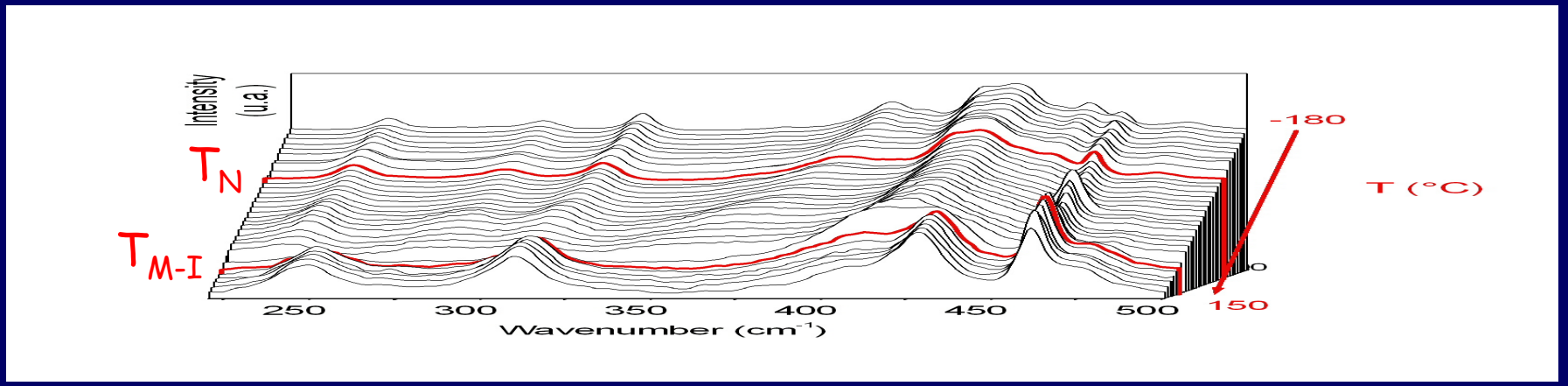


Similar to : M. Zaghrioui, A. Bulou, P. Lacorre, and P. Laffez, Phys. Rev. B **64**, 081102 (2001)

Raman scattering of $SmNiO_3$

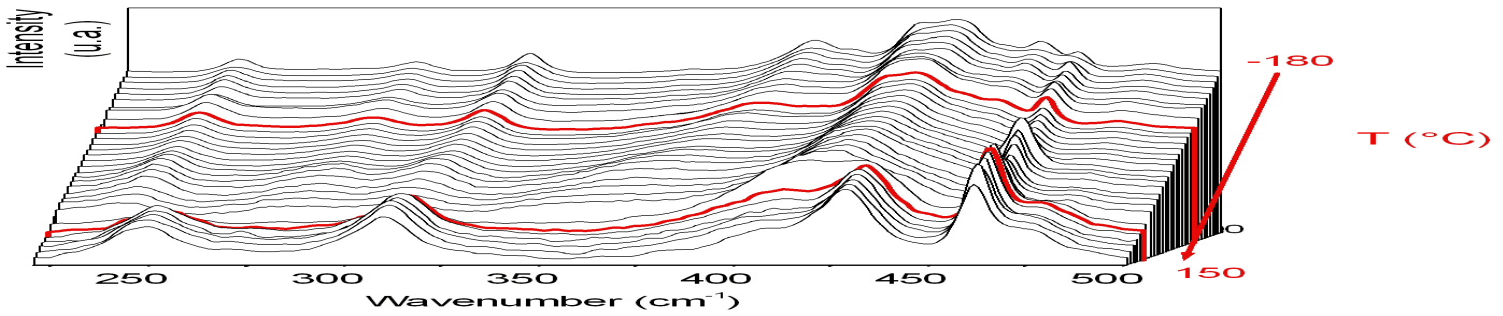




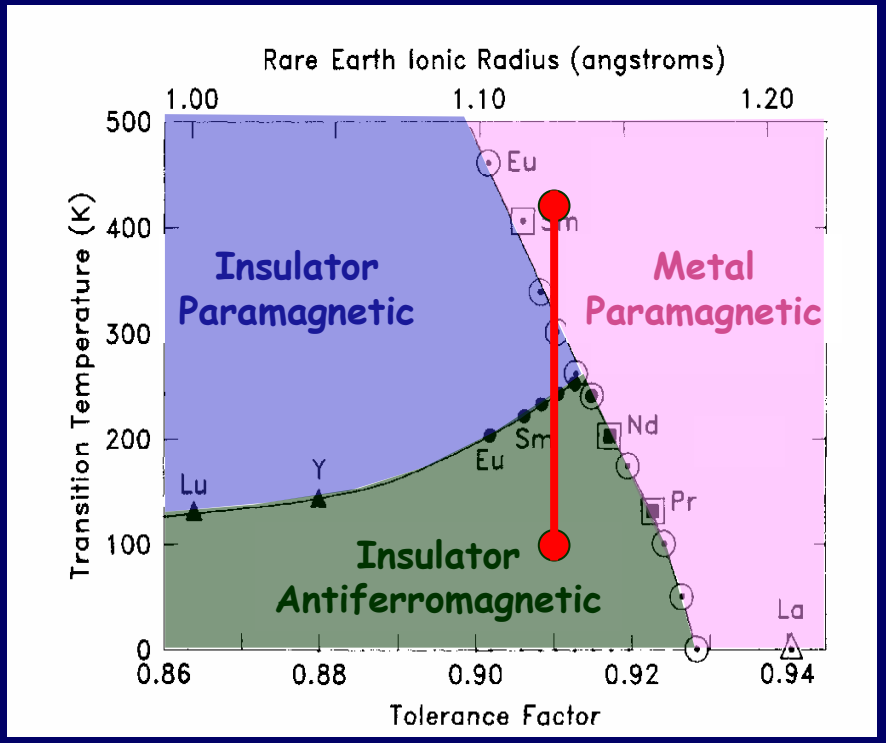


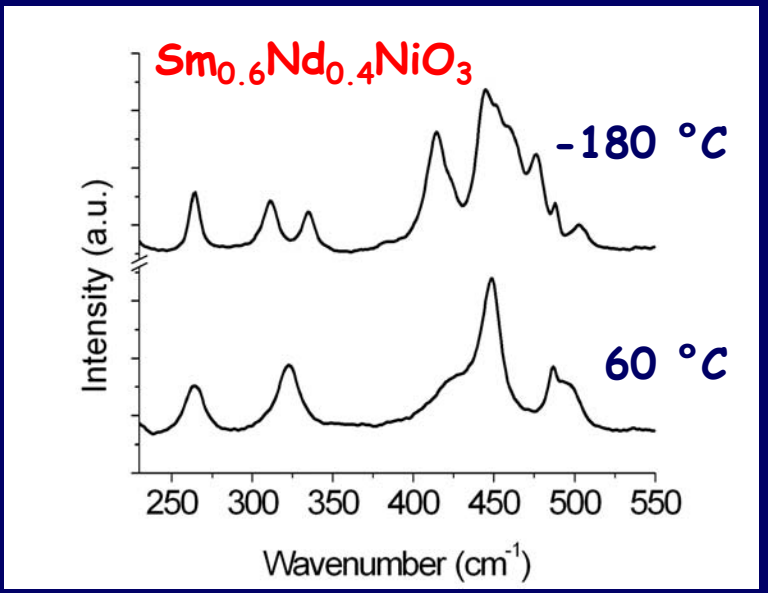
Raman scattering of $SmNiO_3$

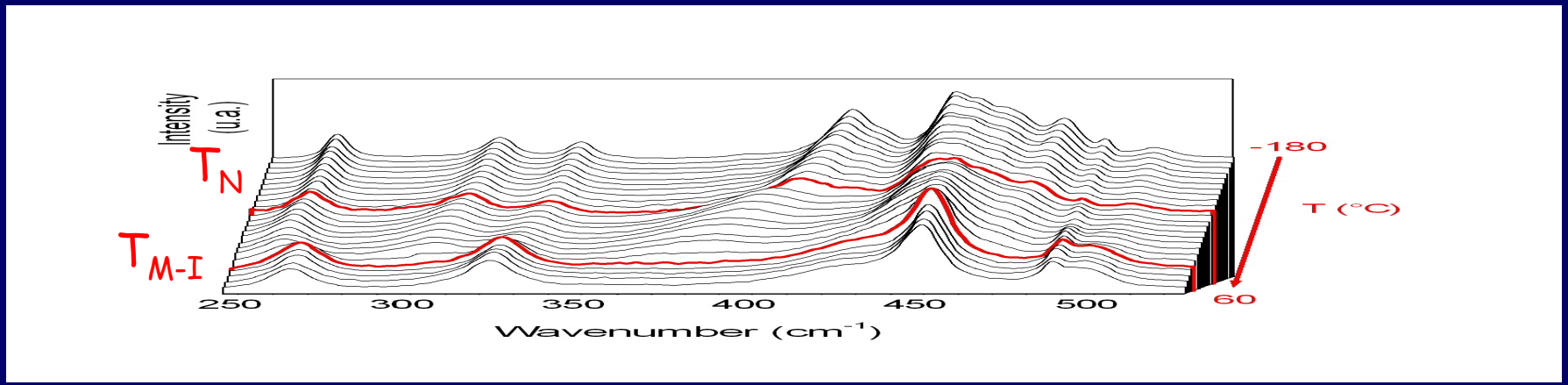
- Evidence for structural phase transition at T_{MI}
- $T_{MI} < T < T_N$: Anharmonic phonon softening



Raman scattering of $Sm_{0.6}Nd_{0.4}NiO_3$

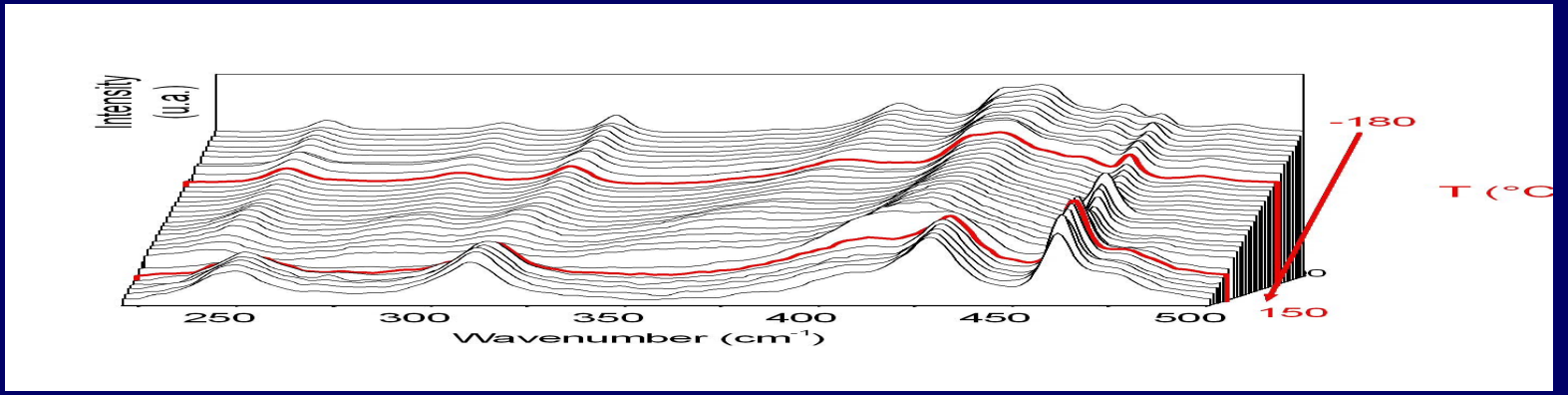






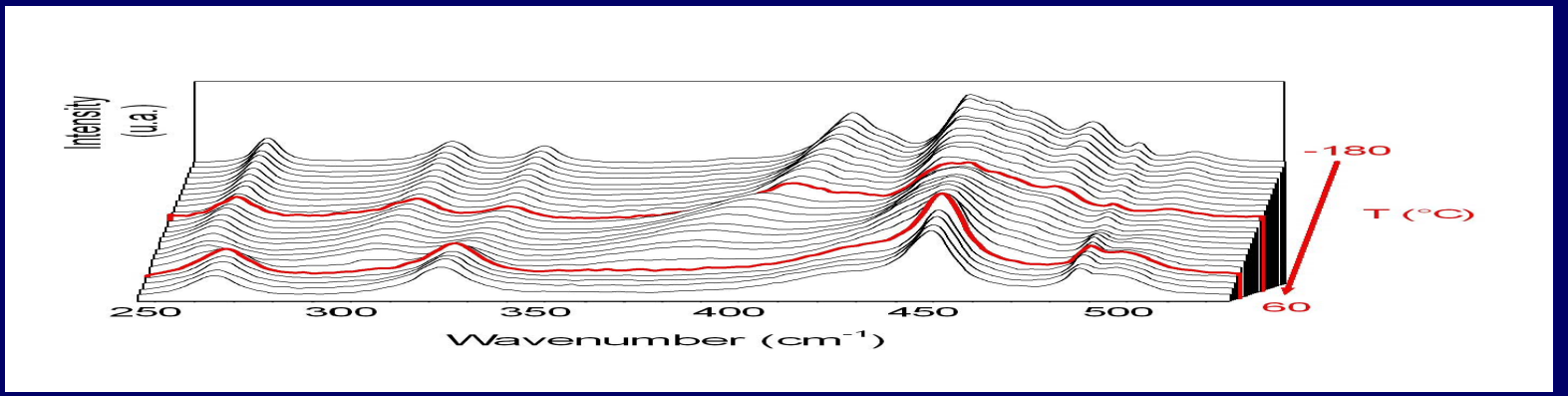
$SmNiO_3$

$T_{MI} \neq T_N$



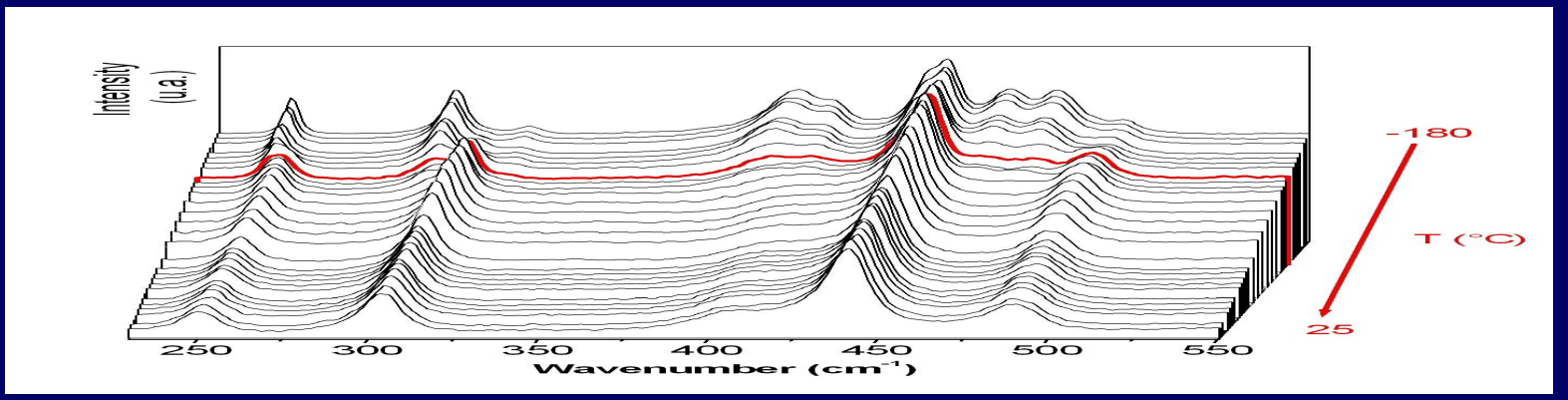
$Sm_{0.6}Nd_{0.4}NiO_3$

$T_{MI} \neq T_N$



$NdNiO_3$

$T_{MI} = T_N$

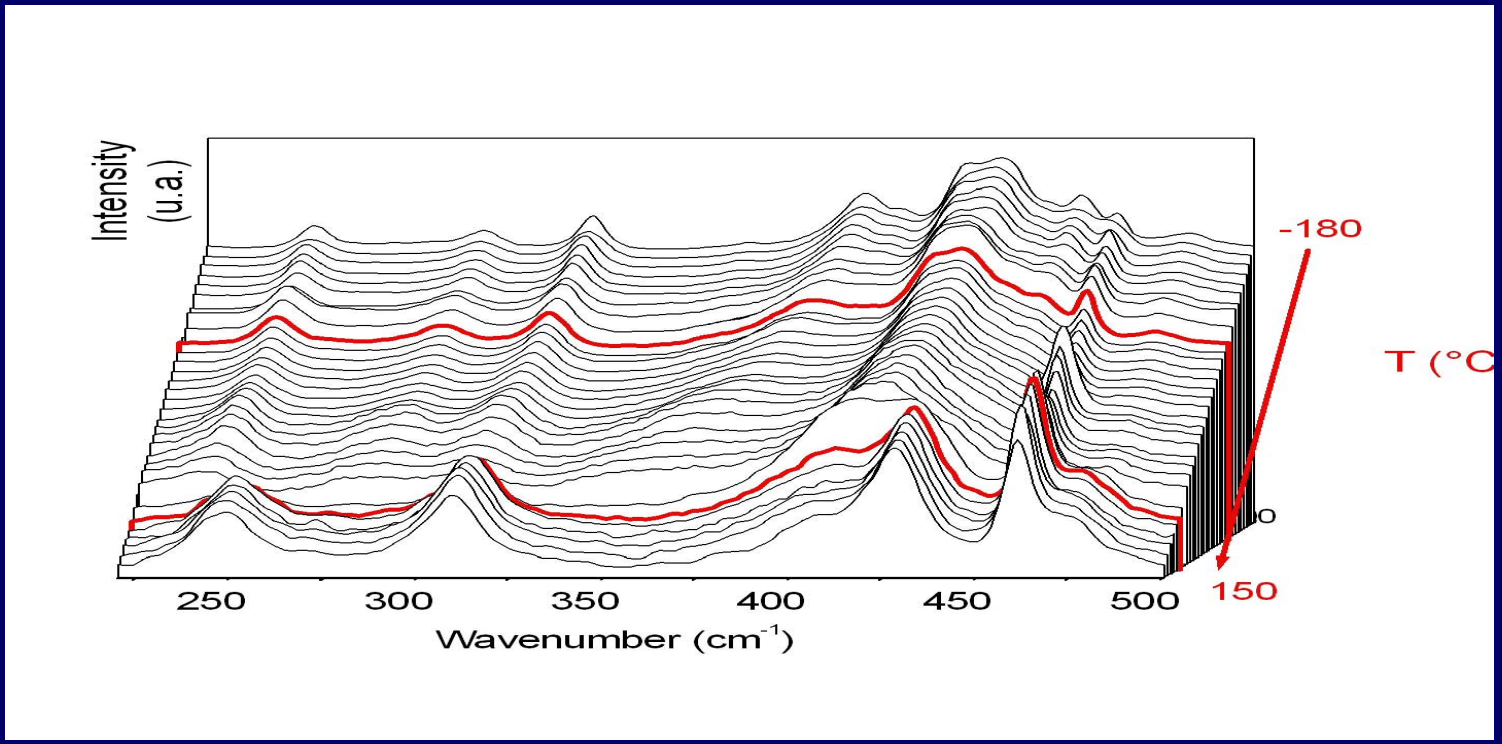


Different temperature-dependent Raman signatures

Metal – insulator transition is not the same for all $RNiO_3$!

Understanding of

the peculiar phonon softening ?



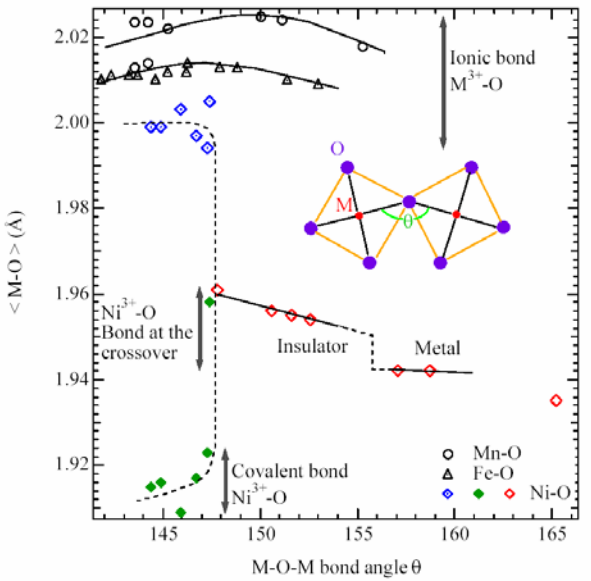
Structural phase transition or magneto-striction or spin-phonon coupling ? ➔ No

One potential ingredient: Long-range ↔ Short range order

PHYSICAL REVIEW B **69**, 153105 (2004)

Chemical bonding and electronic structure of $RNiO_3$ (R = rare earth)

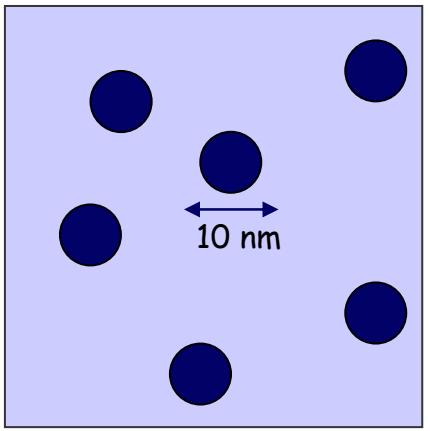
J.-S. Zhou and J. B. Goodenough
Texas Materials Institute, ETC 9.102, University of Texas at Austin, 1 University Station, C2201, Austin, Texas 78712, USA



PHYSICAL REVIEW B **71**, 012104 (2005)

Short-range charge order in $RNiO_3$ perovskites (R = Pr, Nd, Eu, Y) probed by x-ray-absorption spectroscopy

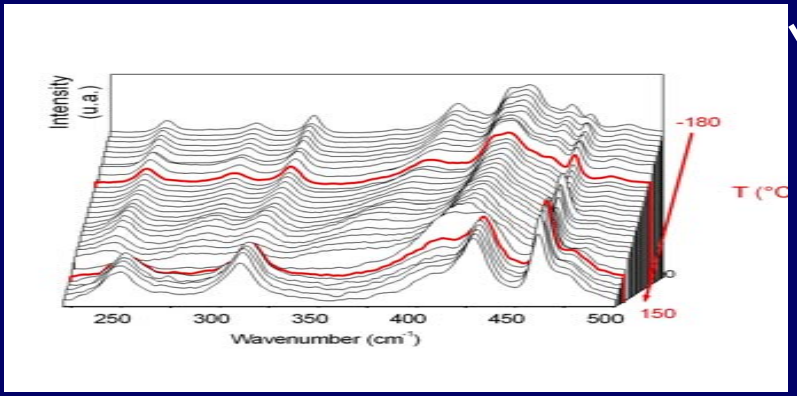
Cínthia Piamonteze,[1,2] Hélio C. N. Tolentino,[1] Aline Y. Ramos,[1,3] Nestor E. Massa,[4] Jose A. Alonso,[5] Maria J. Martínez-Lope,[5] and Maria T. Casais[5]
[1]*Laboratório Nacional Luz Síncrotron, Caixa Postal 6192, 13084-971 Campinas/SP, Brazil*
[2]*IFGW/UNICAMP, 13083-970 Campinas/SP, Brazil*
[3]*LMCP-UMR, 7590 CNRS, Paris, France*
[4]*LANAIS, CEQUINOR, UNLP, C.C. 962, 1900 La Plata, Argentina*
[5]*Instituto de Ciencia de Materiales de Madrid, C.S.I.C., Cantoblanco, E-28049 Madrid, Spain*



Local clusters do exist → Change in size (and charge) with temperature ?

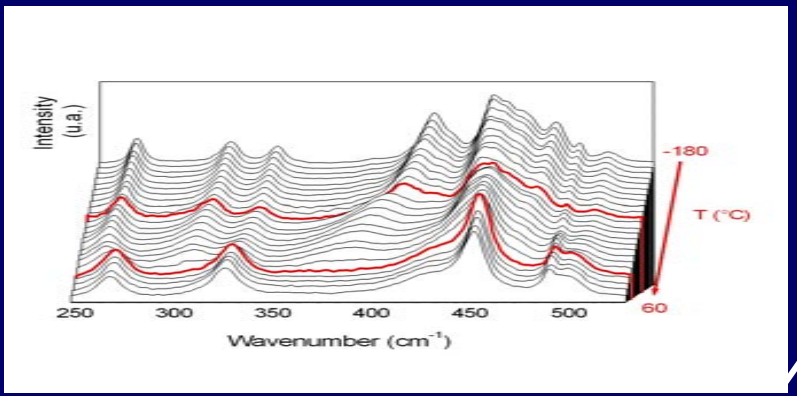
$SmNiO_3$

$T_{MI} \neq T_N$



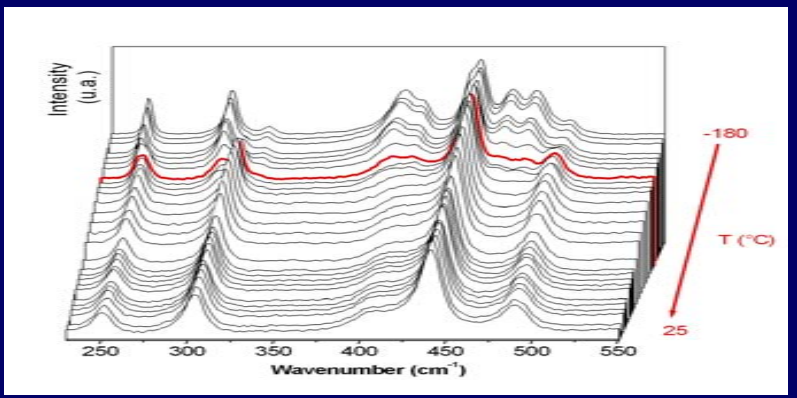
$Sm_{0.6}Nd_{0.4}NiO_3$

$T_{MI} \neq T_N$

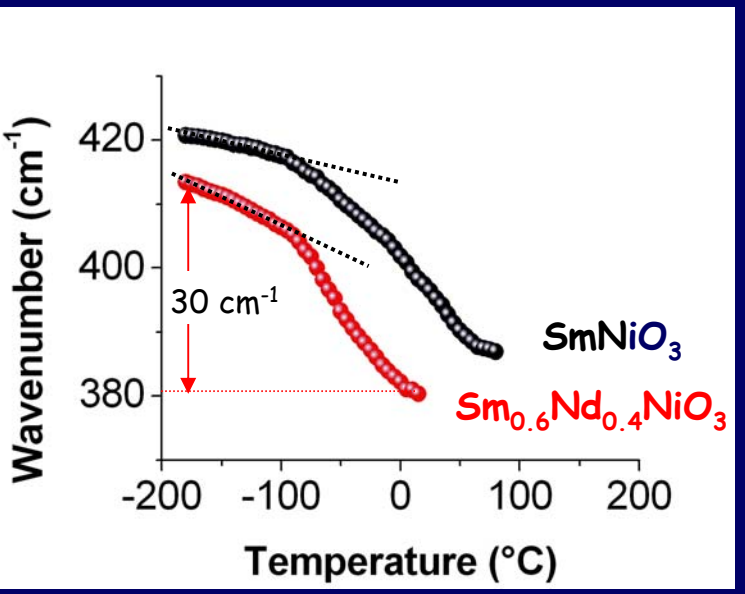


$NdNiO_3$

$T_{MI} = T_N$



Softening accelerates at T_N



(Local ?) Magnetism plays a role

Modification of a specific bonding

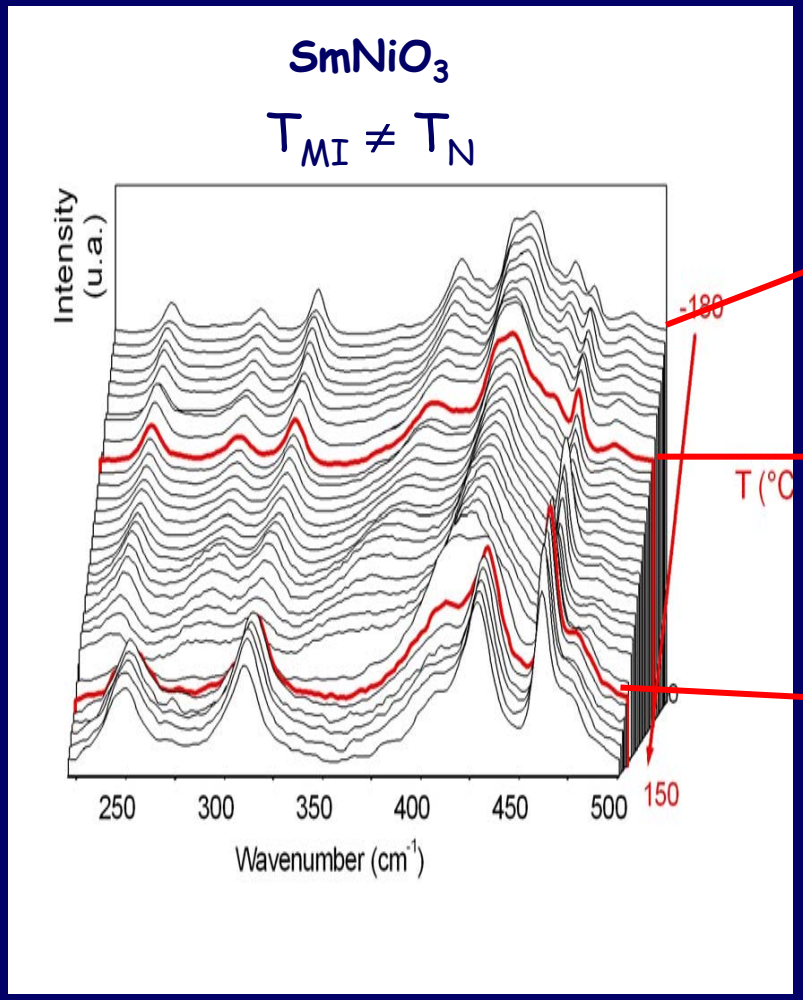
Eigenvector calculations needed

Order parameter

- Octahedra tilt ?
- Charge order ?

Suggestion of charge order as order parameter:
F.P. de la Cruz *et al.* Phys. Rev. B **66**, 153104 (2002)

Hypothesis: Increasing charge order?



Long-range (monoclinic)

$Ni^{3+\delta}$ + $Ni^{3-\delta}$

T_N

Increasing δ and/or size of clusters (monoclinic)

$Ni^{3+\delta}$ + $Ni^{3-\delta}$

T_{MI}

Long-range (orthorhombic)

Ni^{3+}

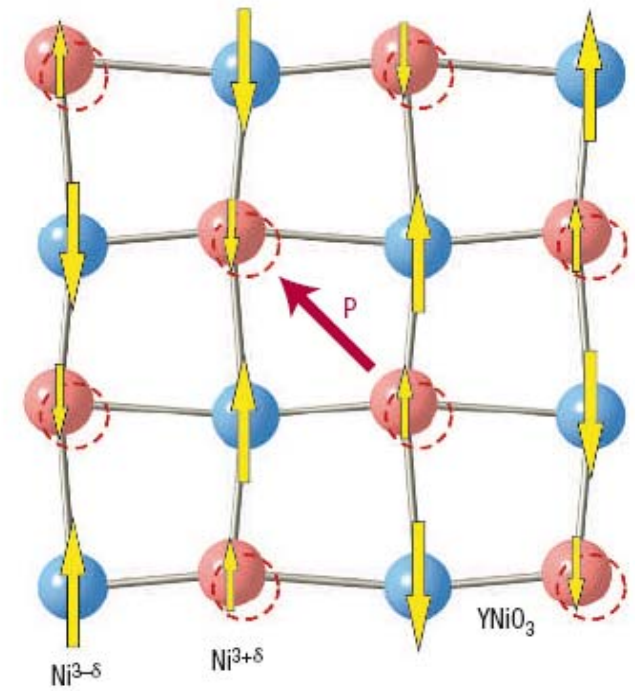
Charge order as order parameter ? → Phonon softening = Change in chemical bonding

Going further…: Coupling in a multiferroic regime ?

nature materials | VOL 6 | JANUARY 2007

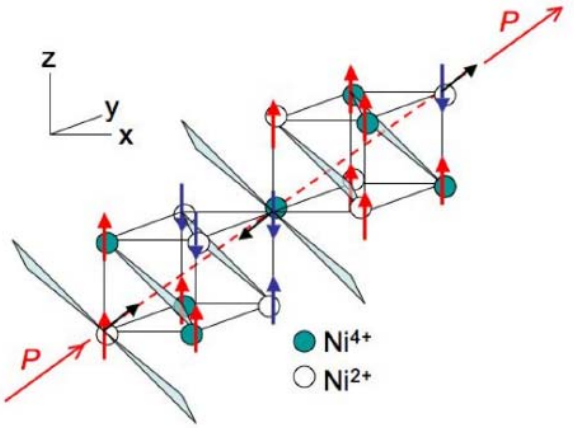
Multiferroics: a magnetic twist for ferroelectricity

SANG-WOOK CHEONG[1,2] AND MAXIM MOSTOVOY[3]



J. Van den Brink, D.I. Khomskii, *J. Phys.: Cond Mat.*, (2008) accepted
➔ CondMat:0803.2964

Multiferroicity due to charge ordering



Advances in perovskite nickelate research

G. Catalan, Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3AQ

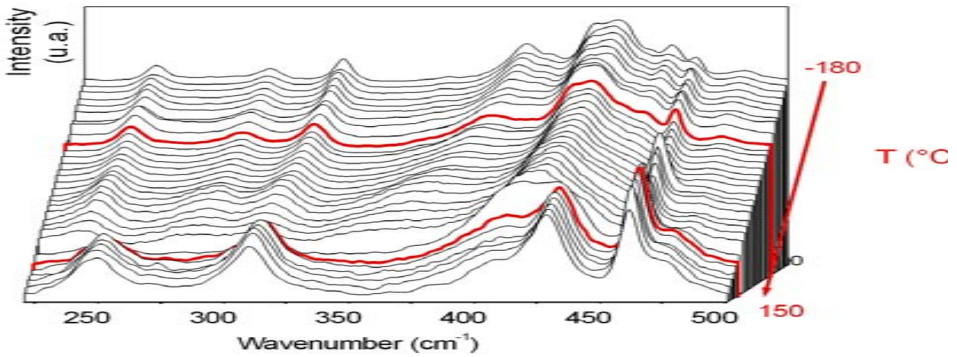
G.Catalan, *Phase Transit.* **81** (2008)

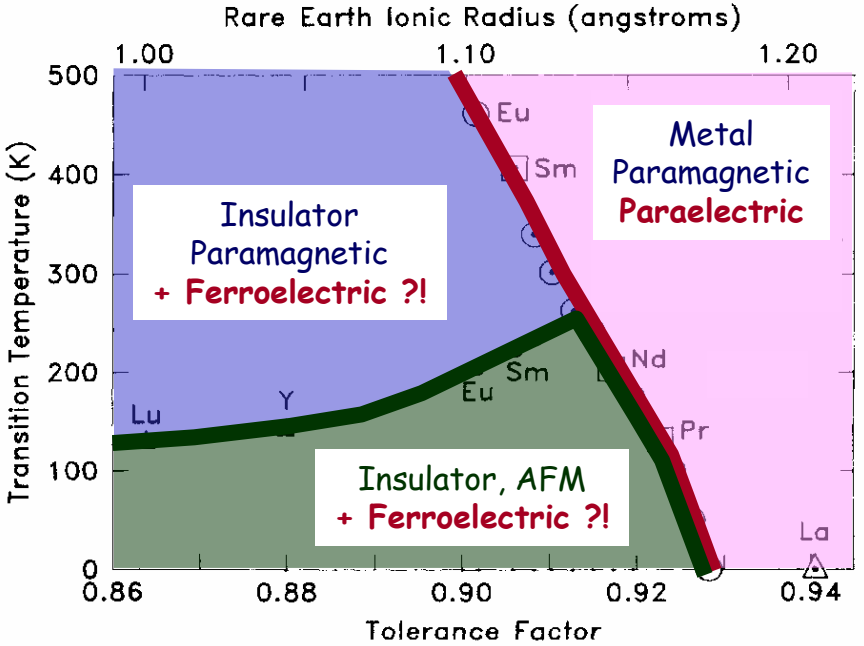
Not yet experimentally verified !

« Multiferroic scenario »

$SmNiO_3$

$T_{MI} \neq T_N$





Phonon frequencies are affected by the correlation of spins

$\omega = \omega_0 + \lambda \langle S_i \cdot S_j \rangle$

but: Spin-phonon coupling ***alone*** cannot explain the softening

Hypothesis: Onset of (local) magnetism in presence of ferroelectric instability

➔ Interactions of order parameters? Enhanced spin-phonon coupling?

Concluding remarks

- RE-Nickelates: Still a playground for experimentalists (and theoreticians)
- $SmNiO_3$ ≈ $Sm_{0.6}Nd_{0.4}NiO_3$ Structural phase transition at T_{MI}
- $SmNiO_3$ ≠ $NdNiO_3$ Different mechanism at MI transitions
- MI transition in Nickelates: should be re-investigated
- Intriguing Phonon softening ➔ An experimental hint for multiferroicity ?!