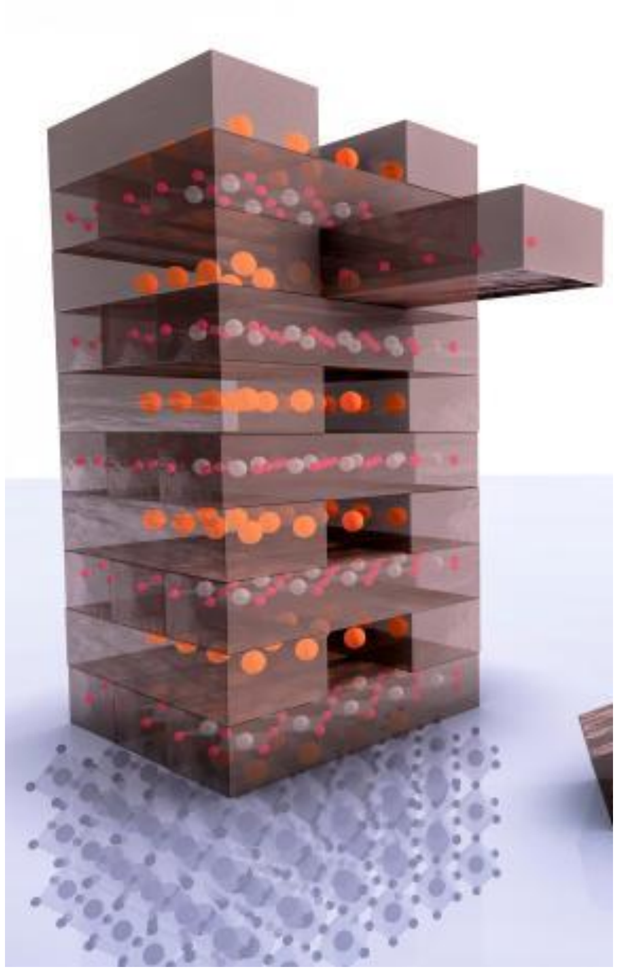
Topotactic engineering for oxide quantum materials

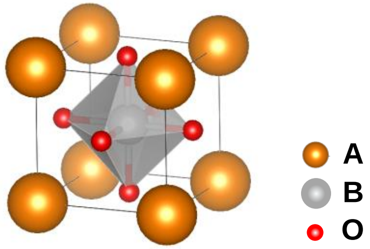
Woo Jin Kim

School of Materials Science and Engineering

Topochemical reduction (‘Jenga chemistry’)

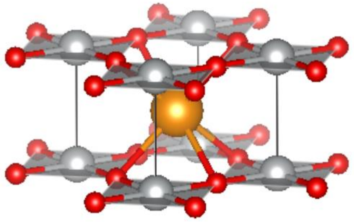


ABO_3 (perovskite)



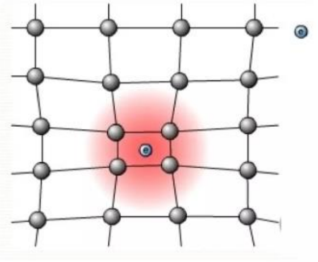
Topotactic engineering

ABO_2 (infinite-layered)



Low-dimensional quantum materials

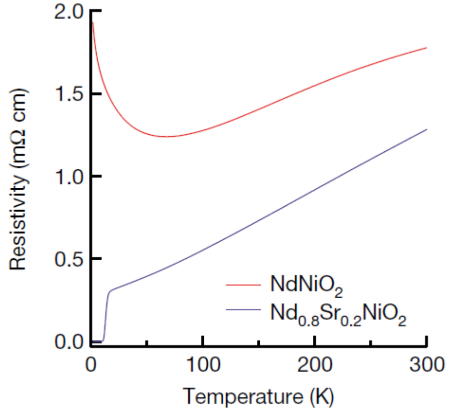
Geometrically frustrated Jahn-Teller order



Large electron-lattice coupling

$CaCoO_2$

Unconventional superconductor



$NdNiO_2$

https://www6.slac.stanford.edu/news/2019-08-28-first-report-superconductivity-nickel-oxide-material

Atomic scale precision heterostructure synthesis (pulsed laser deposition)

Target ablation during PLD-growth

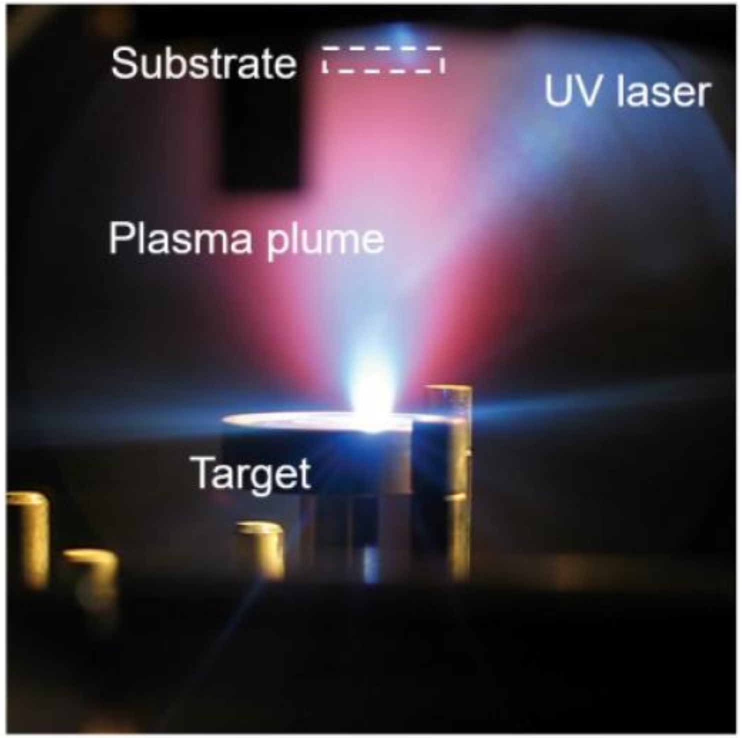
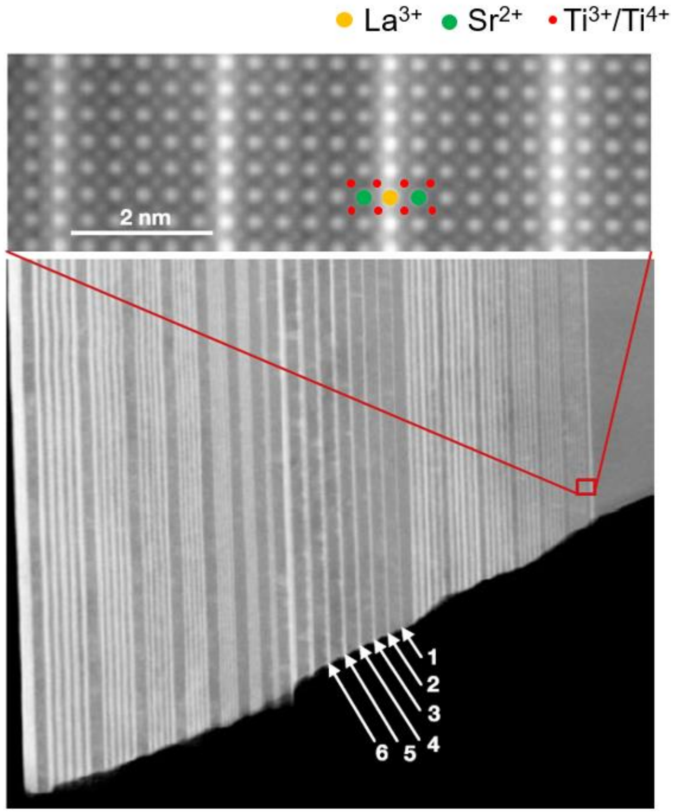


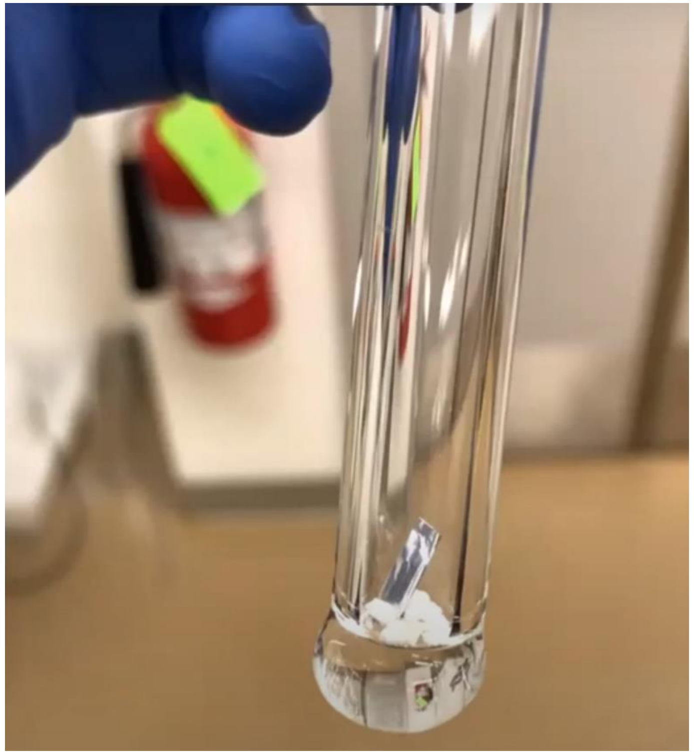
Image from Coherent (www.coherent.com)



H. Y. Hwang *et al.*, Nat. Mater. **11**, 103 (2012).

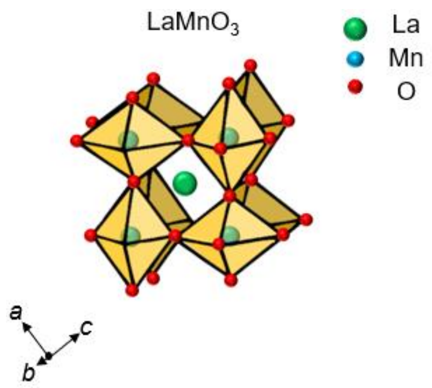
\+

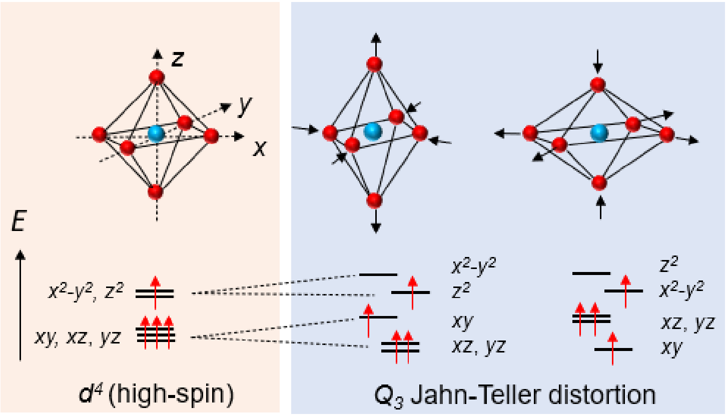
Topotactic reduction engineering



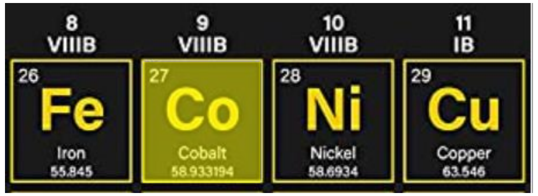
annealing at ~240 – 280 ^{o}C with CaH_2

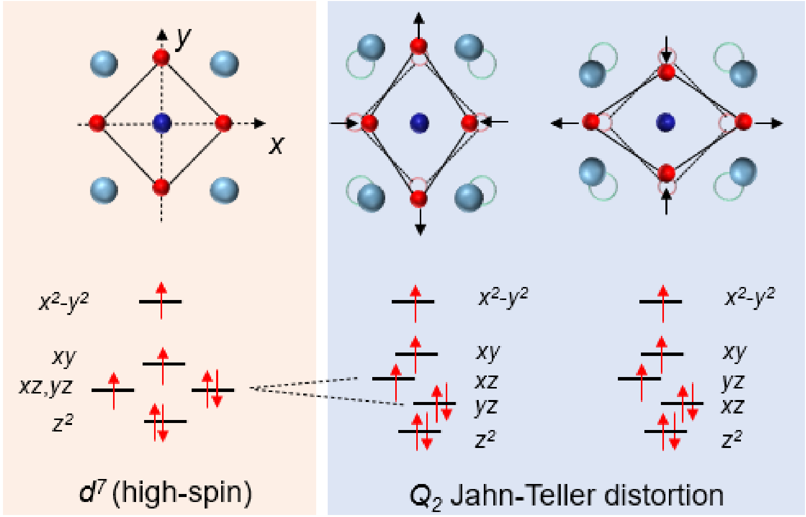
Cooperative Jahn-Teller distortions in correlated systems



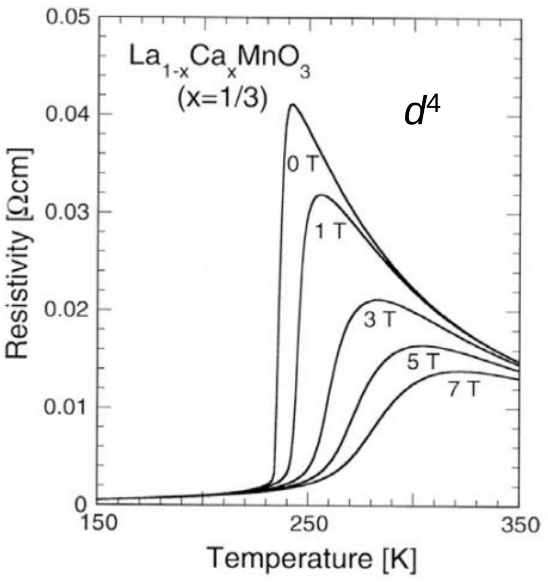


What if in 2D?

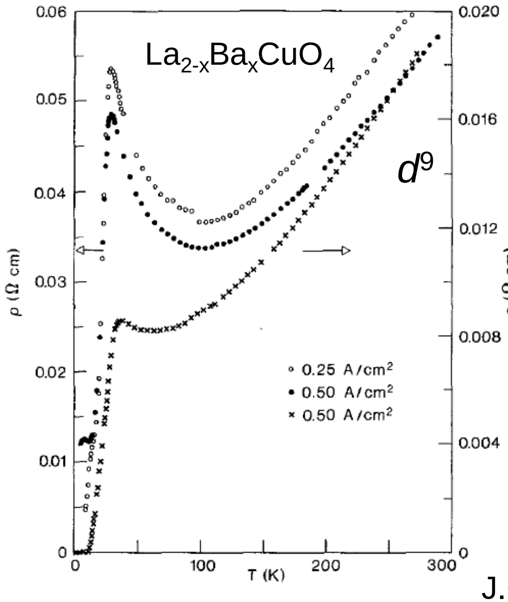


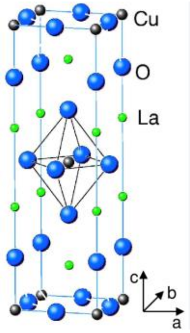


Colossal magnetoresistance



High T_c superconductor

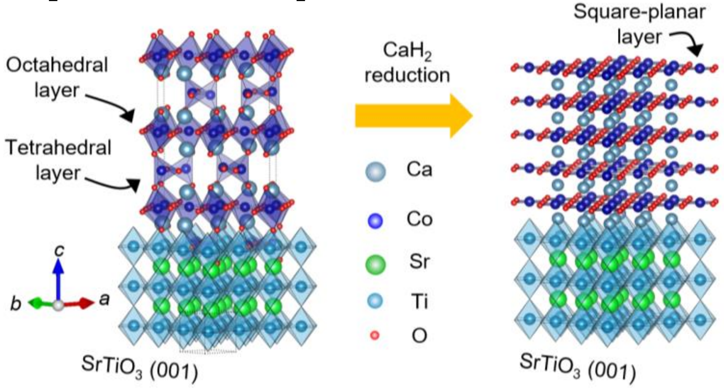




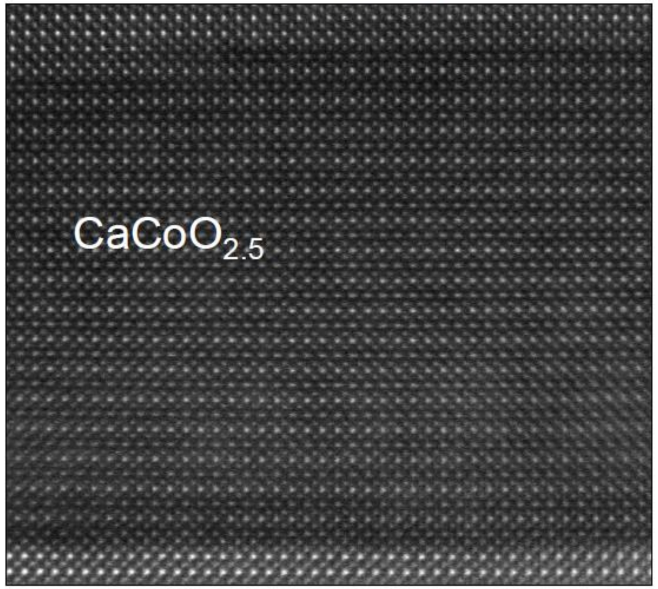
"Hole doped"

Y. Tokura, *Rep. Prog. Phys.* **69**, 797–851 (2006).
J.G. Bednorz and K.A. Miiller, *Z. Phys. B - Condensed Matter* **64**, 189-193 (1986).

Dramatic in-plane superlattice modulations in $CaCoO_2$ thin films

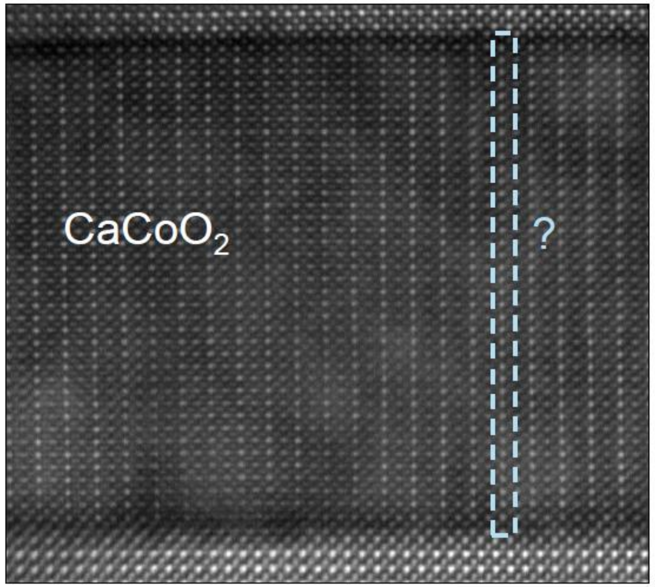


$[100]_t$ zone axis

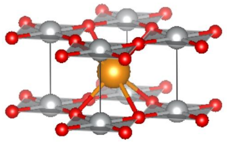


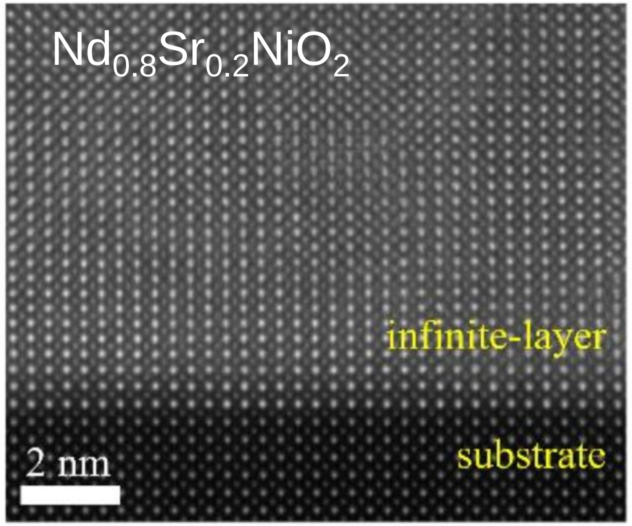
CaH_2 reduction

$[100]_t$ zone axis



$\neq$

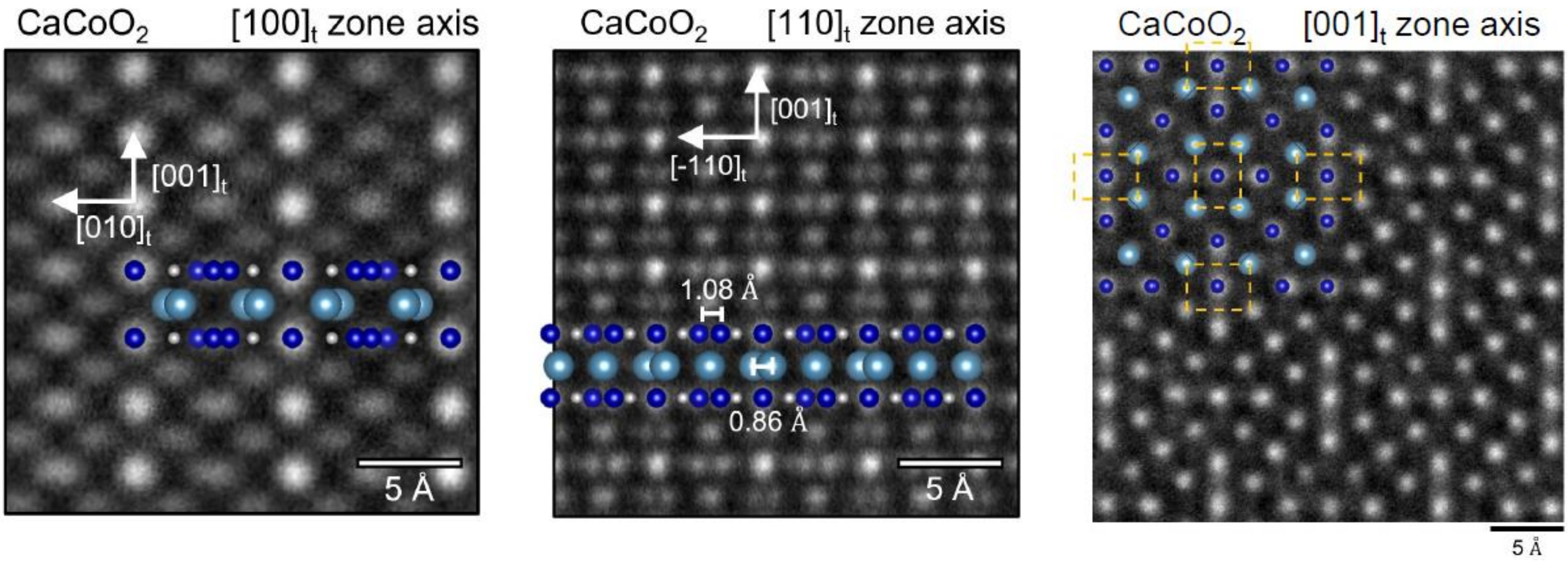




K. Lee *et al*., *APL Materials* **8**, 041107 (2020).

Scanning transmission electron microscopy measurements show a distinguishable atomic arrangement from the normal infinite layer structure.

Ångstrom scale atomic displacements in $CaCoO_2$

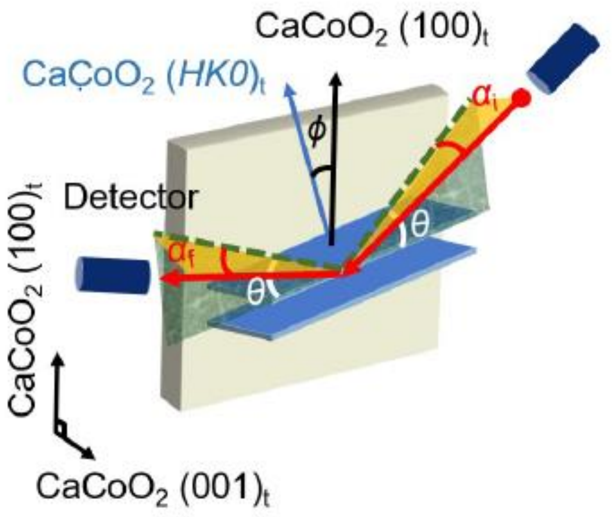


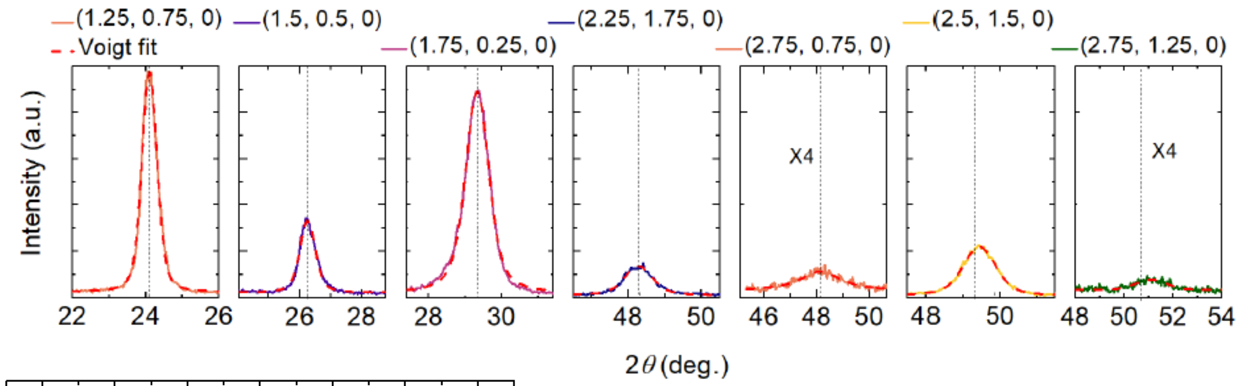
Symmetry group: $P42_12$

$2\sqrt{2}a_t \times 2\sqrt{2}a_t \times c_t$ ($a = b = 2\sqrt{2}a_t = 10.78$ Å and $c = c_t = 3.27$ Å)

Structural refinement of the oxygen positions

Grazing incidence X-ray diffraction



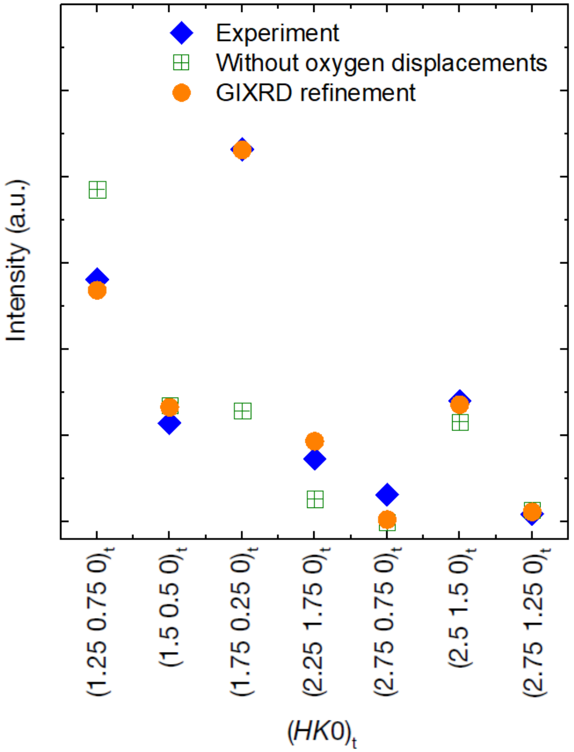


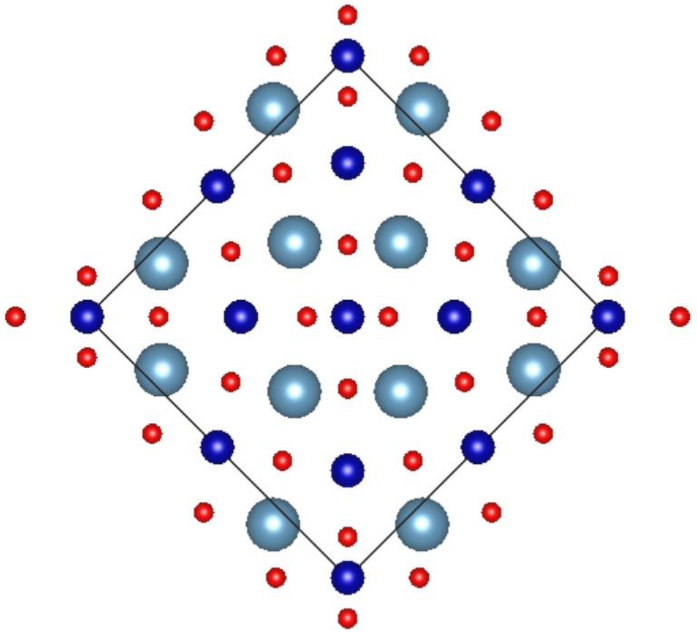
*XRD intensity

$$I_{hkl} = A|F_{hkl}|^2 p_{hkl} L_p(\theta)$$

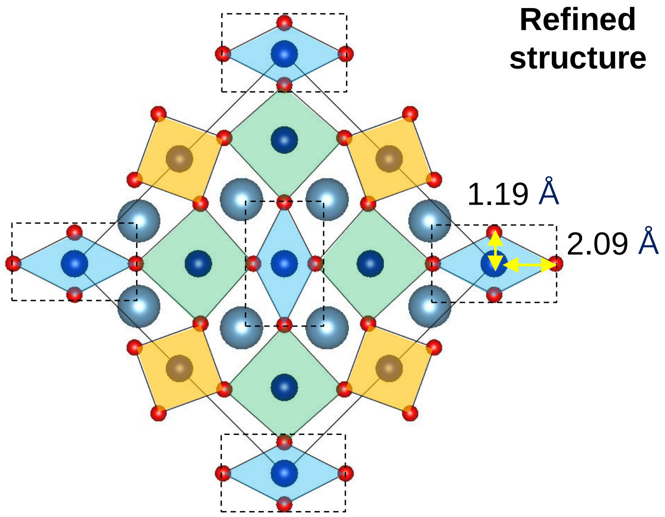
*Rietveld method (Least squares method)

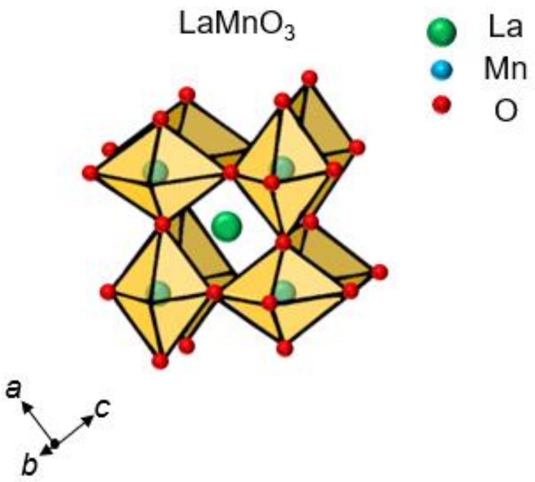
$$M = \sum_i W_i \{ I_i^{obs} - I_i^{calc} \}^2$$

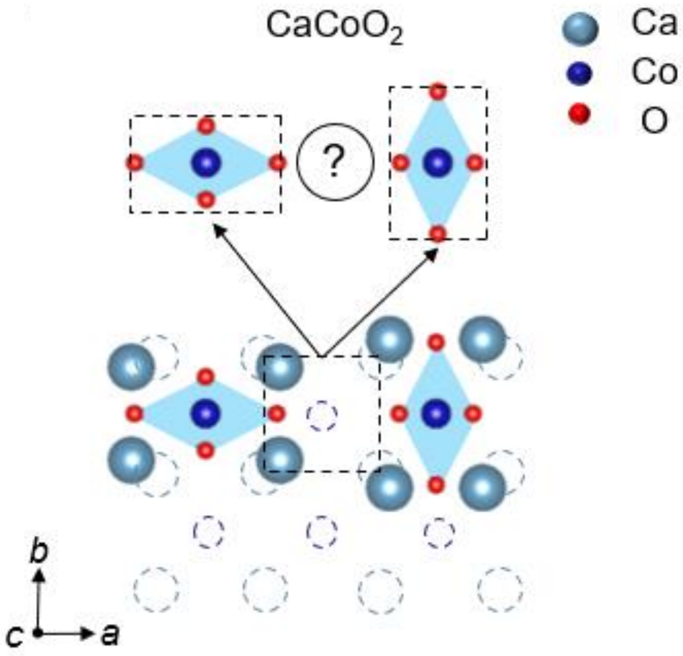


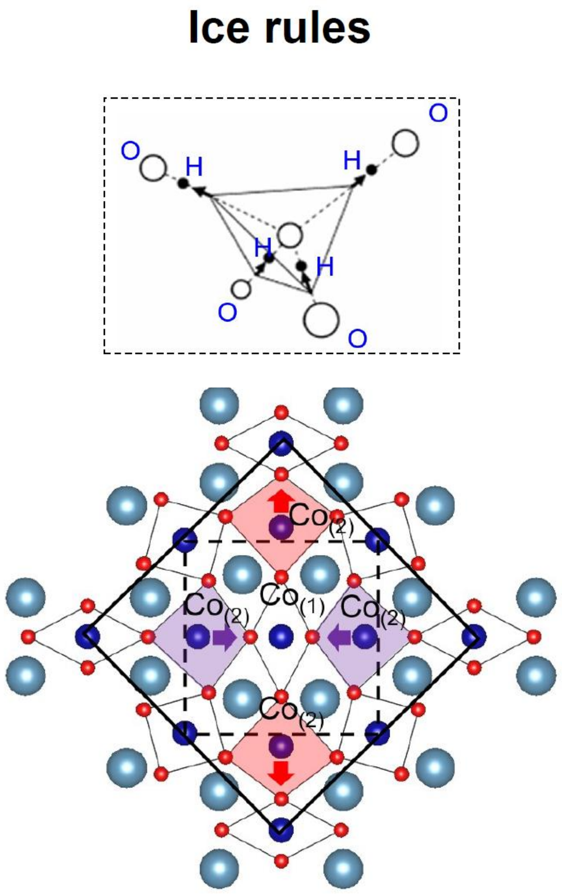


Why are only 25% of CoO_4 site strongly Jahn-Teller distorted?









Geometric frustration from the Ca layer
- strong coupling due to absence of apical oxygen

P. Schiffer *et al*., *Phys. Rev. Lett.* **75**, 18 (1994).

L. Pauling *J. Am. Chem. Soc.* **57**, 2680–2684 (1935).

Nickelate superconductor

4	5	6	7	8	9	10	11	12
IVB	VB	VIB	VIIB		VIII		IB	IIB
22 $^3F_2$	23 $^4F_{3/2}$	24 $^7S_3$	25 $^6S_{5/2}$	26 $^5D_4$	27 $^4F_{9/2}$	28 $^3F_4$	29 $^2S_{1/2}$	30 $^1S_0$
Ti	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.38
$[Ar]3d^2 4s^2$	$[Ar]3d^3 4s^2$	$[Ar]3d^5 4s$	$[Ar]3d^5 4s^2$	$[Ar]3d^6 4s^2$	$[Ar]3d^7 4s^2$	$[Ar]3d^8 4s^2$	$[Ar]3d^{10} 4s$	$[Ar]3d^{10} 4s^2$
6.8281	6.7462	6.7665	7.4340	7.9025	7.8810	7.6399	7.7264	9.3942

PHYSICAL REVIEW B VOLUME 59, NUMBER 12 15 MARCH 1999-II

Electronic structure of possible nickelate analogs to the cuprates

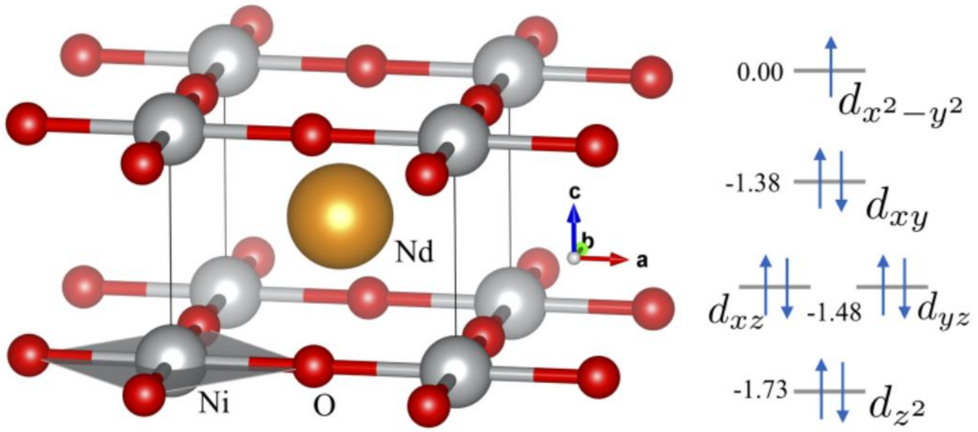
V. I. Anisimov
Institute of Metal Physics, Ekaterinburg, GSP-170, Russia
and Theoretische Physik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland

D. Bukhvalov
Institute of Metal Physics, Ekaterinburg, GSP-170, Russia

T. M. Rice
Theoretische Physik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland
(Received 26 June 1998)

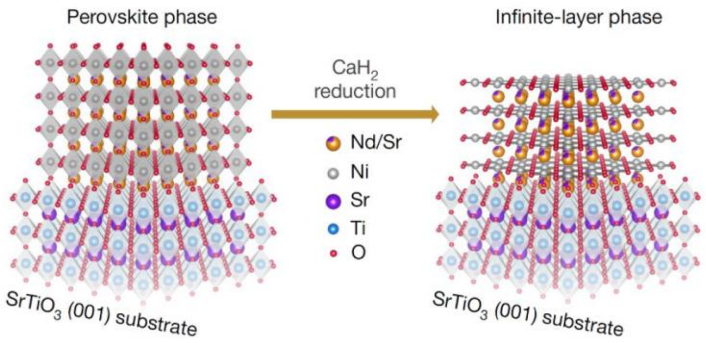
$CaCuO_2$
- CuO_2 square planes
- $3d^9$ electronic configuration (Cu^{2+})

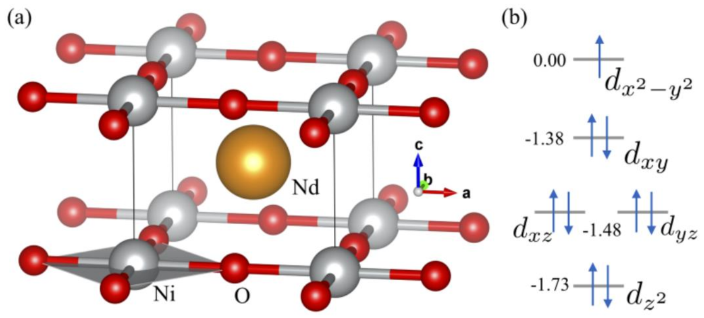
Infinite-layer $LnNiO_2$
- NiO_2 square planes
- $3d^9$ electronic configuration (Ni^{1+})

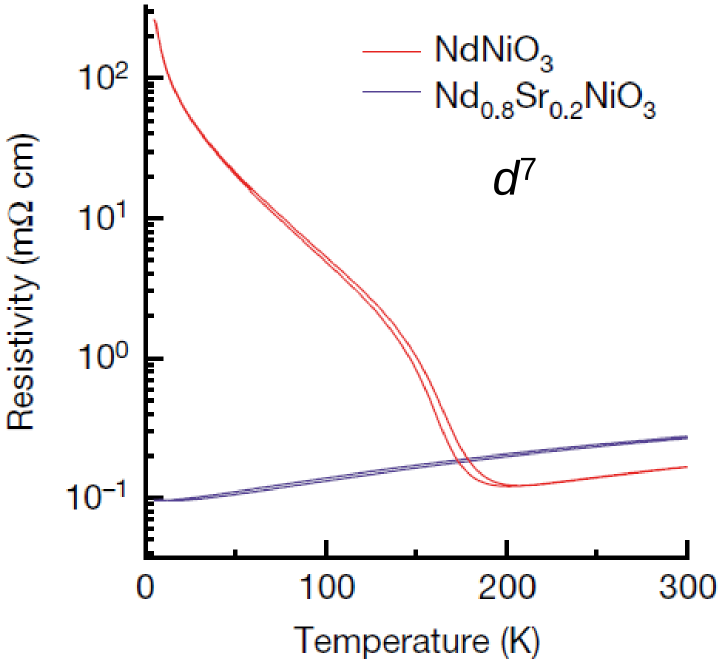


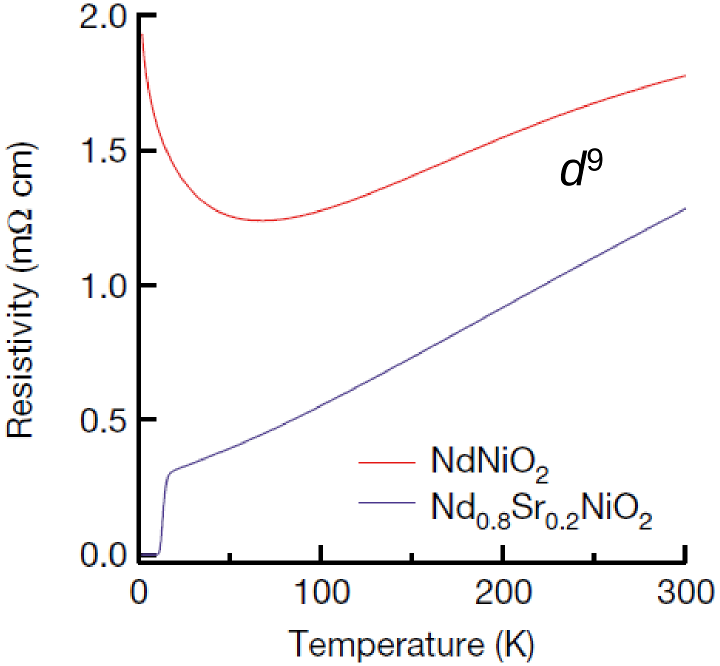
X. X. Wu *et al.*, *Phy. Rev. B* **101**, 060504(R) (2020).

Discovery of nickelate superconductors





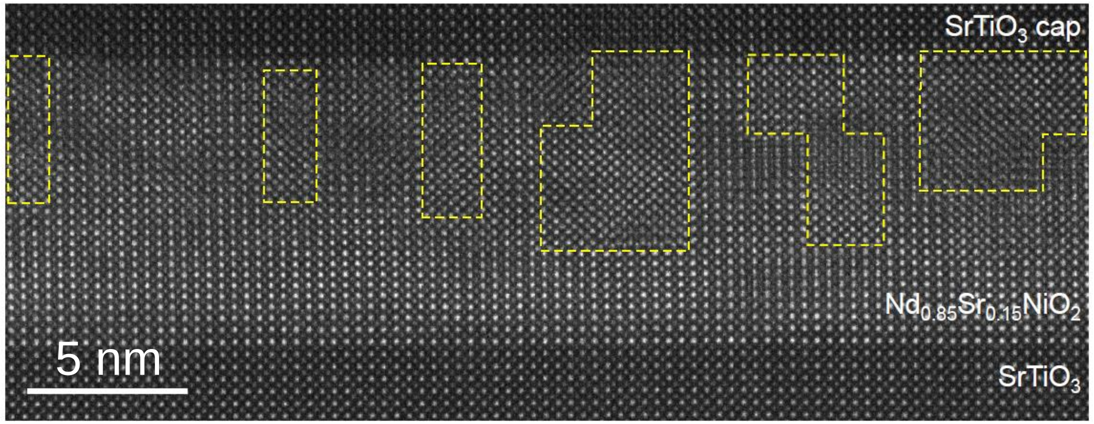




D. Li. *et al*., Nature **572**, 624 (2019).

X. X. Wu *et al*., Phy. Rev. B **101**, 060504(R) (2020).

‘Intrinsic’ or ‘extrinsic’ transport behavior?



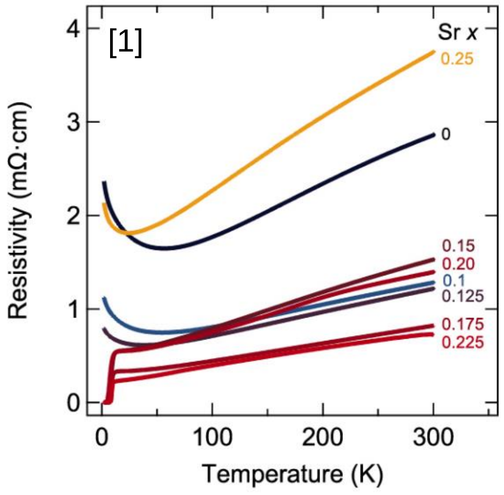
Crystalline imperfections

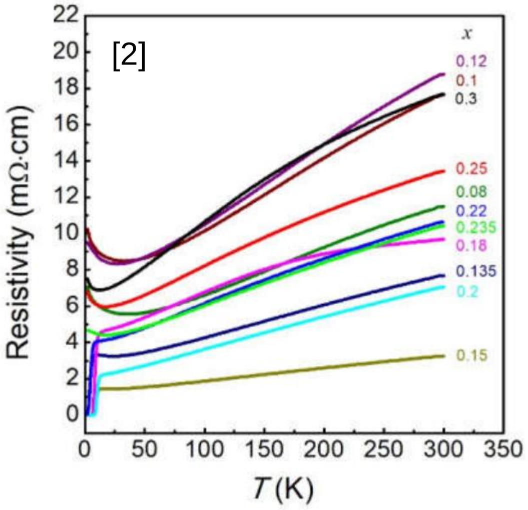
[1] D. Li, B. Wang *et al*., Phys. Rev. Lett. **19**, 381 (2020)

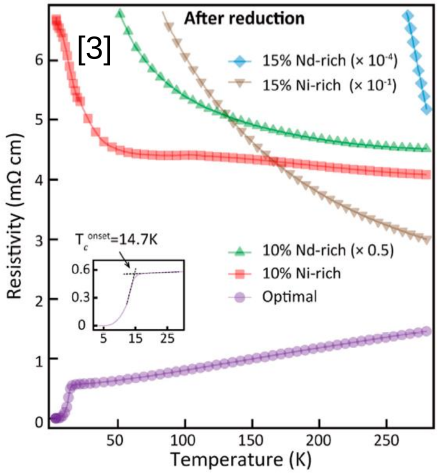
[2] S. Zeng *et al*., Phys. Rev. Lett. **125**, 147003 (2020)

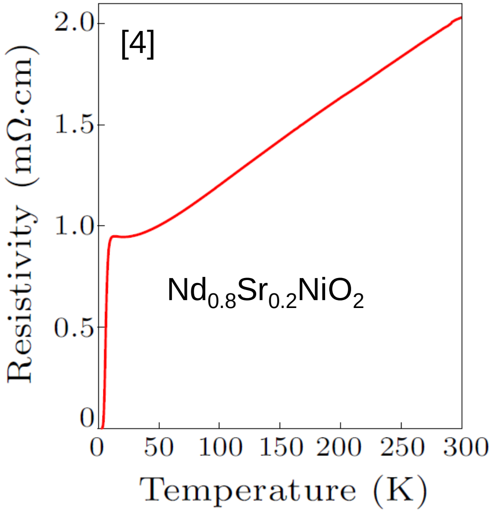
[3] Y. Li *et al*., Front. Phys. **9**, 719534 (2021)

[4] Q. Gao *et al*., Chinese Phys. Lett. **38**, 077401 (2021)

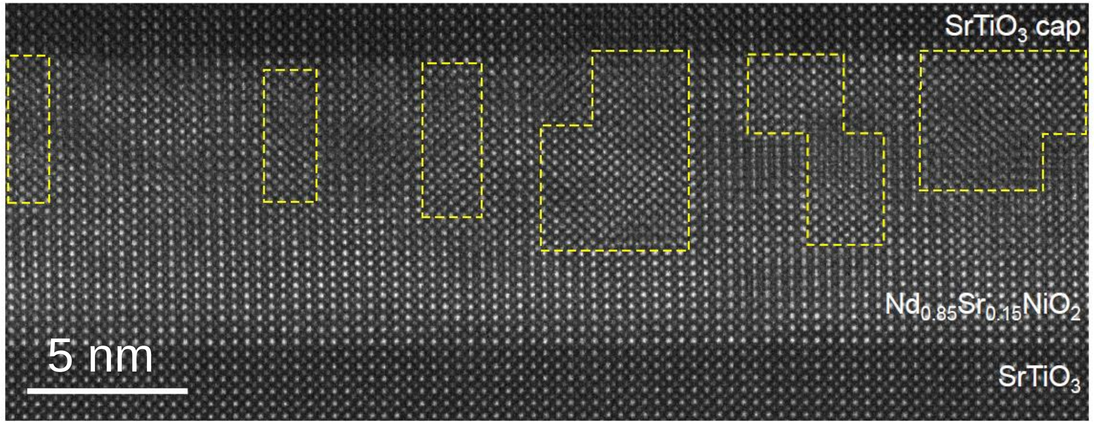




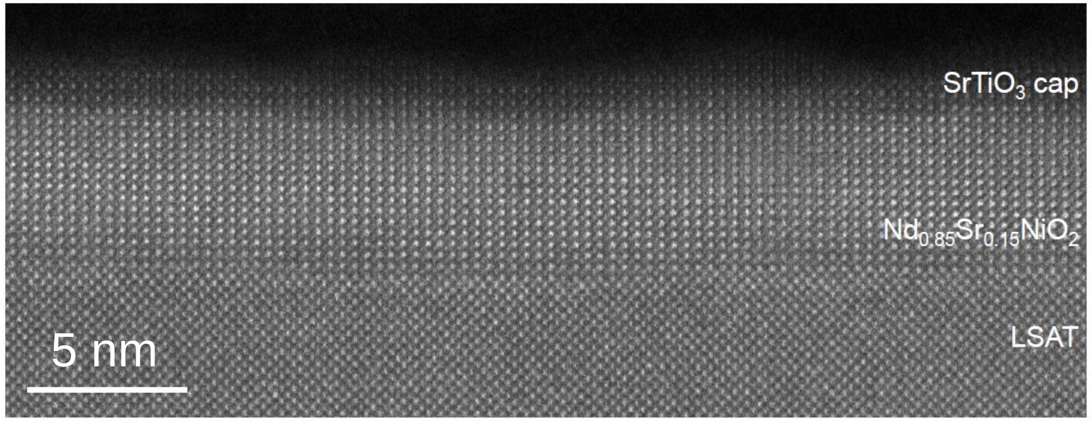


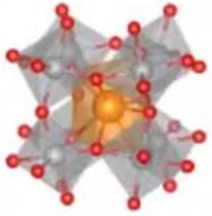


Reducing the lattice mismatch for better sample quality: $SrTiO_3$ → $(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.7}$

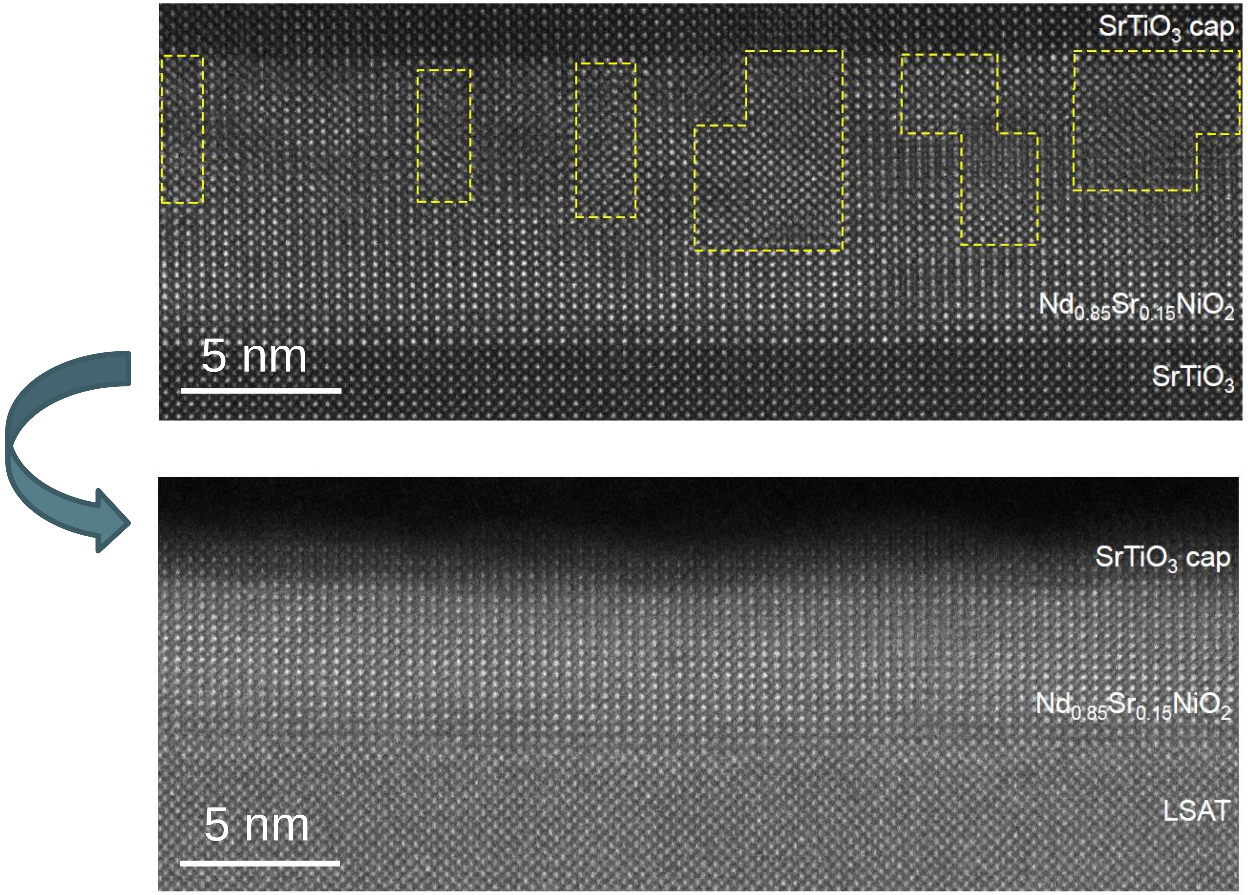


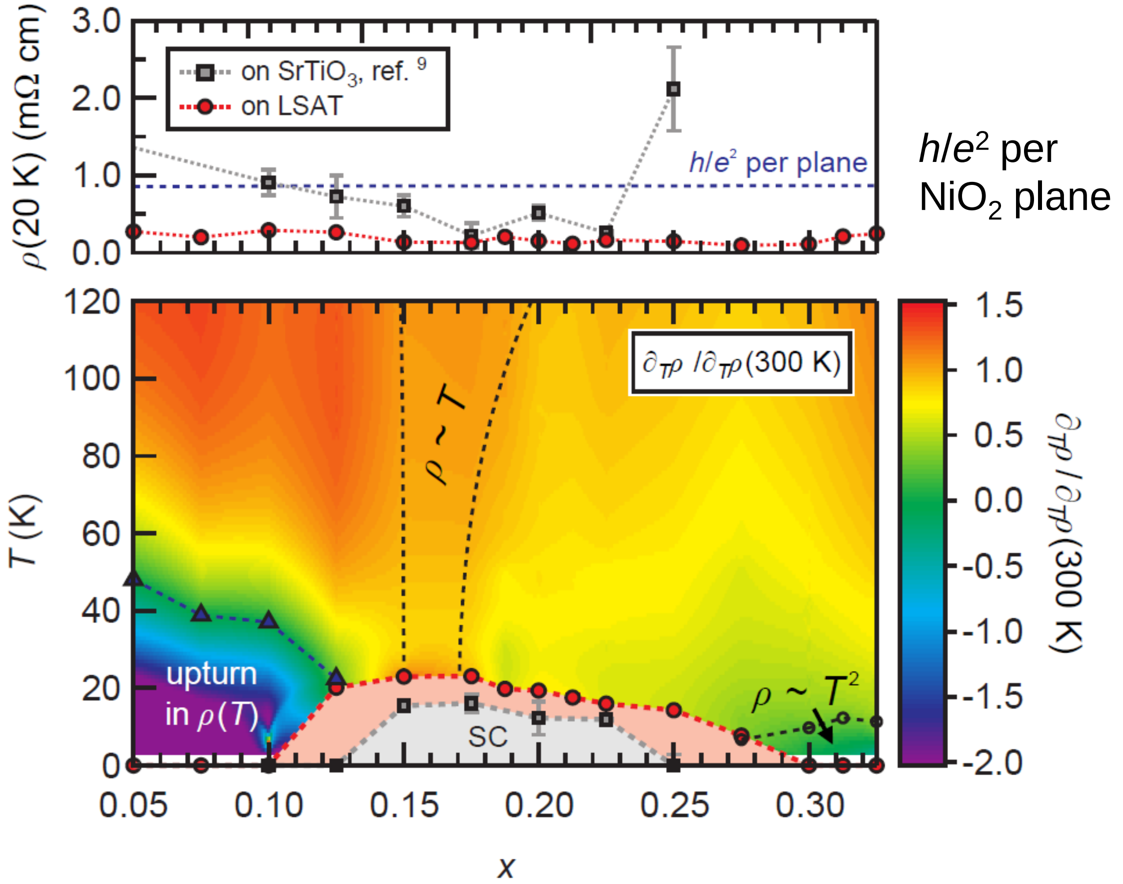
Crystalline imperfections



Phase	Mismatch on $SrTiO_3$	Mismatch on LSAT
 perovskite $a = 3.807$ Å[1]	+2.6% →	+1.6%

Intrinsic superconducting phase diagram of infinite later nickelate

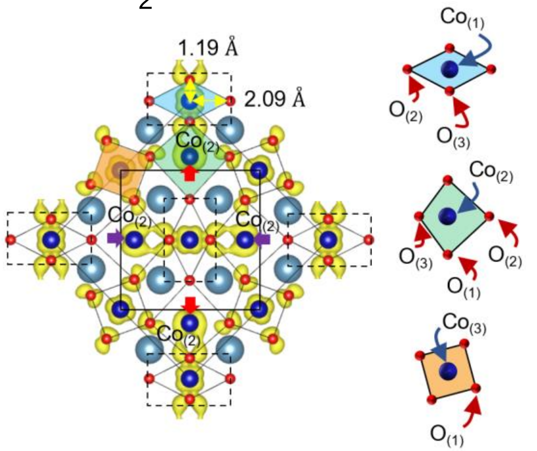




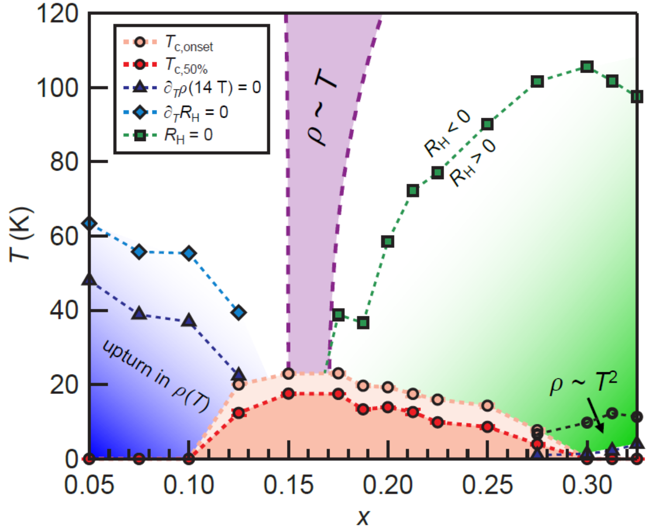
- Normal state resistivity (at T = 20 K) for film on LSAT become lower than that for film on STO.
- Superconducting dome width become larger.

Summary and outlook

$CaCoO_2$



(Nd,Sr)NiO_2



- ✓ Infinite layered cobaltate is a new compound for realizing the first 2D-JTE with strong inter-layer coupling.
- ✓ This gave us a broad understanding how Jahn-Teller order in 2D-lattice affect its lattice and electronic structure.
- ✓ Nickelate study is a good example stressing importance of thin-film quality to study intrinsic transport properties.
- ✓ Superconducting phase diagram of nickelate provide an insight on underlying pairing mechanism.

→ Topotactic engineering opens the new material platform for novel ground states.

W. J. Kim *et al.*, *Nature* **615**, 237-243 (2023).

K. Lee, W. J. Kim and H. Y. Hwang *et al.*, *Nature* **619**, 288-292 (2023).

Acknowledgements

Synthesis, structure, transport and etc. (Harold Hwang Group in Stanford)

Kyuho Lee, Motoki Osada, Yonghun Lee, Varun Harabola, Kevin Crust, Ruijuan Xu, Bai Yang Wang, Jennifer Fowli, Yijun Yu and Harold Hwang

XAS (Stanford/SLAC)

Jun Sik Lee, Cheng-Tai Kuo, Sang-Jun Lee

GIXRD (PAL)

Byeong-Gwan Cho

STEM-EELS (Kourkoutis Group in Cornell)

Michelle Smeaton   Berit H. Goodge   Lena F. Kourkoutis

Theory (The Devereaux Group)

Chunjing Jia   Brian Moritz   Thomas Devereaux

SIMS (Oak Ridge National Lab.)

Anton Ielev