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SMR/455 - 4

EXPERIMENTAL WORKSHOP ON HIGH TEMPERATURE SUPERCONDUCTORS & RELATED MATERIALS (BASIC ACTIVITIES)

12 - 30 MARCH 1990

METAL OXIDES: NORMAL-STATE PROPERTIES

LECTURE II

TRANSITION-METAL (d-BLOCK) OXIDES

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LECTURE II

TRANSITION-METAL (d-BLOCK) OXIDES

Band theory applicable to outer s and p electrons

Hamiltonian for d^n

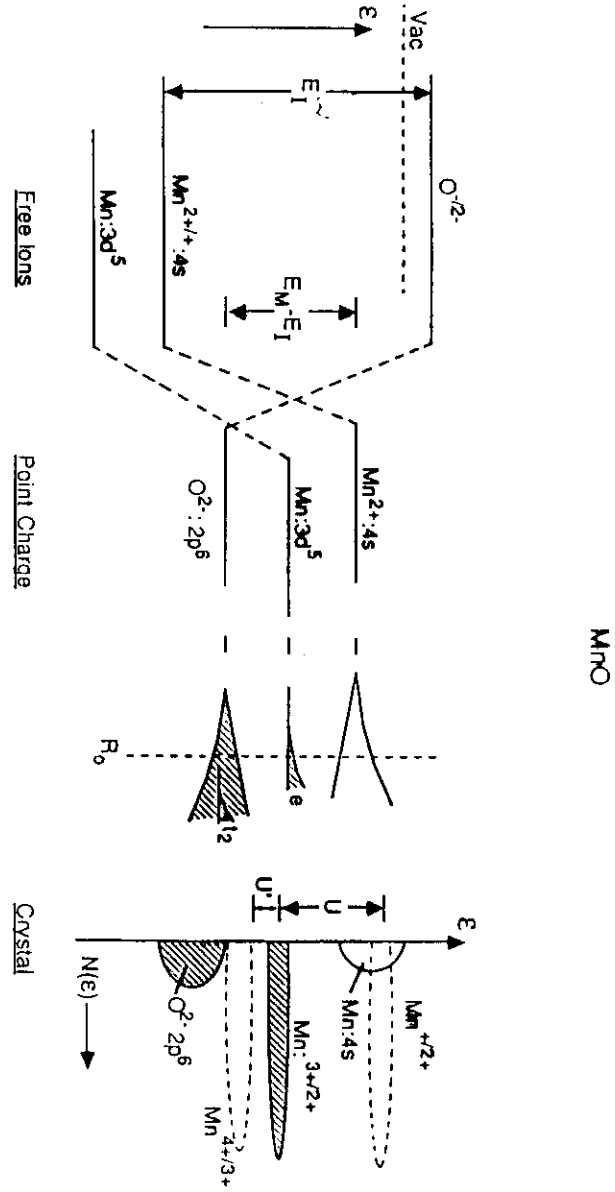
$$H=H_0+(V_{el}+\Delta_c)+(\Delta_{LS}+\Delta_{nc}+H_Z)$$

Procedure:

First, construct crystal-field wave functions; these contain covalent mixing with O-2s and 2p.

Second, consider intermetal interactions on an array of equivalent metal atoms. The nearest-neighbor interaction parameters $b\sim\varepsilon(\Psi_i,\Psi_j)$ utilize the crystal-field Ψ's. Properties depend upon relative magnitudes of

$W \approx 2zb$	*versus*	U or U'
$\tau_h \approx \hbar/zb$	*versus*	ω_R^{-1}
E_M	*versus*	E_I



ATOMIC d WAVEFUNCTIONS

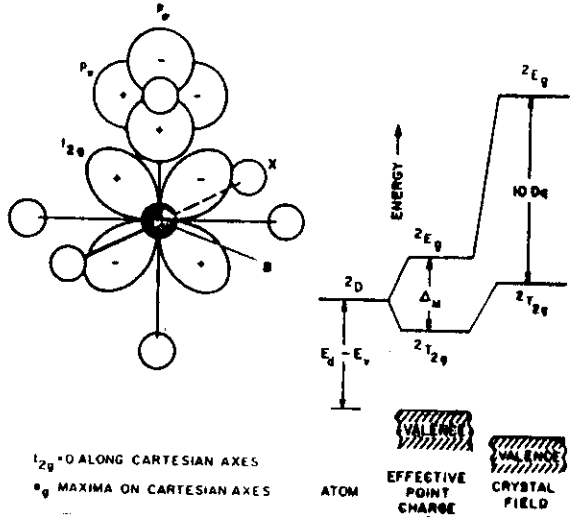
$(L_z f = -i\hbar\partial f/\partial\phi = m\hbar f)$

$f_0 \sim \{(z^2-x^2) + (z^2-y^2)\}/r^2 = 3\cos^2\theta - 1;$ $\quad m = 0$

$f_{\pm1} \sim 2(zx \pm iyz)/r^2 = \sin 2\theta \exp(\pm i\phi);$ $\quad m = \pm 1$

$f_{\pm2} \sim \{(x^2 - y^2) \pm ixy\}/r^2 = \sin^2\theta \exp(\pm i2\phi);$ $\quad m = \pm 2$

OCTAHEDRAL-SITE WAVEFUNCTIONS



$$\Psi_e = N_e (f_e - \lambda_s\phi_s - \lambda_\sigma\phi_\sigma)$$

$$\Psi_t = N_t (f_t - \lambda_\pi\phi_\pi)$$

Where ϕ are symmetrized O-2s, 2p

$\lambda = b^{ca}/\Delta E$ are covalent-mixing parameters.

$$10Dq = \Delta_c = \Delta_m + \frac{1}{2}(\lambda_\sigma^2 - \lambda_\pi^2)(E_M - E_I) + \frac{1}{2}\lambda_s^2\Delta E \qquad (\lambda_\pi < \lambda_\sigma)$$

$$U_{eff} = U' + \begin{cases} 0 \\ \Delta_c \\ \Delta_{ex} \end{cases} \quad \text{where} \quad \begin{cases} U' \text{ reduced by covalence} \\ \Lambda_{ex} \text{ reduced by covalence} \end{cases}$$

DISTINGUISHING d^n CONFIGURATIONS

Atomic U	Localized d^n	Itinerant d
Large	<——— 3d ———>	
Medium	<——— 4d ———>	
Small	<——5d ———>	

Note: b^{cc} larger for lighter 3d elements with lower velence.
b^{cac} larger for heavier 3d elements with higher velence.
$U_{eff} = U'$ for d^1, d^2 d^4 and low-spin d^5, d^7 configurations.

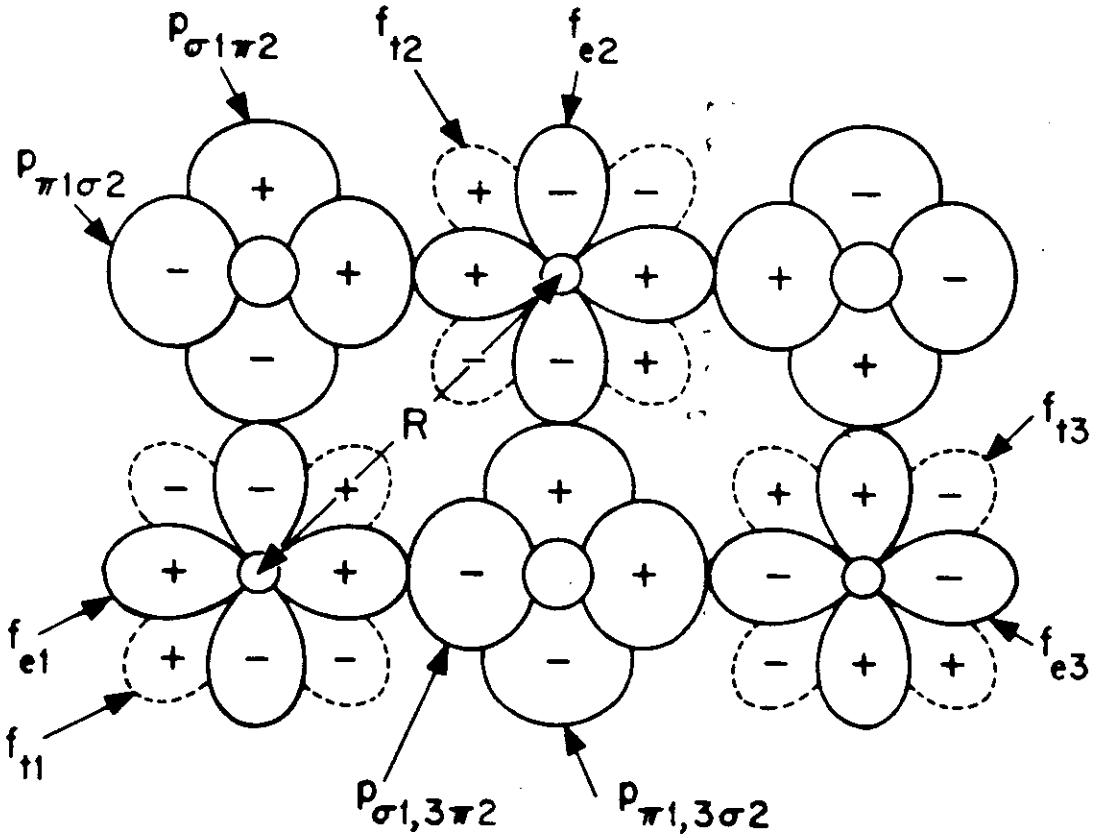
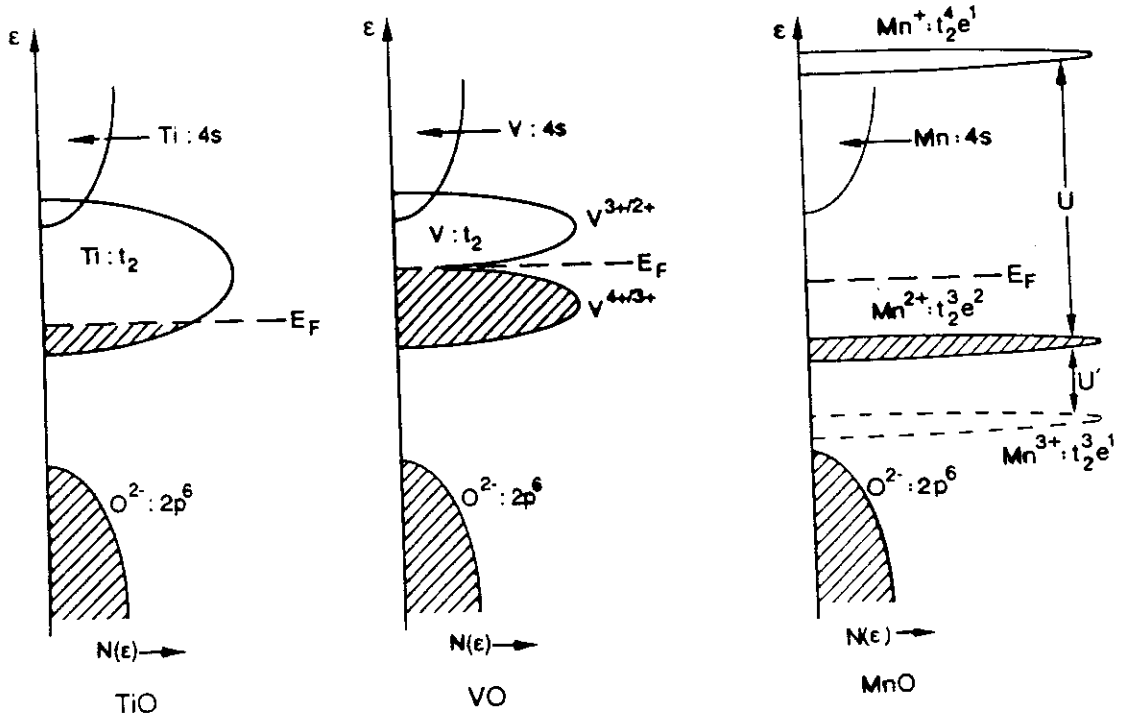


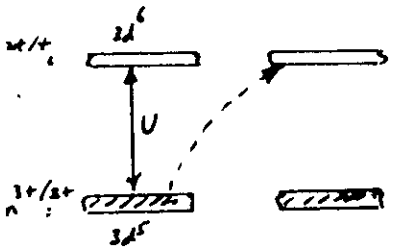
Fig. 14



Interatomic Interactions for Half-Filled Orbitals

Superexchange: $(W < U)$ — M-M or M-X-M

$$\begin{cases} \alpha = \alpha' \cos(\theta/2) + \beta' \sin(\theta/2) \\ \beta = -\alpha' \sin(\theta/2) + \beta' \cos(\theta/2) \end{cases}$$



$$\Delta\varepsilon = -|t^{\alpha\beta}|^2/U$$

$$= -\frac{b^2}{U}\sin^2\left(\frac{\theta}{2}\right)$$

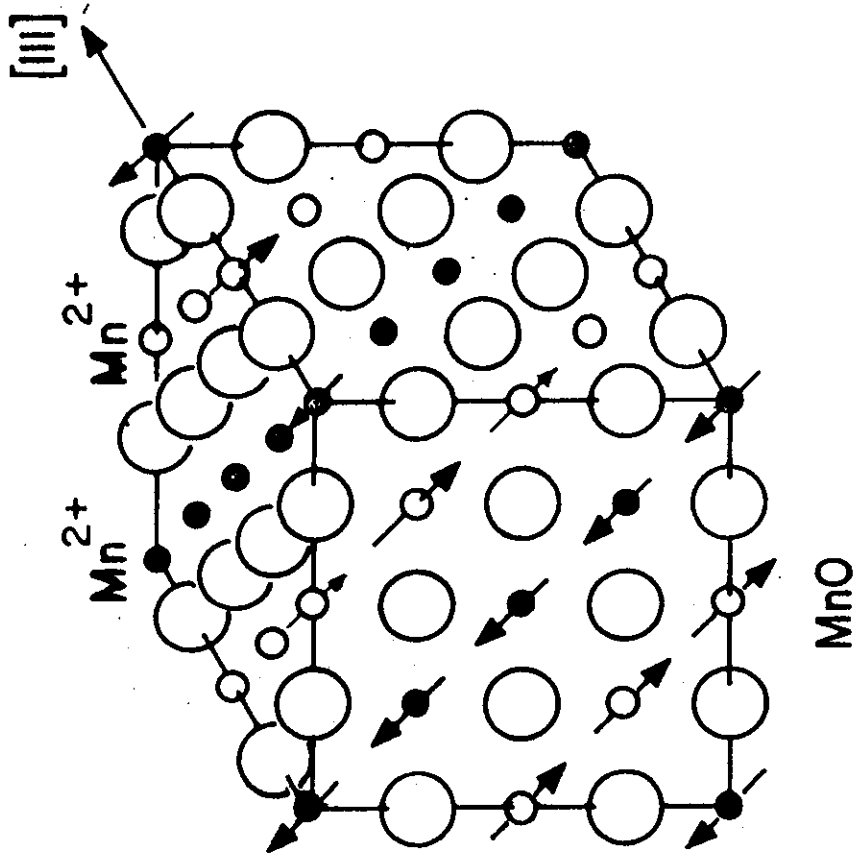
$$= \text{Const.} + \frac{b^2}{2U}\cos\theta$$

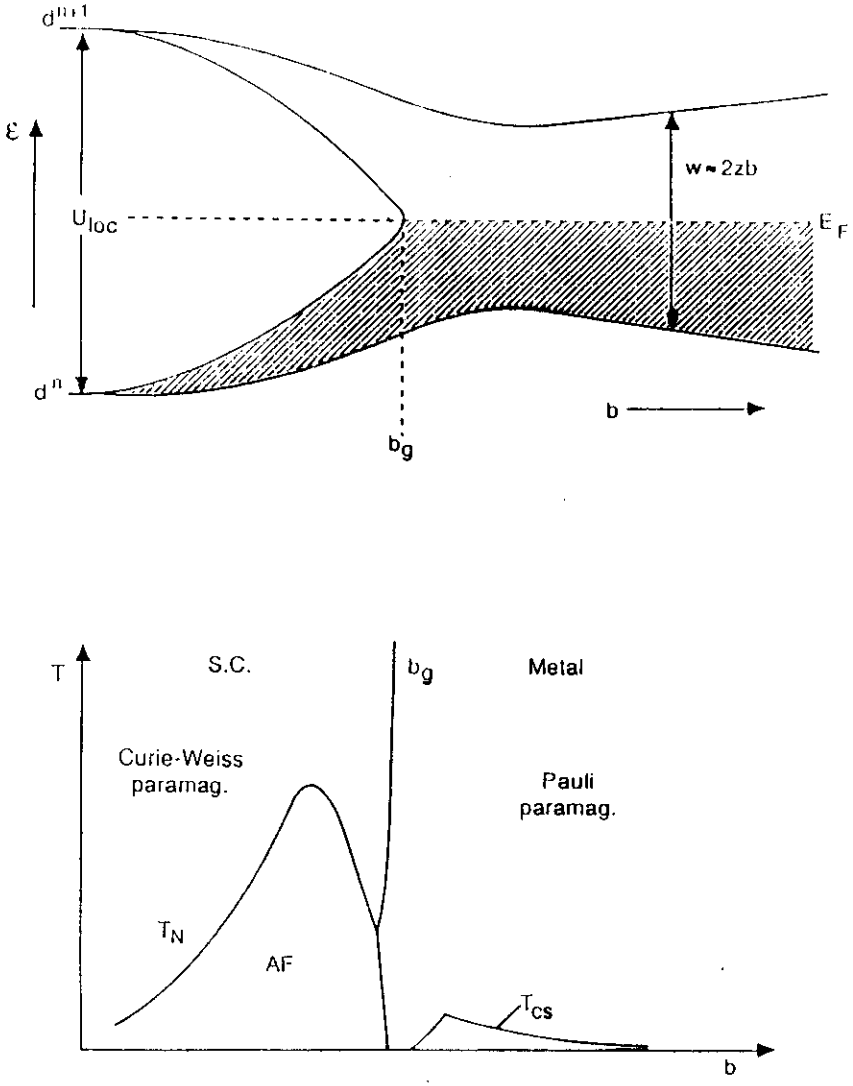
$$\Delta\varepsilon^{s}_{AB} = -2J_{AB}\,\underset{\sim}{S}_A \cdot \underset{\sim}{S}_B = \frac{b^2}{2U}\cos\theta$$

$$\therefore\ J_{AB} = -\frac{2b^2}{(45^\circ)U} < 0$$

Tight Binding: $(W > U)$

$$W \cong 12b \qquad b_{ij} \equiv (\psi_i, \mathcal{H}'\psi_j) \approx \varepsilon_{ij}(\psi_i|\psi_j)$$





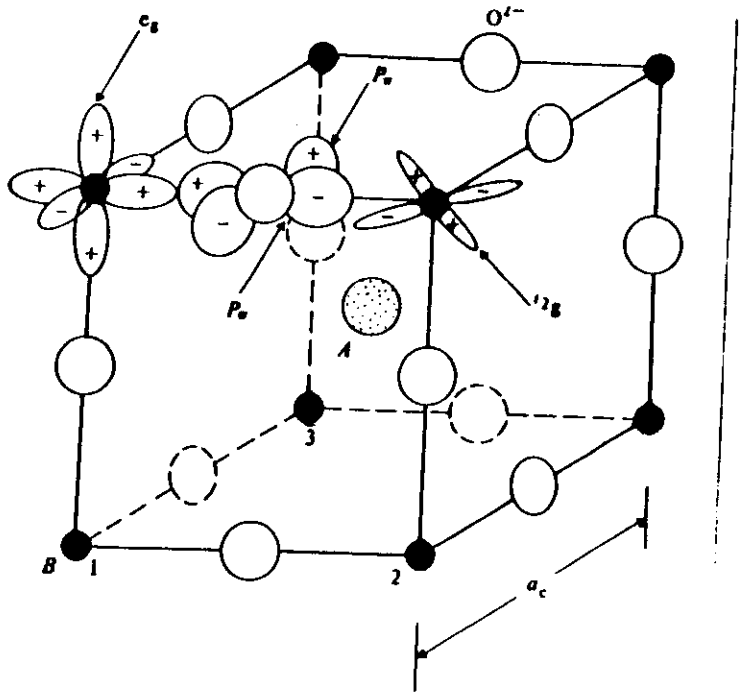


Fig. 3. The cubic-perovskite structure.

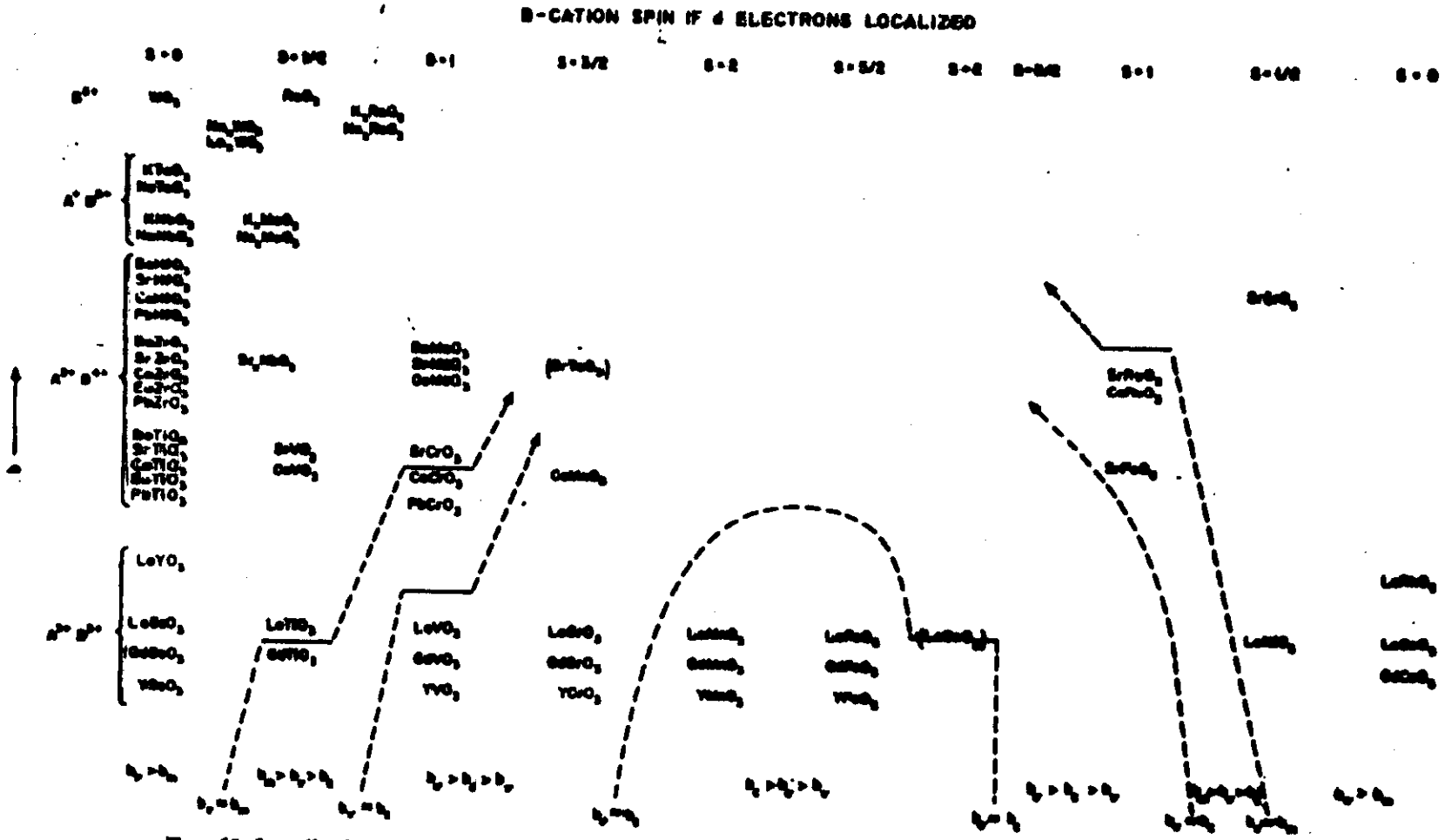


FIG. 65. Localized vs. collective *d* electrons in transition-metal oxides with the perovskite or ReO_3 structure.

MIXED VALENCE

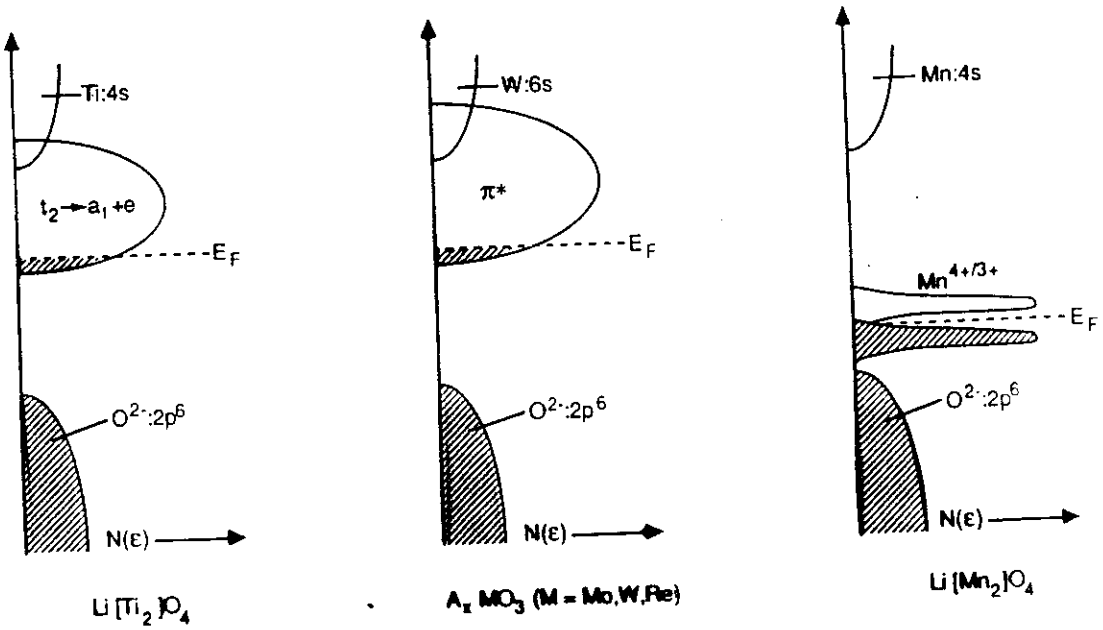
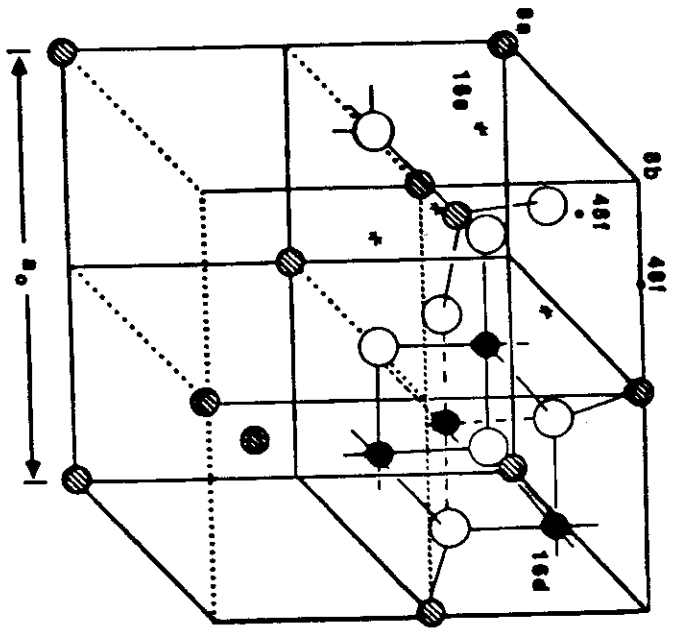


Fig. 17

$\tau_L < \omega_R^{-1}$

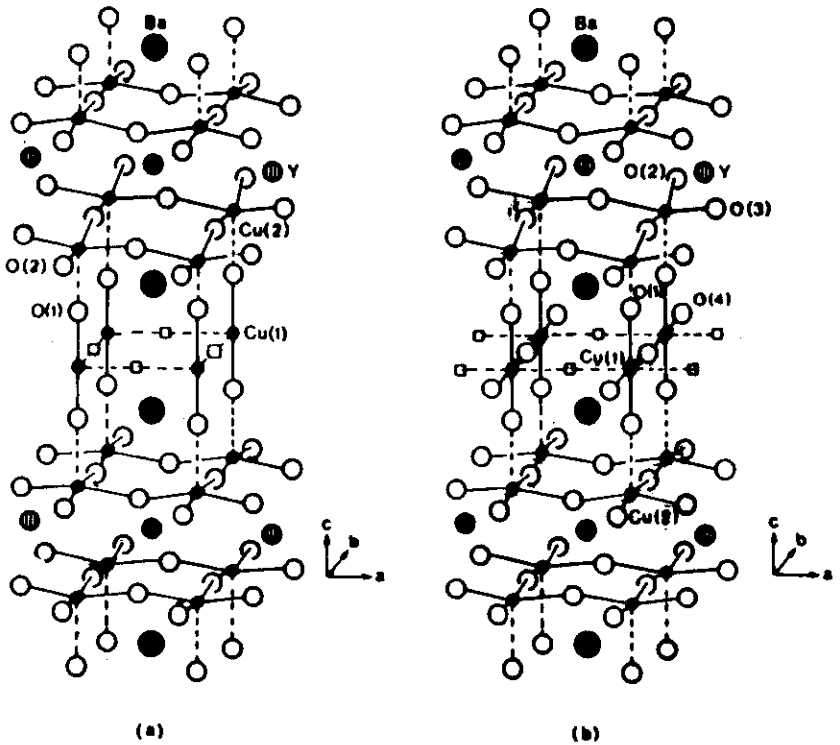
$\tau_L > \omega_R^{-1}$



$Li_{1+x}[V^{4+}_{1-x} V^{3+}_{1+x}]O_4 \quad 0 \le x \le 1$

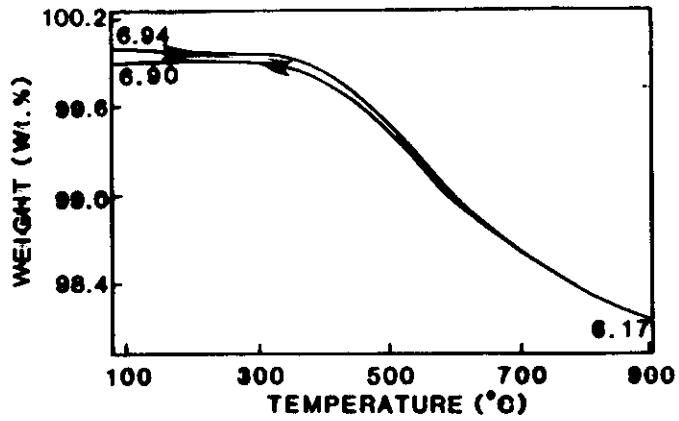
Mott ($x=0$) → AF insulator ($x=1$)

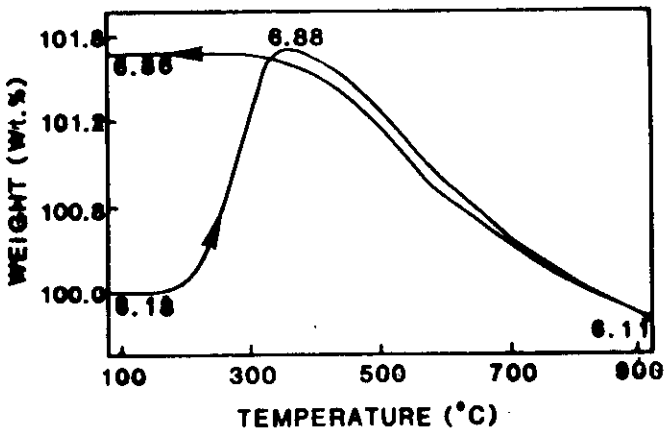
ρ_{imp} : Curie-Weiss for all x

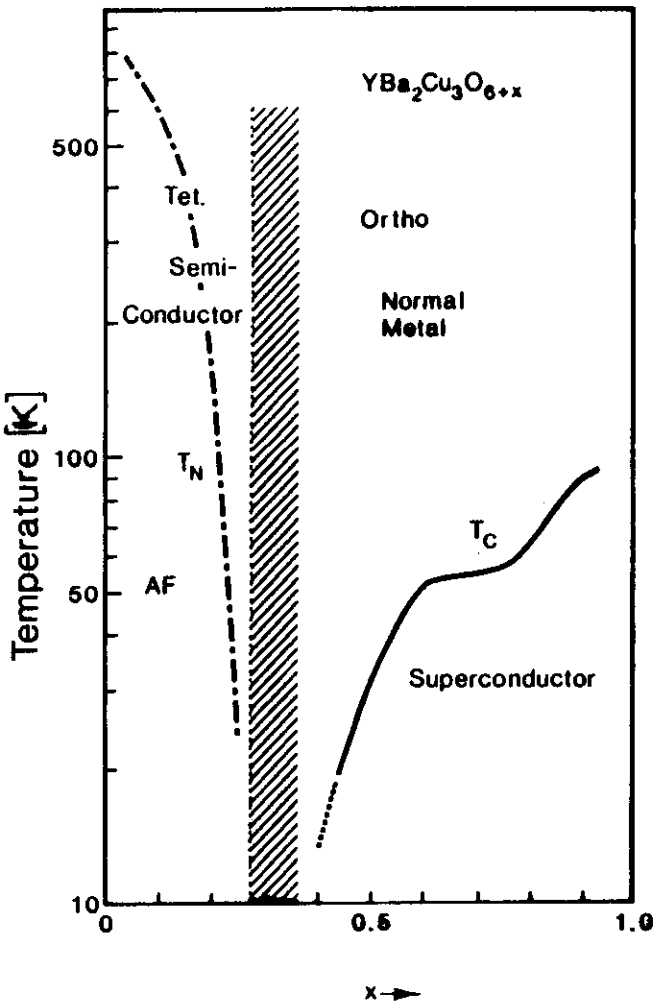


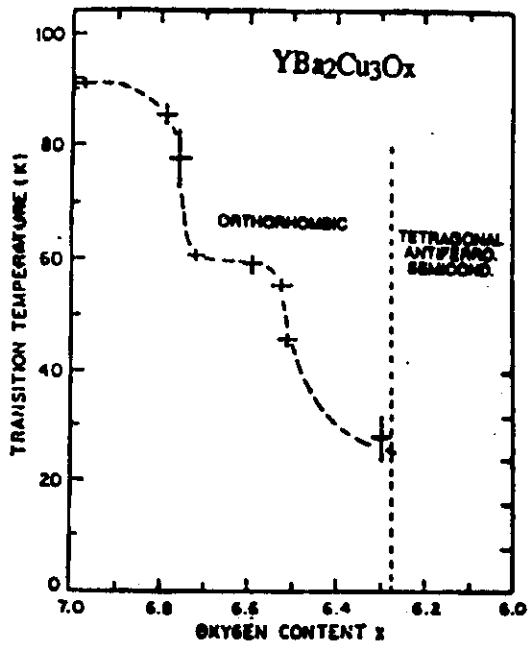
$YBa_2Cu_3O_6$

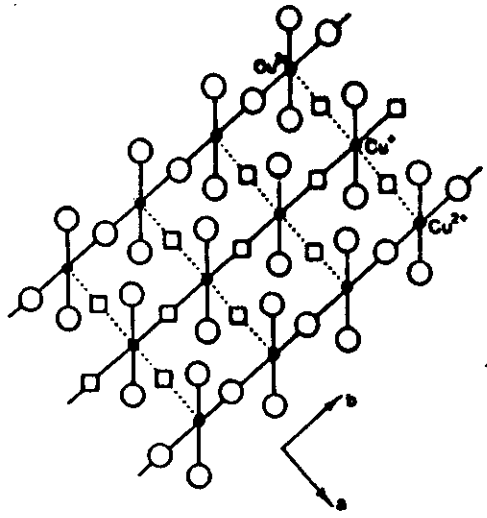
$YBa_2Cu_2O_7$



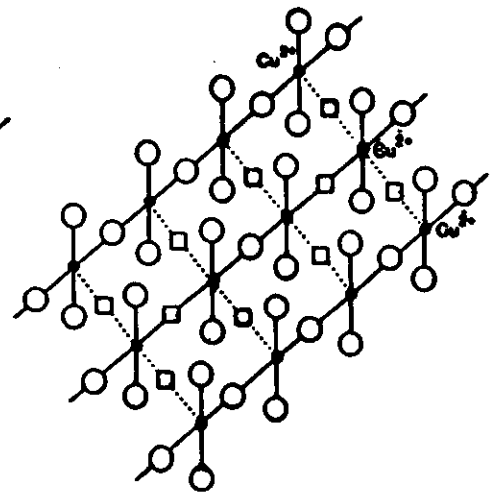




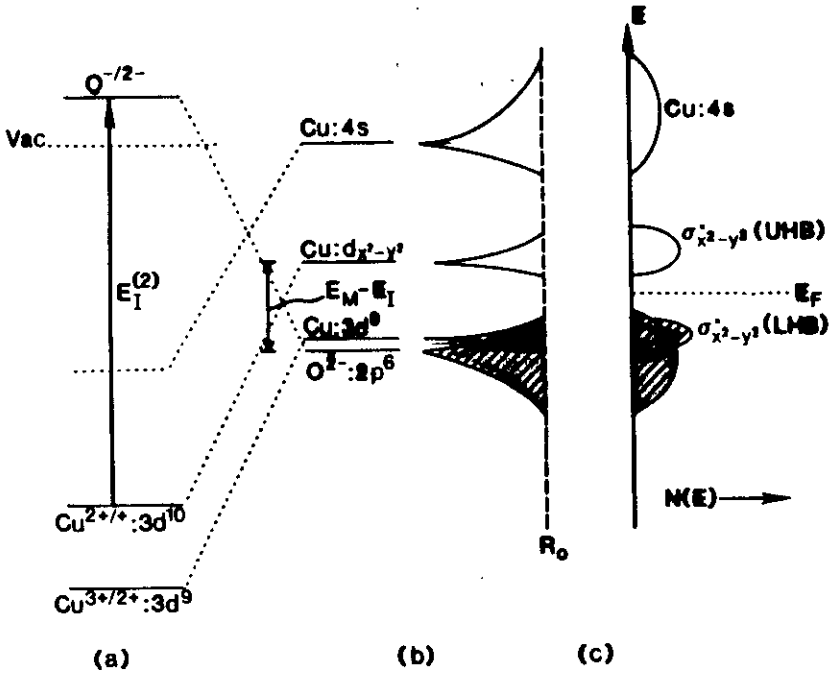




$YBa_2Cu_3O_{6.5}$
Interchain ordering



$YBa_2Cu_3O_{6.75}$
Interchain & Intrachain ordering


O^-/2-
Vac
E_I^(2)
Cu^2+/+:3d^10
Cu^3+/2+:3d^9
(a)
Cu:4s
Cu:d_x²-y²
E_M-E_I
Cu:3d^9
O^2-:2p^6
R_o
(b)
E
Cu:4s
σ*_x²-y² (UHB)
E_F
σ*_x²-y² (LHB)
N(E)
(c)