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UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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

CHEMICAL UNDERSTANDING OF PHYSICAL PROPERTIES

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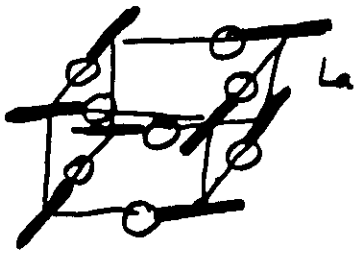
"CHEMICAL" UNDERSTANDING OF PHYSICAL PROPERTIES

Electrical Magnetic Properties of $LaBO_3$ (perovskites)

Electronic		T_c	$S(S+1)$	ρ (ohm cm)	
$t_{2g}^1 e_g^0$	$LaTiO_3$	100K* weak ferro magnetism	0.75	10^{-2}	$S = 1/2$
$t_{2g}^2 e_g^0$	$LaVO_3$	140 (T_N)	2	10^2	$S > 1/2$
$t_{2g}^3 e_g^1$	$LaMnO_3$	110 K	6	10^2	
$t_{2g}^3 e_g^0$	$LaCrO_3$	298K	15/4	$> 10^6$	
$t_{2g}^3 e_g^2$	$LaFeO_3$	750K	35/4	$7 \; 10^6$	
$t_{2g}^6 e_g^0$	$LaCoO_3$	— low-spin high-spin	-	10^2	
$t_{2g}^6 e_g^1$	$LaNiO_3$	metal	$\chi_{para} \sim 700 \times 10^{-6}$	10^{-3}	$S = 1/2$

T_N (V_2O_3, MnO_2, CrO_2, Fe_2O_3) $\approx$ T_N ($LaVO_3$, $LaCrO_3$, $LaMnO_3$, $LaFeO_3$)



$LaMnO_3$.

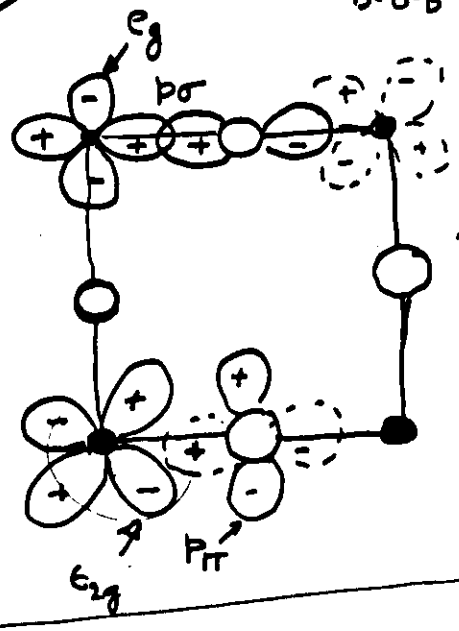
Ferromagnetic layers coupled antiferromagnetically

Criteria for metallicity

ρ +ve TCR or finite σ at $T = 0$ K?

χ small and temperature independent

optical properties.



B-O-B Transfer integral larger for σ bonding than π bonding

$LaCrO_3$ only t_{2g}

$LaFeO_3$ $t_{2g}^3 + e_g^2$

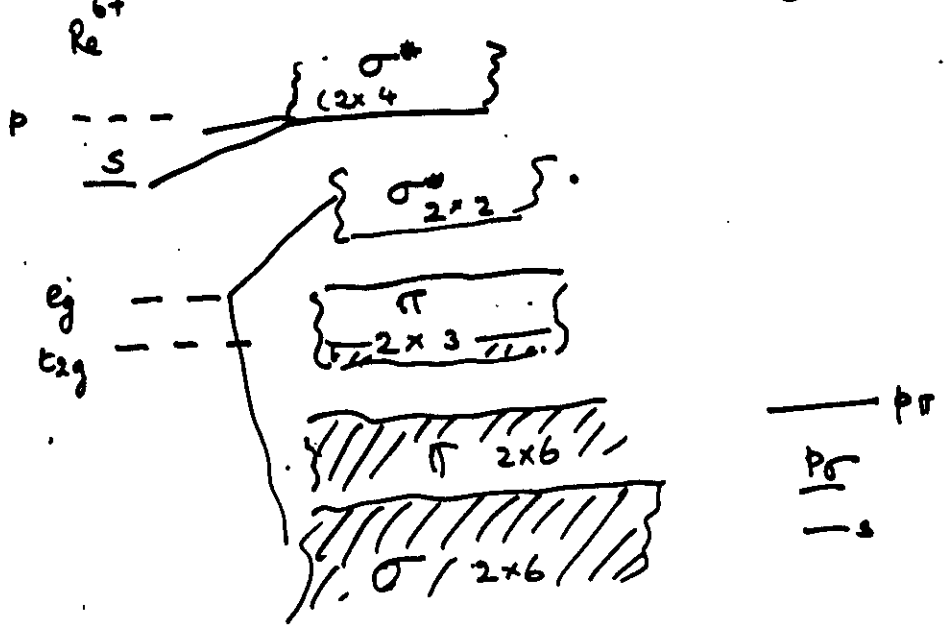
T_N $LaCrO_3$ < T_N $LaFeO_3$

$T_N \propto z J S(S+1)$

$J = \frac{b^2}{U}$ b = transfer integral

T_N of $LaVO_3$, $LaCrO_3$, $LaFeO_3$ $\propto S(S+1)$

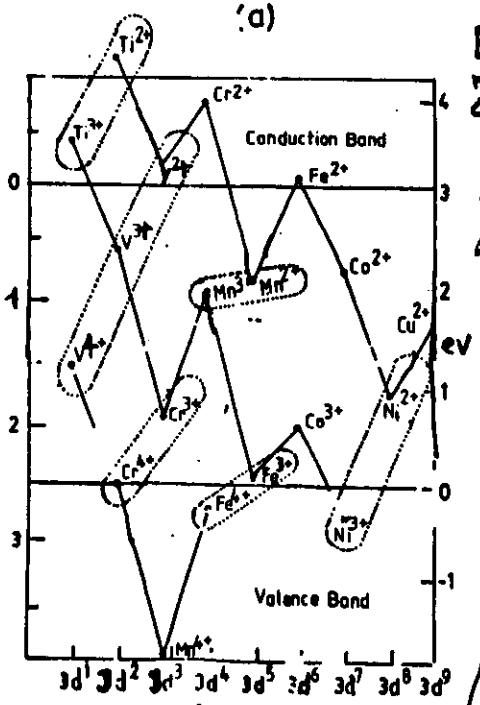
O^{2-}



band diagram of ReO_3

After Goodenough Progr. Solid State Chemistry Vol. 5, 1972

strong hybridisation ~~width~~ of oxygen-metal responsible for metallicity in oxides with cations in high oxidation states



Energy levels of metal ions in oxides (TiO_2)

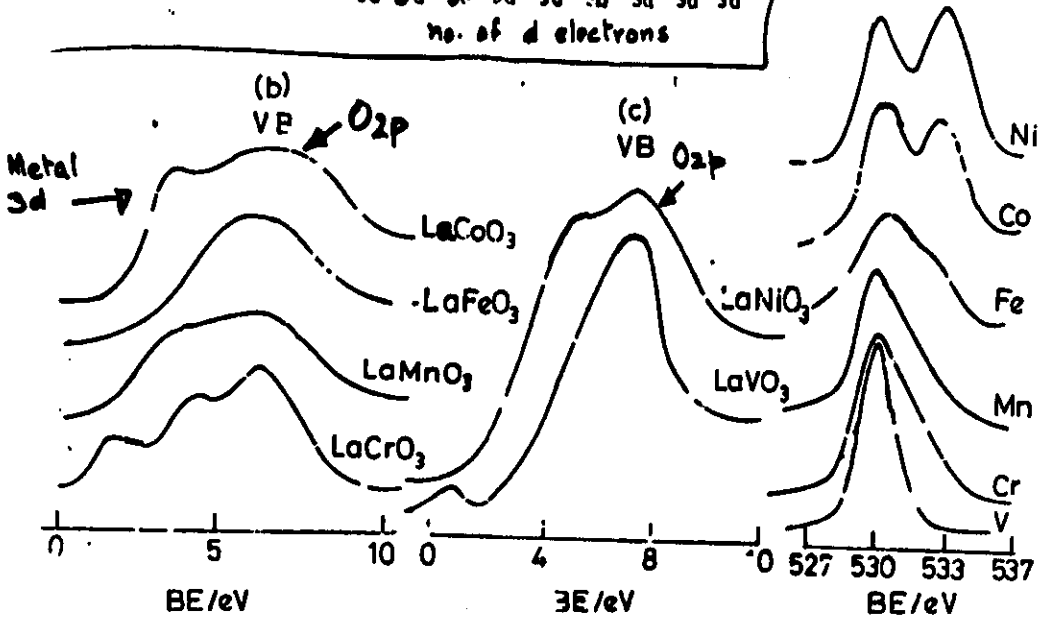
Mizushima et al

J. Phys. Chem. Solids 40, 1129 (1979)

Compounds with metal ions located in valence band are metallic. e.g., $LaNiO_3$, $SrFeO_3$, Cu CrO_3 etc

Mixed Valence of Oxygen?

XPS O(1s)



Ganguly & Hegde Phys. Rev. B37, 5107 (1988)

Double Valence Fluctuation

$Pb^{4+} + 2O^{2-} \rightleftharpoons Pb^{2+} + O_2^{2-}$

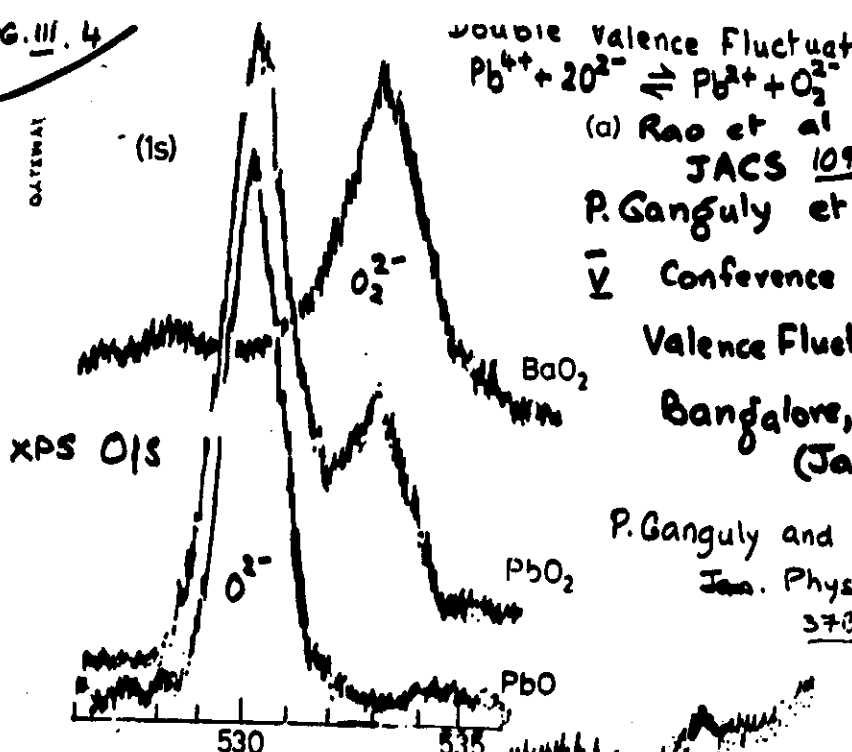
(a) Rao et al (1987) JACS 109, 6893

P. Ganguly et al

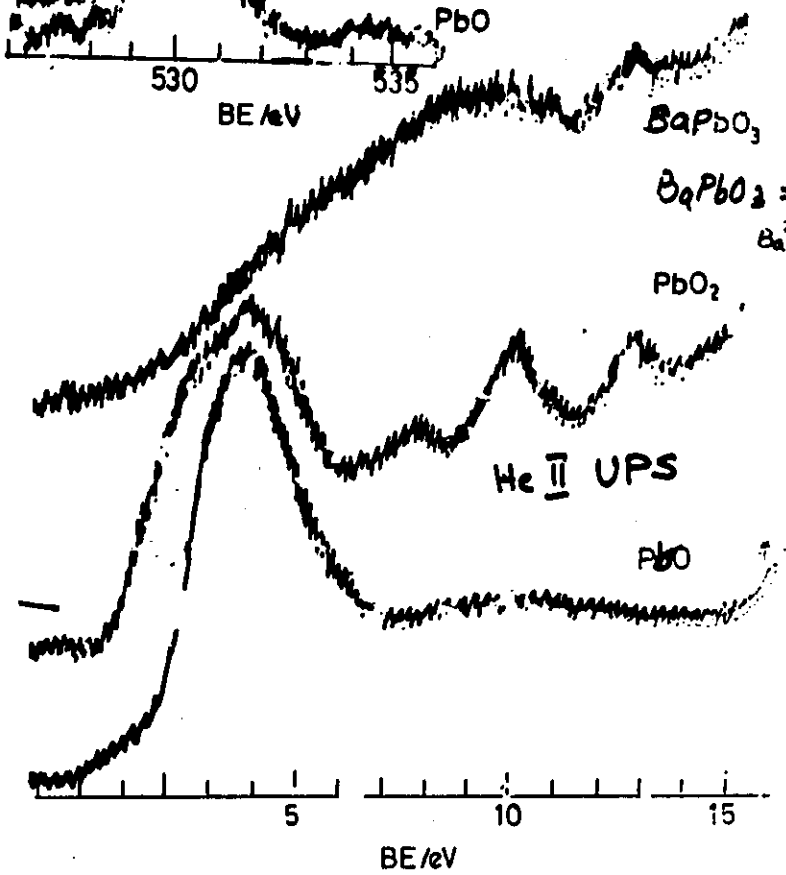
V Conference on Valence Fluctuations

Bangalore, 1987 (Jan.)

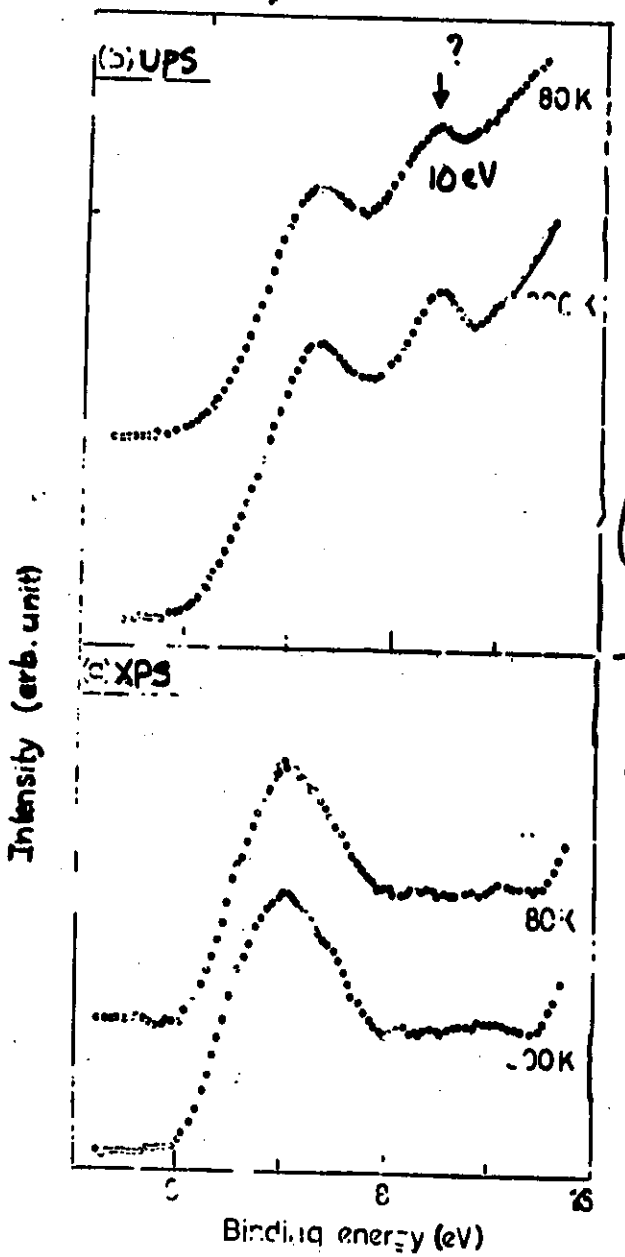
P. Ganguly and M.S. Hegde Jour. Phys. Rev. 1988 37B, 5107



Double



UPS, XPS results on $La_{2-x}Sr_xCu_2O_4$
Sarma and Rao, J. Phys. C.



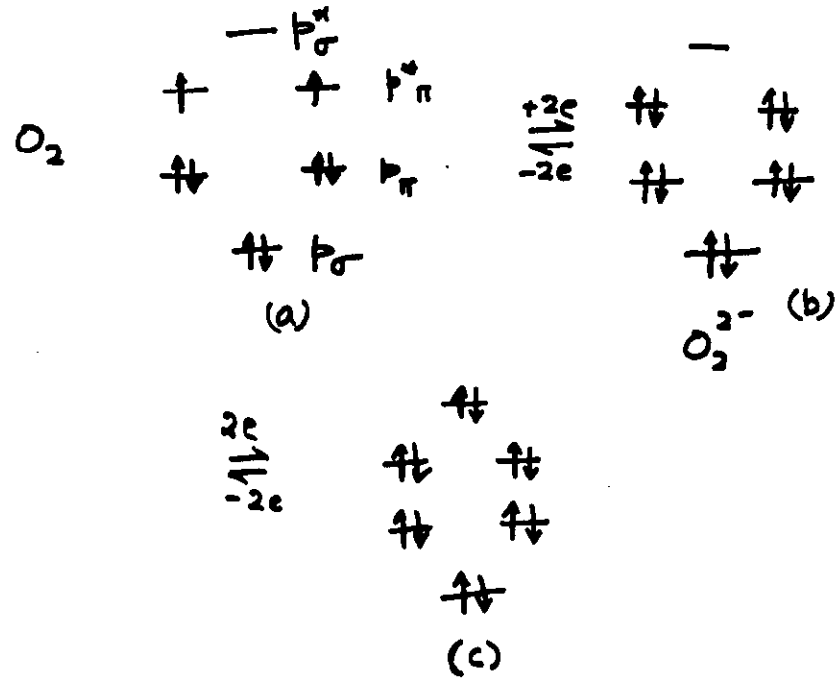
10eV peak in all Cu(II) compounds with strong hybridisation eg. La_2CuO_4, Ca_2CuO_3. Nd_2CuO_4 etc. (Sreedhar and Ganguly unpublished)

O^- ?

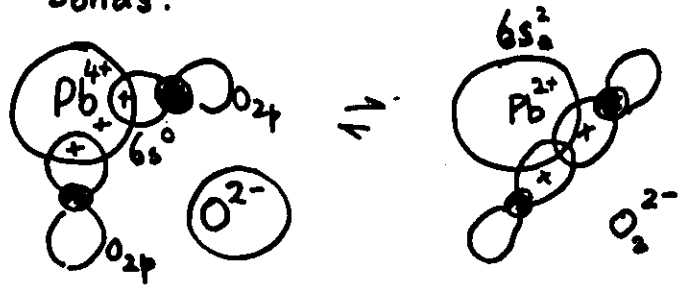
XPS Valence nearly the same in all copper (II) oxides.

$3d^9$ level located inside O2p band

Can Cu^{3+} ions be created



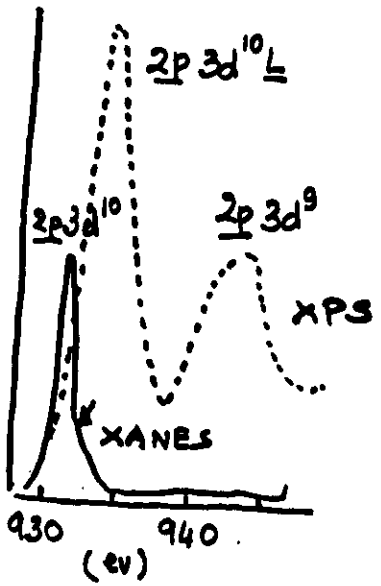
Top of valence band anti-bonding in character. holes in valence band creates bonds. O-O bonds vs Cu-O bonds. If Cu^{2+}; Cu-O bonds. If Cu^{1+} O-O bonds?



No Cu^{3+} in $YBa_2Cu_3O_7$

Sarma, Sreedhar, Ganguly, Rao. Phys. Rev. 1987 from absence of shift of Cu $2p_{3/2}$ binding energy.

Bianconi et al through XPS and $L_{2,3}$ XANES studies ($2p\,3d^n \rightarrow \underline{2p}\,3d^{n+1}$) (Trieste meeting, 1987)



XANES shows no $\underline{2p}\,3d^9$ final state hence no $2p3d^9_f$ (Cu^{3+}) initial state.

Instead $\underline{2p}\,3d^{10}\underline{L}$ (holes)

feature

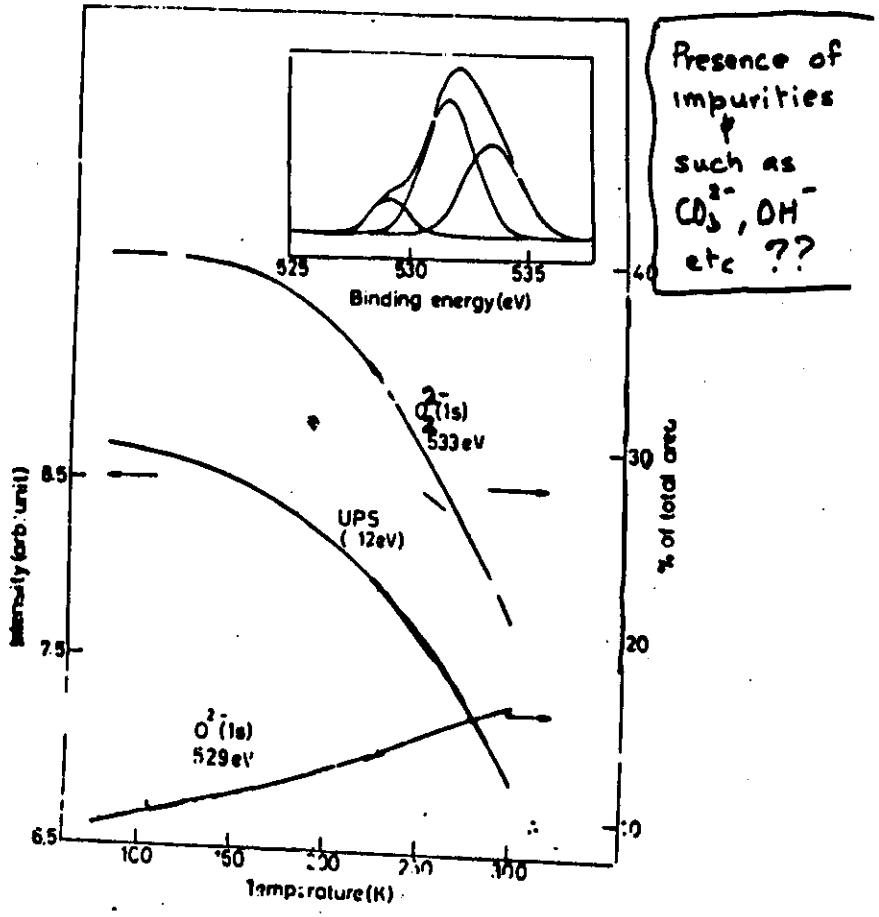
$\underline{2p}_{\#}\,3d^9\underline{L} \rightarrow \underline{2p}\,3d^{10}\underline{L}$

DO THE LIGAND HOLES DIMERISE

$2O^- \rightleftharpoons O_2^{2-}$ (peroxide)

O1s Band in $YBa_2Cu_3O_7$

Is O^{2-} (528ev), O^- 531eV, O_2^{2-} 553 eV ?



Presence of impurities such as CO_3^{2-}, OH^- etc ??

FIG. 2

Temperature-variation of the 529 and 533 eV features in O(1s) level due to O^{2-} and O_2^{2-} -type species respectively in the X-ray photoelectron spectrum. Change in intensity of the Fermi spectrum at 2 eV binding energy due to O^{2-} formation is also shown. Inset shows the O(1s) level at 80K as three Gaussians fitted by a least-squared-error method.

Sarma et al. [redacted]. (1987) BSL 2371 (1988)
Phys Rev

Rao et al MRB
Mater. Res. Bull. (1987)

Is Cu^{3+} stable in oxides under favourable conditions

$La_2Li_{0.5}M_{0.5}O_4$ ($M = Co^{3+}, Ni^{3+}, Cu^{3+}$)

shows systematics consistent with existence of diamagnetic Cu^{3+} ions ($t_{2g}^6, d_{x^2-y^2}^0 d_{z^2}^0$)

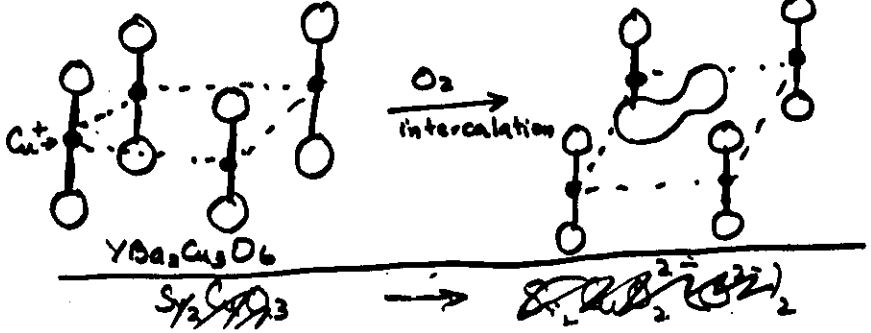
systematics consistent with presence of Cu^{3+}

	c/a	χ_{300K}	ν_{M-O}	Opt.
Co^{3+}	3·26	dia	664	480nm 520nm
Ni^{3+}	3·35	$\mu_{eff} = 1·73$	680	505nm. 630nm
Cu^{3+}	3·54	dia	694	580nm 7800nm

Li NMR same in all the compounds

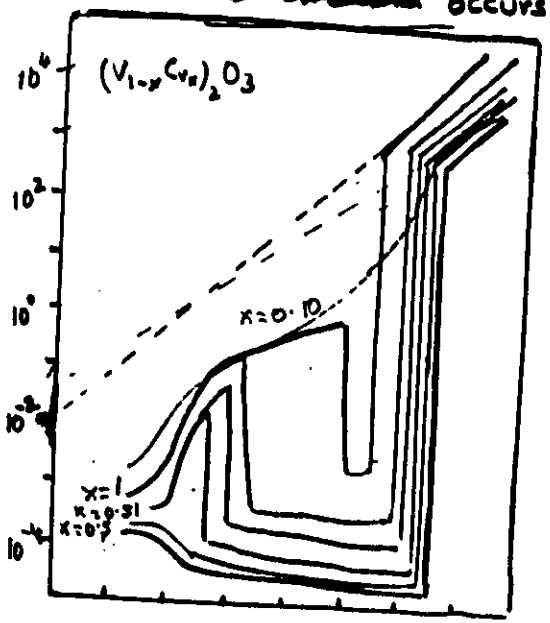
WHY SHOULD WE NOT GET Cu^{3+} in OXIDES especially since $Cu^{3+}-O^{2-}$ attractive energy is more than $Cu^{2+}-O^{-}$ } when no. of O ions conserve $La_{2x}Sr_xCuO_4$

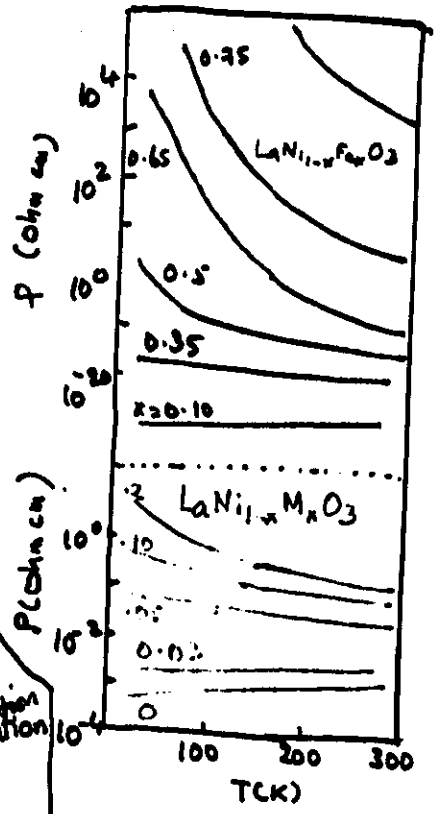
So we would do have a situation where $Cu^{2+}-O^{2-}$ becomes $Cu^{2+}-O_2^{2-}$ on oxygen incorporation. where no loss of attractive energy is involved

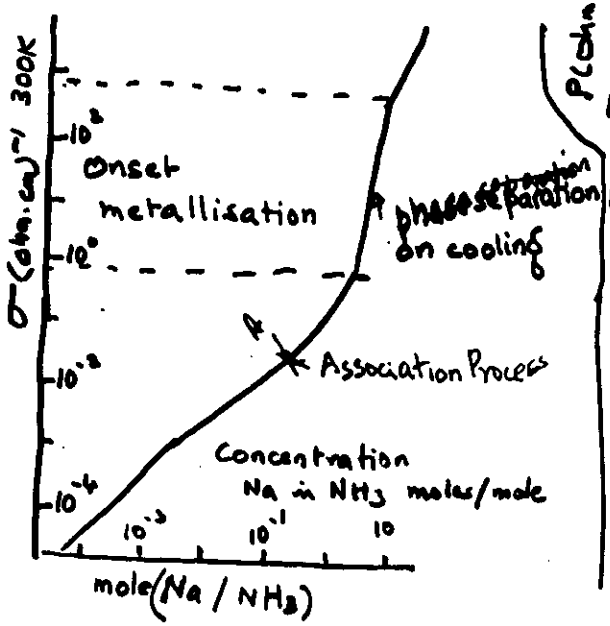


METAL-INSULATOR TRANSITION

IN CHANGE OF SIGN IN TCR occurs when $\rho \sim 2\times10^{-2}$ ohm. cm.







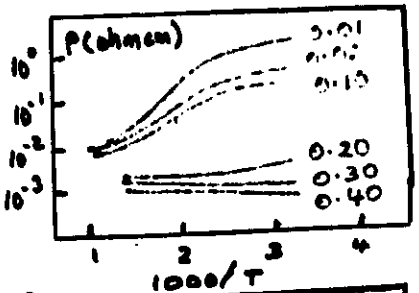
Note region between $\rho = 10^{-1} - 10^{-3}$ ohm cm may also be considered to be metallic or associated with metallisation.

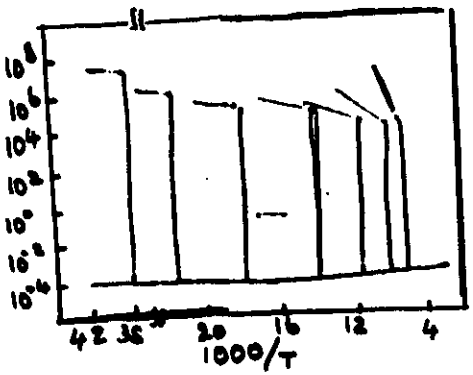
see Rao & Edwards Metallic and non-metallic states of matter. Taylor & Francis, London (1985)

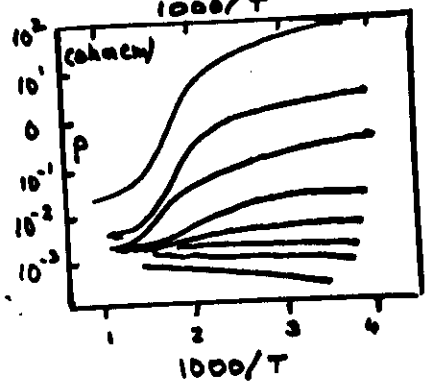
TCR changes sign
when $\rho \sim 10^{-3}$ ohm.cm. both as
function of temp. and concentration.

$V_{2-2y}O_3$

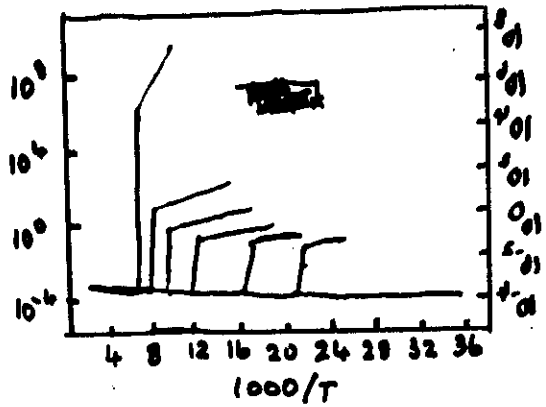
$La_{1-x}Sr_xCrO_3$







$La_{1-x}Sr_xVO_3$



$(Ti_xV_{1-x})_2O_3$.

METAL - INSULATOR TRANSITION

see Hirsch. Comments Cond. Mat Hev. Phys. 15, 249 (1987) and references therein

∴ Why is NiO not a metal

$Ni^+ \xleftarrow{+e} Ni^{2+} \longrightarrow Ni^{3+} + e$ energy I

energy E

$U = I - E$

$U \rightarrow \frac{1}{2}(B_1 + B_2)$ if positive
energy gap exists
if not - metal

Si and Ge became metals by doping

doping with phosphorus:
donor / equivalent to swollen hydrogen atom

METAL - INSULATOR TRANSITION AS FUNCTION OF DOPING - function of r

Electron gas screens positive charge of donors

$$V(r) = \frac{e^2}{\varepsilon r}\exp(-qr)$$

ε = dielectric constant $\left(\frac{1}{q^2} = \frac{4\pi e^2}{\varepsilon}\cdot\frac{3n}{2\varepsilon_F}\right)$

q = Thomas. Fermi screening constant

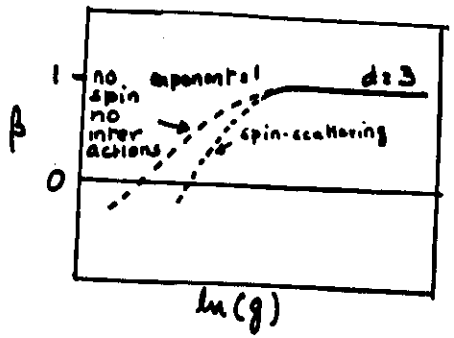
$n_c^{1/3} a_H = 0.25$ $a_H = \hbar^2\varepsilon/me^2$

a_H : Bohr radius of donor

RANDOMNESS

Absence of diffusion on random lattices

T=0 Theory
Scaling theory



$G(L)$ = conductance

$g(L) = G(L)/(e^2/h)$

$\beta = [d(g)/dL][L/g]$

$L = (D/f)^{1/2}$

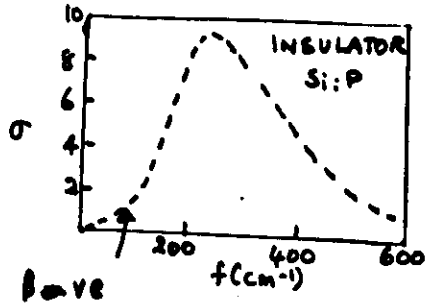
D = electron diffusion coefficient

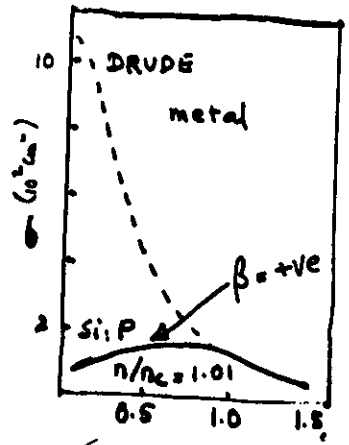
f = frequency

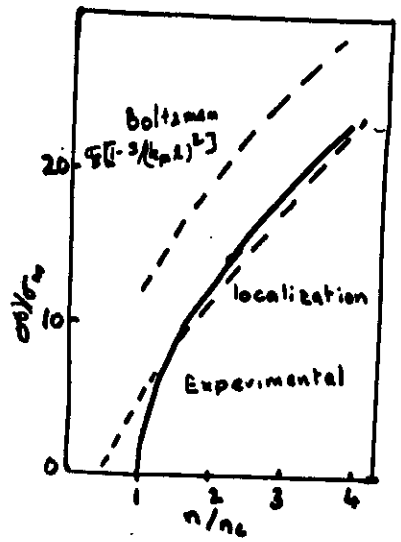
β negative insulator

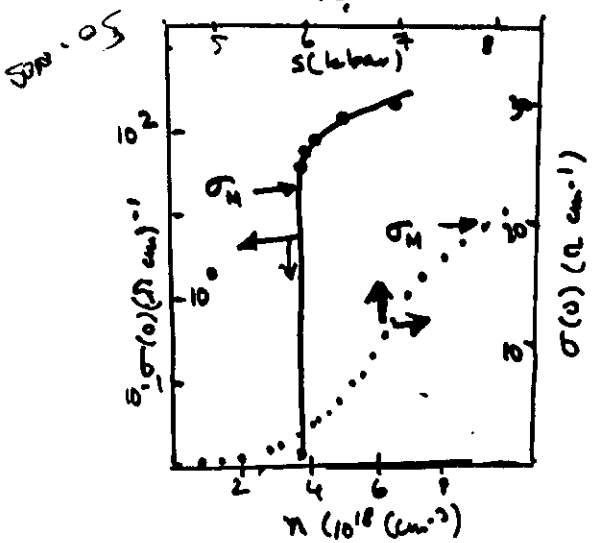
+ve metal

$\beta = 0$ defines critical conductance ($= 0$)









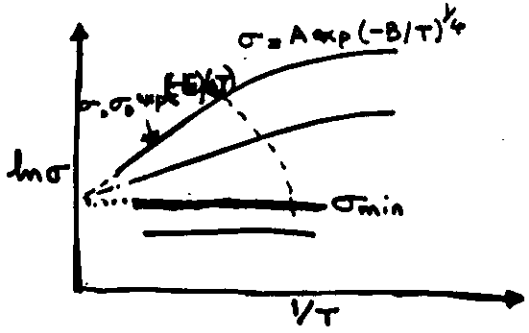
Mott's minimum metallic Conductivity

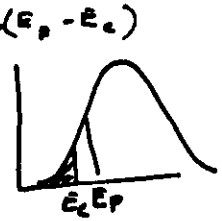
Mean free path cannot be less than interatomic spacing

$$\sigma = \frac{1}{3}\frac{e^2}{\hbar a} \approx 5000\ (\Omega^{-1}cm^{-1}) \qquad a = 3\text{-}4A^\circ$$

From Anderson localisation criterion

$$\sigma_{min} : \frac{1}{\rho} = \frac{1}{3}\frac{e^2}{\hbar a} \approx .03\frac{e^2}{\hbar a} \approx 500\ \Omega^{-1}cm^{-1} \qquad a = 3.4A^\circ$$





From Scaling Theory

$$\sigma = 0.03\, e^2/\hbar\xi$$

ξ = localisation length for $E_F - E_c$ below mobility edge

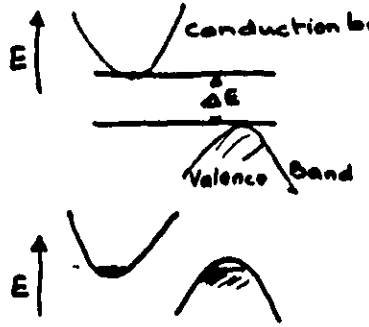
If L_i is inelastic diffusion length.

$$\sigma = 0.03\, e^2/\hbar L_i \quad \text{when } L_i < \xi$$

For Temp. dependence of L_i determines σ

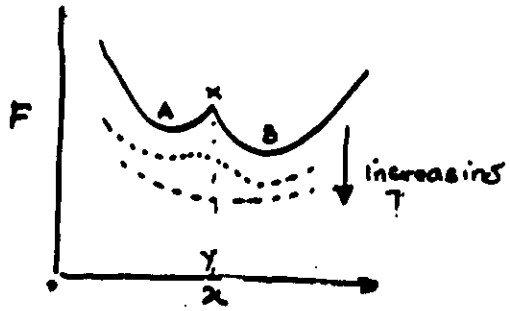
$L_i \propto (T)^{-1}$ or $(T^{-1/2})$

as E_F approaches E_c negative TCR ?



Band-crossing M-I transition is discontinuous

FOR DISCONINUOUS TRANSITION THE PLOT OF FREE ENERGY AGAINST ANY VARIABLE x AFFECTING THE BAND GAP MUST SHOW A KINK AT TRANSITION



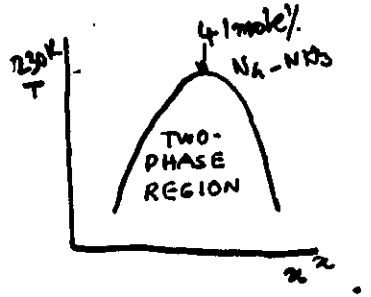
$Na_x WO_3$

$x = .20 \ldots .8$

$K_{0.30} MoO_3$

$K_{0.23} MoO_3$

$La Ni_{1-x} Al_x O_3$.



Possibility of phase segregation in composition-controlled metal insulator transition.

$\sigma = ne^2 D/k_B T = ne^2 \nu a_0^2 / k_B T : ne^2 \nu_0 a_0^2 \exp(-\Delta/k_B T)$

frequency of hopping given from the exchange energy

$J = h\nu$

From diffusion equations (Zener, 1951)

$$\sigma = \alpha \frac{k T_c}{T} \cdot \frac{e^2}{\hbar a}$$

$\sigma = 10^{+3}$ ohm^{-1} cm^{-1} for $\nu \sim 10^{14}$ sec^{-1} $\nu > \omega_0$

$$\sigma = \frac{ne^2\tau}{m^*}$$

$\tau \sim 10^{-14}$ sec, $m^* \sim 10$

$\sigma = 10^2$ ohm^{-1} cm^{-1} OXIDES

$\tau \sim 10^{-14}$ sec $m^* \sim 1$

$\sigma = 10^4$ ohm^{-1} cm^{-1}

amorphous metals

MOOIJ CRITERION

$\sigma = 10^1$ ohm^{-1} cm^{-1}

$\frac{\tau}{m^*} = 10^{-13}$, $\tau = 10^{-14}$ sec, $m^* = 100\, m_e$

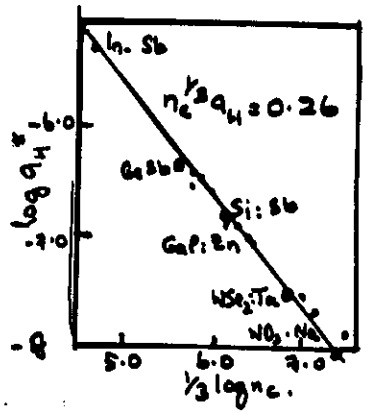
OR

$\nu = 10^{12}$ sec^{-1}

$\nu < \omega_0$ (vibrational frequency)

between 10^1 & 10^3 ohm^{-1} cm^{-1} residence time is comparable to transit time

correlated hopping.



Edwards & Sienko.
Phys. Rw. B17, 2575 (1978)

HERZFELD CRITERION

Edwards & Sienko Accs. Chem. Res. 15, 87 (1982)

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} n\alpha_0 \qquad n \to n_c = \frac{3}{(4\pi\alpha_0)}, \quad \varepsilon \to \infty$$

$\vec{p} = e\vec{r}$ = dipole associated with displacement $\vec{r}$

$\vec{E}^0$ = external electric field.

$$m\ddot{\vec{p}} + m\omega_0^2 \vec{p} = e^2 E^0$$

ω_0 = characteristic frequency

Effective field (Lorentz field) $\vec{E}^{Lo} = \vec{E} + \left(\frac{4\pi}{3}\right) n \langle \vec{p} \rangle$

$$m\ddot{p} = e^2 E - m\omega_0^2 \vec{p} + \left(\frac{4\pi}{3}\right) n e^2 \langle \vec{p} \rangle$$

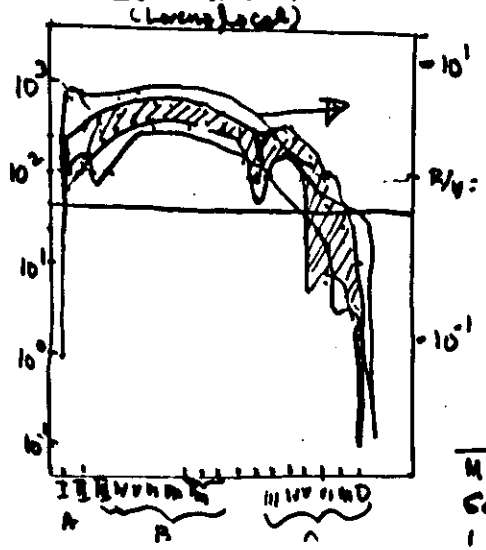
$$(m/q)\ddot{p} = F$$

$\langle F \rangle = 0$ (bound valence electron)

$$\langle p \rangle = \frac{\alpha_0}{1 - (4\pi/3) n\alpha_0} \vec{E}$$

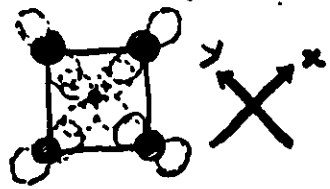
$$\alpha_0 = e^2/(m\omega_0^2)$$

$$(\varepsilon - 1)/(\varepsilon + 2) = R/V \qquad R = \frac{4\pi N_A \alpha_0}{3}$$

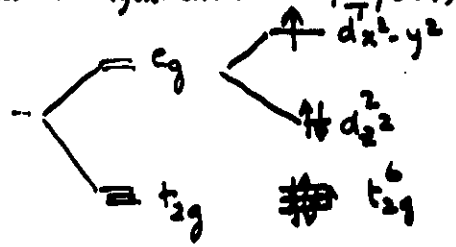


Minimum band width?
Ganguly Proc. Ind. Acad. Sci 96, 533 (1986)

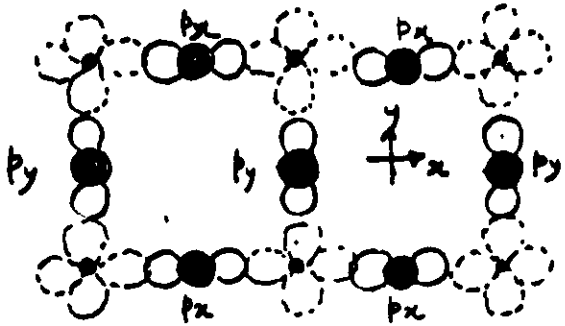
Structures built up from square-planar CuO_4 units (Müller-Buschbaum. Angew. Chem. 1977, 16, 674)



● - oxygen anion
● - copper ion
- $d_{x^2-y^2}$ orbital
- O 2p orbital

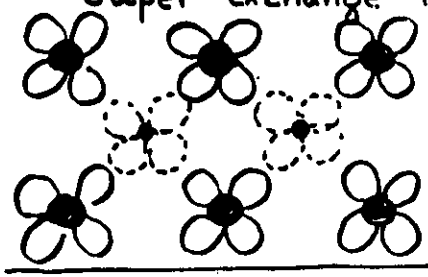


Super exchange involving non-orthogonal orbitals
180° Cu-O-Cu linkages.



ANTIFERROMAG.
(H_2)

Super exchange involving orthogonal orbitals
90° Cu-O-Cu linkages



FERROMAG.
(O_2)

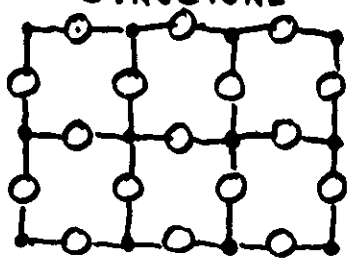
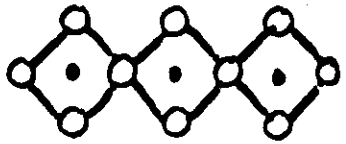
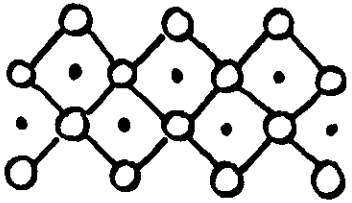
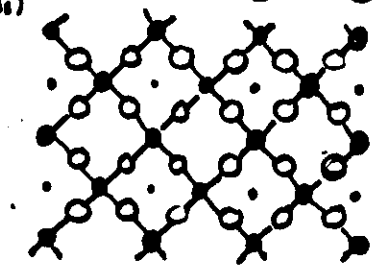
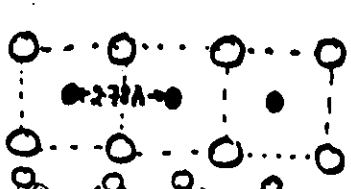
$$\chi = \frac{C}{T - \theta}$$

Curie-Weiss law

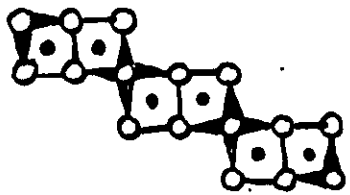
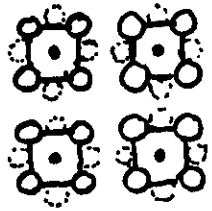
θ +ve ferro
−ve antiferro

$C = 0.37$ for Cu^{2+} spin only

$$\chi_\perp = \frac{2}{3}\chi(T_N) = \frac{C}{3T_N}$$

COMPOUND	STRUCTURE	Magnetic Susceptibility (g.at.Cu)	T_N (likely)
$Sr_2Cu_2O_2Cl_2$ Cu-O distance = 1.98 Å		~200×10⁻⁶ emu/ (300K). Temp. dependent C = .03	
Nd_2CuO_4 1.97 Å°	»	very small from Cu^{2+} ($T < 650K$)	650 K log fit 1/T contribution from Cu^{2+}
Ca_2CuO_3		temp. ind. Susceptibility 120×10⁻⁶ emu	1000K from $\chi(T=0)$ $\chi_\perp = \frac{C}{3T_N}$
Sr_2CuO_3	»	temp. dependent C = .03	
$SrCuO_2$		temp. ind. 100×10⁻⁶ emu	
$MgCu_2O_3$ (long + short bonds) ∥ ⊥		strong temp. dependence $\chi > \frac{C}{T^{0.5}}$	
$Ba_2Cu_3O_4Cl_2$		C and Θ strongly temp. dependent for 100<T<300 K C = 0.20 at T = 300K	60K from χ_{max}
Li_2CuO_2	 2.78 Å	Curie-Weiss C = .37 Θ = −40K not ferromagnetic	< 12K
$BaCuO_2$		C = .37, Θ = 80K Anomaly at 80K	not ferromagnetic.

NO EPR SIGNAL DETECTABLE IN ANY OF THESE COMPOUNDS (80,-300K)

$Y_2Cu_2O_5$ Cu^{2+} in nearly tetrahedral		Curie Weiss T > 80K C = .57 Θ = 40	< 12 K
Y_2BaCuO_5 (2.04 Å°) " "La_2BaCuO_5" (1.87 Å°)		Curie law (T > 100K) C = .37 Y χ_{max} 30K La sharp increase at 40K, field dependence	30 - 40K
Bi_2CuO_4 Cu-Cu = 2.85 Å		C-W law above 200K C = 1.73, Θ = 40K Bonner-Fischer 1d Heisenberg from T = 50K to T = 200K χ_{max} at 50K Fit to $\chi = \frac{0.042}{T} + \frac{0.67}{1+\frac{2}{3}\exp\left(\frac{100}{4T}\right)}$	T_N = 50K

ALL SHOW STRONG EPR SIGNALS

$Cu^{2+} \rightleftharpoons Cu^{1+} + Cu^{3+}$ d^8 low spin

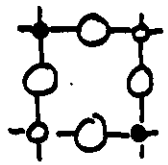
IN Y_2BaCuO_5, "La_2BaCuO_5", Bi_2CuO_4, Cu^{2+} IONS ARE NOT EXACTLY IN SQUARE-PLANAR COORDINATION

CONCLUSIONS FROM MAGNETIC SUSCEPTIBILITY STUDIES

a) Compounds with extended Cu-O-Cu 180° linear interactions have very small susceptibilities. probably due to high magnetic (antiferro) coupling temperatures. when it involves short (≤ 2.00 Å) Cu-O bonds

(b) Compounds with 90° Cu-O-Cu interactions show strong temperature-dependence of the susceptibility. Strong Cu-O overlap does not lead to disappearance of moment

(c) Compounds with only Cu-O-O-Cu interactions show indications of antiferromagnetic coupling below 30-50 K.



nnn frustration

interplanar Cu-O-O-Cu Bose condensation

(d) Reluctance to form a ferromagnetic ground state despite fairly high paramagnetic Curie temperature (θ = 40K, $Y_2Cu_2O_5$; θ = 80K for $BaCuO_2$)

(e) S = ½ Heisenberg in Bi_2CuO_4
Sreedhar et. al. J. Phys. C. 1987

Sreedhar & Ganguly, Inorg. Chem. in press

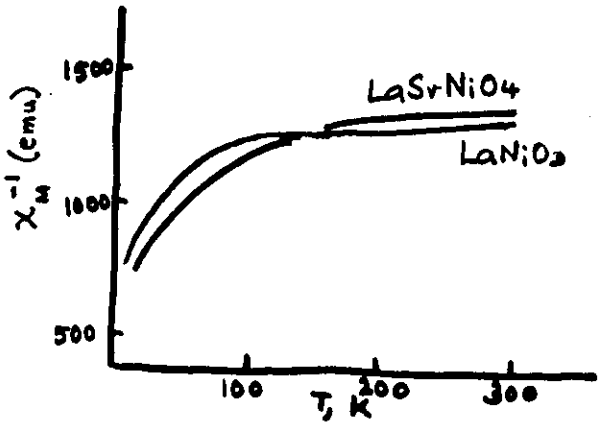
TWO DIMENSIONS vs THREE DIMENSION

$SrABO_4$ (ABO_3)

P. Ganguly. Proc. Ind. Natn. Sci. Acad. 52A, 1986, p.135

MAGNETIC PROPERTIES UNCHANGED

Except for decrease in θ (T_c, T_N) consistent with decrease in number of nearest neighbours



EXAMPLES

$LaNiO_3$	$SrLaNiO_4$
$La_{0.5}Sr_{0.5}CoO_3$	$Sr_{1.5}La_{0.5}CoO_4$
$La_{0.5}Sr_{0.5}MnO_3$	$Sr_{1.5}La_{0.5}MnO_4$
$LaFeO_3$	$SrLaFeO_4$

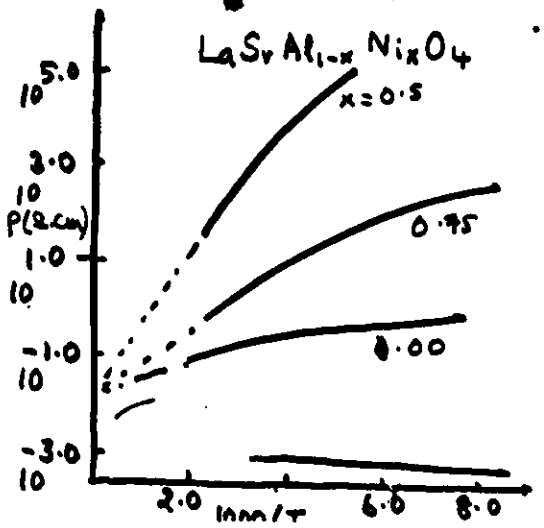
NOTE in copper compounds (High T_c)

$\chi \approx \frac{1}{6} \chi_{LaSrNiO_4}$

ELEC. TRANSPORT PROPERTIES CHANGED.

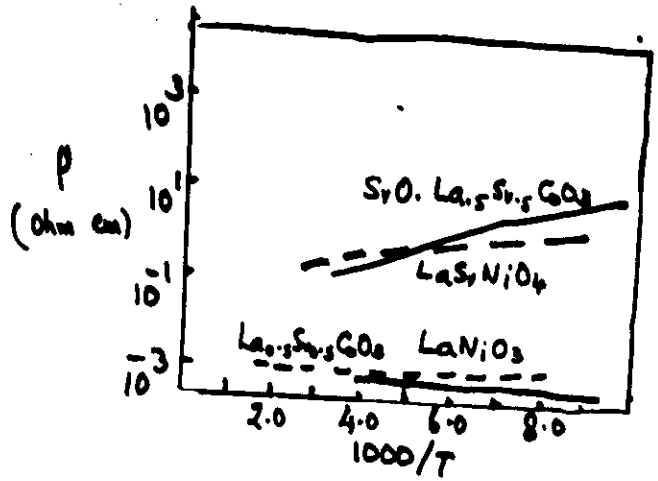
WORST $BaPbO_3$ $\rho \sim 10^{-4}\,\Omega$.cm Ba_2PbO_4 $> 10^{10}\,\Omega$.cm.

BEST Sr_2RuO_4 $\rho \sim 10^{-4}\,\Omega$.cm Sr_2RuO_4 $> 10^{-1}\,\Omega$ cm (T = 80K)

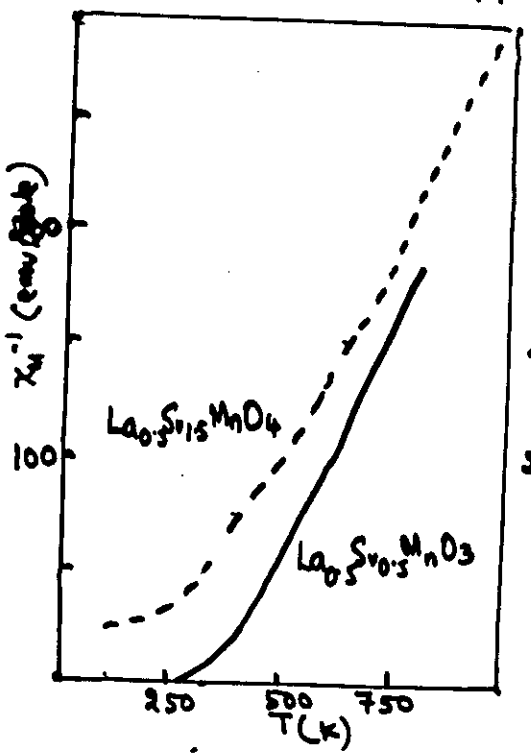


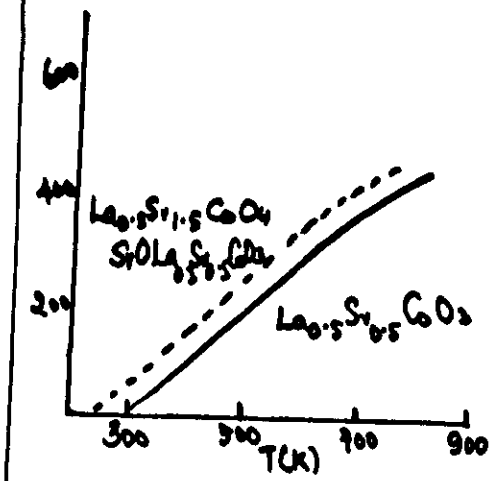
Transfer integral, t, is unaffected but 'polaronic effects reduce bandwidth that affects electrical transport.

MORAL: Require higher t for metallisation



MAGNETIC PROPERTIES NOT AFFECTED MUCH (transfer integral)
TRANSPORT PROPERTIES AFFECTED DRAMATICALLY (polaronic effects)





CONCLUSIONS

i) High AF ordering temperature possible. Favours $Cu^{2+}\uparrow$ $Cu^{2+}\downarrow$ pairing

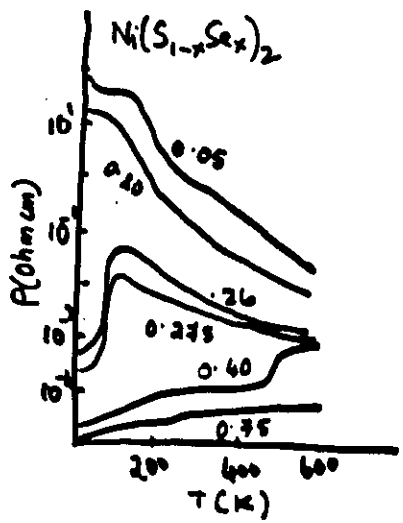
ii) Holes in O^{2-} and formation of O_2^{2-} possible $2O^{2-} \underset{+2e}{\overset{-2e}{\rightleftharpoons}} O_2^{2-}$

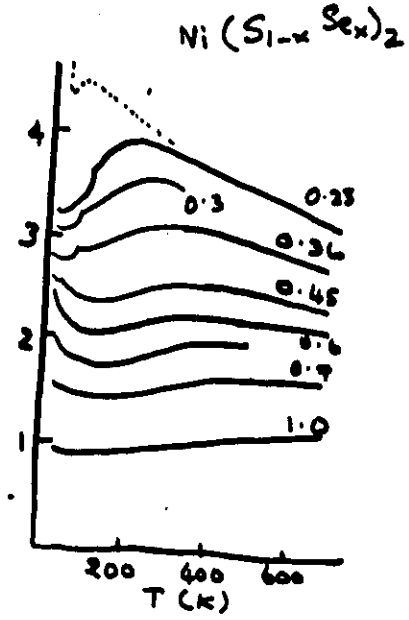
iii) Possibility of $Cu^{1+}, Cu^{3+} \rightleftharpoons Cu^{3+}, Cu^{1+}$
short Cu-O distance d^{10} d^8 d^9 d^{10}

iv) Three dimensionality or next-nearest neighbour interactions near 30-50K (50 K, $BaCuO_2$)

v) Cu-O system possible because above factors may be satisfied.
La^{3+}, Y^{3+} favours Cu^{1+}, ~~not~~ (good)
K^+ favours Cu^{2+} (not good)
$KCu^{3+}O_2$, $SrCu^{2+}O_2$, $YCu^{1+}O_2$

vi) 2d ? d^9 in octahedra,
Ni^{1+} in chalcogenides (S, Se, Te)





From. Wilson.
"Metallic non-metallic states of matter"
Eds. Rao and Edwards. P.P.
Taylor and Francis, London (1985)