# TOPOCHEMICAL REACTIONS IN IRON SILICIDES AND NICKELATES : CHEMICAL BONDING, 2D CHARACTER, *SUPERCONDUCTIVITY* AND ANALOGY WITH *CUPRATES*

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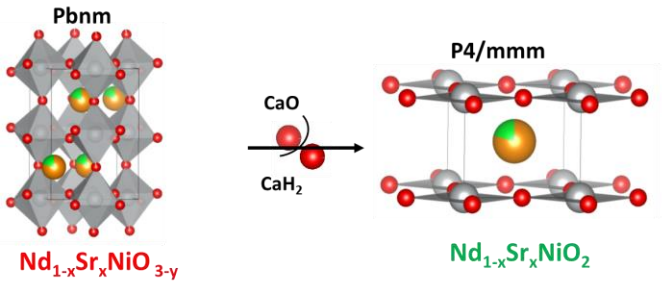
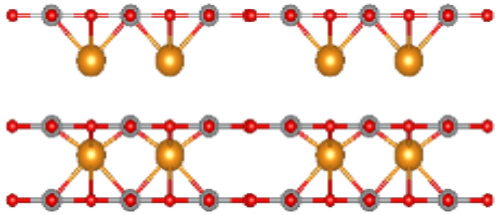
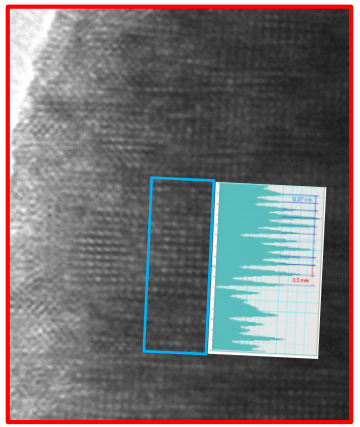
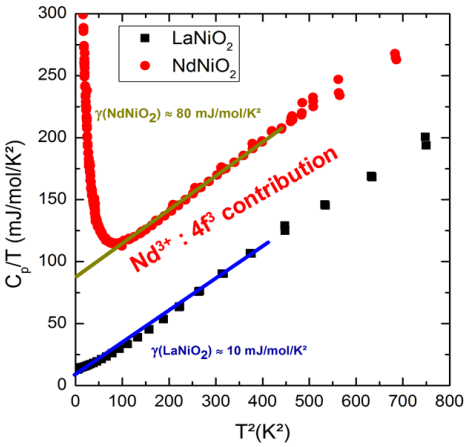






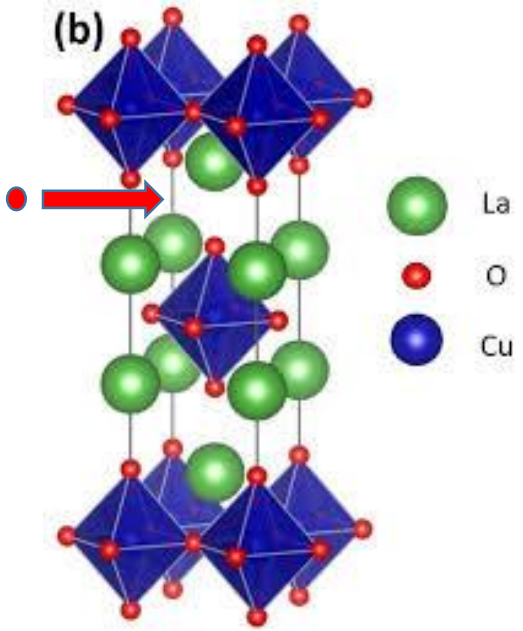

GDR Meetic, Plenary Conference, Latresne-Bordeaux, May 30th- June 2nd 2023

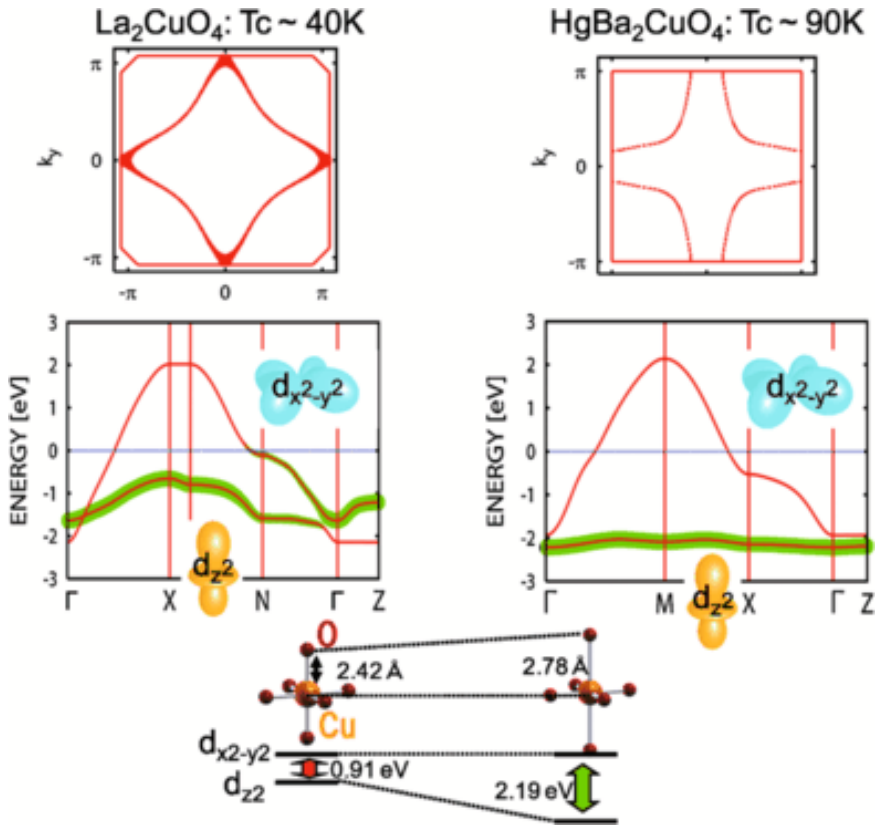
# *Introduction :* Cuprates and High Tc *superconductivity*

**Oxygen intercalation**, ***Cu-O charge transfer***, ***$CuO_4$ square planar ($D_{4h}$)***, ***Jahn-Teller (JT) distortion*** and Fermi Surface

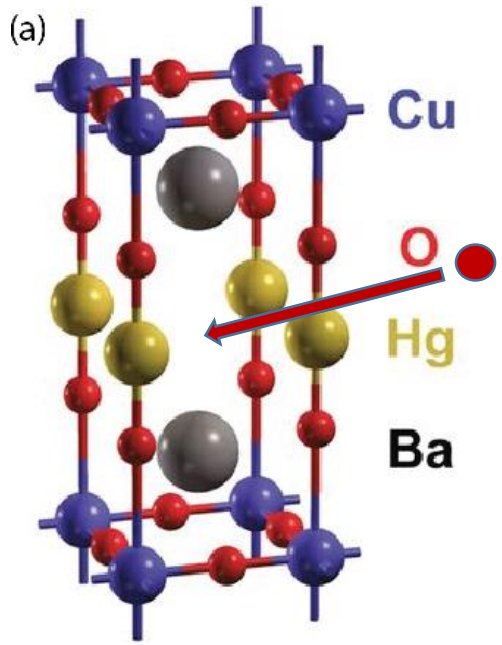
Long range **hopping t'** / Nearest neighbors *hopping t* ↑ → Tc ↑

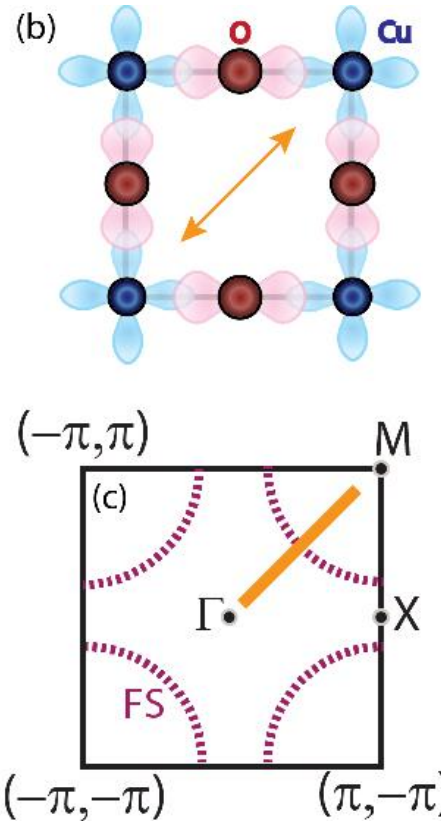
## $La_2CuO_{4+x}$




## $HgBa_2CuO_{4+x}$




A perspective of superconductivity as multiband phenomena : cuprates, iron and aromatic systems
H. Aoki. J Supercond Nov Magn, (2012), 25, -1247

# Fluorine intercalation in cuprates : how creating holes for superconductivity ?

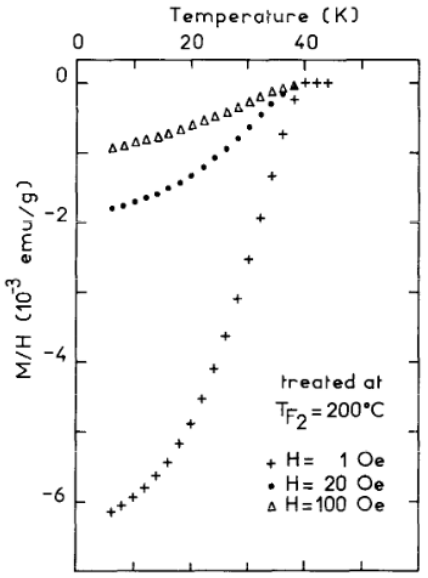
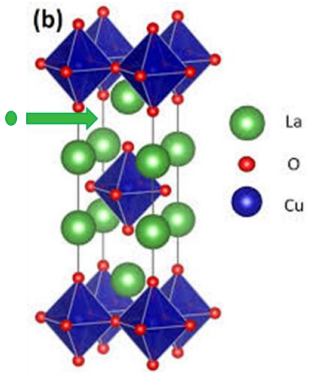
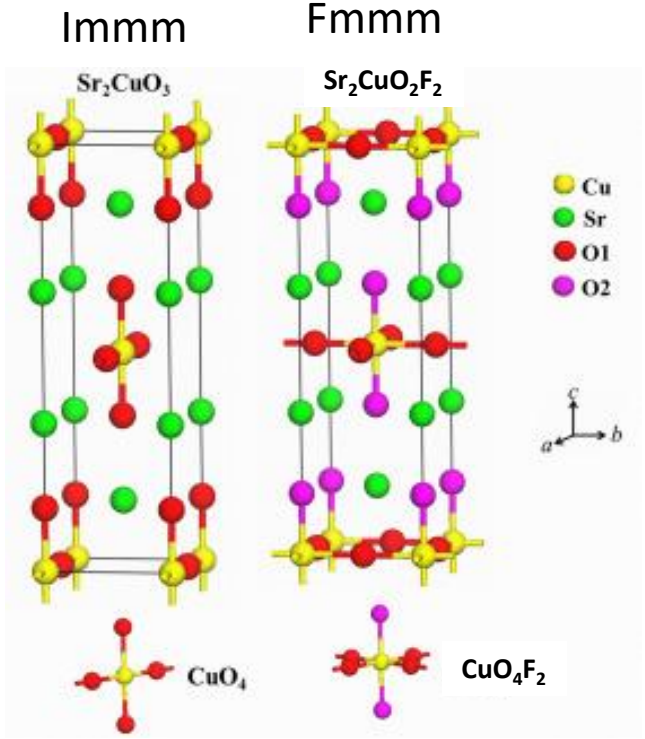
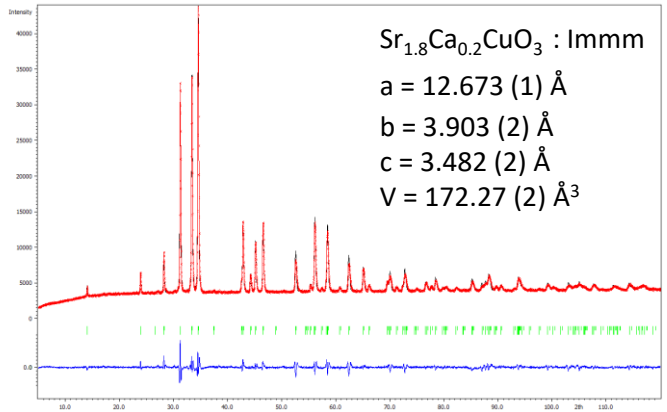



Fig. 2. Magnetic susceptibility for an $F_2$-treated $La_2CuO_4$ sample recorded at various applied magnetic fields.



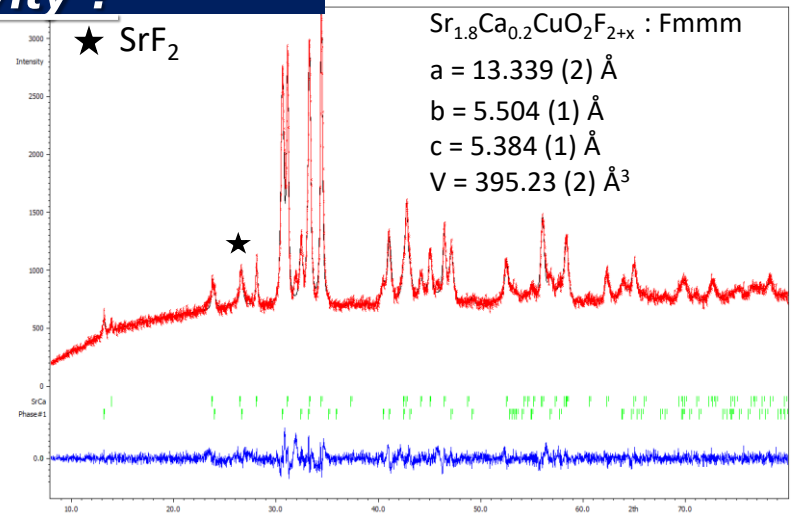




**Low temperature (200°C)**
**$F_2$-direct Fluorination, Tc=40K**
**$La_2Cu(O,F)_{4+y}$**
**B. Chevalier , A. Tressaud et al.**
**Physica C, 167 (1990), 97-101**

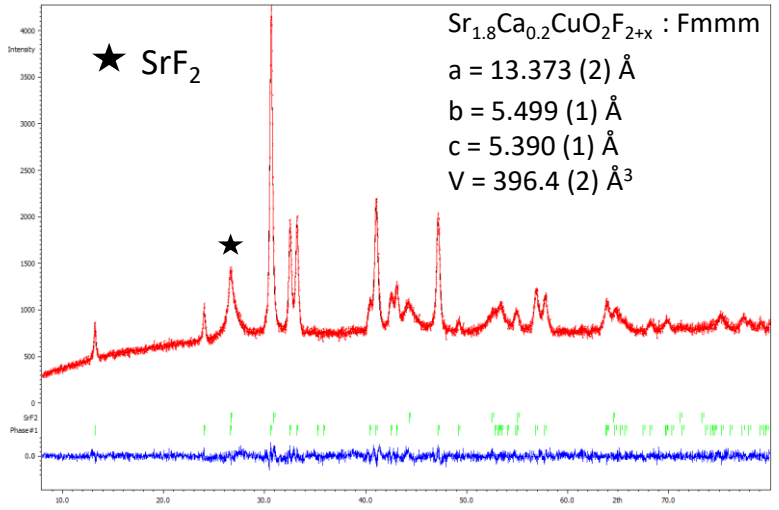



## Topochemical reactions

**Synthesis and superconducting properties of strontium copper oxyfluorides**
**Optimum Tc= 47 K**
**M. Al-Mammouri et al. Nature (1994) 369, 382-384**




*1%$F_2$, 15min, T=200°C : 2 phases Immm (Pristine) + Fmmm*

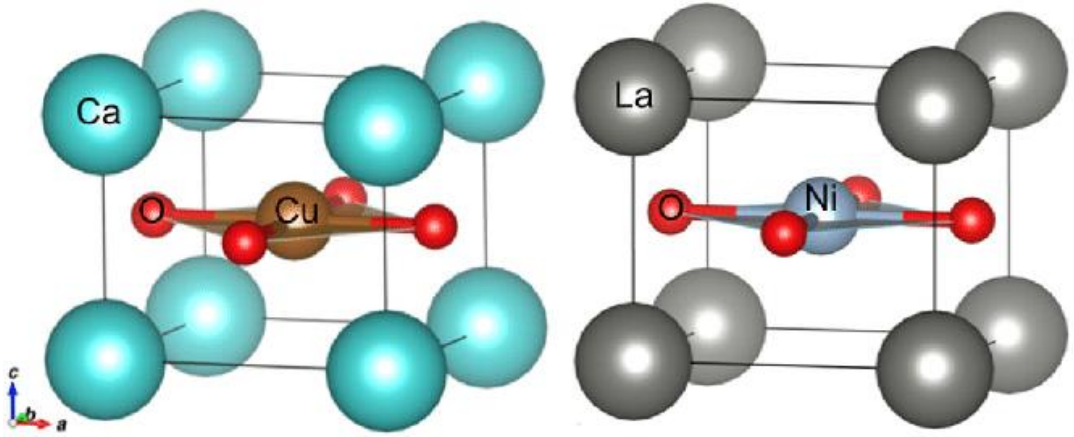


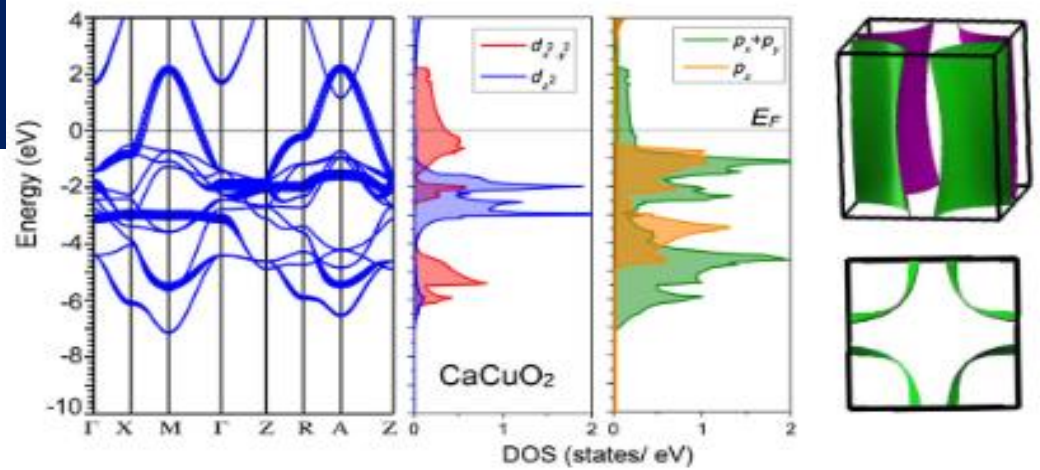

*5% $F_2$, 15min, T=200°C : 1 phase Fmmm*

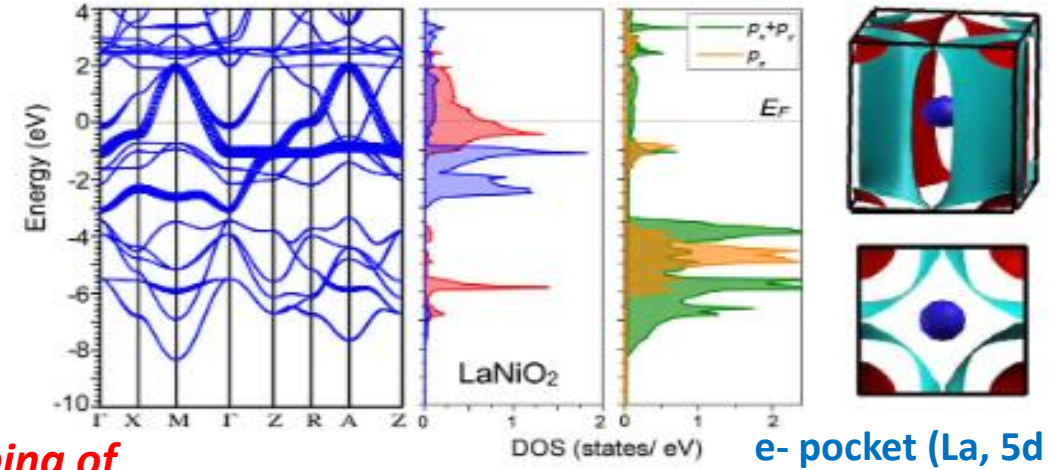
# The square planar ($D_{4h}$, JT) : similarities and difference between $CaCuO_2$ and $LaNiO_2$ (P4/mmm)

***Stronger Cu(d)-O(p) hybridization (lower charge transfer energy) >> Ni(d)-O(p) → local moment magnetism***

- Higher superexchange coupling J ($CaCuO_2$) >> J ($LaNiO_2$)
- **$5dz^2$ (La, RE) band contribution at $E_F$ in $La(RE)NiO_2$**

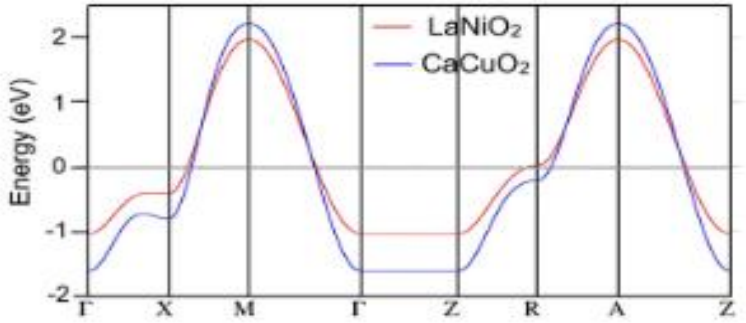



e- pocket (La, 5d bands)

***Self-doping of the Ni $d_{x2-y2}$ band***




***Higher dispersion of Cu($d_{x2-y2}$) orbitals***

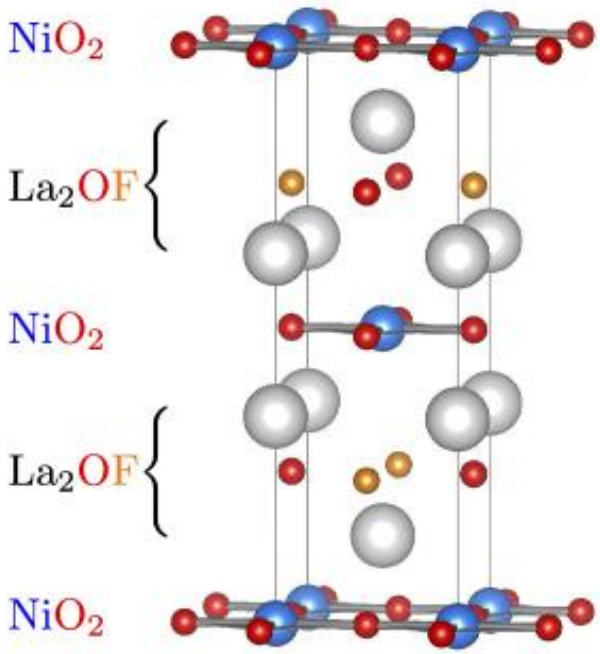
Similarities and differences between $LaNiO_2$ and $CaCuO_2$ and implications for superconductivity
A.S. Botana and M.R. Norman
Phys Rev 10, 011024, (2020)

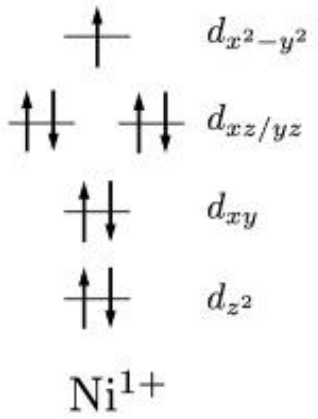
# Imagining a new phase : $La_2NiO_3F$ (T' $Nd_2CuO_4$)

**Enhancement (competitive bonds) of $NiO_2$ 2D character → cuprates**



**increasing the ionic character of R-O/F bonding in RP phases**




**Incorporation of Fluorine in Fluorite-type blocks**

FIG. 1. (a) Ball-and-stick model of the single-layer T'-type $La_2NiO_3F$ where single $NiO_2$ layers are separated by $La_2OF$ fluorite blocks (the conventional unit cell is indicated by the lines). (b) Nominal $3d^9$ electronic configuration of the $Ni^{1+}$ atom in this single-layer T'-type class of nickelates.

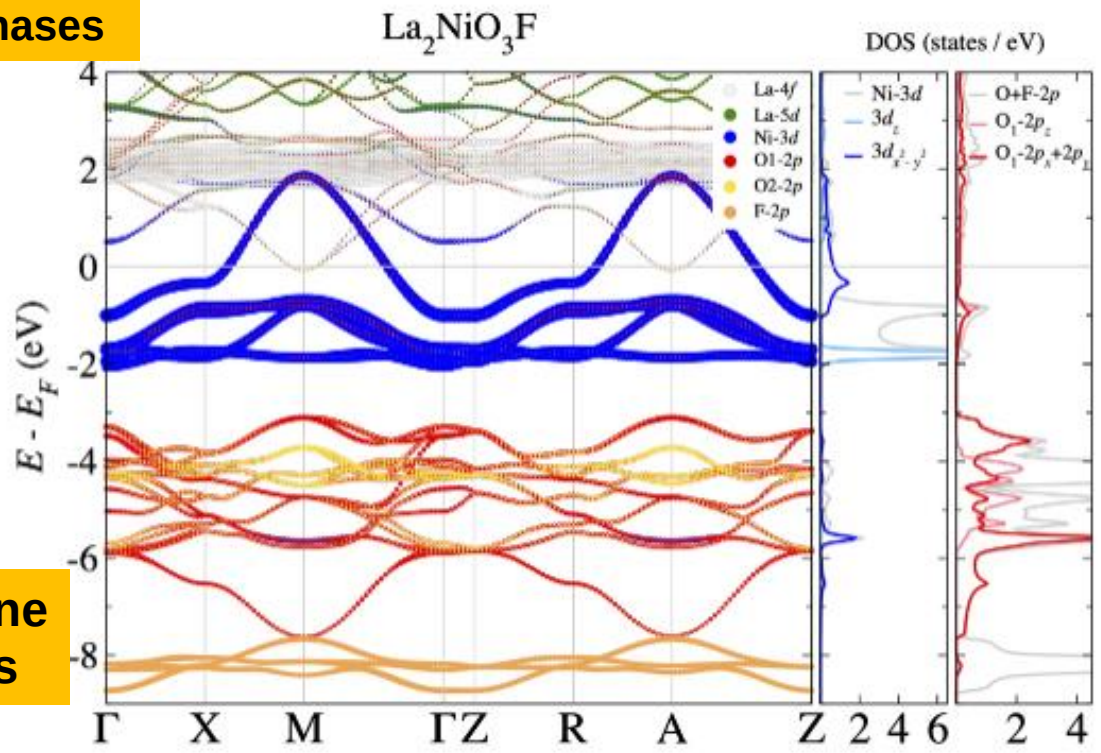



FIG. 2. Band structure and orbital resolved density of states (DOS) of $La_2NiO_3F$ ($I4/mmm$ space group $a = 3.9925$ Å, $c = 12.5150$ Å [23]). O1 refers to the oxygens in the $NiO_2$ layer, while O2 to the fluorite block.

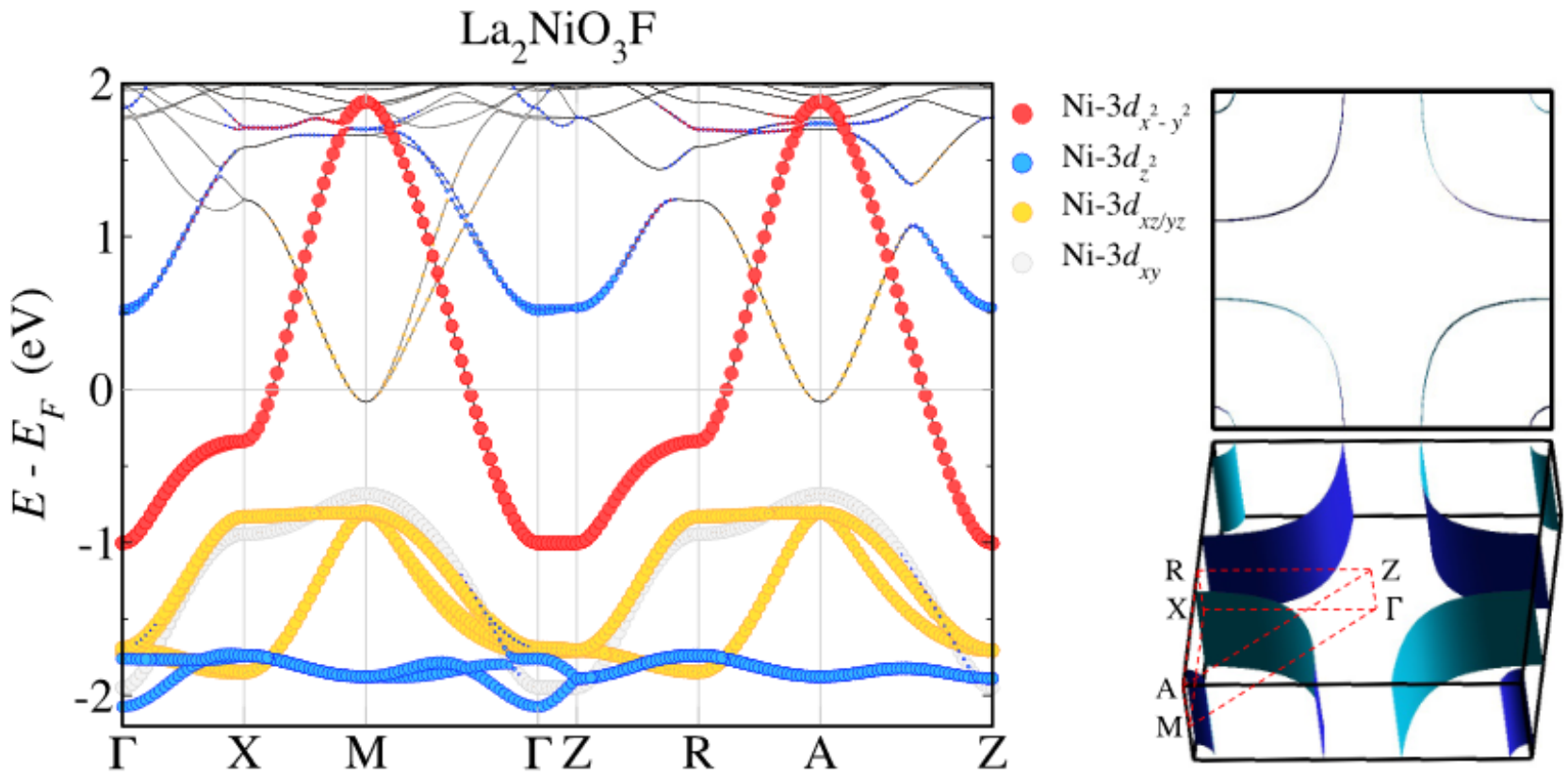
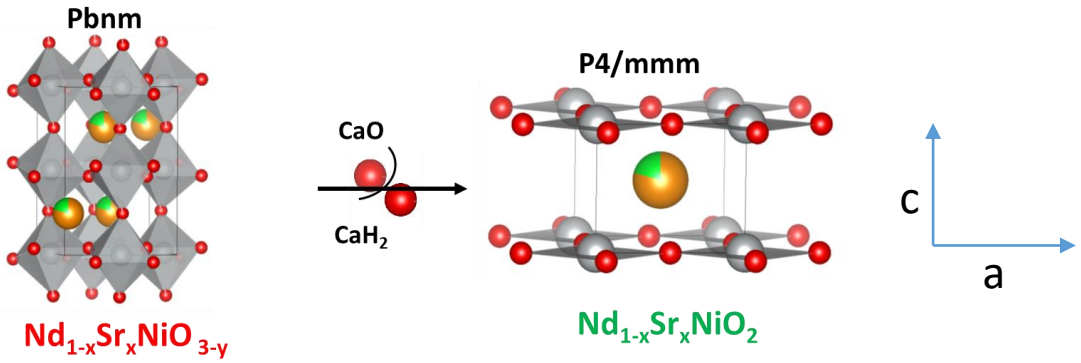
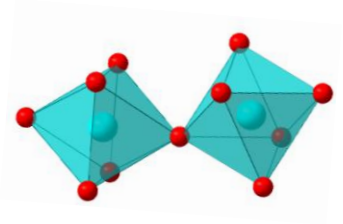



FIG. 3. Band structure near the Fermi energy and Fermi surface of $La_2NiO_3F$ (top and perspective views).

# Topotactic reduction ($CaH_2$) of bulk- $RE_{1-x}SrNiO_3$ (RE = La, Nd) perovskite

**$RE_{1-x}SrNiO_3$ perovskite (RE = La, Nd) :**
HP $O_2$ (T=900°C, 250 bars), **Sr Solubility limit = 0.07**

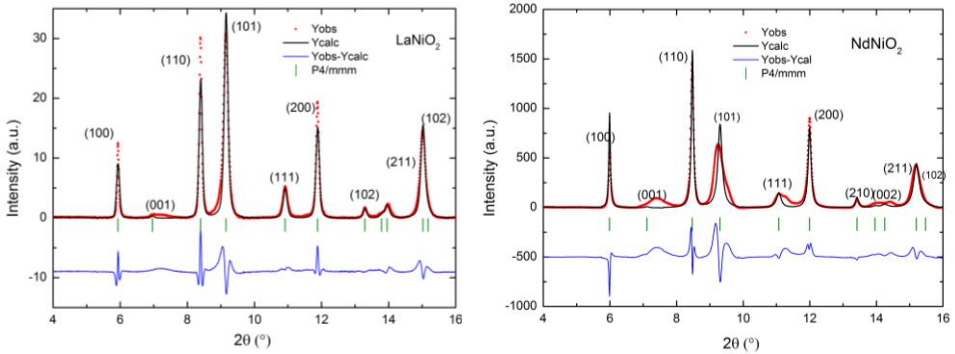


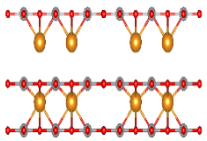
**Stacking faults related to steric effect**

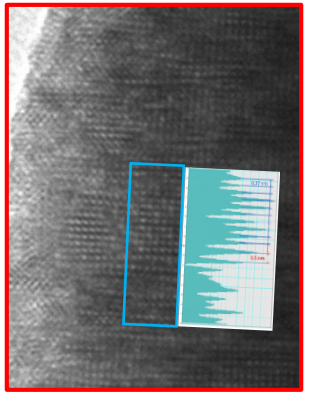
**The lower the <Ni-O-Ni> angle** into **pristine O3**
**The higher the stacking faults rate** in **IL O2**
**(decrease under pressure)**
**Nd** > Pr* > Nd/Sr > La
**Stronger Nd-$NiO_2$ interactions at local scale**

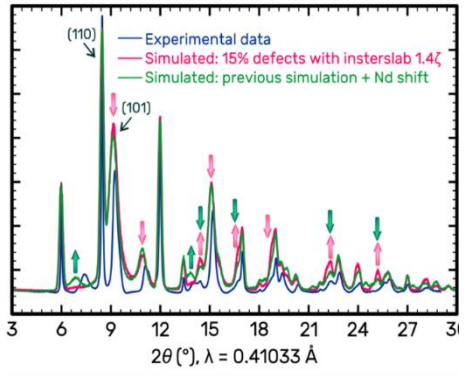
**$RE_{1-x}Sr_xNiO_2$ infinite layers (RE = La, Nd) :**
Reduction ($CaH_2$), T=250°C)
**XRD : Anisotropic size broadening (110) vs (101)**
**+ strong variation of (110)/(101) intensity ratio**

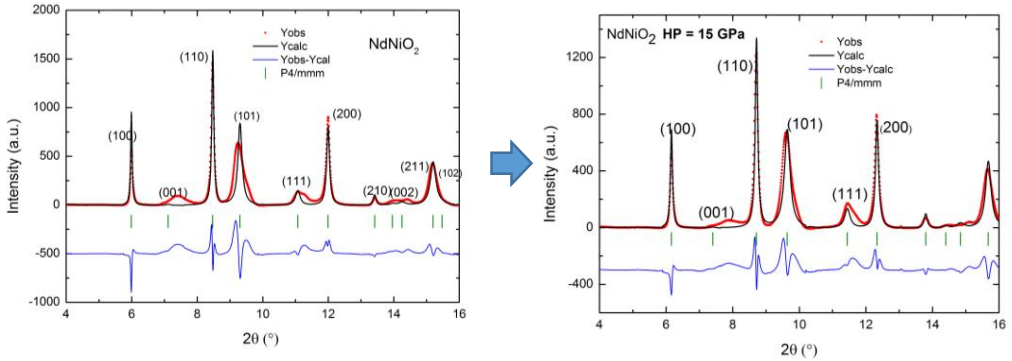



**Occurrence of stacking faults in $NdNiO_2$**
**along c direction (Nd)**
**(FAULTS-XRD & HRTEM)**







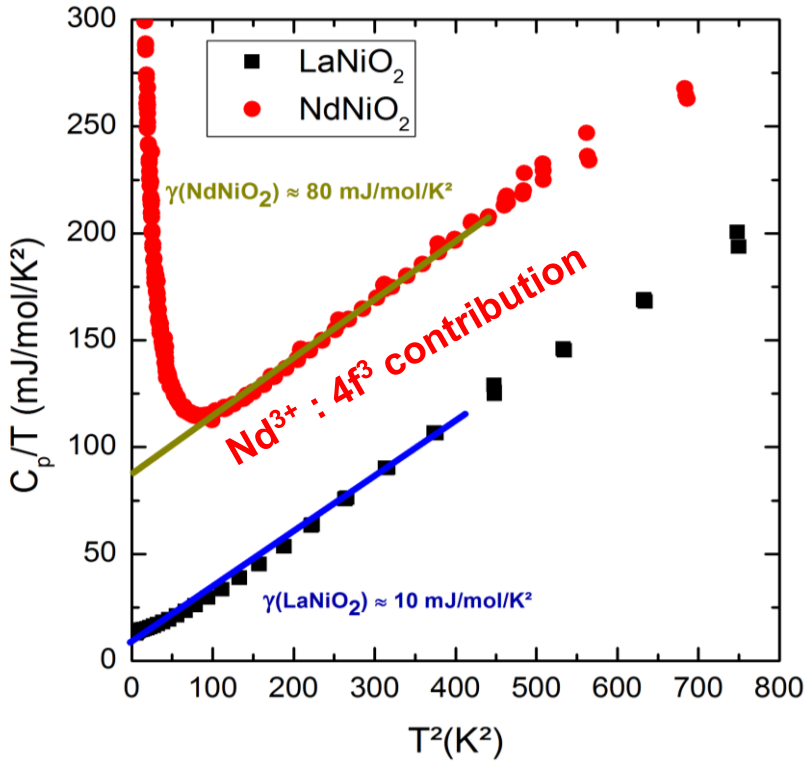




**Decrease of stacking faults under pressure in $NdNiO_2$ along c direction (Nd)**

# $Nd(Sr)NiO_2$ vs $LaNiO_2$ : transport and magnetic properties

## Electronic Specific heat

$C_p = \gamma T + \beta T^3 \rightarrow \frac{C_p}{T} = \gamma + \beta T^2$, *at low temperature*



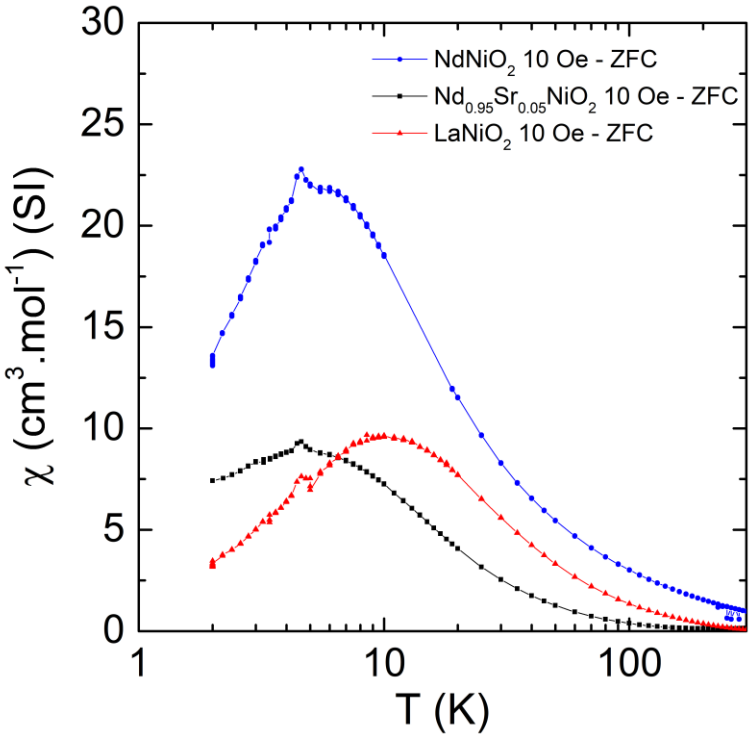

- ***Metallic state :*** $\gamma \propto N(E_F) \propto$ ***m* (effective mass)***

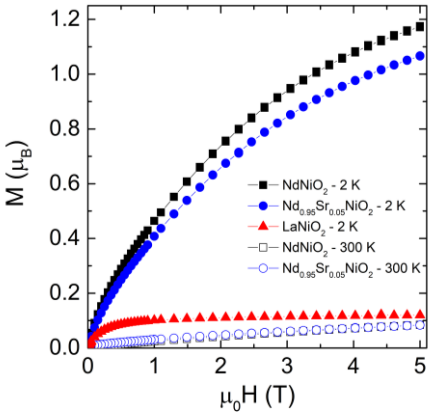
***DFT calculation :*** $N(E_F)$ = 1 state/eV/$LaNiO_2$ → $\gamma$ (DFT) = 2.4 mJ/mol/K²

$\gamma(NdNiO_2) \approx 8x\gamma(LaNiO_2)$

- Low T upturn : Magnetic order (T < 2K) and/or Schottky anomaly

## DC Magnetic susceptibility




- M = f(H) : local magnetic interactions
- **Spin glass behavior **** with spin freezing temperature :

$T_f$ = 12K ($LaNiO_2$), 6K ($NdNiO_2$), 5K ($Nd_{0.95}Sr_{0.05}NiO_2$)

$CaCuO_2$ : AF ordering $T_N$= 442 K


* Hepting, M. *et al. Electronic structure of the parent compounds of superconducting infinite-layer nickelates. Nature Materials.* 19 (2020). 381-385

** Lin, H. *et al. Universal spin-glass behaviour in bulk $LaNiO_2$, $PrNiO_2$ and $NdNiO_2$. New J. Phys.* 24 (2022), 013022

# $Nd(Sr)NiO_2$ vs $LaNiO_2$ : Cp/T = f(T) vs magnetic field

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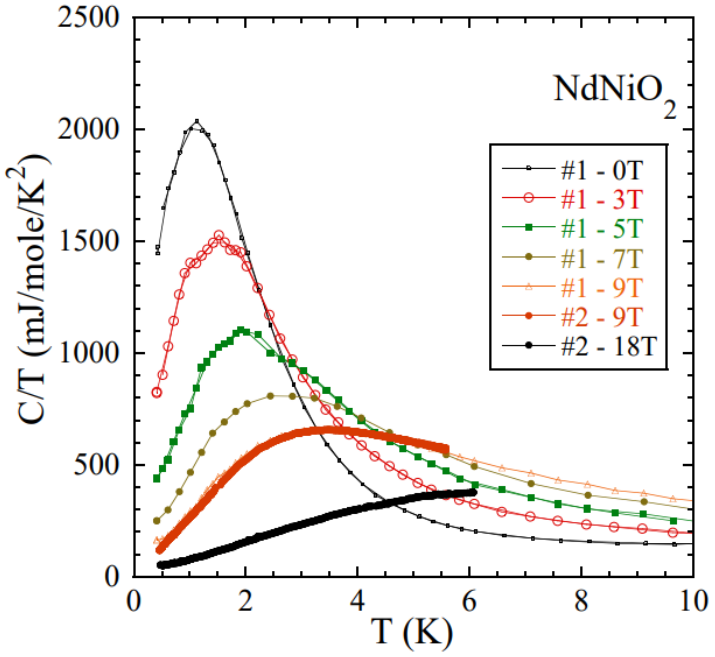
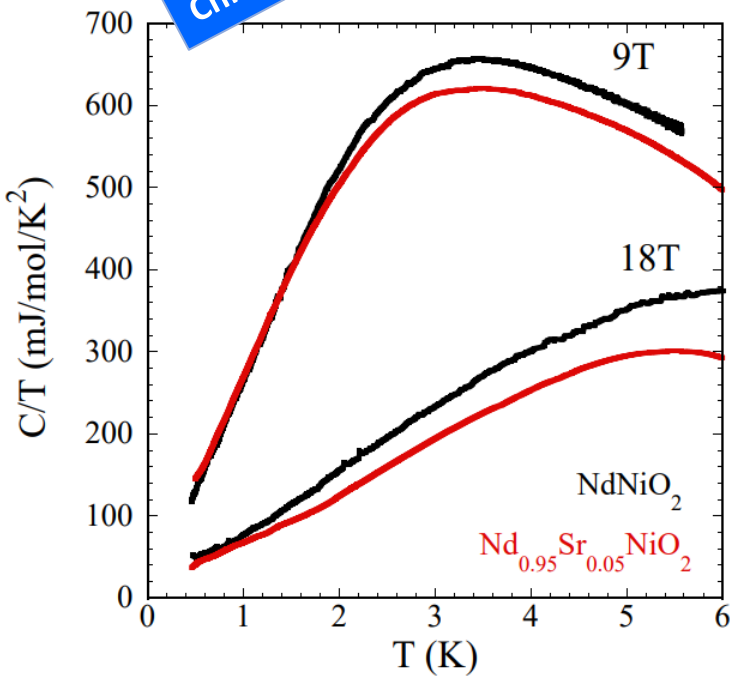
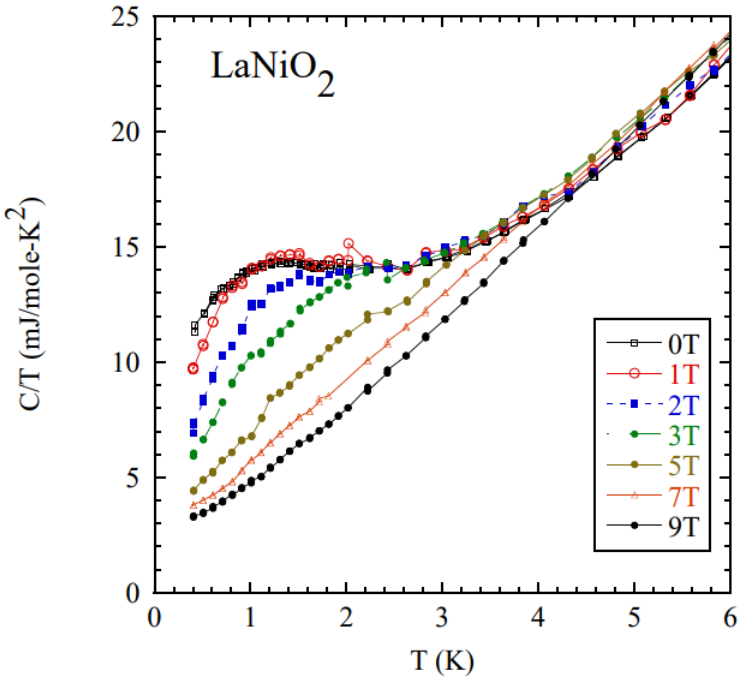
Christophe Marcenat@Institut Neel

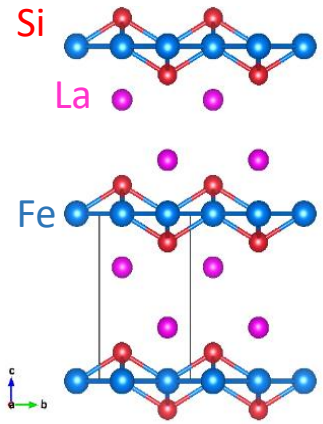


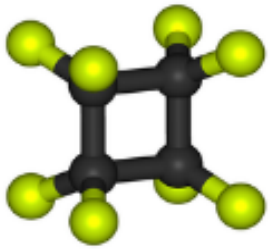



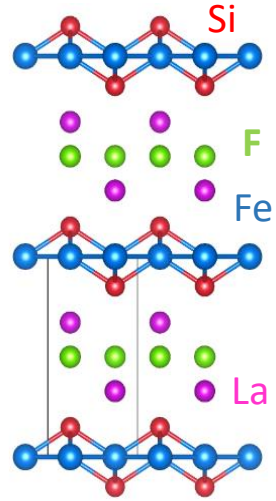

- ***Crystal field splitting*** of $Nd^{3+}$ at low T ($^4I_{9/2}$ GS Kramers doublet) ***and Schottky-like anomaly***
- The two level Schottky anomaly becomes ***more indistinctive*** as increasing magnetic field (Zeeman)
- $NdNiO_2$ and $Nd_{1-x}Sr_xNiO_2$ : Cp/T = f(T) ***almost similar behaviors despite stacking faults observed in $NdNiO_2$***
- Variation of Cp/T vs T in $LaNiO_2$ : **local magnetic excitations** $Ni^+(S=1/2)$ → cuprates

# From $(Cu)NiO_4$ $D_{4h}$ site in IL-Perovskite to $FeSi(As)_4$ Td site in anti-PbFCl ($FeSiLaF_x$)



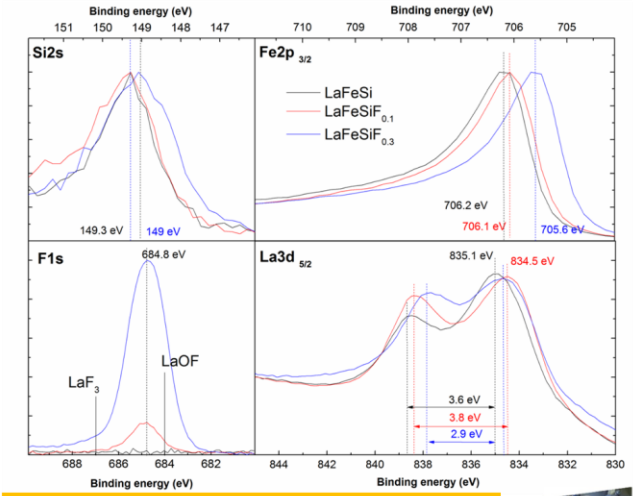



**T=450°C-500°C**
**$C_4F_8$, flow, 10-30ml/min**
**1-4h**




Dissociation of covalent C-F bonds
at the surface of LaFeSi →
Topotactic intercalation of **$F^-$ anions in Td ($La_4$) site**

**Topotactic fluorination of intermetallics as a new route to quantum materials.**
**J-B. Vaney et al. *Nature Comm,* 2022, 13, 1462-1471**




**XPS analysis :**
Increase of Fe-Si covalency with F content
A more pronounced overlap between La and Si
F 1s binding energies constant with x content

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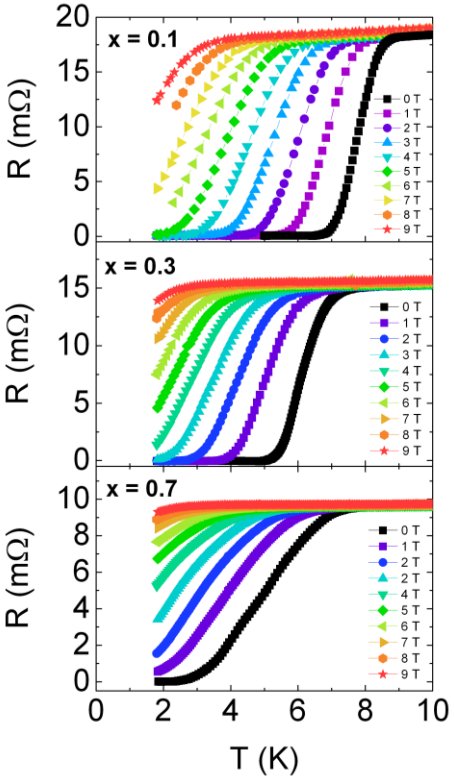
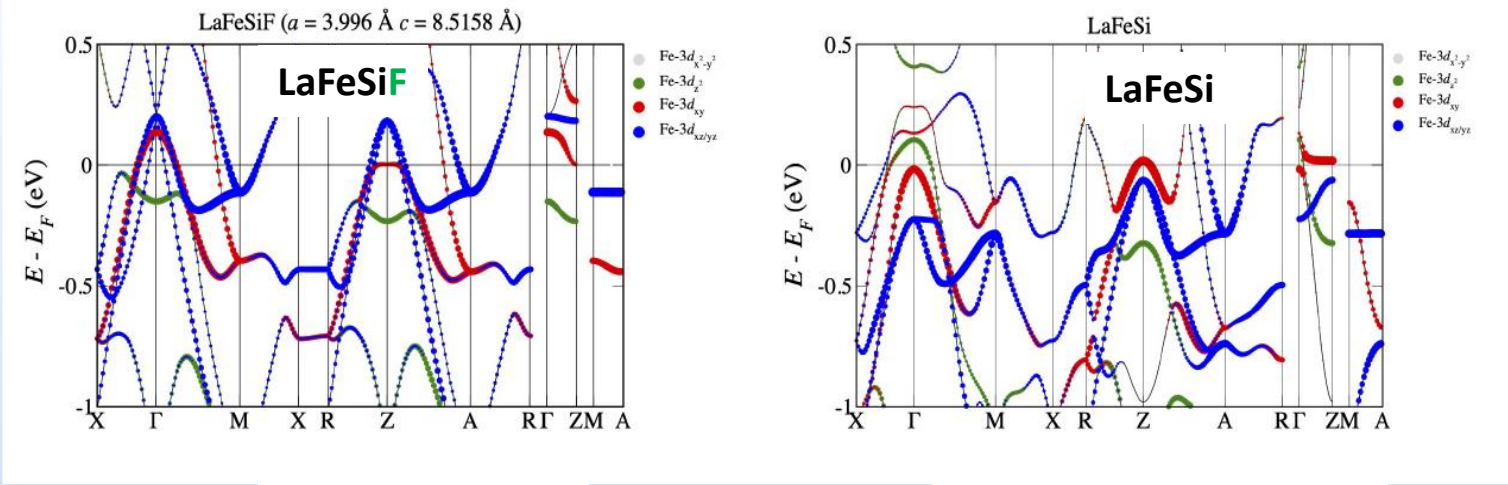
@Placamat

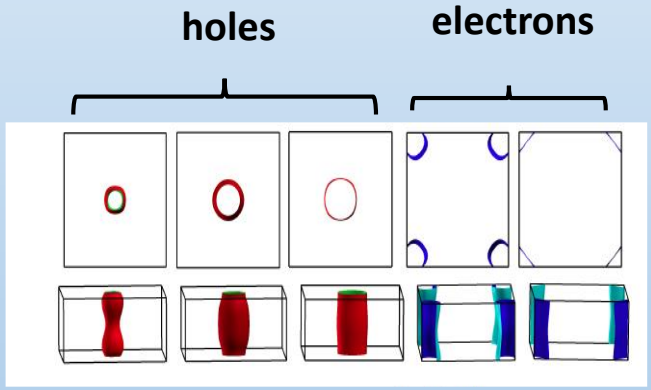


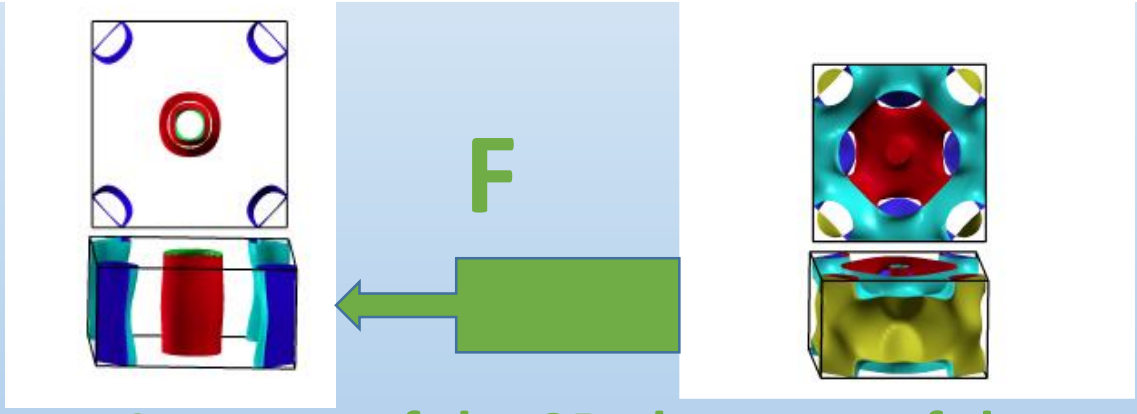
# Electronic structure (Band diagram and Fermi surface)

*A. Cano & F. Bernardini*




- ✓ Metallic
- ✓ Multi-band
- ✓ 3d (Fe) states




Increase of the 2D character of the Fermi surface

Similar to $LaFeAsO_{0.85}F_{0.15}$ (Tc=26 K). by direct synthesis, never topotactic!

→ $T_c$ decreases with Fluorine content

→ Increase of metallicity in FeSi sheets with F content => Inductive effect & Electronic correlations

# Conclusion :
## Anharmonic stabilization with various breathing mode of Oxygen- Copper, Nickel, Iron , Hydrogen in square coordination

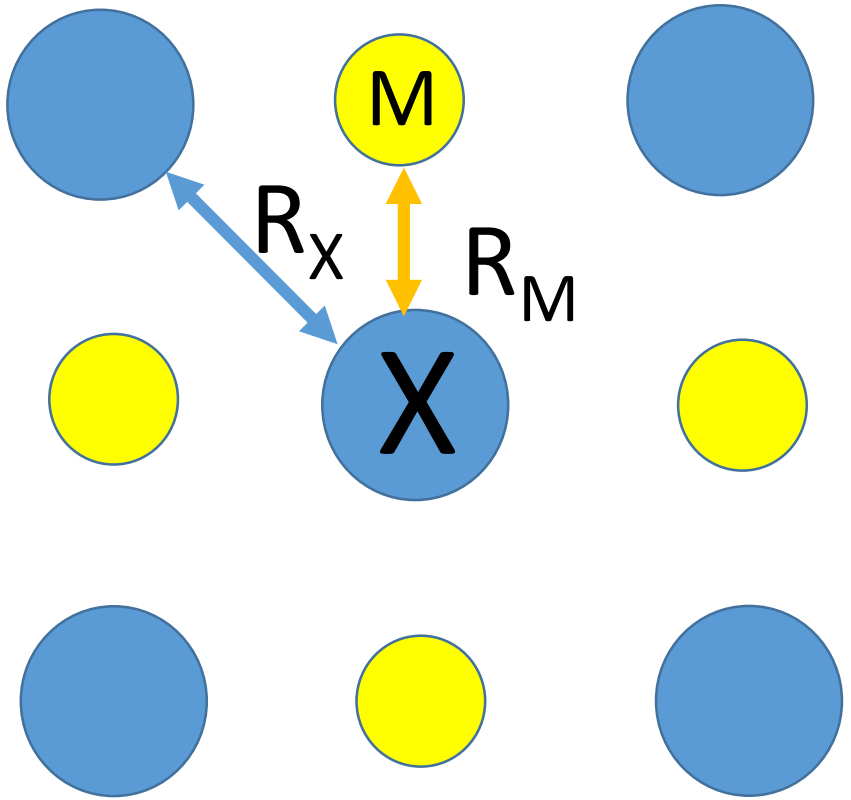
## *What's next ?*

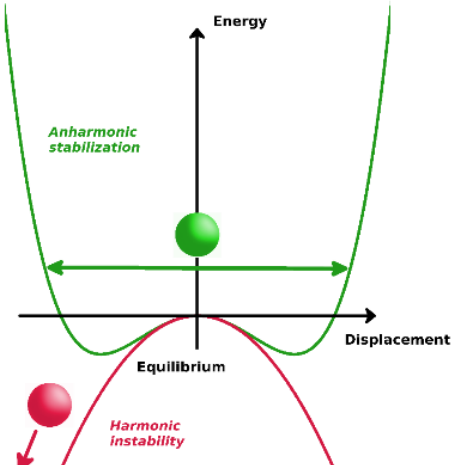
## Mixing Anions X to enhance square planar configuration

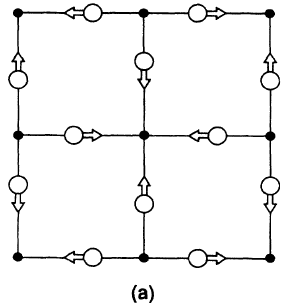
Electronegativity &
**Madelung Potential**

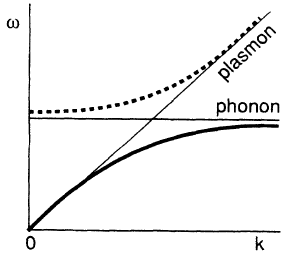
Polarizability &
**Van der Walls Forces**

**Symmetry**



# Acknowledgments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**Sophie TENCE (Fluoride-Silicide)**

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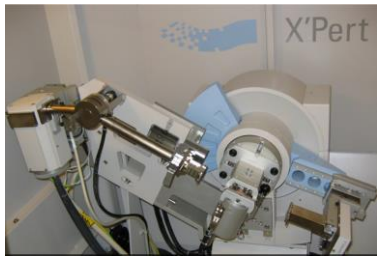


**Pierre RODIERE (Nickelate)**

Rafik BALLOU (CF calculation)

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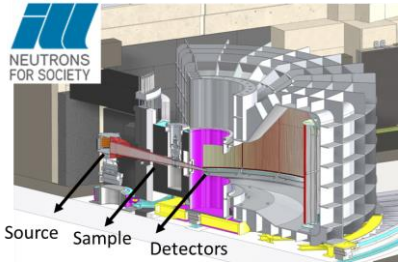


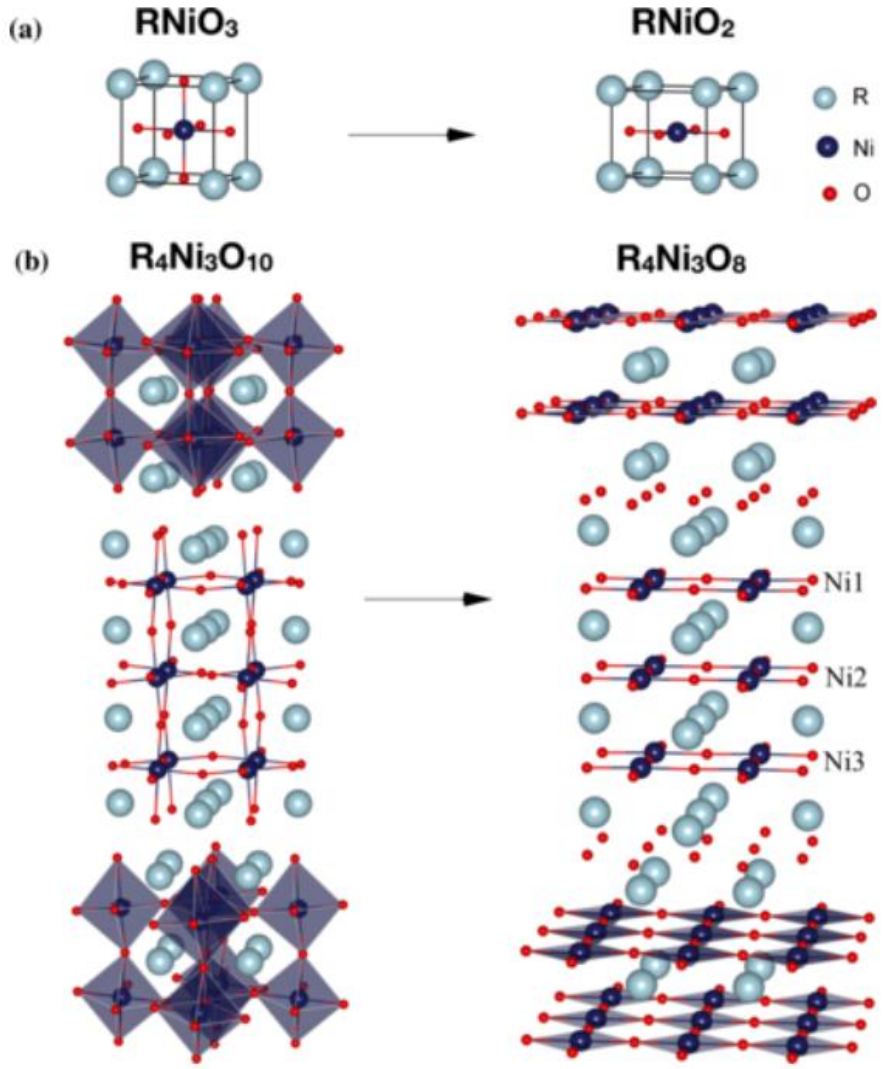

**ILL**

Emmanuelle SUARD (D2B)

Prime

Projets de recherche interdisciplinaires multi-équipes

# Topochemical reduction of Perovkite vs RP phases : 2D character, $NiO_2$ IL and R influence




**$RNiO_2$, IL**

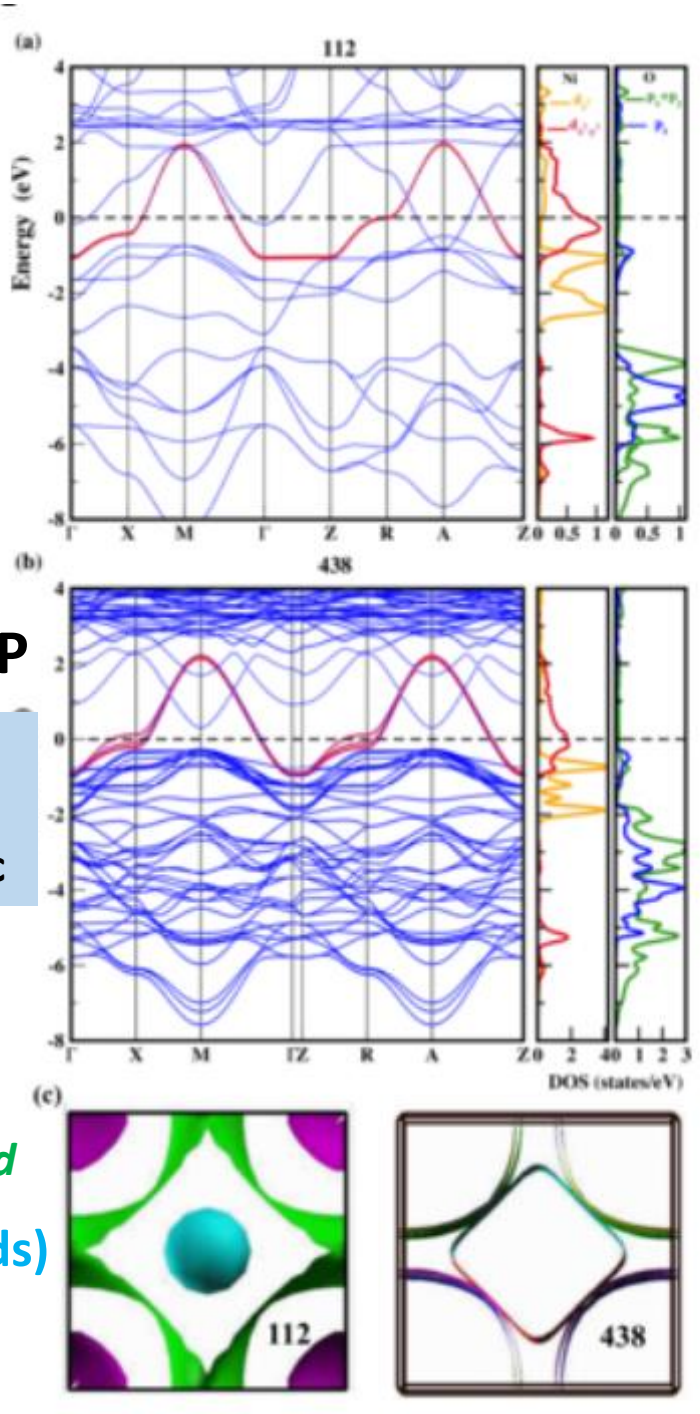
**$R_4Ni_3O_8$, RP**

**Destabilization of R-d bands above $E_F$**
**R-O becomes more ionic**

Stronger Ni-O hybridization

***Self-doping of the Ni $d_{x2-y2}$ band***

**e- pocket (R, d bands)**




Theoritical investigations of superconductivity in trilayer square-planar nickelates
E.M. Nica et al. Phys Rev B, 102, (2020), 020504

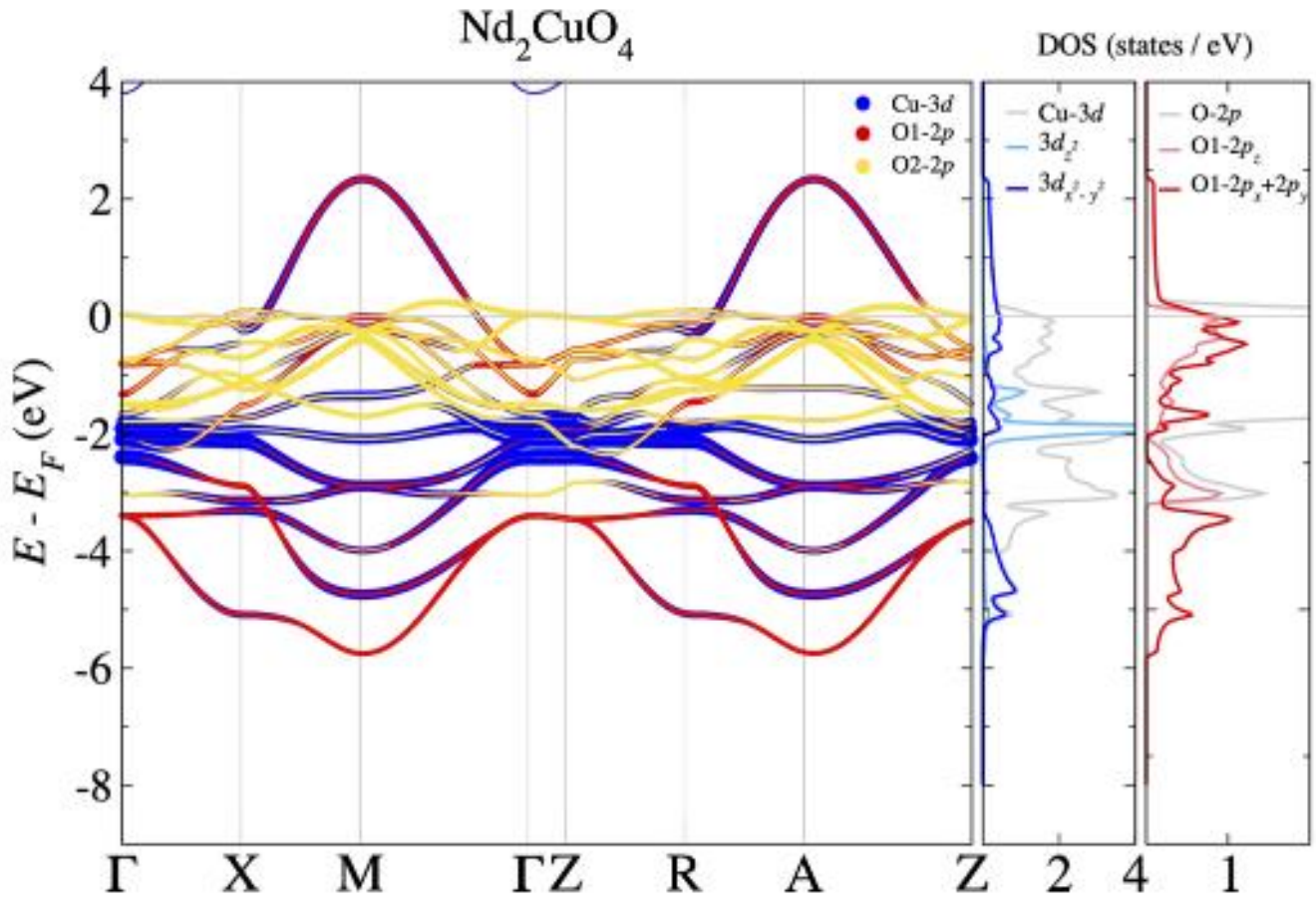
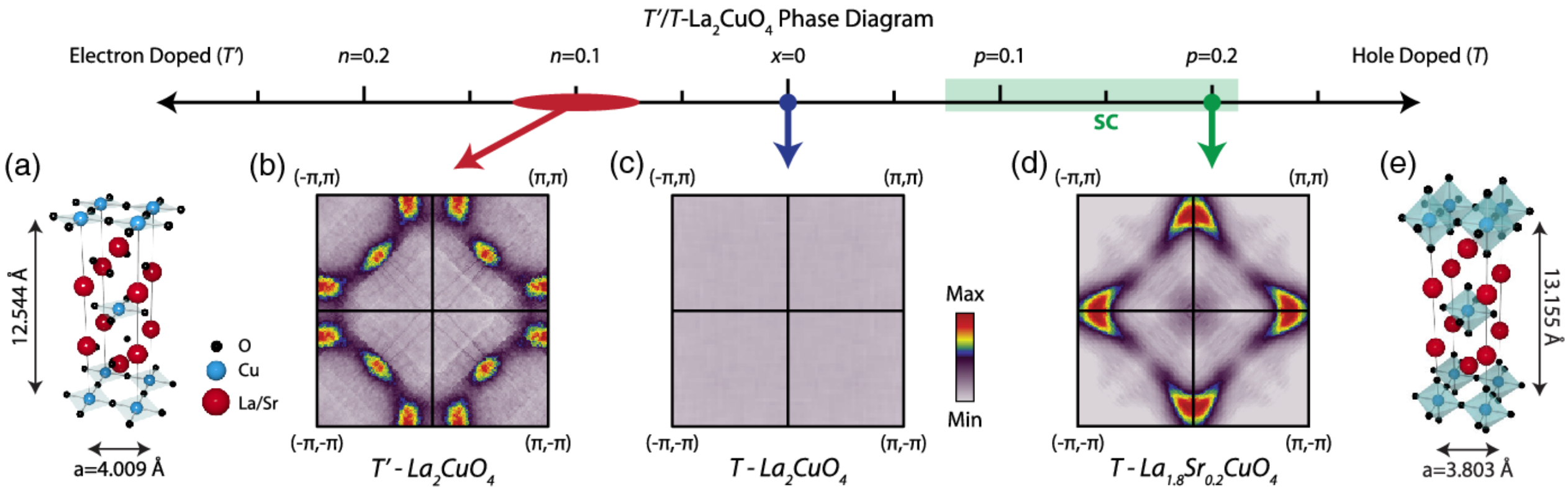
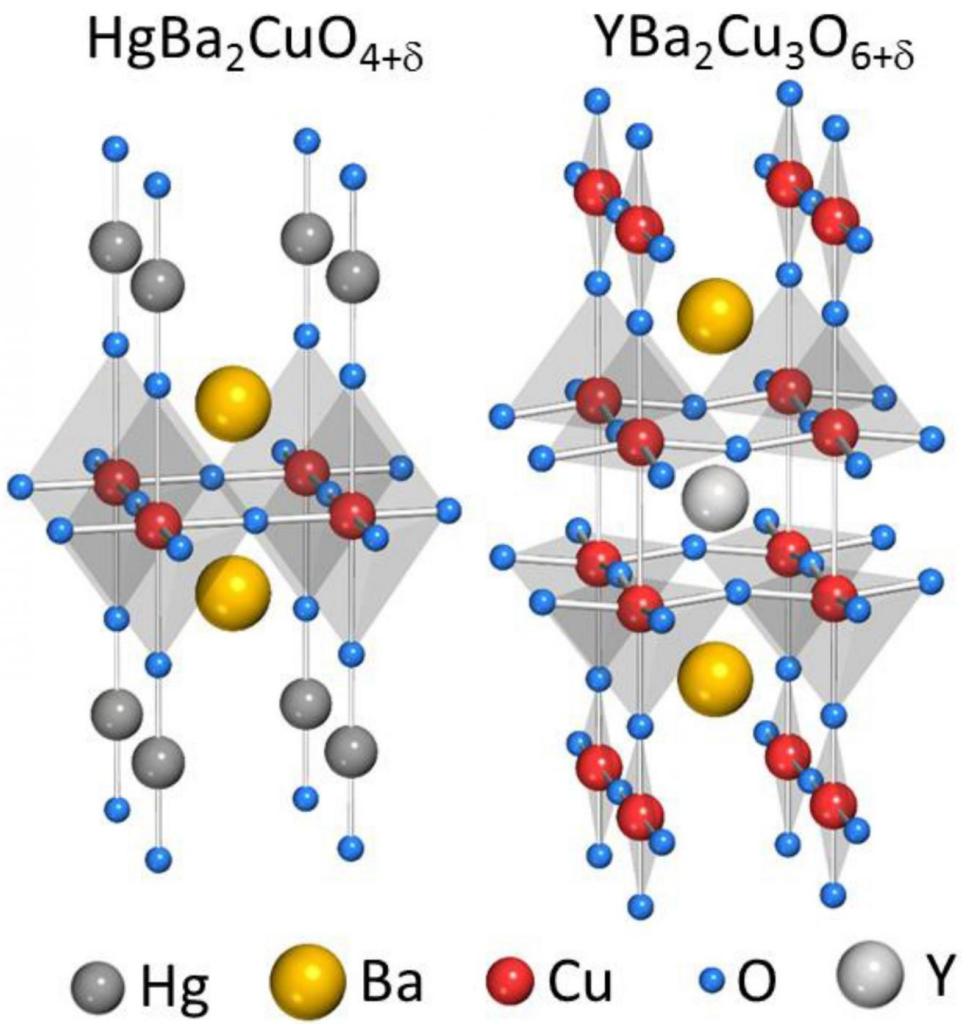
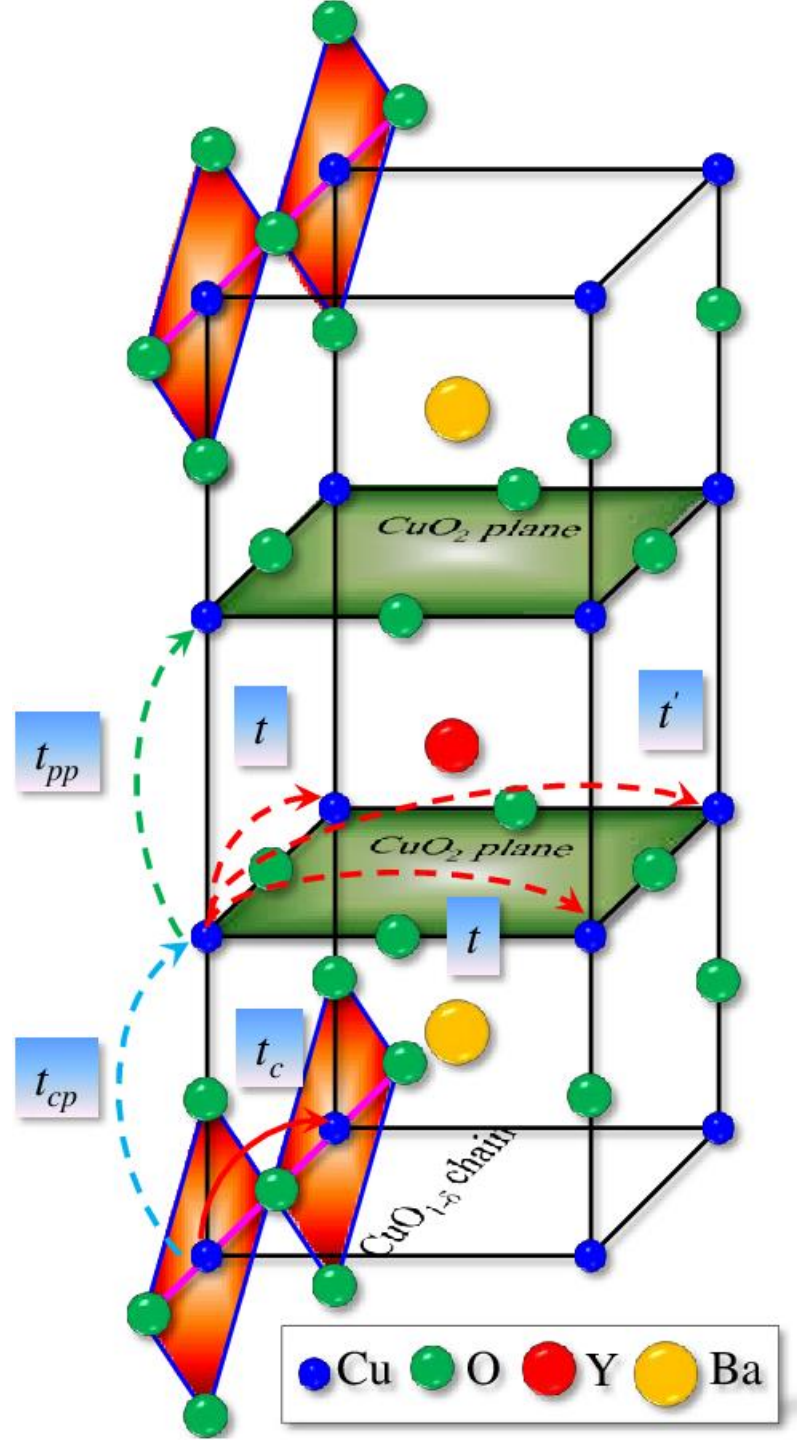



FIG. 4. Band structure and orbital resolved density of states (DOS) of $Nd_2CuO_4$. O1 refers to the oxygens in the $CuO_2$ layer while O2 to the fluorite block.


T′/T-La2CuO4 Phase Diagram
Electron Doped (T′)
n=0.2
n=0.1
x=0
p=0.1
p=0.2
Hole Doped (T)
SC
(a)
12.544 Å
a=4.009 Å
O
Cu
La/Sr
(b)
(-π,π)
(π,π)
(-π,-π)
(π,-π)
T′ - La2CuO4
(c)
(-π,π)
(π,π)
(-π,-π)
(π,-π)
T - La2CuO4
Max
Min
(d)
(-π,π)
(π,π)
(-π,-π)
(π,-π)
T - La1.8Sr0.2CuO4
(e)
13.155 Å
a=3.803 Å

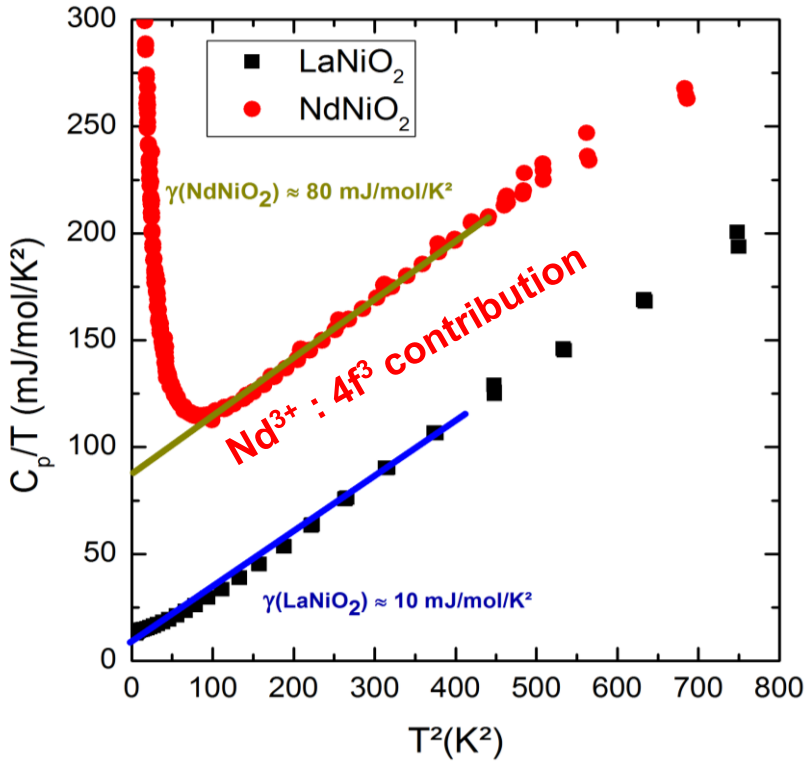

$HgBa_2CuO_{4+\delta}$
$YBa_2Cu_3O_{6+\delta}$
Hg
Ba
Cu
O
Y


$CuO_2$ plane
$CuO_2$ plane
$t_{pp}$
$t$
$t'$
$t$
$t_c$
$t_{cp}$
$CuO_{1-\delta}$ chain
Cu
O
Y
Ba

# $Nd(Sr)NiO_2$ vs $LaNiO_2$ : transport and magnetic properties

## Electronic Specific heat

$C_p = \gamma T + \beta T^3 \rightarrow \frac{C_p}{T} = \gamma + \beta T^2$, *at low temperature*



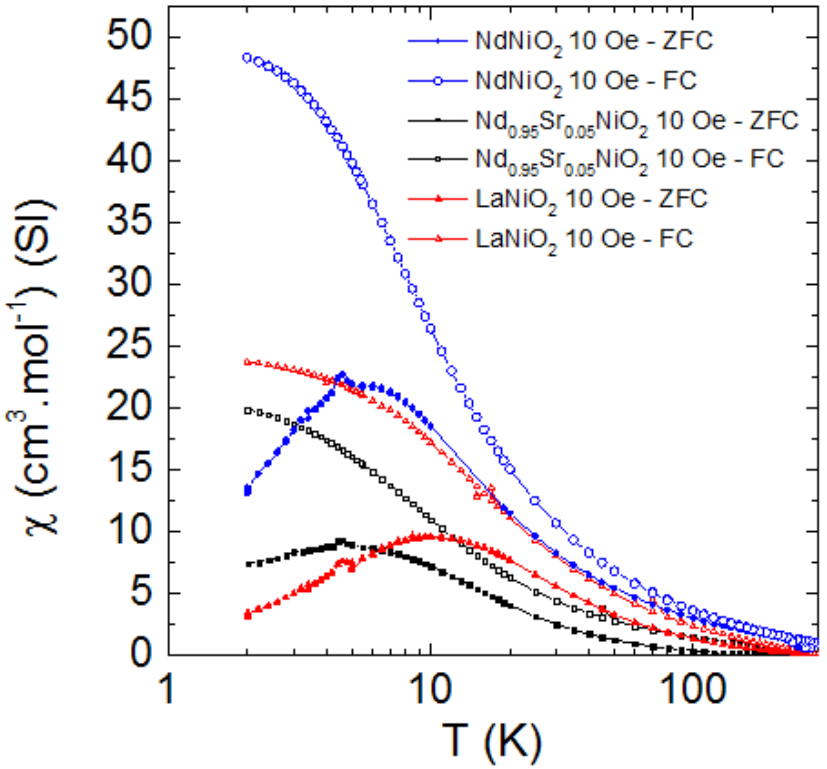

- ***Metallic state : $\gamma \propto N(E_F) \propto m^*$ (effective mass)***

***DFT calculation : $N(E_F)$ = 1 state/eV/$LaNiO_2$ → $\gamma$ (DFT) = 2.4 mJ/mol/K²)***

**$\gamma(NdNiO_2) \approx 8x\gamma(LaNiO_2)$**

- Low T upturn : Magnetic order (T < 2K) and/or Schottky anomaly

## DC Magnetic susceptibility

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$\gamma(NdNiO_2) \approx 8x\gamma(LaNiO_2)$

Low T upturn : Magnetic order (T < 2K) and/or Schottky anomaly

- M = f(H) : local magnetic interactions
- **Spin glass behavior **** with spin freezing temperature :

$T_f$ = 12K ($LaNiO_2$), 6K ($NdNiO_2$), 5K ($Nd_{0.95}Sr_{0.05}NiO_2$)

$CaCuO_2$ : AF ordering $T_N$= 442 K

* Hepting, M. *et al. Electronic structure of the parent compounds of superconducting infinite-layer nickelates. Nature Materials,* 19

** Lin, H. *et al. Universal spin-glass behaviour in bulk $LaNiO_2$, $PrNiO_2$ and $NdNiO_2$. New J. Phys.* 24 (2022),

# Pauling electronegativity $\chi$


1929 (Rules), 1954 (Nobel Prize),
1962 (Nobel peace prize)

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,2 H 1 | | | | | | | | | | | | | | | | | He 2 |
| 0,98 Li 3 | 1,57 Be 4 | | | | | | | | | | | | | 3,04 N 7 | | | Ne |
| 0,93 Na 11 | 1,31 Mg 12 | | | | | | | | | | | 1,61 Al 13 | 1,9 Si 14 | 2,19 P 15 | 2,58 S 16 | 3,16 Cl 17 | Ar |
| 0,82 K 19 | 1 Ca 20 | 1,36 Sc 21 | 1,54 Ti 22 | 1,63 V 23 | 1,66 Cr 24 | 1,55 Mn 25 | 1,83 Fe 26 | 1,88 Co 27 | 1,91 Ni 28 | | | | 2,01 Ge 32 | 2,18 As 33 | 2,55 Se 34 | 2,96 | Kr 36 |
| 0,82 Rb 37 | 0,95 Sr 38 | 1,22 Y 39 | 1,33 Zr 40 | 1,6 Nb 41 | 2,16 Mo 42 | 1,9 Tc 43 | 2,2 Ru 44 | 2,28 Rh 45 | 2,2 Pd 46 | 1,93 Ag 47 | 1,69 Cd 48 | 1,78 In 49 | 1,96 Sn 50 | 2,05 Sb 51 | 2,1 Te 52 | 2,66 I 53 | Xe 54 |
| 0,79 Cs 55 | 0,89 Ba 56 | 1,1 La 57 | 1,3 Hf 72 | 1,5 Ta 73 | 1,7 W 74 | 1,9 Re 75 | 2,2 Os 76 | 2,2 Ir 77 | 2,2 Pt 78 | 2,4 Au 79 | 1,9 Hg 80 | 1,8 Tl 81 | 1,8 Pb 82 | 1,9 Bi 83 | 2 Po 84 | 2,2 At 55 | Rn 86 |
| 0,7 Fr 87 | 0,9 Ra 88 | 1,1 Ac 89 | Rf 104 | Db 105 | Sg 106 | Bh 107 | Hs 108 | Mt 109 | Ds 110 | Rg 111 | Cn 112 | 113 | 114 | 115 | 116 | 117 | 118 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,12 Ce 58 | 1,13 Pr 59 | 1,14 Nd 60 | 1,13 Pm 61 | 1,17 Sm 62 | 1,2 Eu 63 | 1,2 Gd 64 | 1,2 Tb 65 | 1,22 Dy 66 | 1,23 Ho 67 | 1,24 Er 68 | 1,25 Tm 69 | 1,1 Yb 70 | 1,27 Lu 71 |
| 1,3 Th 90 | 1,5 Pa 91 | 1,7 U 92 | 1,3 Np 93 | 1,3 Pu 94 | 1,3 Am 95 | 1,3 Cm 96 | 1,3 Bk 97 | 1,3 Cf 98 | 1,3 Es 99 | 1,3 Fm 100 | 1,3 Md 101 | 1,3 No 102 | 1,3 Lr 104 |

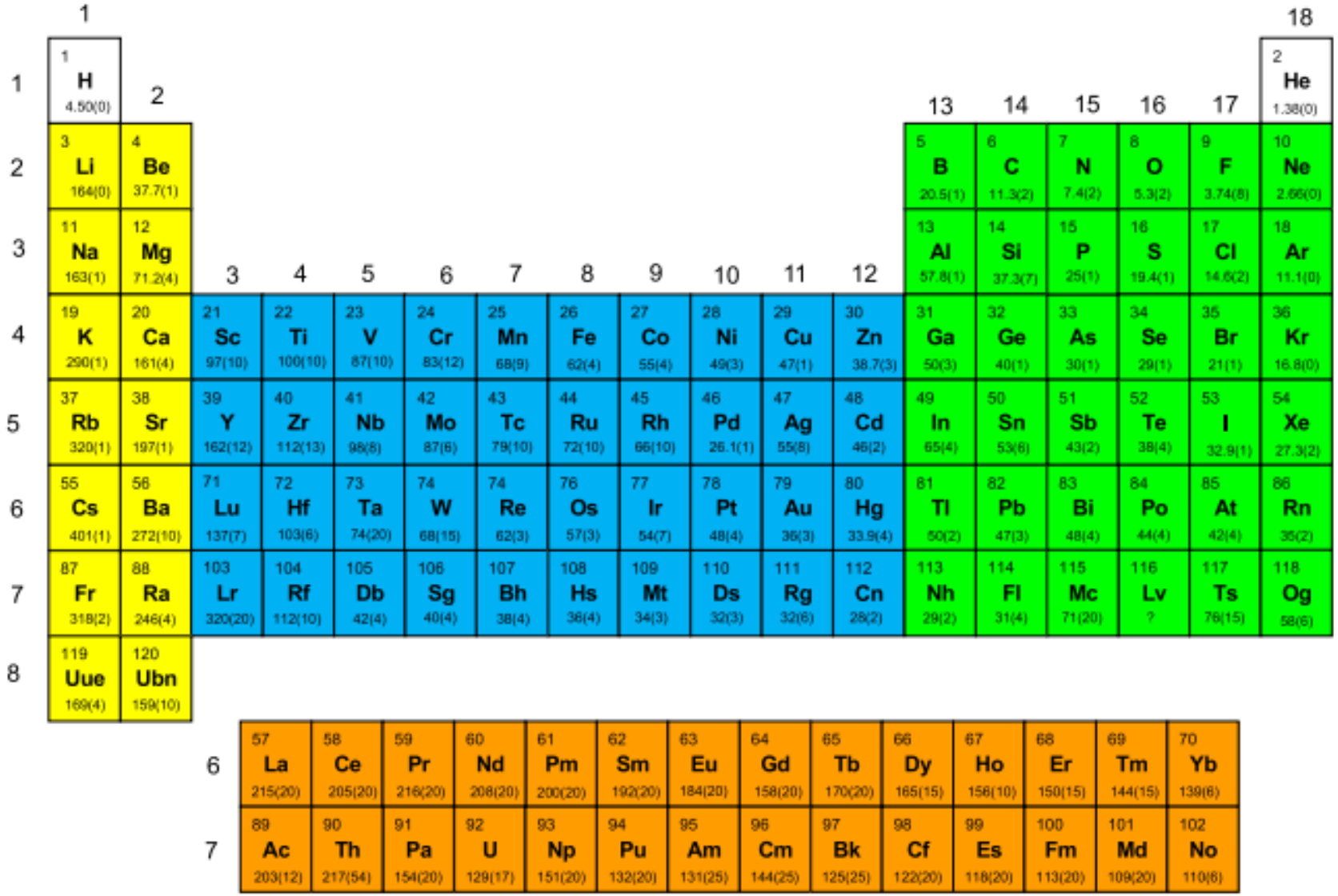
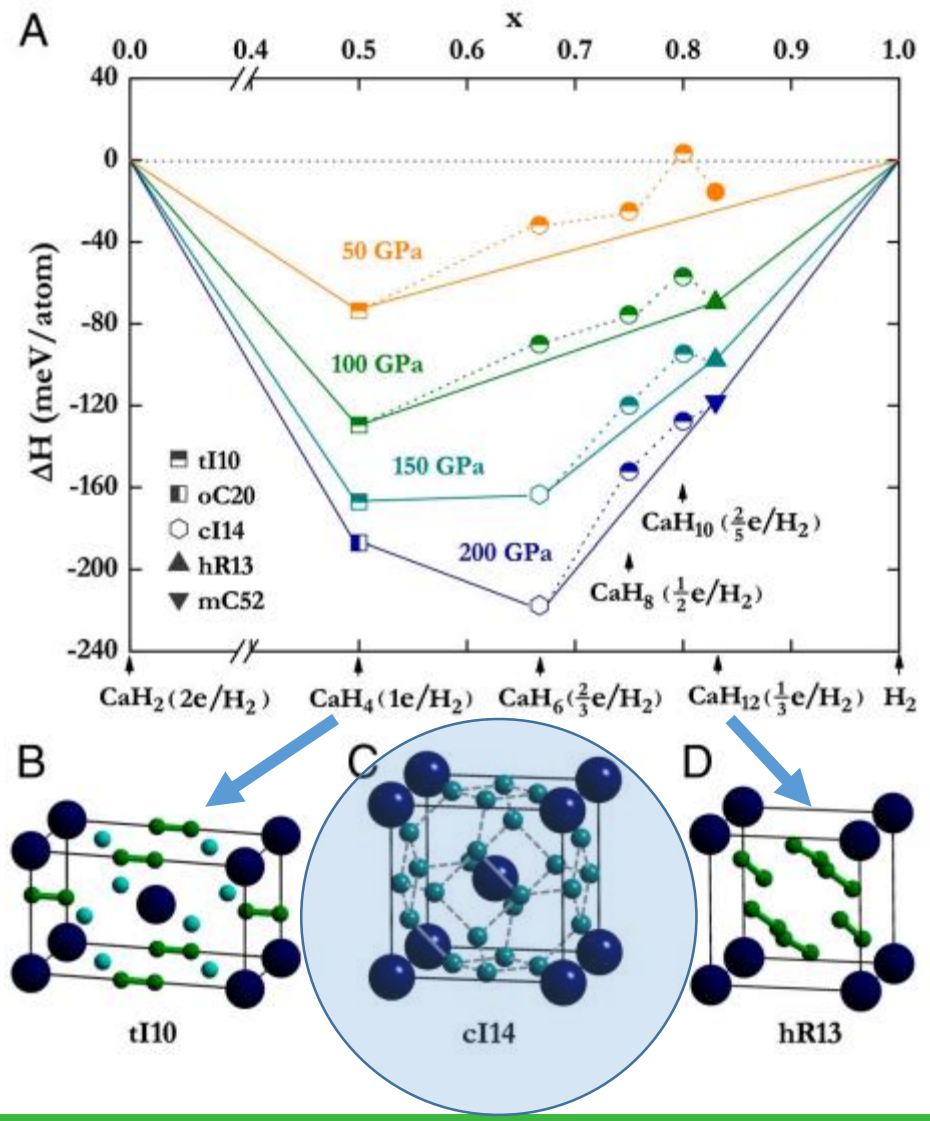



**Figure 1.** Recommended values from Table 1 for the atomic polarizabilities (atomic units; estimated uncertainties in parentheses) of elements $Z = 1$–120. The various blocks of elements are colour-coded: *s*-block, yellow; *p*-block, green; *d*-block, blue; *f*-block, orange.

Peter Schwerdtfeger & Jeffrey K. Nagle (2019) 2018 Table of static dipole polarizabilities of the neutral elements in the periodic table, Molecular Physics, 117:9-12, 1200-1225, DOI: 10.1080/00268976.2018.1535143

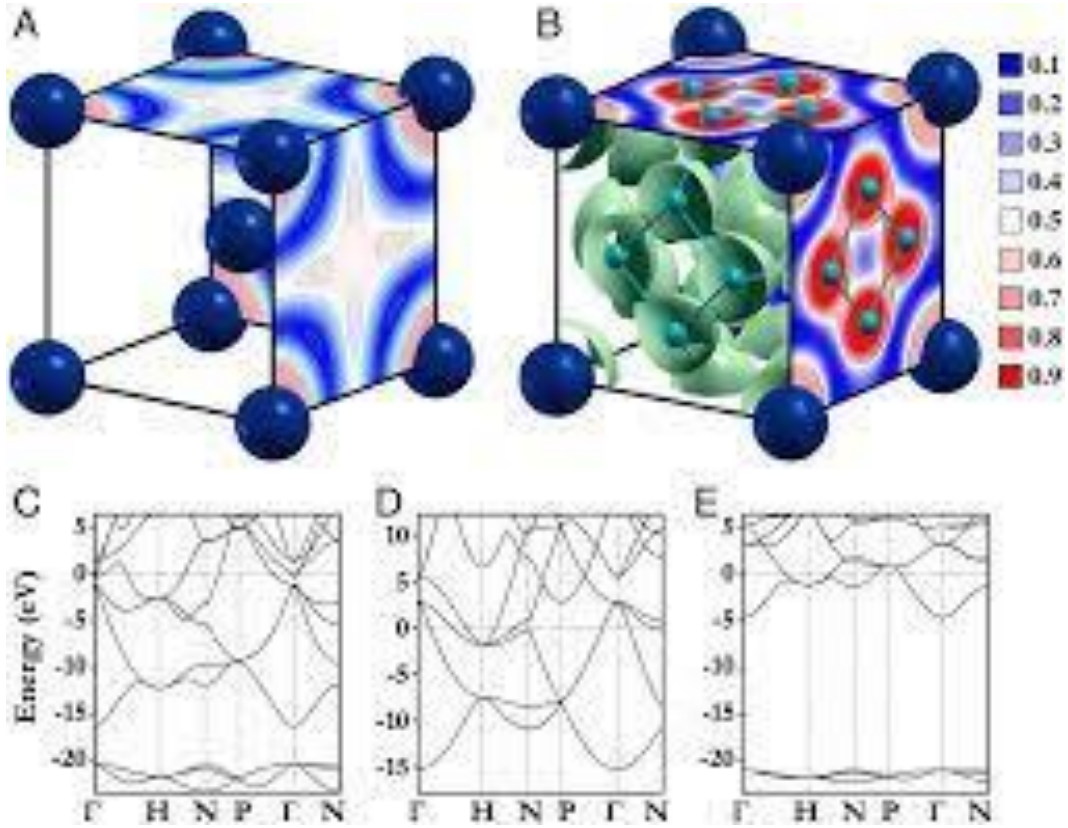
# The $H_4$ unit in $CaH_6$ 'clathrate' hydride with sodalite framework : superconductivity with Tc = 220-235 K at 150 GPa




Superconductive Sodalite-like clathrate calcium hydride at high pressure
PNAS, H. Wang et al. 2012, 109, 17, 6463-6466

ELF of $CaH_0$

***ELF of $CaH_6$***




$CaH_6$ $Ca_0H_6$ $CaH_0$

Band structure

**Optimized H-H distance in square $H_4$ unit**
**H-H ($CaH_6$)= 1.26 Å < H-H ($H_3S$) = 1.54 Å**
**$H_3S$, Im-3m (cI14) : Tc = 190 K at 150 GPa**