Towards new 2D nickelates with superconducting behavior

Alain Demourgues

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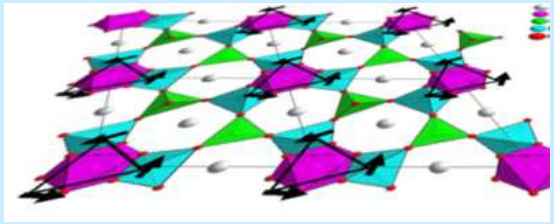

GDR MEETICC

Matériaux, Etats ElecTronIques et Couplages non-Conventionnels

5th of November 2019, Paris

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Pergamon Press plc

ELUSIVE SUPERCONDUCTIVITY IN POLYCRYSTALLINE SAMPLES OF LAYERED LANTHANUM NICKELATES*

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(*Received* 11 *May* 1989 *by C.N.R. Rao*)

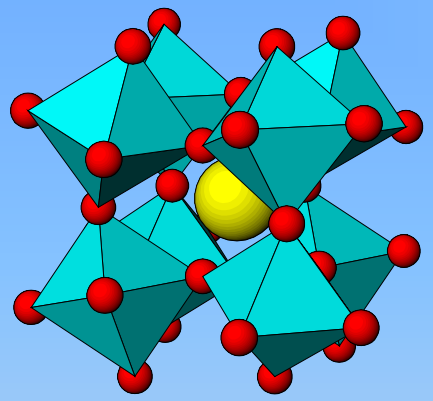
$La_{2-x}NiO_4$, $La_{2-x}Sr_xNiO_4$ and related layered nickelates have been investigated for possible presence of superconductivity. While there is clear onset of diamagnetism around 20 K in many of these nickelates, we do not, however, find any anomaly in the electrical resistivity, magnetoresistance or thermopower around 20 K. High energy spectroscopic studies show Ni to be in the 2+ oxidation state accompanied by a substantial proportion of oxygen holes.

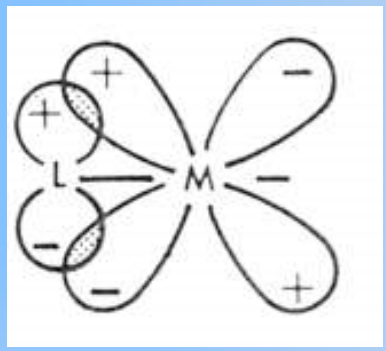
Outline

- ***Foreword*** : From Ni^{3+} (t_2^6 e^1) to Ni^{+} (t_2^6 e^3) perovskite
  U (Hubbard), $W_{\pi,\sigma}$ (bandwidth), Δ (charge transfer)
- ***Foreword :*** Cuprates vs Nickelates
- **Ni-RE hybridization and Charge Density Wawe ?**
- **From Perovskite to Ruddelsden-Popper (n=1, 2, 3, …) networks : towards more 2D frameworks**
- **Towards mixed anions (O, F, S, Se) Nickelates**
- **$[AX_3]$ Perovskite, $[A_2X_4X'_2]$ K_2NiF_4 and $[A_nX_m]$ layers for stacking : Towards new 2D phases**

Band diagram of $RNiO_3$ (Ni^{3+}-t_2^6 e^1- A= La, Sm)

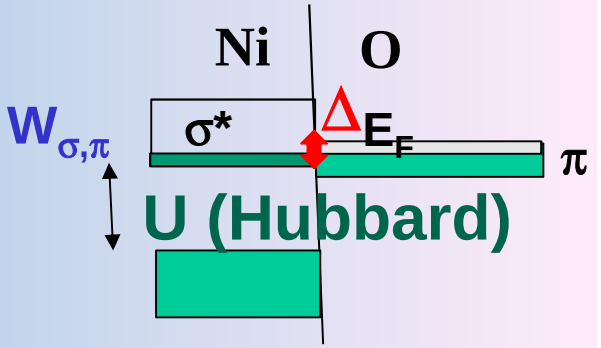
Zaanen-Sawatsky-Allen Scheme !





M-O π Bonding

$\Delta < W < U$ (Metal)



$W < \Delta < U$ (SC)

Competitive bonds between R-O and Ni-O :
(O) p_π orbital for Ni-O <=> (O) p_σ orbital for R-O

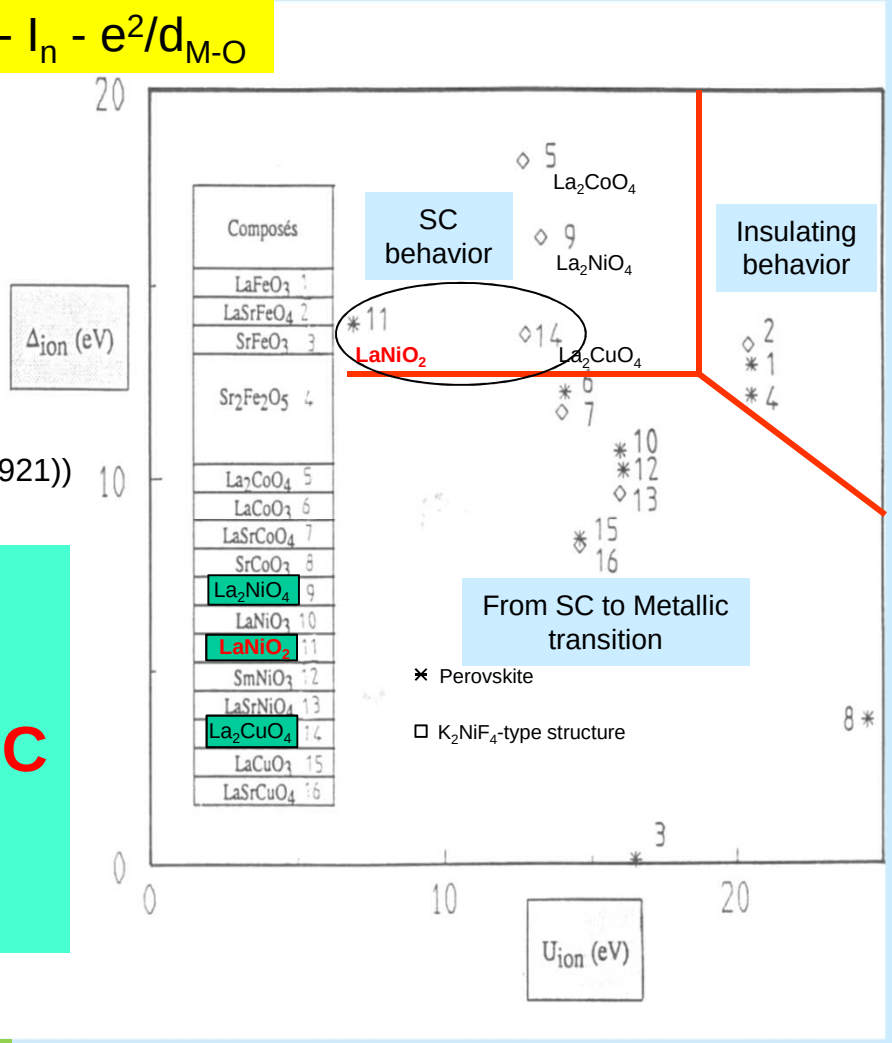
R size ↓ (acidic character ↑) : Covalency of R-O bond (pσ) ↑
W_π (Ni-O) ↓
Ni-O-Ni Angle ↓ orbital overlap (σ) ↓ ***W_σ(Ni-O) ↓***

From ***metallic behavior ($LaNiO_3$)*** to ***semiconducting behavior ($SmNiO_3$)***

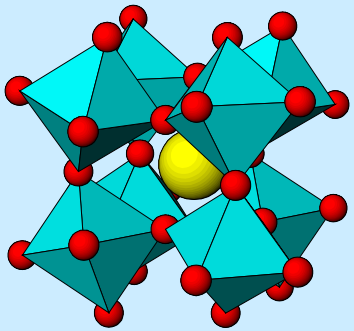
Competition between M-O charge transfer Δ_{ion} and Coulomb repulsion U_{ion}(i.e Hubbard energy) energies in oxides : a ionic view !

$\Delta_{ion} = e\,\Delta(V_{M\text{-}O}) - A(O^-) - I_n - e^2/d_{M\text{-}O}$

Madelung potential difference V_M-V_O
(P.P EWALD method
Ann.Phys, 64, 253 (1921))



Perovskite and K_2NiF_4-type (perovskite layer)



$LaNiO_2$:

W ≤ U < Δ

Mott-Hubbard SC

U < W < Δ

Low U Metal ?

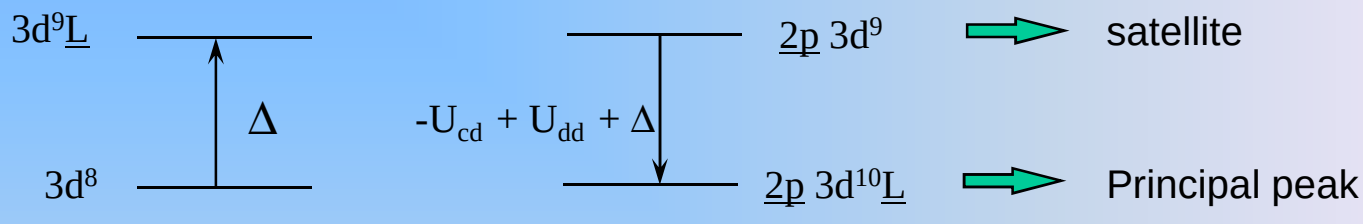
J. Zaanen, G. Sawatsky and J.W. Allen
Phys.Rev.Lett., 55, 418 (1985)

J.B. Torrance, P. Lacorre and R.M. Metzger
J. Sol. Stat.Chem., 90, 168 (1991)

$U_{ion} = I_{n+1} - I_n - e^2/d_{M\text{-}M}$

Charge Transfer calculations : Cu^{3+} $L_{2,3}$ edges XAS

• Cu^{3+} $\alpha\ /3d^8> + \beta\ /3d^9\underline{L}>$ ⟶ $\alpha'\ /\ 2p^5\ 3d^9> + \beta'\ /\ 2p^5\ 3d^{10}\underline{L}>$



$\Delta_{ion} = e\ \Delta(V_{M\text{-}F}) - A(F) - I_n - e^2/d_{M\text{-}F}$

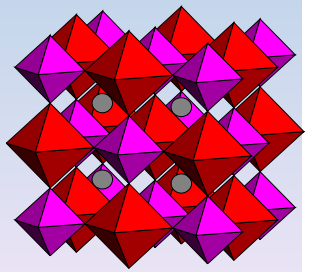


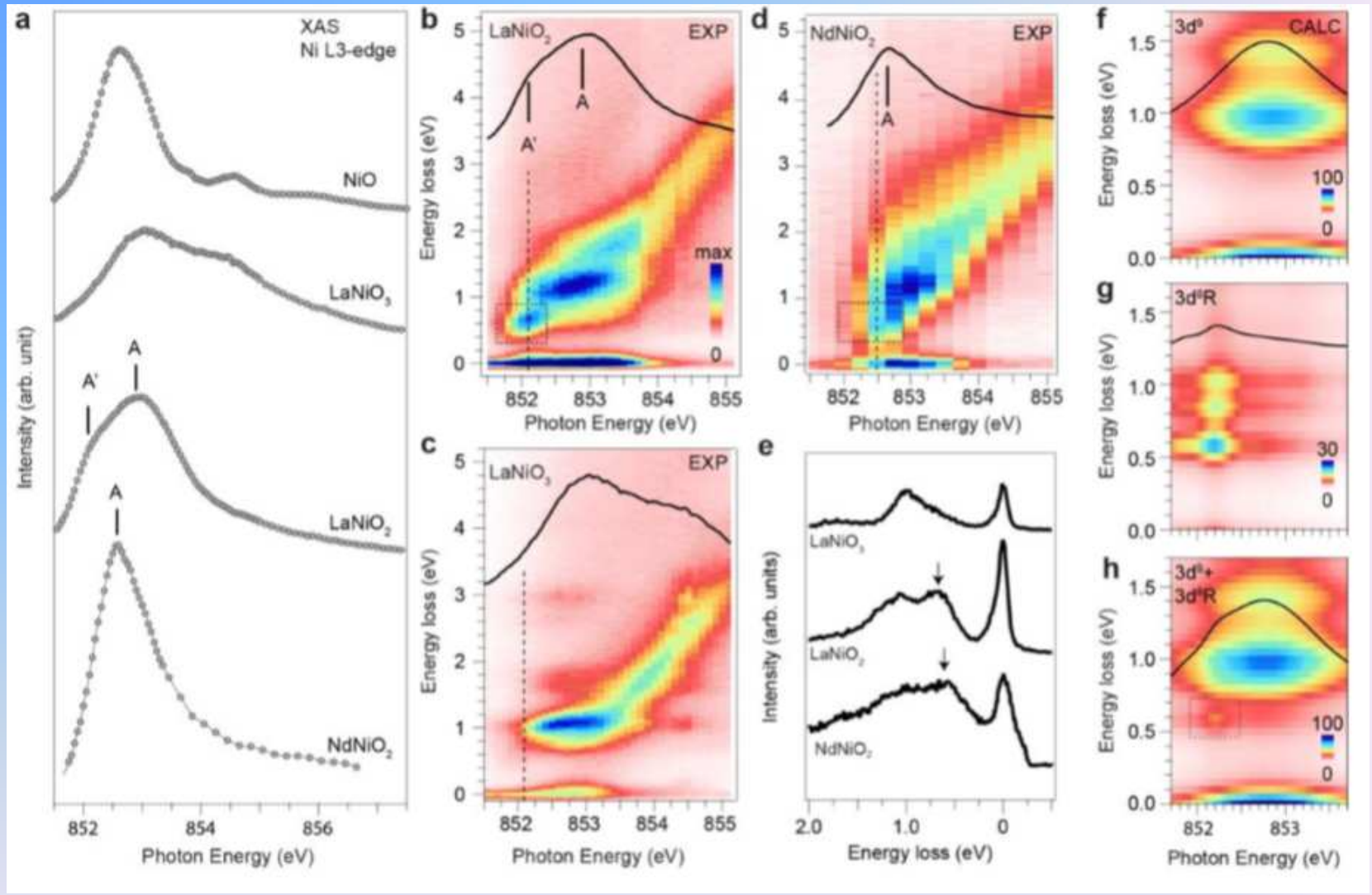
TABLE I. Energetic parameters used to calculate the energy difference between a hole on a fluorine and on a metal site.

Compounds	Ionization energy (eV)	Electrostatic Madelung site potential (V)	$e\Delta V_M$ (eV)	$d_{M\text{-}F}$ (Å)	Charge-transfer energy Δ_{ion} (eV)
$KNiF_3$	18.19	22.19	33.77	2.006	4.98
$KCuF_3$	20.32	22.14	33.74	2.035	2.95
K_2NaNiF_6	35.21	30.90	43.02	1.890	−3.20
K_2NaCuF_6	36.88	30.88	43.00	1.870	−4.97

C. De Nadaï , A. Demourgues et al. Phys Rev B.**63**, (2001) 125123,

only 40% of $3d^8$ configuration (Cu^{3+}) in $K_2NaCu^{III}F_6$.

XAS and RIXS (Ni-L_3-edge)

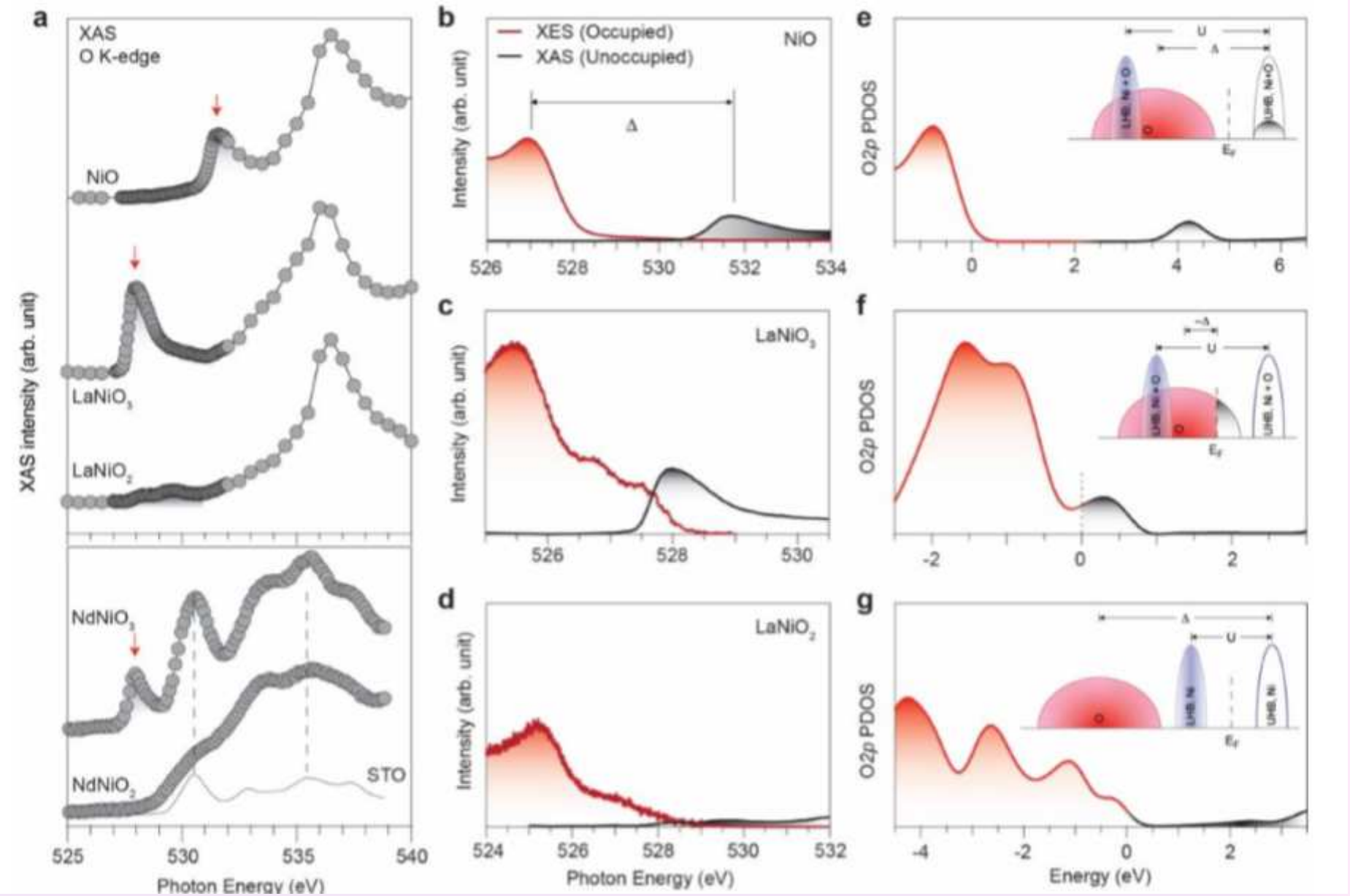


Ni-La and Ni-Nd Hybridization !

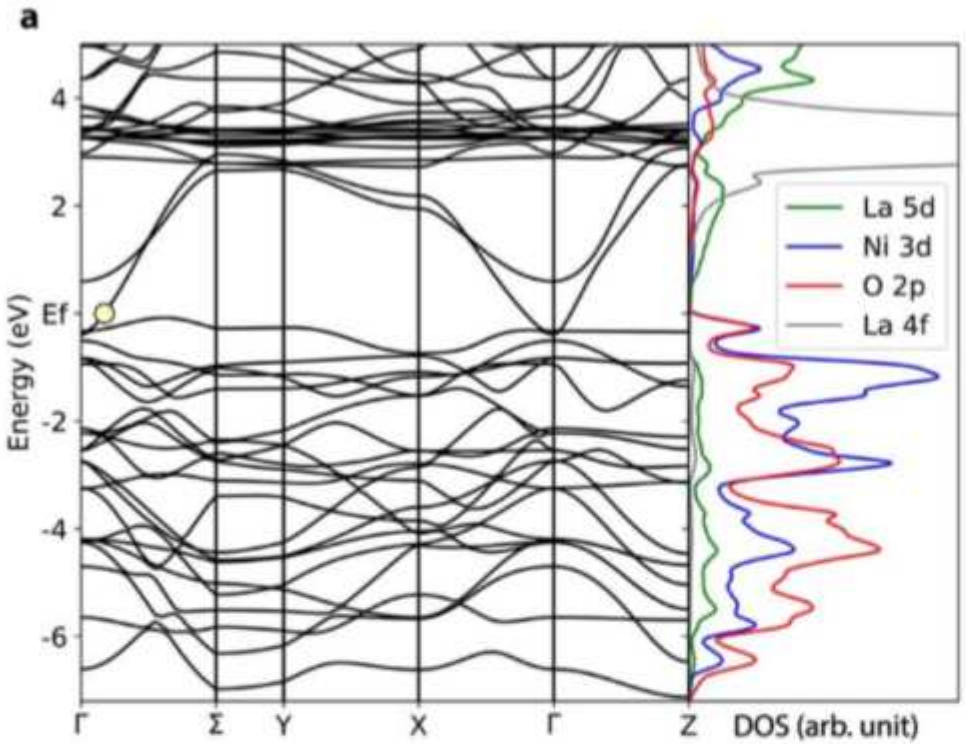
Electronic structure of the parent compound of superconducting infinite-layer nickelates

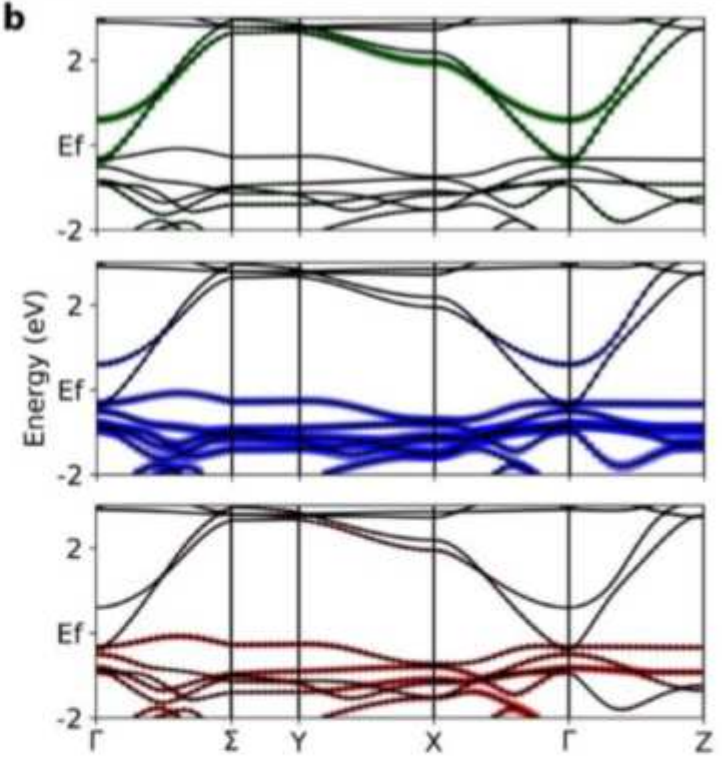
M. Hepting1†, D. Li1, C. J. Jia1, H. Lu1, E. Paris2, Y. Tseng2, X. Feng1, M. Osada1, E. Been1, Y. Hikita1, Y. D. Chuang3, Z. Hussain3, K. J. Zhou4, A. Nag4, M. Garcia-Fernandez4, M. Rossi1, H. Y. Huang5, D. J. Huang5, Z. X. Shen1, T. Schmitt2, H. Y. Hwang1, B. Moritz1, J. Zaanen6, T. P. Devereaux1, and W. S. Lee1*

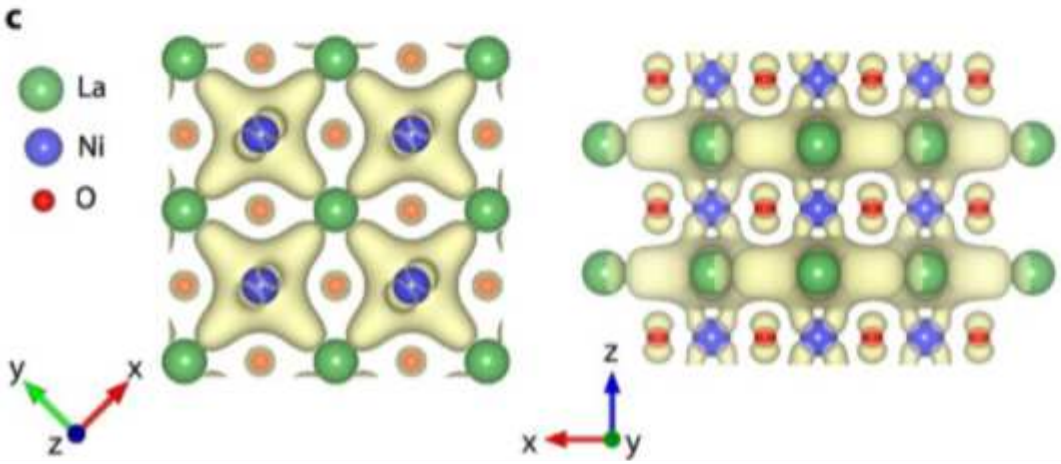
XAS (O-K edge) and DFT+U calculation

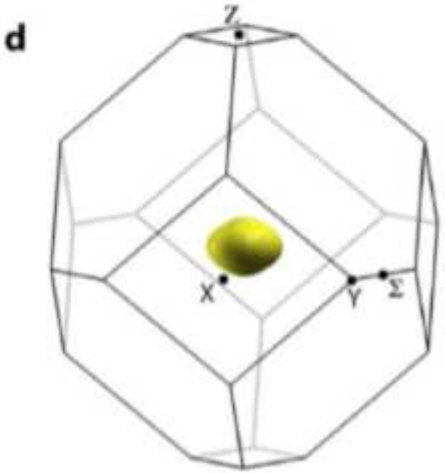


Electronic structure of $LaNiO_2$



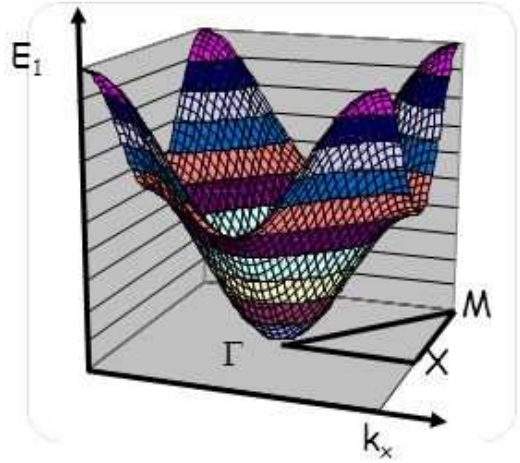


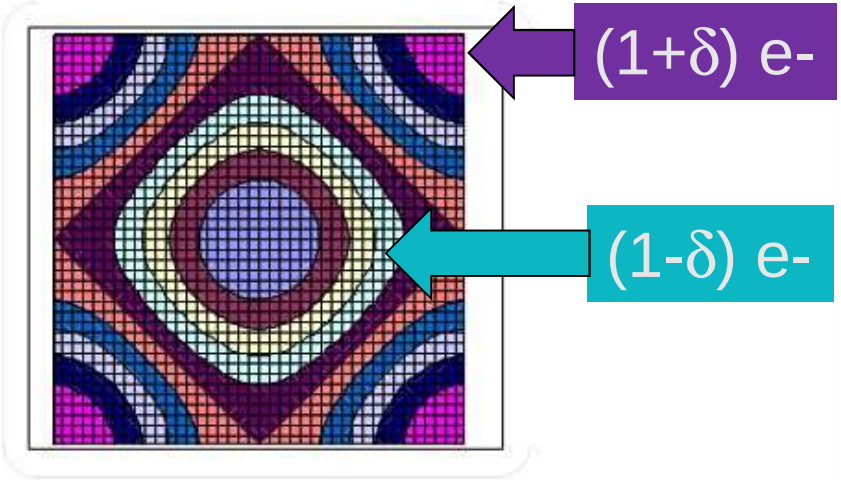




III. Bandes d'Énergie : Surfaces de Fermi

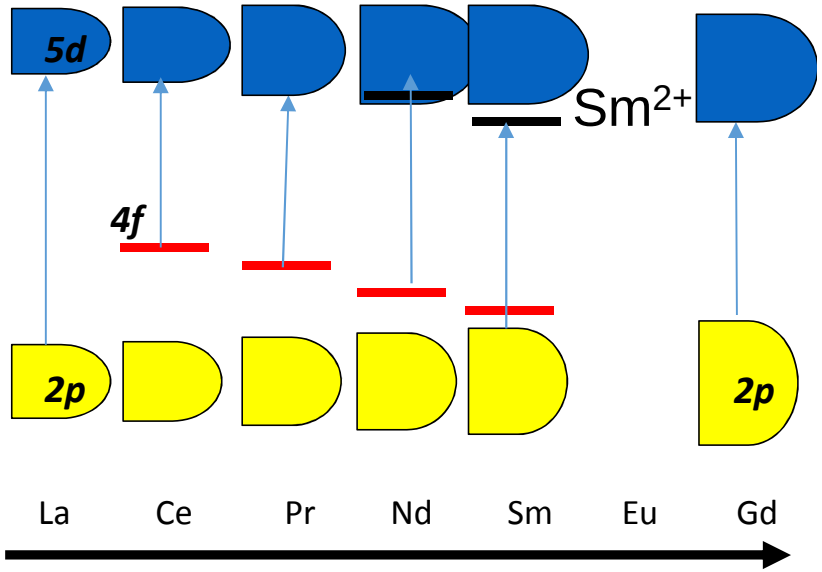
Comment se modifient les lignes d'isoénergie dans le cas de vraies bandes ?
Exemple en 2D : réseau carré plan de paramètre a

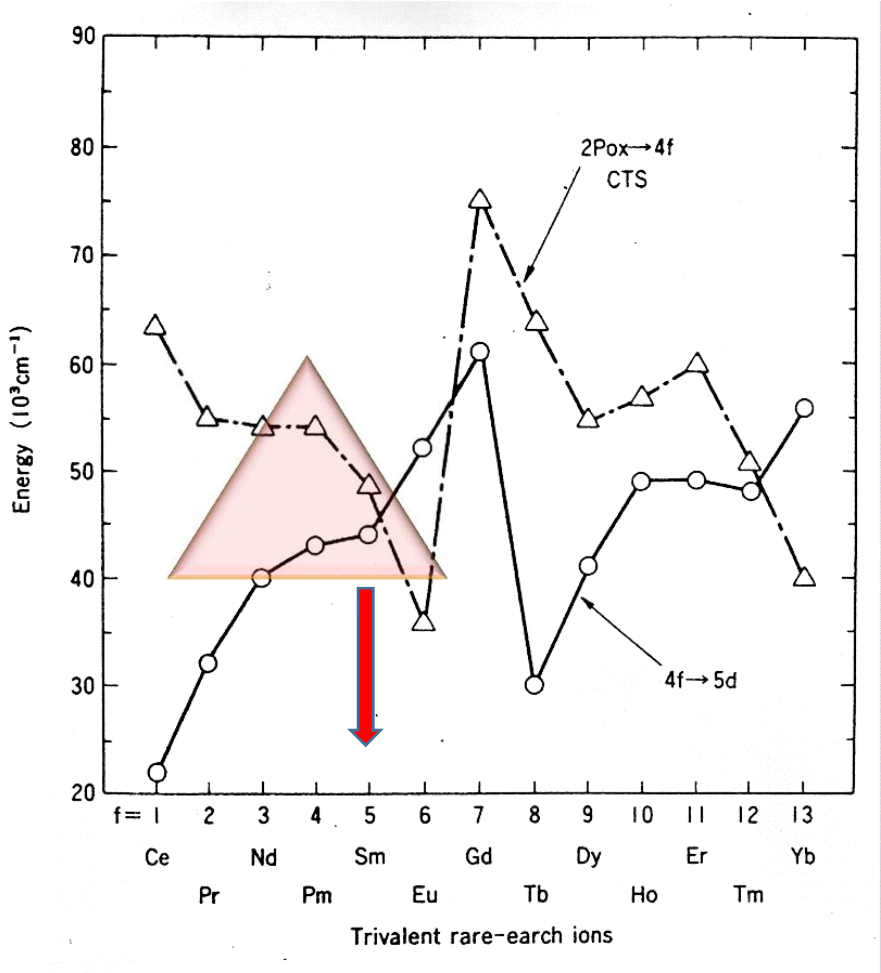




1ère bande

Competition between f-d transitions and Oxygen-RE charge transfer in rare earth sesquioxides





$$Sm_{0.95}Ni^{+1.15}O_2$$

$$Sm^{3+} + Ni^{+} \Leftrightarrow Sm^{2+} + Ni^{2+}$$

Destablization of Charge Density Wave ?

From K_2NiF_4 (RP, n=1, I4/mmm) to P4/nmm (O/F ordering)

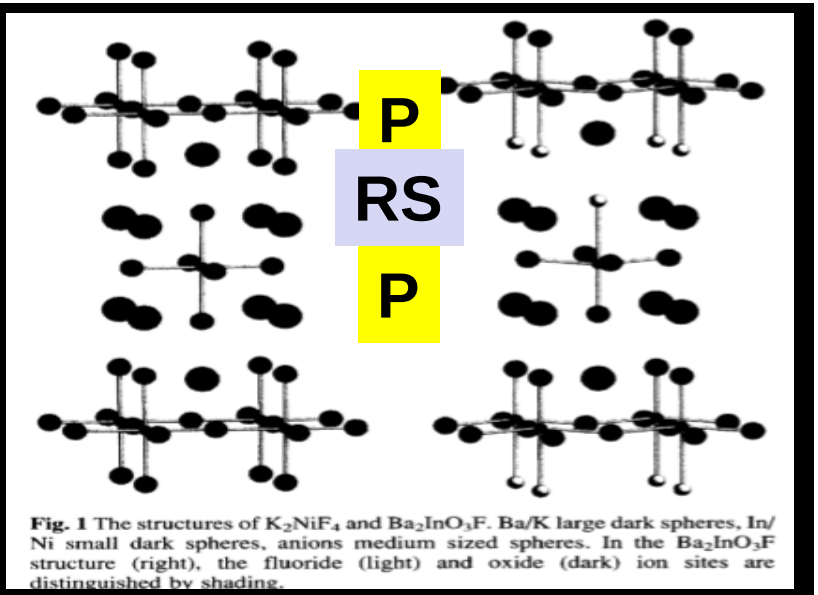


Fig. 1 The structures of K_2NiF_4 and Ba_2InO_3F. Ba/K large dark spheres, In/Ni small dark spheres, anions medium sized spheres. In the Ba_2InO_3F structure (right), the fluoride (light) and oxide (dark) ion sites are distinguished by shading.

From $(La_{1.6}Sr_{0.4})Ni^{+2.6}O_{4.1}$ (RP n=1, I4/mmm) to $(La_{1.6}Sr_{0.4})Ni^{+1.34}O_{3.47}$ (Immm)

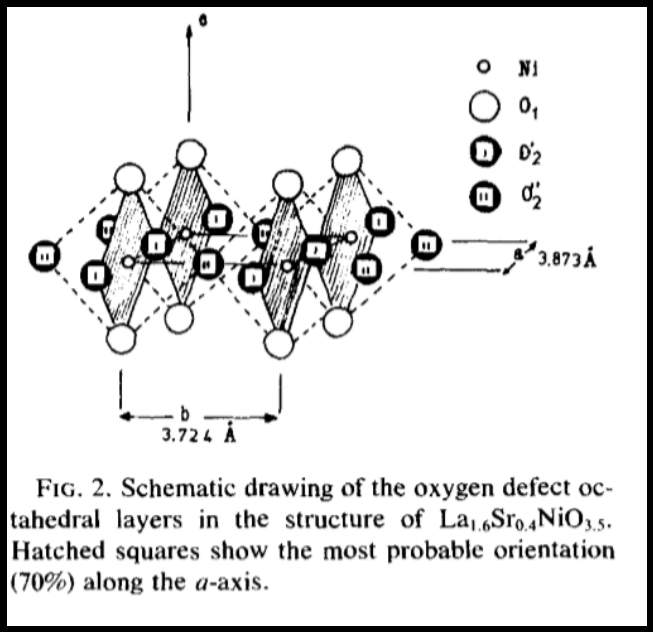


FIG. 2. Schematic drawing of the oxygen defect octahedral layers in the structure of $La_{1.6}Sr_{0.4}NiO_{3.5}$. Hatched squares show the most probable orientation (70%) along the *a*-axis.

From $(LaSr)Ni^{+3}O_4$ (RP n=1, I4/mmm) to $(LaSr)Ni^{+1.2}O_{3.1}$ (Immm)

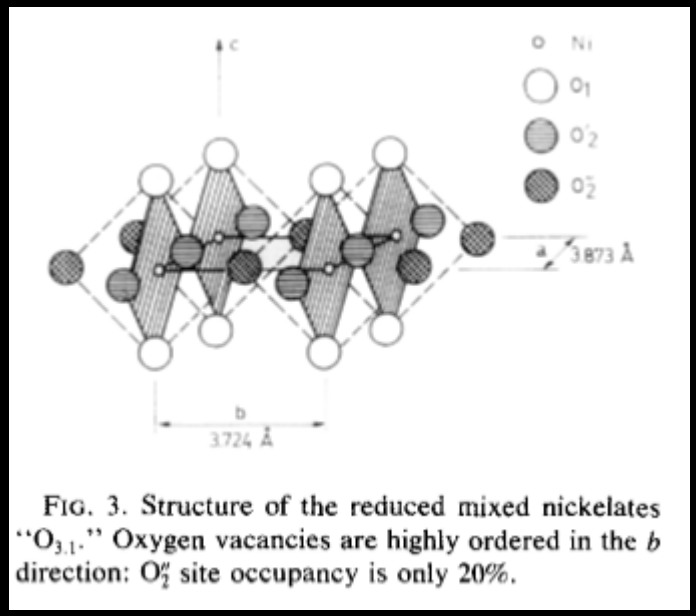


FIG. 3. Structure of the reduced mixed nickelates "$O_{3.1}$." Oxygen vacancies are highly ordered in the *b* direction: O''_2 site occupancy is only 20%.

M. Crespin et al, JSSC, 1990, 84, 165-170
M. Crespin et al. JSSC, 1992, 100, 281-291
R.T. Needs and M.T. Weller J.Chem.Soc, Chem.Comm, 1995, 353-354

Observed in Sr_2CuO_3, $Ba_2CuO_{3.3}$, Physica C, 1988, 152, 39

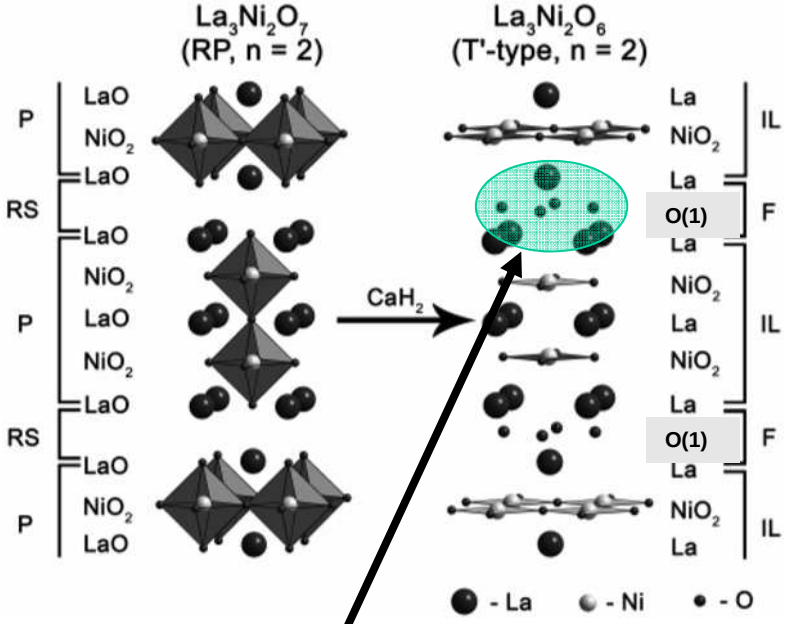


Figure 2. Structure models of $La_3Ni_2O_7$ and $La_3Ni_2O_6$ with denoted layers and structural blocks: P, perovskite; RS, rock salt; IL, infinite layer; F, fluorite.

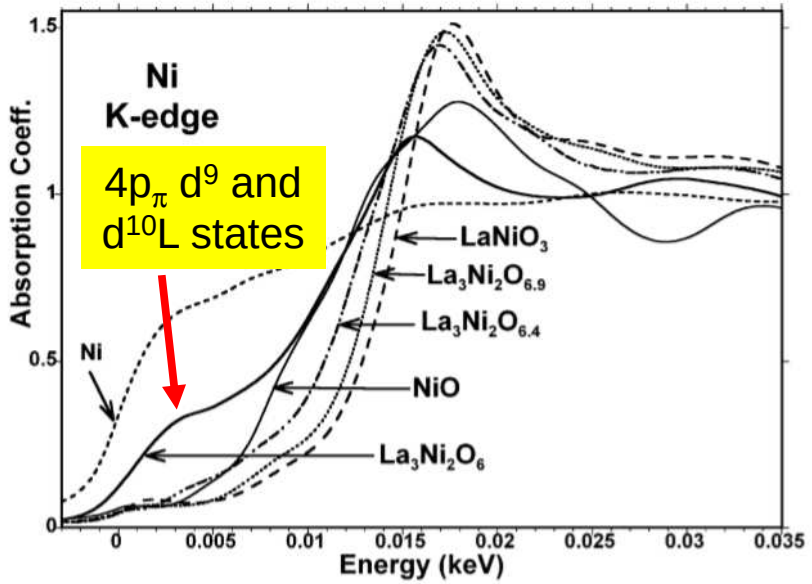


Figure 3. X-ray absorption spectra for $La_3Ni_2O_6$ and for standards.

particular, develops a dramatically down-shifted shoulder, in the 0−5 eV range, which is similar to the XAS shoulder, which

Residual Stress :

4 Shorter La(2)-O(1) bond distance (acidic)
→ Competitive bonds effects leading
to four longer La(2)-O(2) one's !
8 equal La(1)-O(2) bonds in cubic site

Table 1. Crystallographic Data for $La_3Ni_2O_6$ [a]

atom	Wyckoff position	x	y	z	10^2 U (Å)	occ.
La1	2b	0	0	0.5	0.50(3)	1
La2	4e	0	0	0.3170(1)	0.72(2)	1
Ni	4e	0	0	0.0826(1)	0.69(1)	1
O1	4d	0	0.5	0.25	1.04(3)	1
O2	8g	0	0.5	0.0838(1)	0.97(2)	1

[a] Space group: *I4/mmm* (No. 139); $a = 3.9686(1)$ Å, $c = 19.3154(6)$ Å; $\chi^2 = 2.3\%$, $wRp = 3.2\%$, $Rp = 1.3\%$.

V.V. Poltavets, ..,and M. Greenblatt
J.A.C.S, 2006, 128, 9050-9051

Decrease of $4p_\pi(d^9)$ and $(d^{10}L)$ states pre-edge in $La_4Ni^{+1.33}{}_3O_8$ (more 3D) vs $La_3Ni^{1.5+}{}_2O_6$ (more 2D).

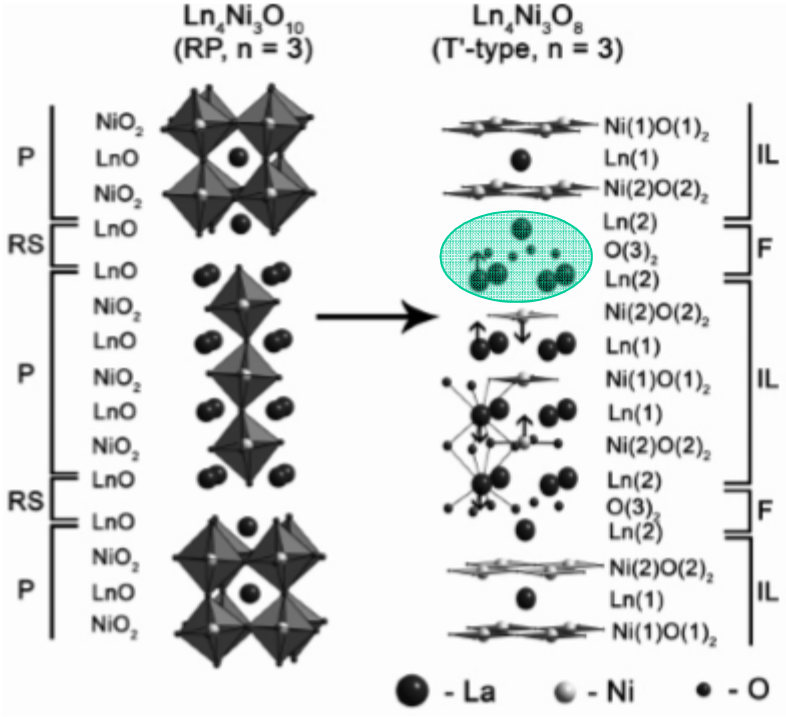


Figure 2. Structure models of $Ln_4Ni_3O_{10}$ and $Ln_4Ni_3O_8$ (Ln = La, Nd) with denoted layers and structural blocks: P, perovskite; RS, rock salt; IL, infinite layer; F, fluorite. The directions of Ln and Ni atoms shifts are shown by arrows.

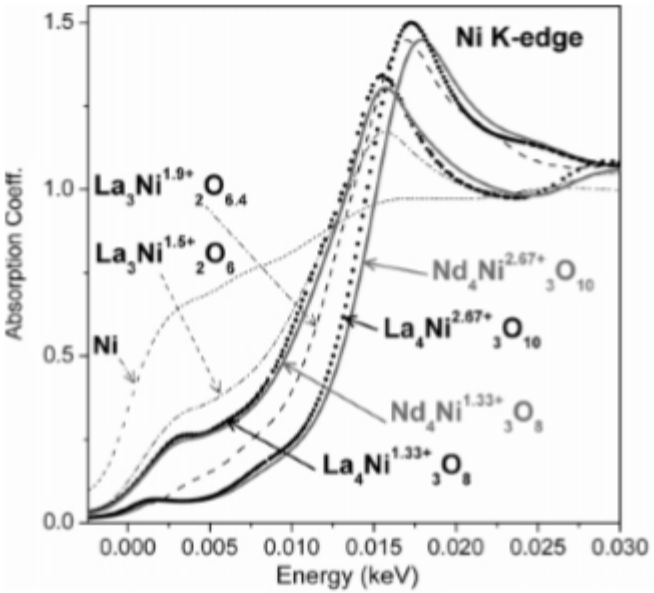
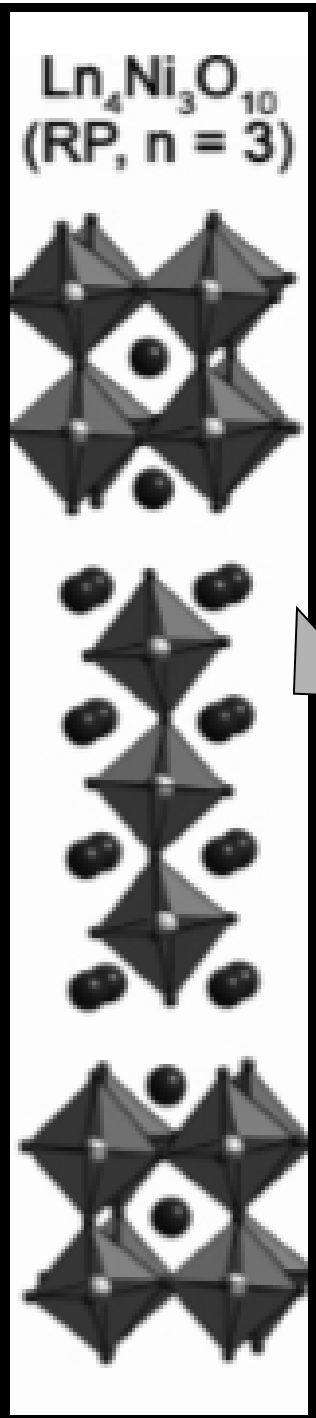
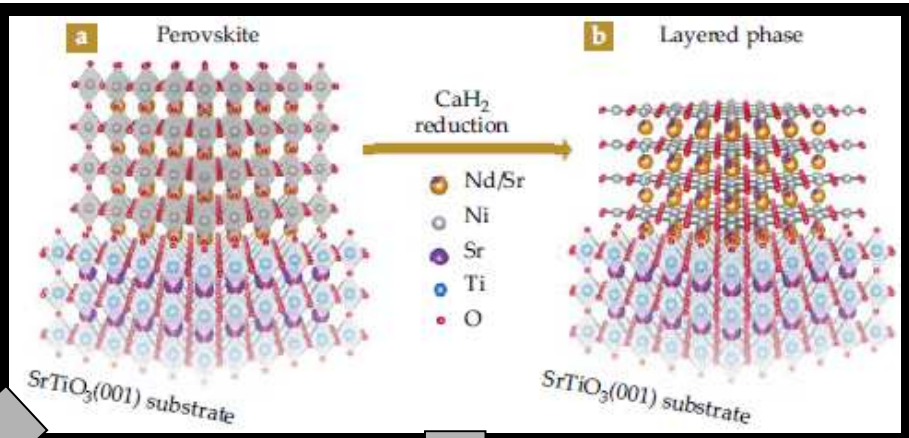


Figure 3. X-ray absorption spectra for $Ln_4Ni_3O_8$ (Ln = La, Nd) and for standards.

V.V. Poltavets, ..,and M. Greenblatt
Inorg.Chem, 2007, 47, 10887-10891

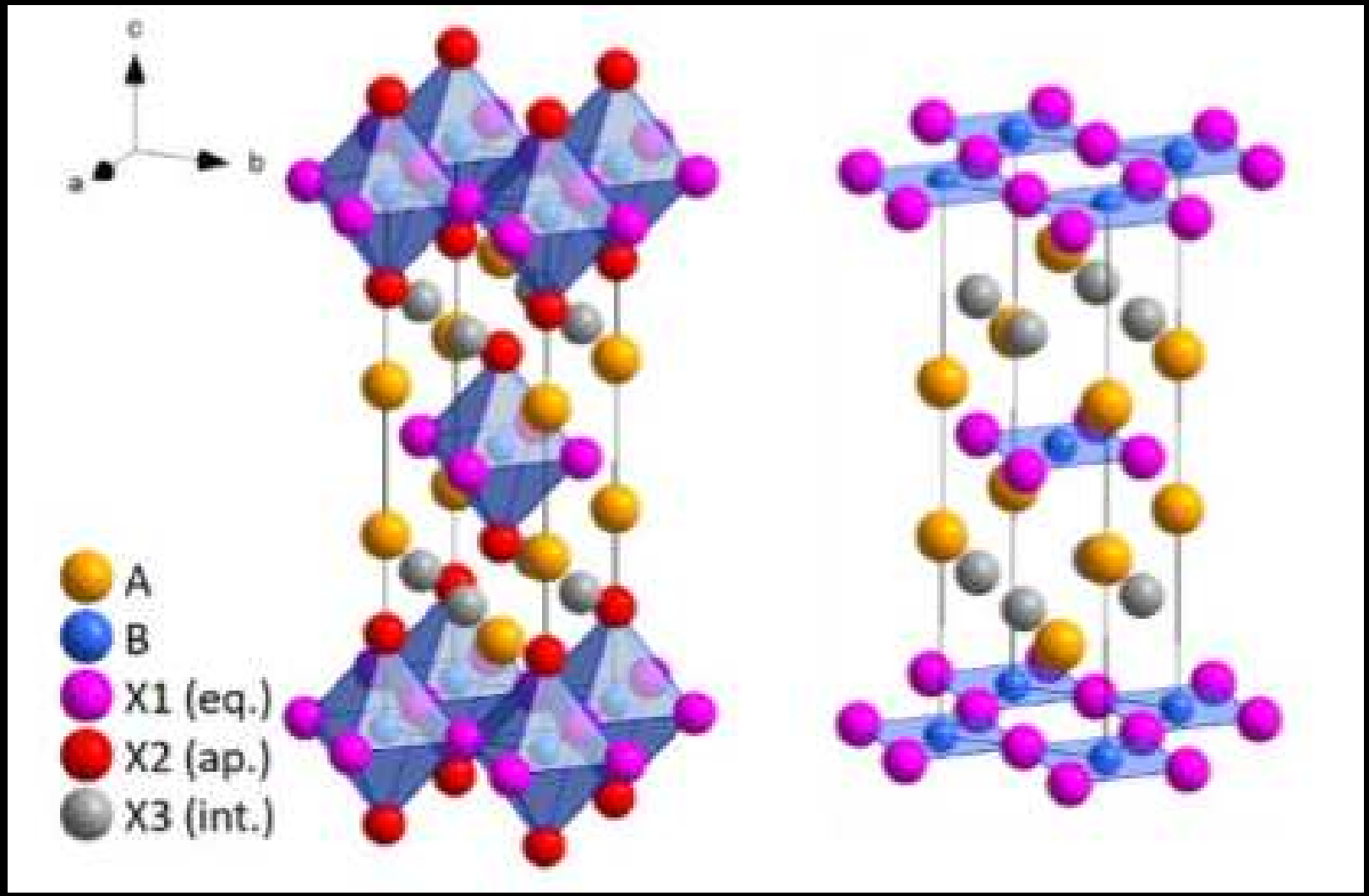




RP , n=3 => 2 $SrTiO_3$ + $LaSrNiO_3$
=> $Sr_3LaTi_2NiO_8$

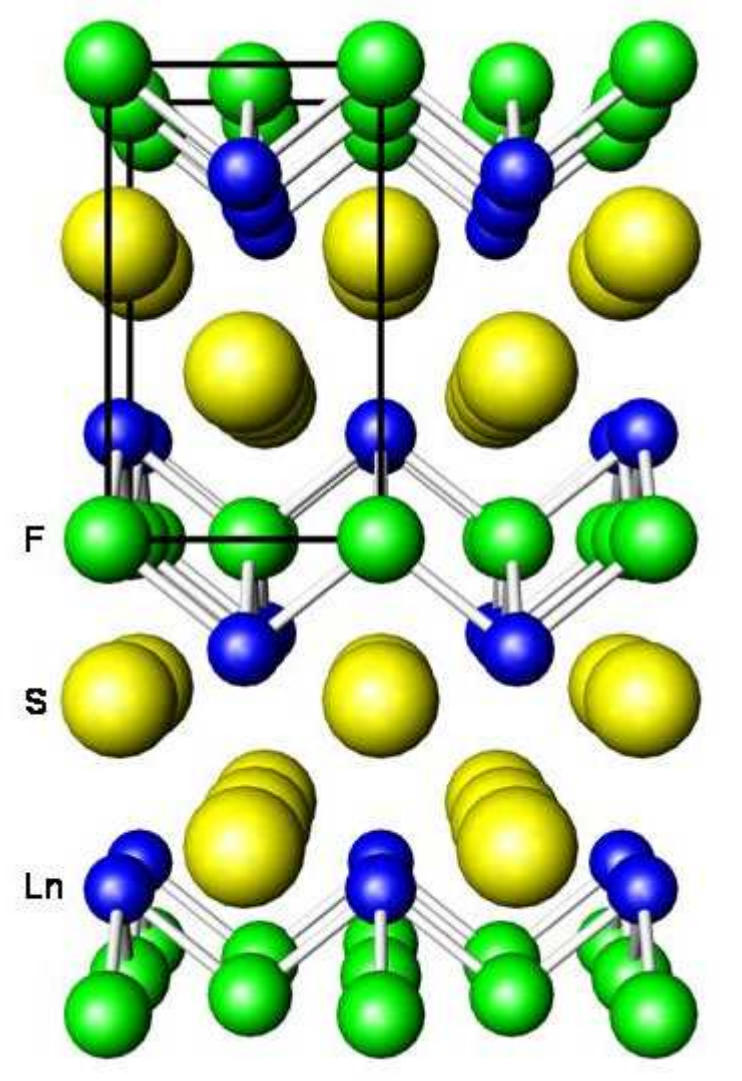
RP , n=4 => 3 $SrTiO_3$ + $LaSrNiO_3$
=> $Sr_4LaTi_3NiO_{12}$

From La_2NiO_{4+x} (I4/mmm) to $La_2NiO_3F_2$ (PVDF treatment, Cccm), then La_2NiO_3F (NaH reduction, I4/mmm, T' = Nd_2CuO_4)

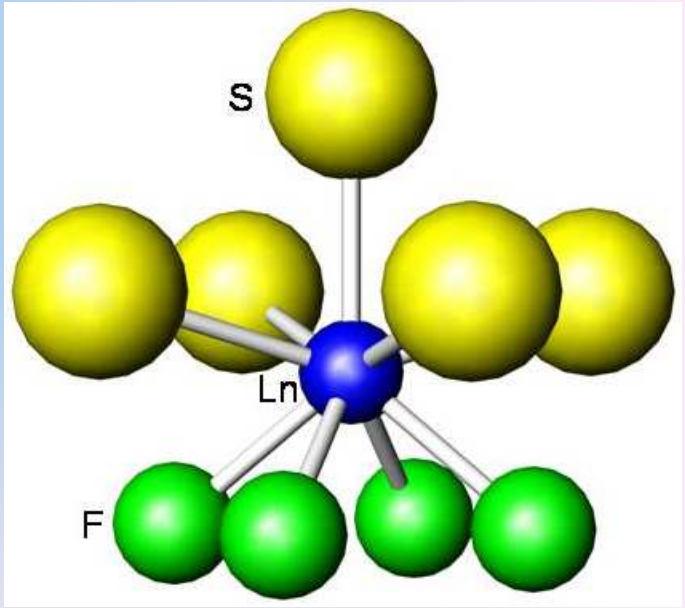


Wissel, K.; Heldt, J.; Groszewicz, P. B.; Dasgupta, S.; Breitzke, H.; Donzelli, M.; Waidha, A. I.; Fortes, A. D.; Rohrer, J.; Slater, P. R.; Buntkowsky, G.; Clemens, O., Topochemical Fluorination of La2NiO4+d: Unprecedented Ordering of Oxide and Fluoride Ions in La2NiO3F2. Inorg. Chem. 2018, 57 (11), 6549-6560.

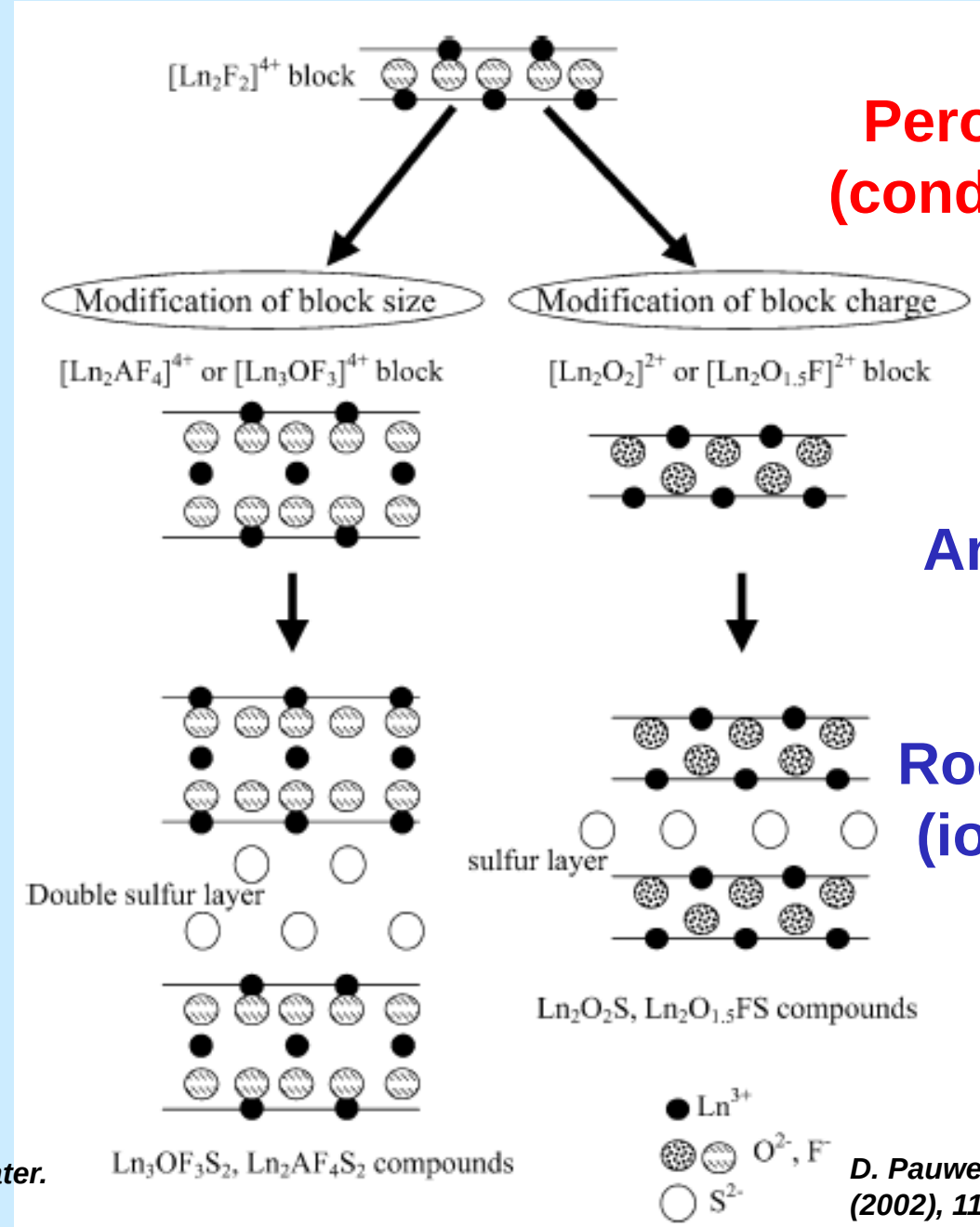
Rare earth fluorosulfides : structural features



Tetragonal P4/nmm (La → Er, Y)
Cell parameters : a ≈ 4 Å, c ≈ 7 Å



Building principle of 2D oxyfluorochalcogenides (2002)



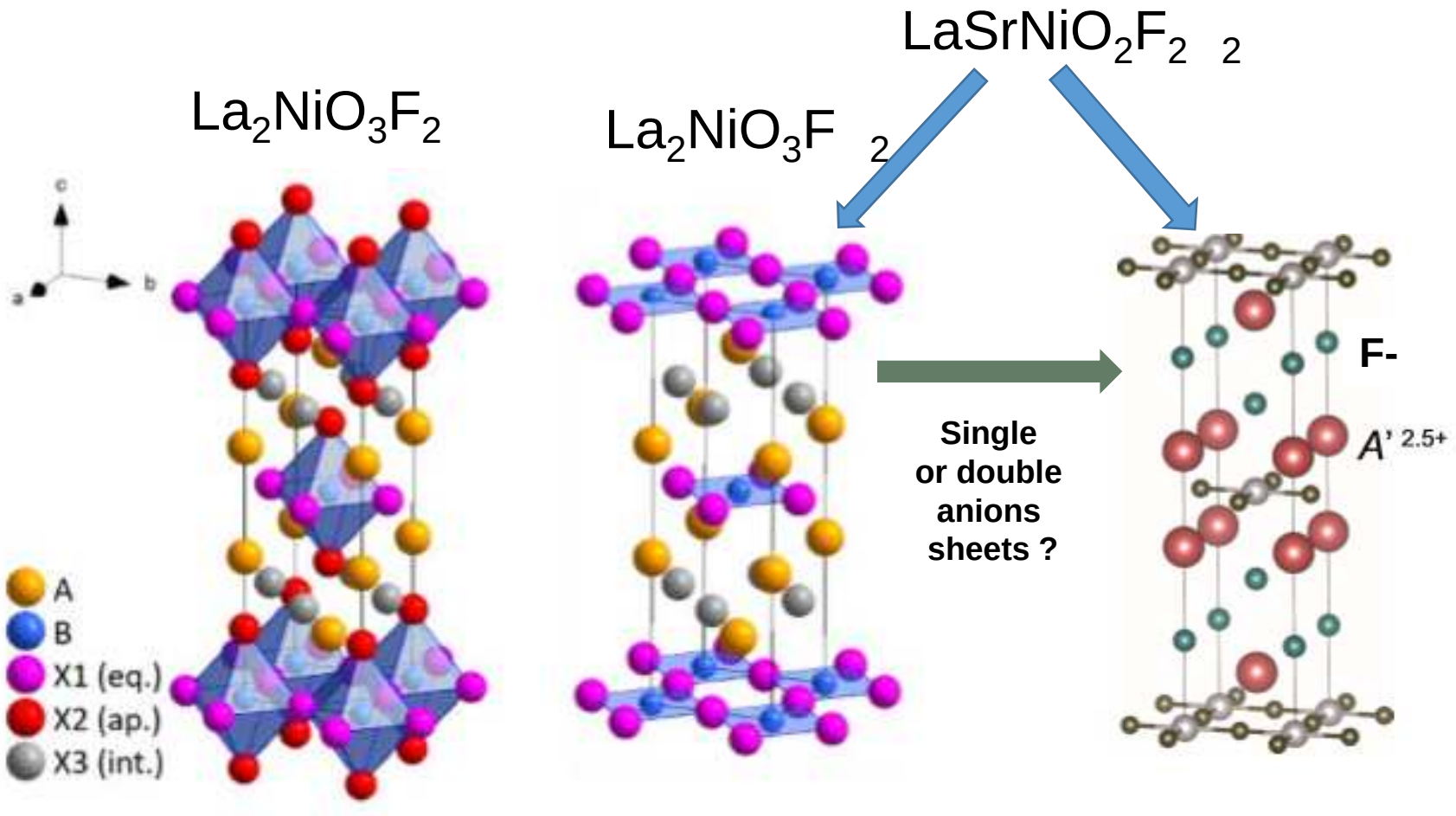
Perovskite layers (conductive sheets)

+

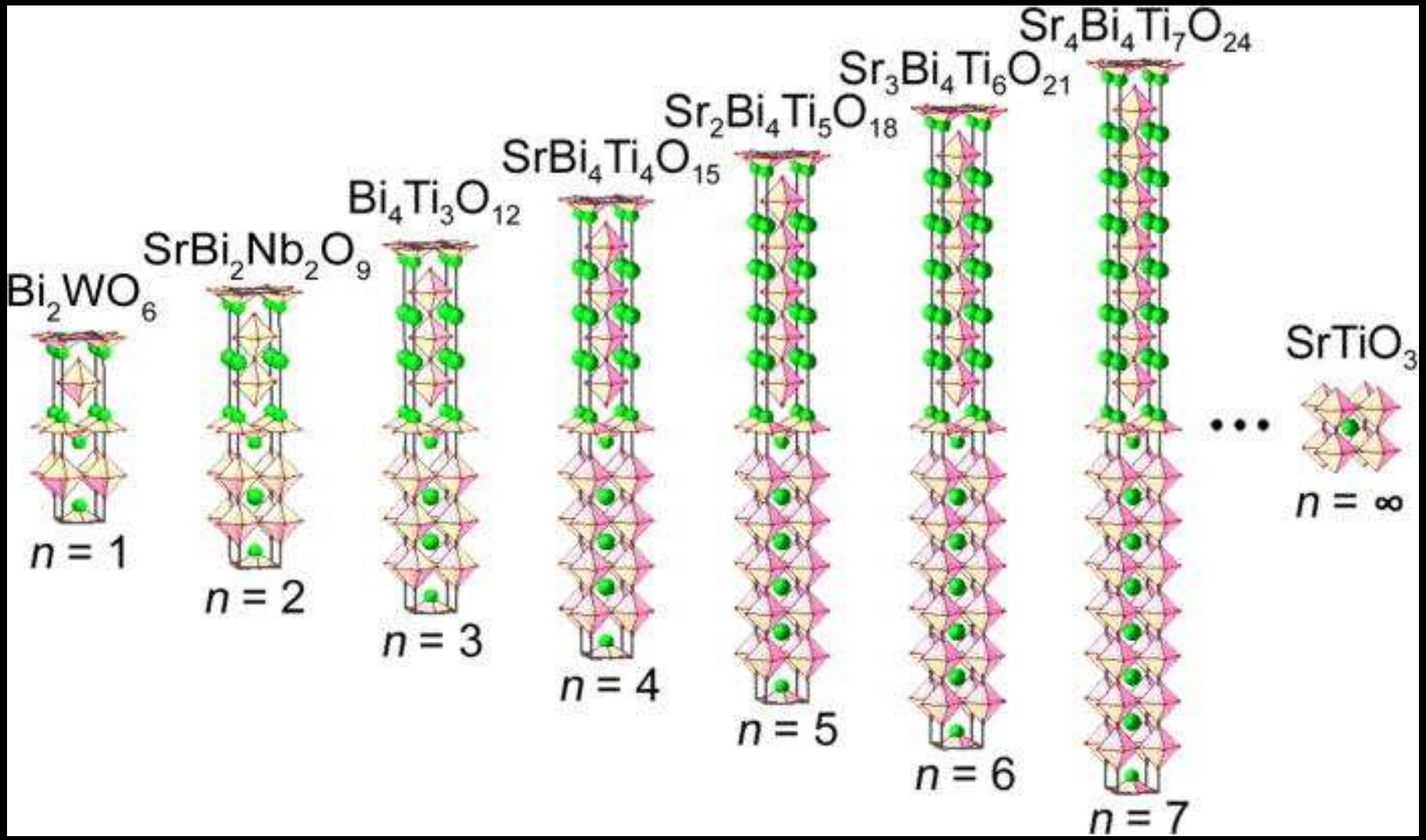
Fluorite/ Anti-Fluorite Blocks or Rocksalt sheet (ionic blocks)

D. Pauwels et al .Chem Mater. (2006),18, 6121-6131

D. Pauwels et al .Solid State Sciences (2002), 11-12,1471-1479.


$La_2NiO_3F_2$
$La_2NiO_3F_2$
$LaSrNiO_2F_2$ 2
c
b
a
A
B
X1 (eq.)
X2 (ap.)
X3 (int.)
Single
or double
anions
sheets ?
F-
A' 2.5+

Aurivillius phases : $[Bi_2O_2]^{2+}[A_{n-1}B_nO_{3n+1}]^{2-}$



From O_h to D_{4h} (Ni^{3+}/Ni^{2+}) : $[Bi_2O_2]^{2+}[A_{n-1}B_nO_{2n+2}]^{2-}$ = (n=3) $Bi_4Ni_3^{2.66+}O_{10}$?

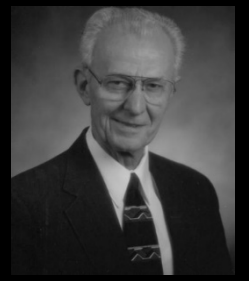
Pauling electronegativity χ

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

2,2 H 1																	He 2
0,98 Li 3	1,57 Be 4											2,04 B 5	2,55 C 6	3,04 N 7	3,44 O 8	3,98 F 9	Ne 10
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 18
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	1,9 Cu 29	1,65 Zn 30	1,81 Ga 31	2,01 Ge 32	2,18 As 33	2,55 Se 34	2,96 Br 35	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	2,1 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

Hard-Soft Acid-Base (**HSAB**) theory
Ralph Pearson (1960)



Energy

Hard acid : $H^+(1s^0)$, $Ti^{4+}(3d^0)$, K^+, Ba^{2+}, La^{3+}

Soft acid : $Fe^{2+}(3d^6)$, $Cu^+(3d^{10})$, $Ni^+(3d^9)$

Soft base : $H^-(1s^2)$, S^{2-}, I^-, SO_4^{2-}, CO_3^{2-}

Hard base : F^-, O^{2-}, OH^-, Cl^-, NH_3

Hard-Hard or Soft-Soft AB react faster leading to stronger bonds !

P4/nmm
p-type (Cu+)-SC + AFM (T_N>300K)

D. Berthebaud et al.
Sol. Stat. Sci. 2014, **36**, 94-100

$Sr_2FeCu_{0.9}O_3Se$
[$Sr_2Ga^{3+}Cu^{+}O_3S$]

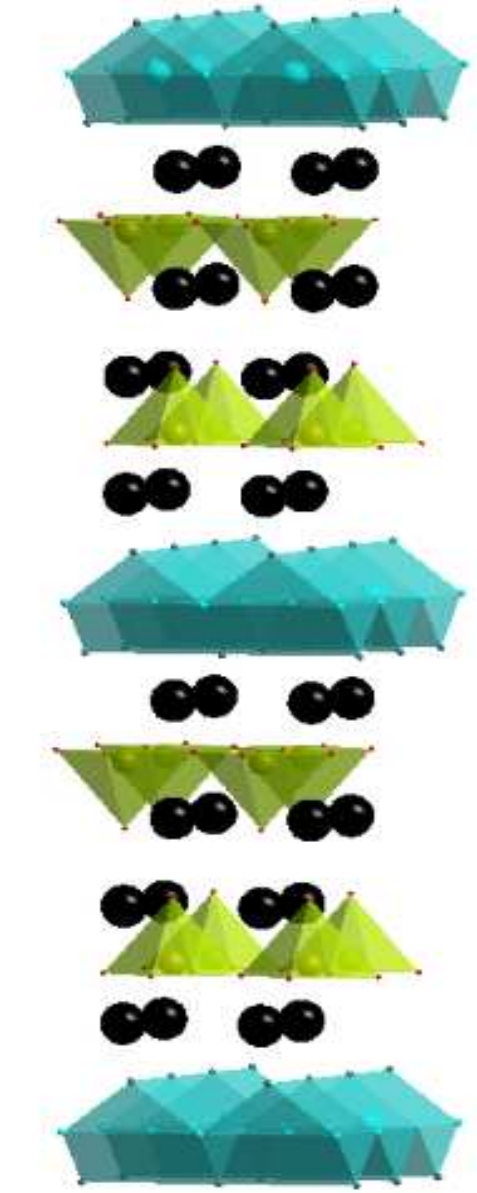


Fig. 1. View of the crystal structure

(NdSr)$Ni^{+,2+}Cu^{2+,+}O_3(S,Se)$?

[Perovskite layers]

[5] NiO_5

[9] $(Nd/Sr)O_9$

[4] $(Nd/Sr)O_4Se$

Ni^{+}/Cu^{2+} or
Ni^{2+}/Cu^{+} ?

+

[AntiFluorite sheets]

[4] $CuSe_4$

Electrostatic valence (Pauling) :
Se(-2) + 2O (-1.51) + O (-2.7) = - 7.72 < 8

[Td] : **Se**Cu_4

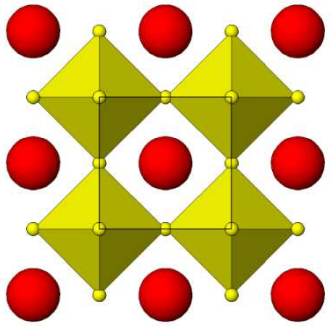
Electrostatic valence (Pauling) :
Se(-1) + 2O (-1.91) + O (-2.9) = - 7.72 < 8

[Oh] x 2: **ONi_2Sr/Nd_4** ,
[Oh] : **$ONiSr/Nd_5$**

AX_3 stacking and Perovskite network

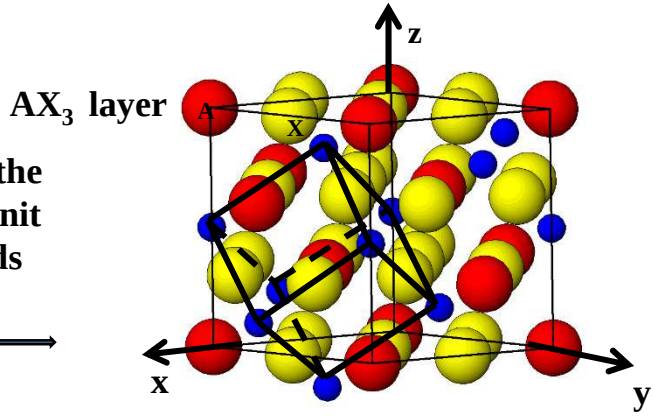
$LaNiO_3$

Ni^{3+} ($t_2^6e^1$)



3C polytype

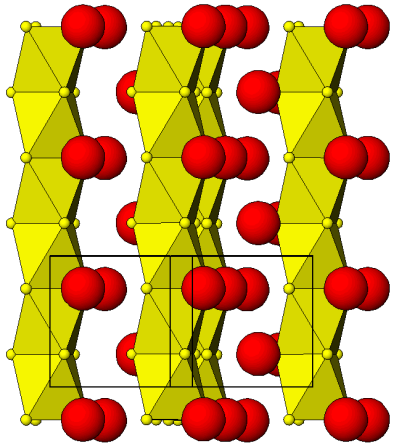
Relationship between the cubic and hexagonal unit cells. z axis corresponds to[111]p



$LaNiO_3$

Ni^{4+} ($t_2^6e^0$)

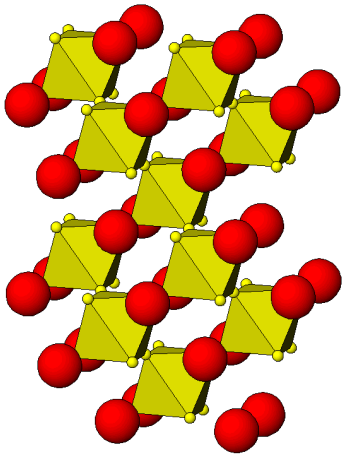
$BaNiO_3$



AX_3 a layer
AX_3 b layer
AX_3 a layer

2H polytype
Chains of face sharing octahedra

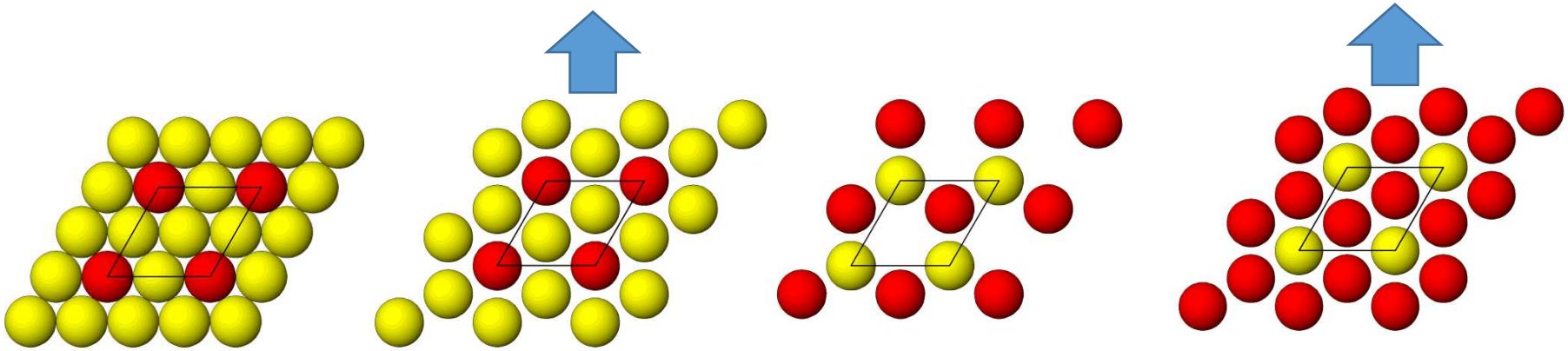
AX_3 a layer
AX_3 b layer
AX_3 c layer
AX_3 a layer



3C polytype
3D corner sharing octahedra

Various $[A_nX_m]$ layers for stacking

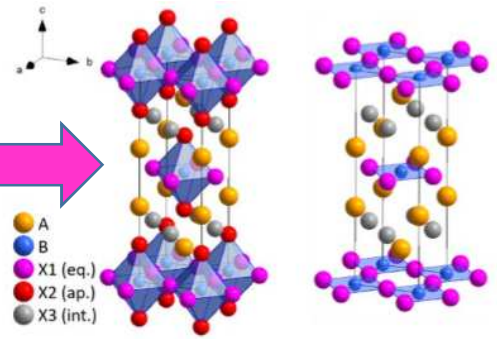
$[La_2(Ni)O_2X_4]^{3+}[NaO_2]^{3-}$ $[NaSr(Ni)O_2X_4]^0[Na_2O]^0$



$[AX_3]$ layer **$[AX_2]$ layer** **$[AX]$ layer** **$[A_2X]$ layer**

$La(Ni)O_2X$ $[Sr_2(Ni)O_2X_2]^+[NaO]^-$

$K_2NIF_4 = La_2NiO_4$ = Closed Stacking of $La_2O_4[X]_2$ layers



Conclusions

- ***Low U-Hubbard energy (~6 eV) Ni^{+} (t_2^6 e^3) perovskite***
  $W_{\pi,\sigma}$ (Bandwidth) ~ U < Δ (CT,O-Ni), ***Mott-Hubbard ?***
- Ni vs Cu : Lower O→ Ni Δ-CT, Stronger Ni-RE Hybridization
- **Destablization of CDW in $Sm_{1-x/3}$ $_{x/3}Ni^{1+x}O_3$?**
- **From Perovskite to Ruddelsden-Popper (n=1, 2, 3, …) networks : $(LaSr)Ni^{1.2+}O_{3.1}$, $La_4Ni_3^{1.33+}O_8$, $Sr_4LaTi_3Ni^{1+}O_{12}$?**
- **Towards mixed anions (O, F, S, Se) Nickelates : La_2NiO_3F, $(NdSr)NiCuO_3(S, Se)$?**
- **$[AX_3]$ Perovskite, $[A_2X_4X'_2]$ K_2NiF_4 and $[A_nX_m]$ layers for stacking : Towards new 2D phases**