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EXPERIMENTAL WORKSHOP ON
HIGH TEMPERATURE SUPERCONDUCTORS
(11 - 22 April 1988)

STRUCTURE-PROPERTY CORRELATIONS IN OXIDES WITH HIGH T_c

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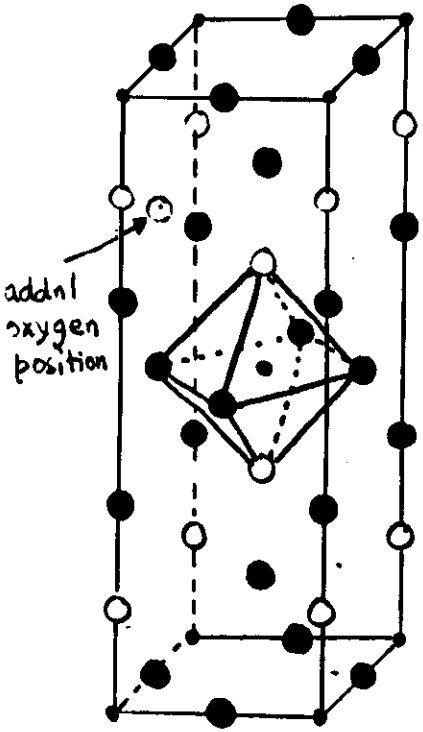
STRUCTURE - PROPERTY CORRELATIONS in OXIDES WITH HIGH T_c.

(Lecture II)

Ganguly & Rao, C.N.R. J. Solid State Chem. (1984)
Singh, Ganguly, Goodenough)

A_2BO_4 oxides



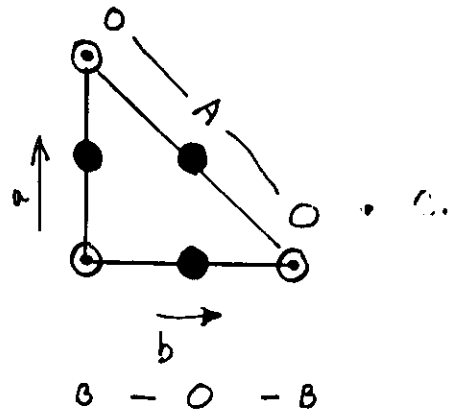
K_2NiF_4 Structure as in La_2CuO_4 (tetragonal)

- • copper
- ●● oxygen I, I'
- ○ oxygen II, II'
- ● Lanthanum, 9-fold coordinated ($d_{x^2-y^2}$ orbitals)
- ○ oxygen II' (not occupied)

In Sr_2CuO_3 ● oxygens are missing. (chains) ($d_{y^2-z^2}$ orbitals)

In Nd_2CuO_4 ○ oxygens are missing. Instead ● O oxygens (at 0, 0, 0.25) are occupied. (planes)

$La-O_{II}$ or $Sr-O_{II}$ bonding vs $Cu-O_{II}$ bonding



Tolerance Factor

$$t = \frac{r_{A-O}}{\sqrt{2}\, r_{B-O}}$$

$0.85 \lesssim t \lesssim 1.02$

Cu^{2+} d^9

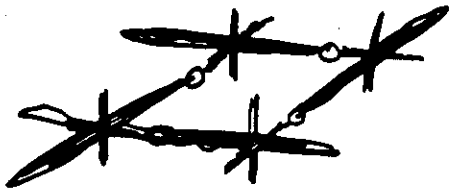
in elongated octahedra or sq. planar

low-tolerance factor as in La_2CuO_4 ($t \approx 0.85$)

favours ferrodistortive ordering of elongated octahedra ($c/a > 1$)

high-tolerance factor as in K_2CuF_4 ($t \sim 1$)

favours antiferrodistortive ordering

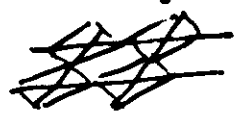


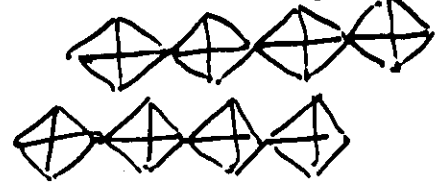
La_2CuO_4 ↔ Nd_2CuO_4

elongated octahedra ↔ sq. planar

La_2CuO_4 ⟷ Sr_2CuO_3

$d_{x^2-y^2}$ $d_{z^2-x^2}$, $d_{y^2-z^2}$



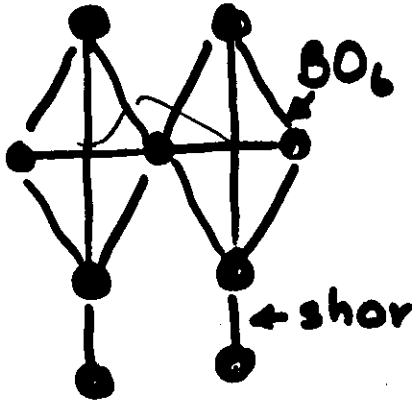


competition in (Sr, La) – O – Cu interactions along c axis

Tolerance factor <1 in almost all A_2BO_4 or ABO_3 oxides

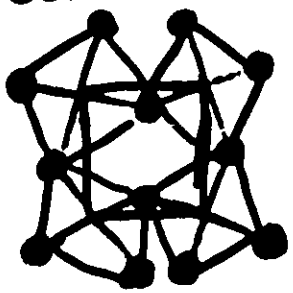
In 2d

- Pressure in ab plane causes elongation of BO_6 octahedra., Jahn-Teller of Cu^{2+} adds to elongation
- short La-O bonds. Cu-O-Cu angle = 180°



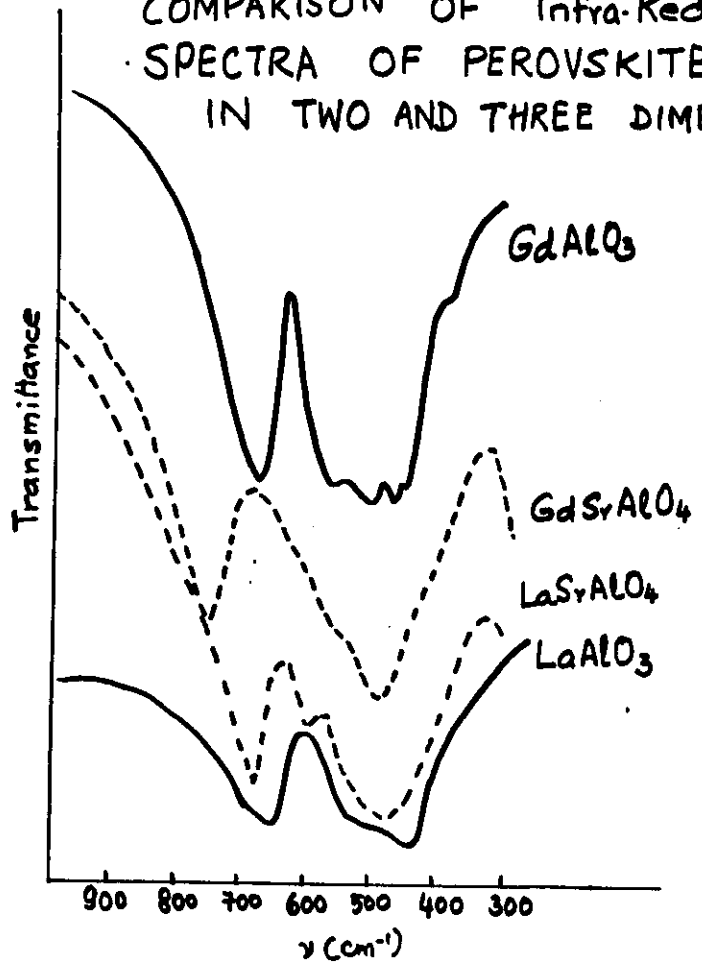
In 3d

- buckling of octahedral network relieves pressure. Individual octahedra remain symmetrical



- B-O-B angle less than 180°

COMPARISON OF Infra-Red SPECTRA OF PEROVSKITES IN TWO AND THREE DIMENSIONS

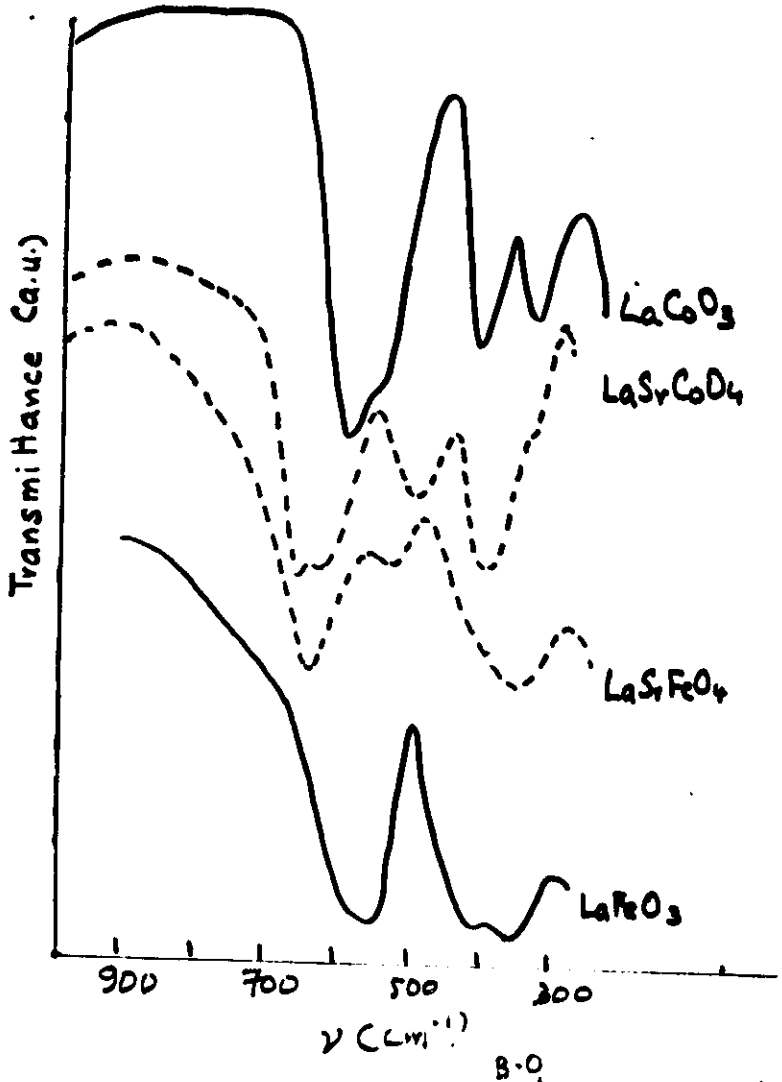


Similar results obtained with other compounds containing iron group transition metal ion.

Highest frequency band could be related to B-O stretching

Reduction in tolerance factor by decreasing size from La to Gd does not affect force constant in 3d perovskite but affects force constant in 2d.

IR Spectra of some ABO_3 and A_2BO_4 oxides

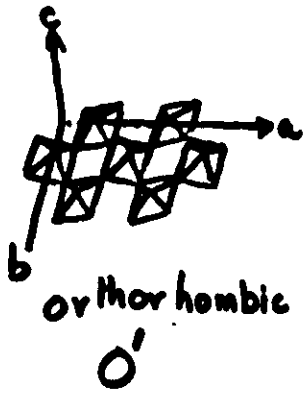


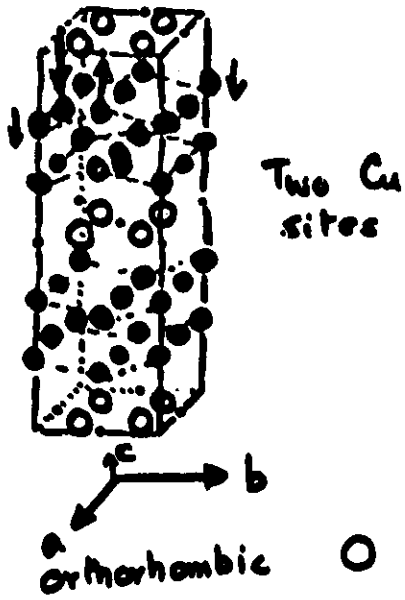
3d oxides have lower force constants than 2d oxides showing influence of more pressure in K_2NiF_4 structures due to rigidity of BO octahedral network..

As t is decreased T → O → O'

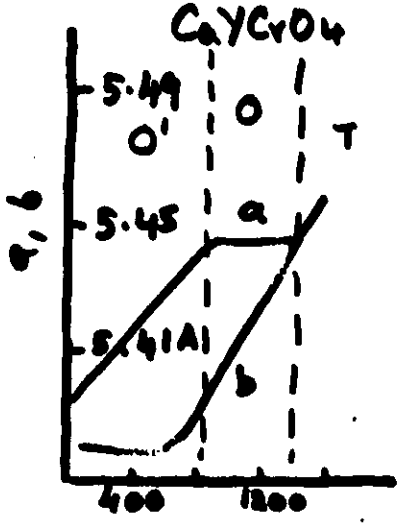
Does $La_2Cu_4O_4$ have an O component

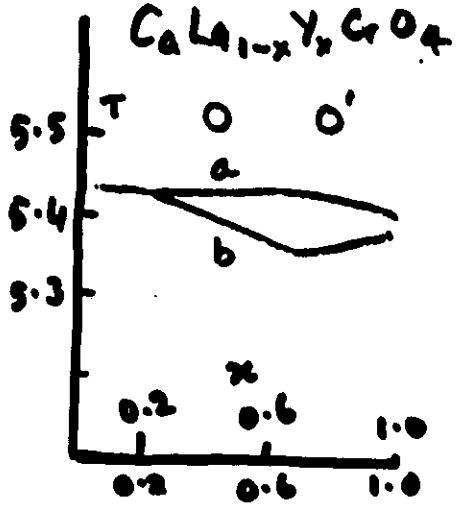
Singh et al, JSSC, 52, 254 (1984)



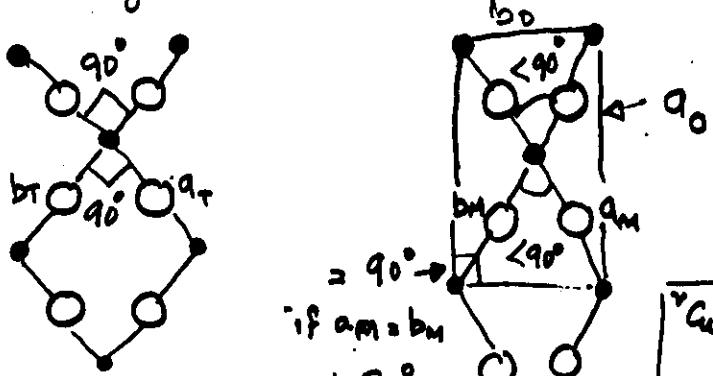


Berjoan et al JSSC 42, 75 (1982)





Tetragonal → Monoclinic



$\nu_{Cu^{2+}} \rightleftarrows \frac{\nu_{Cu^{1+}} + \nu_{Cu^{3+}}}{2}$

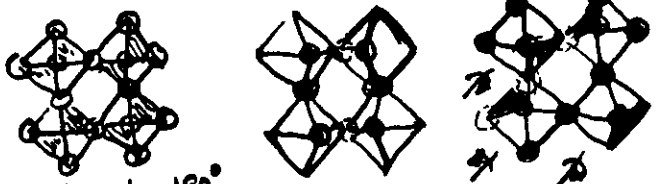
$Cu^{3+} + O^{2-} \rightleftharpoons Cu^{2+} + O^-$

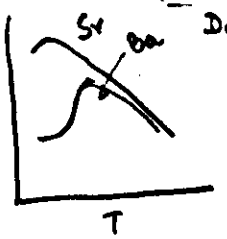
$CuO = (Cu^{1+}Cu^{3+})O^-O^{2-}$

When $t \leq 0.85$ orthorhombic

e.g. La_2NiO_4, La_2CoO_4, La_2CuO_4

B-O-B distance is reduced by decreasing B-O-B angle from 180°. Done by tilting of octahedra





Does change in $(a-b)/(a+b)$ show ... in symmetry

$La_{1.85}M_{0.15}CuO_4$

Changes may be related to ... transition ...

$La_{2-x}Sr_xCu_4O_{4-\delta}$ ($\delta \simeq 0$ for $x < 0.3$; "holes" $\propto x$; $\delta = \frac{x}{2}$ for $x \geq 0.5$; only Cu^{2+})

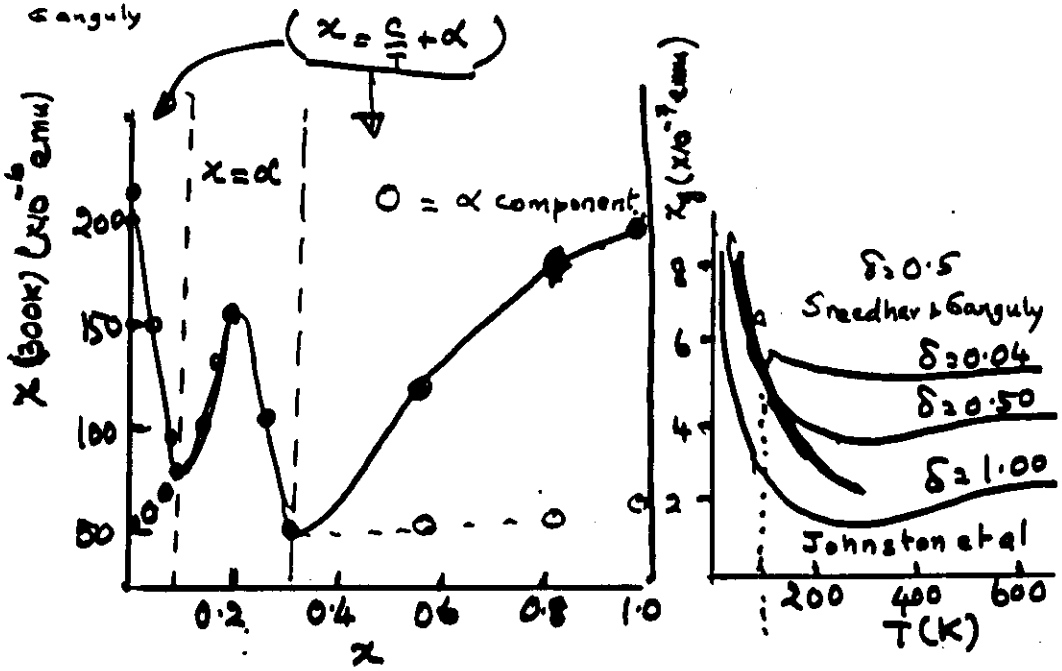
$x = 0.18$-0.20 max. T_c.

$T_c \to 0$ for $x \simeq 0.3$

at 300K MAGNETIC SUSCEPTIBILITY reaches maximum near $x \approx 0.20$ } Transition from half-filled to quarter-filled Bands

Similarly with $YBa_2Cu_3O_7$

Sreedhar and Ganguly



SUSCEPTIBILITY IN METALLIC PHASE OF $LA_{2-x}Sr_{0.3}Cu_4O_4$ ~ that of Copper. (50×10^{-6} emu) compared to $LaNiO_3$ (Ni^{3+}, $s = \frac{1}{2}$), (600×10^{-6} emu) RESISTIVITIES ARE COMPARABLE

DISPROPORTIONATION

La_2NiO_4 & La_2CuO_4 have tolerance factors closest to the lower limit

$$t \geq \frac{r_A - O}{\sqrt{2}\, r_B - O} \approx 0.85 \quad (La_2NiO_4, La_2CuO_4)$$

IS DISPROPORTIONATION POSSIBLE SINCE THIS WOULD IMPROVE TOLERANCE FACTOR

$$t_{Cu^{2+}} < t_{Cu^{+}, Cu^{3+}\,(LS)}$$

$$r_{Cu^{2+}} > \frac{r_{Cu^{+}} + r_{Cu^{3+}}}{2}$$

DOES LOW-DIMENSIONAL SYSTEM FAVOUR DISPROPORTIONATION OR SOMETHING CLOSE TO THE FORMATION OF CHARGE DENSITY WAVES.

e.g. $2Cu^{2+} \rightarrow Cu^{(2+\delta)+} + Cu^{(2-\delta)+}$

La_2CuO_4 $\rho \sim 10^{-1}\ \Omega.cm.$, $\chi \sim 200\times10^{-6}$ emu.

$\tau_{res} \sim 10^{-12}$ sec

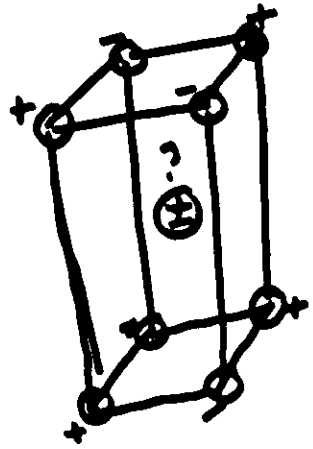
$W_b \sim 0.01$ eV?

$\chi_{PP} \quad \frac{C}{T_P} = \frac{.37}{T_P}$

$T_P = 1800K$

IS THE LOCAL SYMMETRY IN K_2NiF_4 STRUCTURE THE SAME AS THAT REFLECTED BY THE SPACE GROUP

FRUSTRATION OF ANTIFERROMAGNETIC ORDERING IN 3D

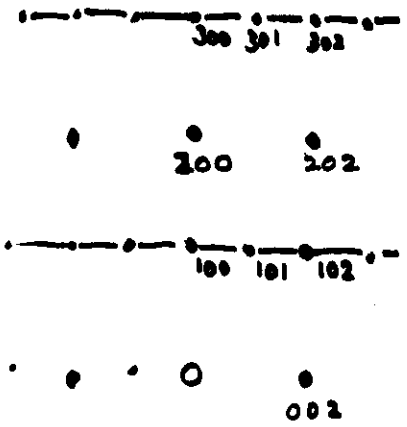


FRUSTRATION REFLECTED IN ABS. OF CATIONIC ORDERING ALSO IN COMPOUNDS SUCH AS

$La_2Li^{+}_{0.5}M^{3+}_{0.5}O_4$

$Sr_2M^{3+}Ti^{4+}O_4$

BUT TWO-DIMENSIONAL ORDER IS PRESENT



orthorhombic
unit cell
$a_o = \sqrt{2}\, a_T$
$200_O \equiv 110\ T$

Neutron-Diffraction from Single Crystals of K_2NiF_4 illustrating 2d antiferromagnetic ordering
- 3d Bragg reflection spots
- Superlattice reflections
— streaking indicating 2d ordering

SIMILAR ELECTRON DIFFRACTION PATTERN WITH STREAKING SEEN IN $La_2Li_{0.5}Co_{0.5}O_4$. Two-dimensional ordering actually seen in high resolution electron microscope

ACCOMODATION OF EXCESS OXYGEN

$La_2NiO_{4+\delta}$ and $La_2CoO_{4+\delta}$ have usually excess oxygen ($\delta \neq 0$)

$\delta \simeq 0.125$ for Ni
$\delta \leq 0.25$ for Co

Density measurements on single crystals of $La_2NiO_{4+\delta}$ clearly showed that density is greater than the x-ray density suggesting the excess oxygen is present as <u>interstitial</u> oxygen

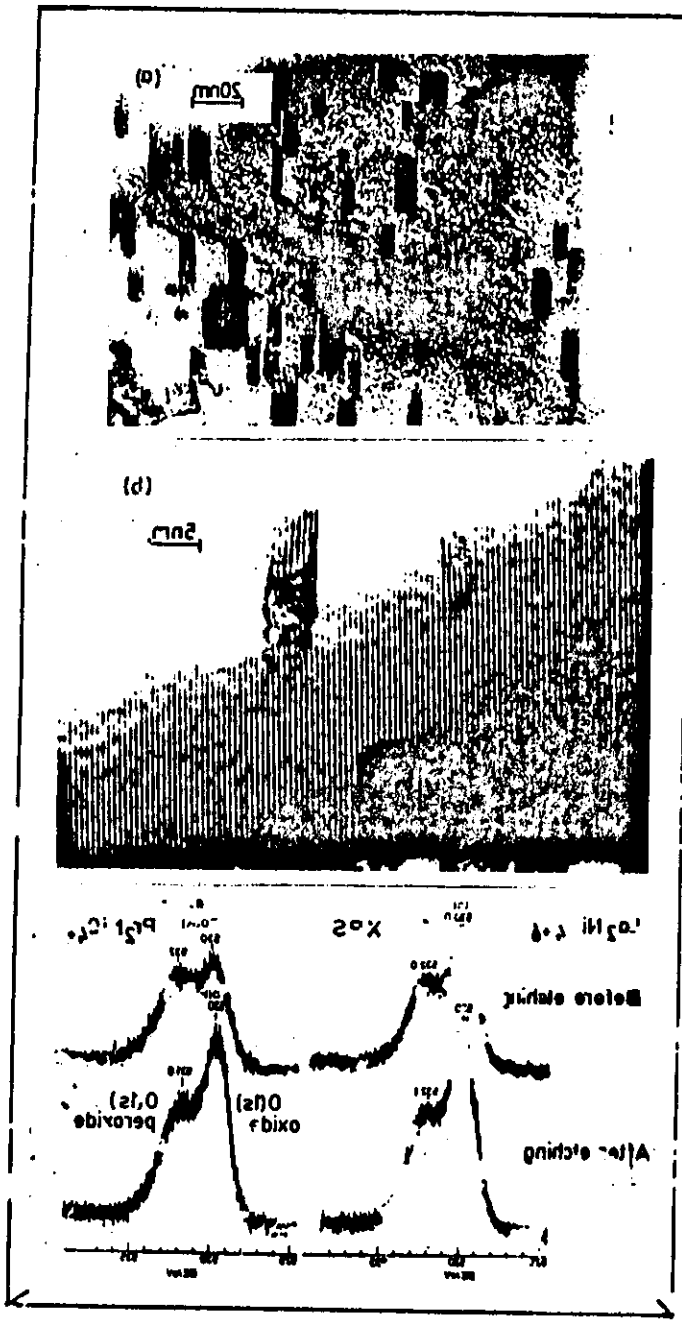
PROBABLY AS PEROXIDE

αLa_2NiO_4 monoclinic distortion

$La_2NiO_{4.125}$ tetragonal

The two exist as two distinct phases when δ is varied between 0 and 0.125

La_2CuO_4 is superconducting
Beille et al C.R. Acad. Sc. Paris. 304 (II) 1099 (1987)
presence of peroxide



excess O_2, peroxidic

$La_2NiO_{4.12}$ (T)

La_2NiO_4 (O)

$La_2NiO_{4+\delta}$ for $0 < \delta < 0.125$ mixture of T and O this seems to show that $\delta = 0.125$ due to peroxide is a distinct composition. Similarly $\delta = 0.125$ and $\delta = 0.25$ in $La_2CoO_{4+\delta}$

NEW PRINCIPLE ?

STABILITY AT LOW TOLERANCE FACTORS

La_2NiO_4, Nd_2NiO_4, La_2CoO_4 etc } low tolerance factor have excess oxygen

Tolerance factor increases on introduction of holes due to excess oxygen. Structure is thus stabilised

$Nd_2NiO_4 \longrightarrow Nd_2O_3 + NiO$ on standing

Similarly $Sr_2Fe_{0.5}Ta_{0.5}O_4 \rightarrow \underset{R}{SrO} + \underset{P}{SrFe_{0.5}Ta_{0.5}O_3}$

$La_2NiO_4 = (\overset{3+}{La}\overset{2-}{O})^+ (LaNiO_3)^-$

$\underset{c}{\leftrightarrow}$ axis + - + - + - + - long-range order due to electrostatic forces between layers.

$Sr_2BO_4 = (SrO)^{\delta}_{2}(SrBO_3)^{\delta}$

o o o o o o o o no long-range order; less stable

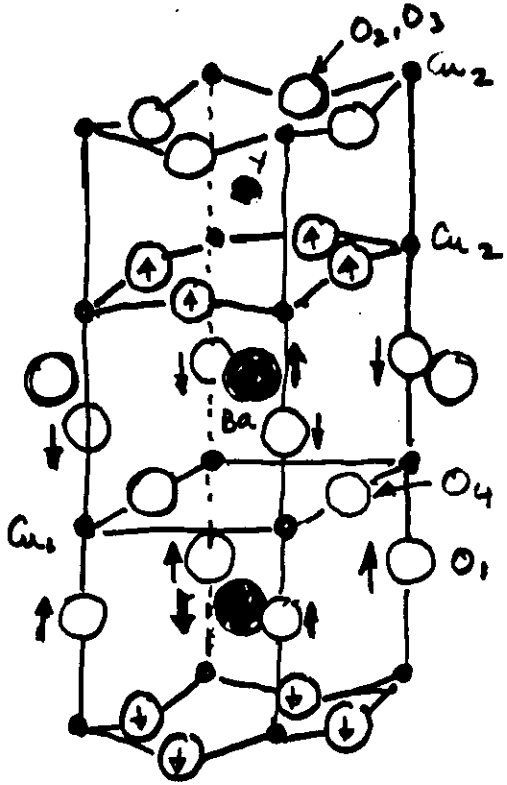
In absence

Size of Ba^{2+} ions ~ 1·50 Å° (radius)

size of O^{2-} ions ~ 1·40 Å° (radius)

Ba-O distance ~ 2·90 Å°

$Ba-O_{2,3}$ ~ 2·90 Å
$Ba-O_1$
$Ba-O_4$ ~ 2·74 Å°

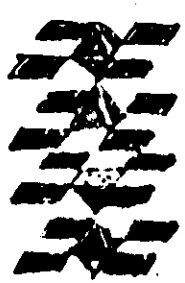


Large size of Ba forces displacements of O_1 towards Cu_1

$\Rightarrow Cu_1-O_1-Cu_2$ and $Cu_1-O_4-Cu_2$ angle = 180° because of presence of Ba ions in all directions.

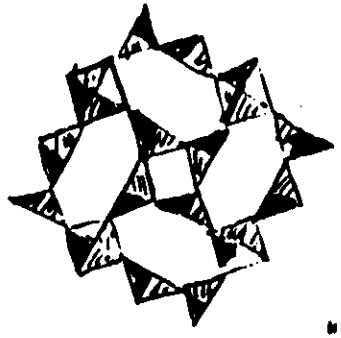
short Cu-O4 distance imposed by Ba replacement of Ba by Sr, La etc may relax the constraint. Giving rise to different orbital ordering schemes?

Proposed Structures showing different arrangements in polyhedra



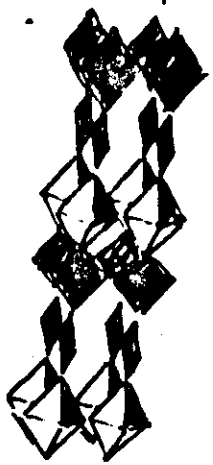
"$La_3Ba_3Cu_6O_{14}$"

Same motif in $La_2Ni_2O_5$

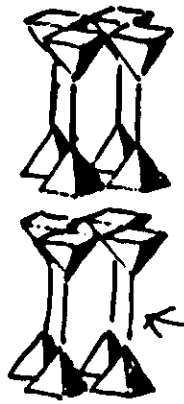


"$La_4BaCu_5O_{13}$"

"$YBa_2Cu_3O_7$"



Rellevetal for $YBa_2Cu_3O_7$



$YBa_2Cu_3O_6$

Notice pore of ~2·75 Å radius which may intercalate gases

Ba requires nine-fold coordination

so we want $BaCuO_{2.25}$

Function of Y may be to give the extra oxygen in $BaCuO_2$ to provide a 9-fold coordination for oxygen

Each Y gives 0.5 excess oxygen

so we have $(YCuO_2)(BaCuO_{2.25})_2$

$\Vert\Vert$

$YBa_2Cu_3O_{6.5}$

as the composition in which all Cu^{2+} ions have valency 2.

$YBa_2Cu_3O_{6.5}$ intercalates O_2 to $YBa_2Cu_3O_7$

However, Ba can go to Y sites but not it seem vice versa.

Thus $Y_{1-x}Ba_{2+x}Cu_3O_{7\pm\delta}$ is known.

$La_{1\pm x}Ba_{2\mp x}Cu_3O_{7\pm\delta}$ are also known

$LaNiO_3$ vs $YNiO_3$

~~insula~~ metal	insulator
prepared at ambient (1 atm) pressures	requires high pressure.

Small A ions such as Y^{3+}, (maybe Ca^{2+}) impose eight-fold coordinated A site

Perovskite $LaNiO_3$

(a)

O-positions vacant in $LaNi^{+}O_2$

Ni^{+} isoelectronic with Cu^{2+}

$3d^9$

● = Ni

◎ = La

○ = O

(b)

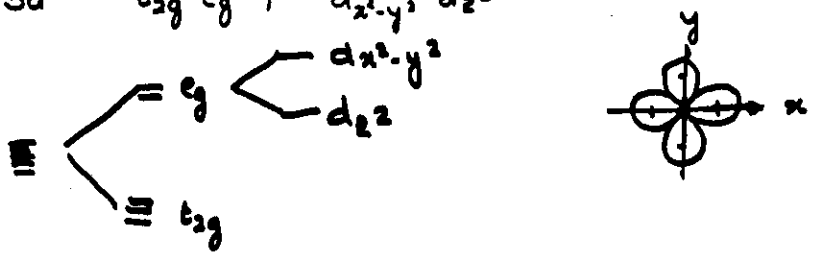
$La_2Ni_2O_5$

alternation of octahedra and tetrahedra

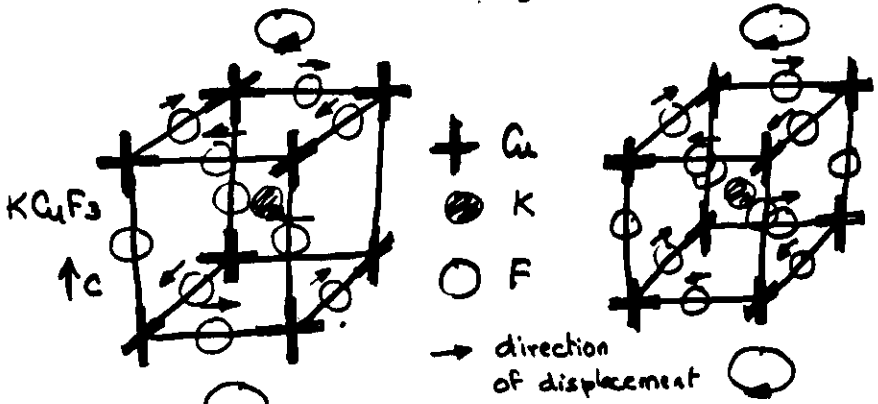
Ni^{2+} isoelectronic with Cu^{3+}

Cu^{2+} is a Jahn-Teller ion

$3d^9$ $t_{2g}^6 e_g^3$, $d_{x^2-y^2}^1 d_{z^2}^2$

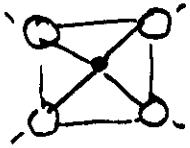


octahedra elongation along z axis.



$c/a < 1$ polytypism from different orbital ordering schemes

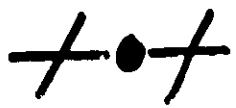
In oxides CuO_4 square-planar units are preferred. When constrained to be in ~~square-planar~~ octahedral environment octahedra are elongated.



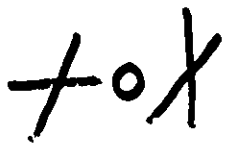
Four free links. 2d network

a) ORDER ORBITALS. FILL OXYGEN so that $c = 3a$

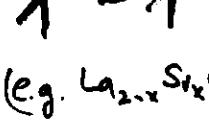
b) CONSTRAINTS FOR OXYGEN POSITIONS BEING OCCUPIED



i) positions located between lobes of two half-filled orbitals are to be occupied and would be most tightly bound



ii) positions between half-filled and ~~empty~~ one filled orbitals to be occupied next and would be more loosely bound



iii) positions between filled orbitals would be the last to be occupied

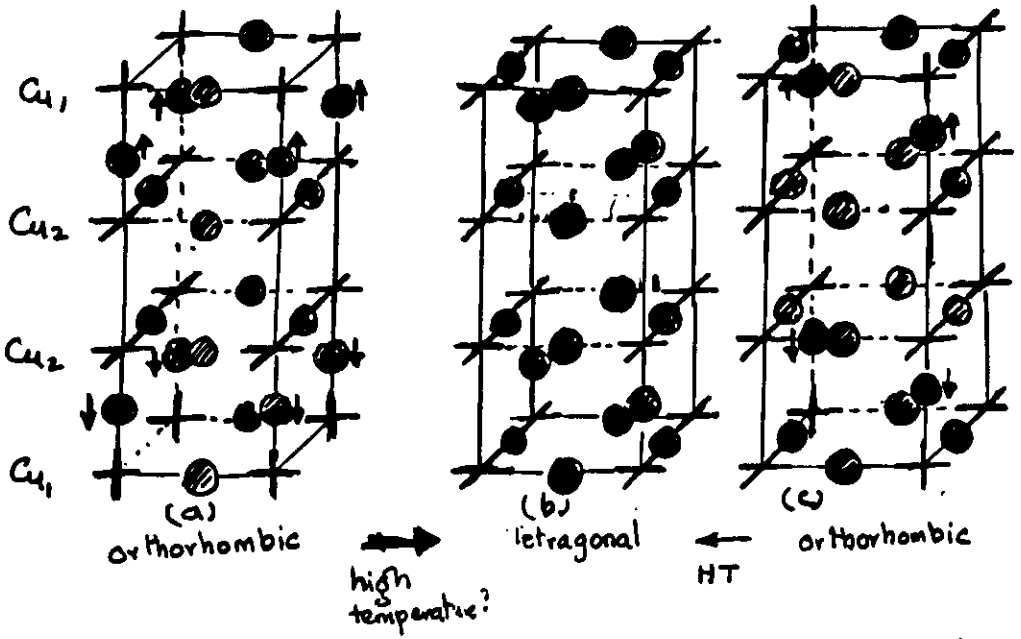
(e.g. $La_{2-x}Sr_xCuO_4$)

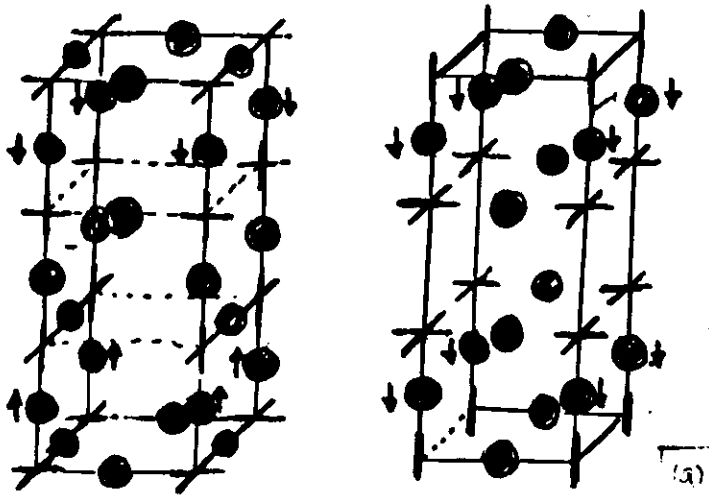
Additional Constraint

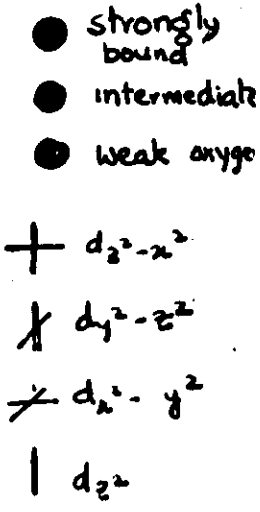
Y to have eight fold co-ordination

Possible/possible orbital ordering schemes

→ b axis







(d) and (e) consistent with neutron diffraction structure and displacement of O_I ions.