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SMR/455 - 3

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

12 - 30 MARCH 1990

METAL OXIDES: NORMAL-STATE PROPERTIES

LECTURE I

PRELIMINARIES

MAIN-GROUP AND RARE-EARTH OXIDES

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These are preliminary lecture notes, intended only for distribution to participants.

METAL OXIDES: NORMAL-STATE PROPERTIES

LECTURE I

PRELIMINARIES

MAIN-GROUP AND RARE-EARTH OXIDES

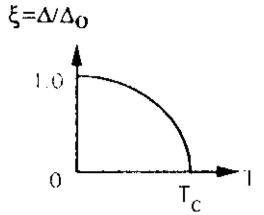
SUPERCONDUCTIVITY

A many-body phenomenon - but it manifests a condensation from a metallic normal state where single-particle theory is applicable

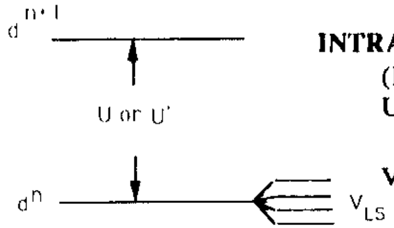
OXIDES

	Insulators		Metals
Single-Valent:	MgO, EuO, MnO		GdO, TiO
	SnO_2	VO_2	PbO_2
Mixed-Valent:	$Mn^{2+}[Mn_2^{3+}]O_4$		
	$Li[Mn^{4+}Mn^{3+}]O_4$		
	$Fe^{3+}[Fe^{3+}Fe^{2+}]O_4$		
	$Li[V_2^{3.5+}]O_4$		
			$Li[Ti_2^{3.5+}]O_4$

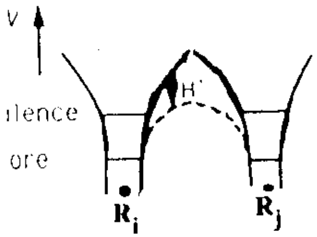
COMPETING ENERGIES



HEAT: TΔS
Controls solid-state transition
e.g. Superconductor transition

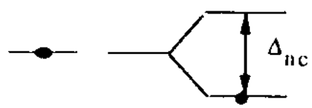


INTRAATOMIC: U or U', $V_{LS}=\lambda L\cdot S$
(Present in atom, weakened in solid)
U= on-site correlation energy
$\sim (c^2/r_{ij})\exp(-\gamma r_{ij})$
V_{LS}=multiplet splitting

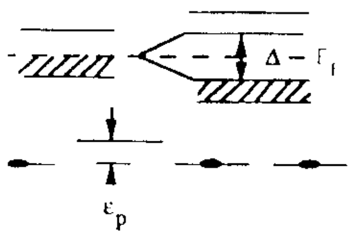


INTERATOMIC: $b_{ij}\equiv(\Psi_i, H'\Psi_j)\approx\varepsilon(\Psi_i, \Psi_j)$
b^{ca}=cation-anion (gives Δ_c, Δ_{nc}),
covalent-mixing parameter $\lambda\equiv b^{ca}/\Delta E$
b^{cc}=cation-cation $\sim\varepsilon\exp(-R/\rho)$
R=cation-cation separation
b^{cac}=cation-anion-cation $\sim\varepsilon\lambda^2$

ELECTRON-LATTICE: Δ_{nc}, Δ_{SDW}, Δ_{CDW}, ε_p



Jahn-Teller Δ_{nc} removes orbital degeneracy
CDW or SDW changes translational period.
(commensurate and incommensurate)
small polaron ≡ "dressed" electron



SINGLE-VALENT COMPOUNDS

(Tight-binding bandwidth: W ≈ 2zb)

	Localized Electrons		**Itinerant Electrons**
Theory:			
	crystal-field	**(Hubbard)***	**Band**
	n-fold configurations	quasiparticles	electrons/holes
	U>>W	U≈W	U<<W
	$4f^n$ ⟵	d	⟶ s, p
Properties:	μ_A, J_{ij}		—
	magnetic order $T<T_C,T_N$	SDW/CDW	BCS supercond.
	χ_m: Curie-Weiss	enhanced	Pauli
	Bravais (sub)lattice: insulator	s.c./metal	metal
Examples:	EuO, MnO	V_2O_3	TiO

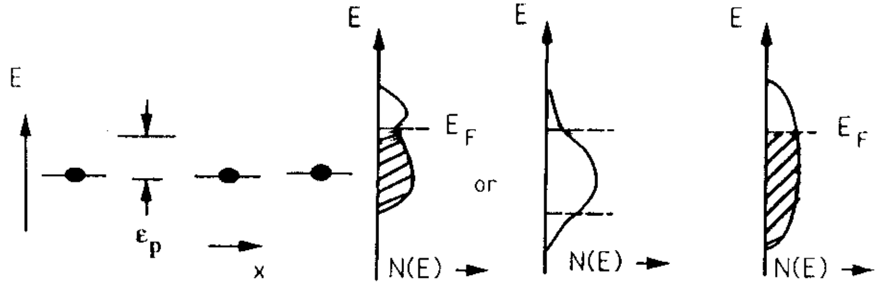
* For non-degenerate, half-filled band

MIXED-VALENT COMPOUNDS

(ω_R^{-1}=Period of trapping lattice vibration)
(τ_h=Interatomic-hopping time)

Small Polarons **Itinerant Electrons**

$\tau_h >> \omega_R^{-1}$ $\tau_h \approx \omega_R^{-1}$ $\tau_h << \omega_R^{-1}$



Mobility:

$\mu=eD/kT$ $\mu=eD_0/kT$ $\mu=e\tau_s/m^*$

or variable-range hopping

or short-range charge/spin fluctuation

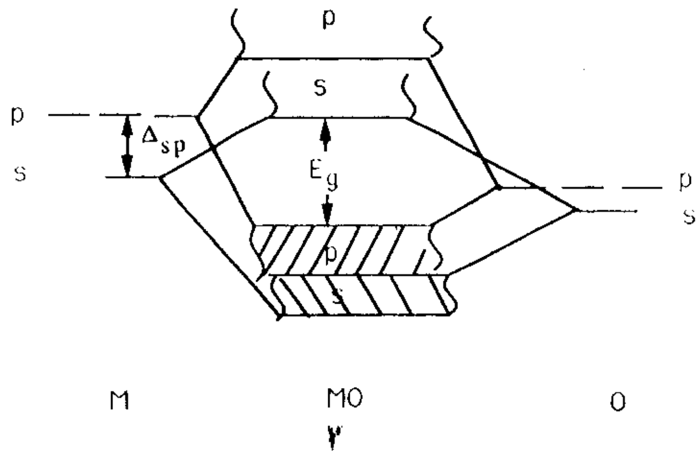
MAIN-GROUP OXIDES

Band Theory Applies

Oxygen: 2s, 2p valence electrons

Metal: only s, p valence electrons outside closed shells.

Non-Bravais Lattice (M and O distinguishable atoms)

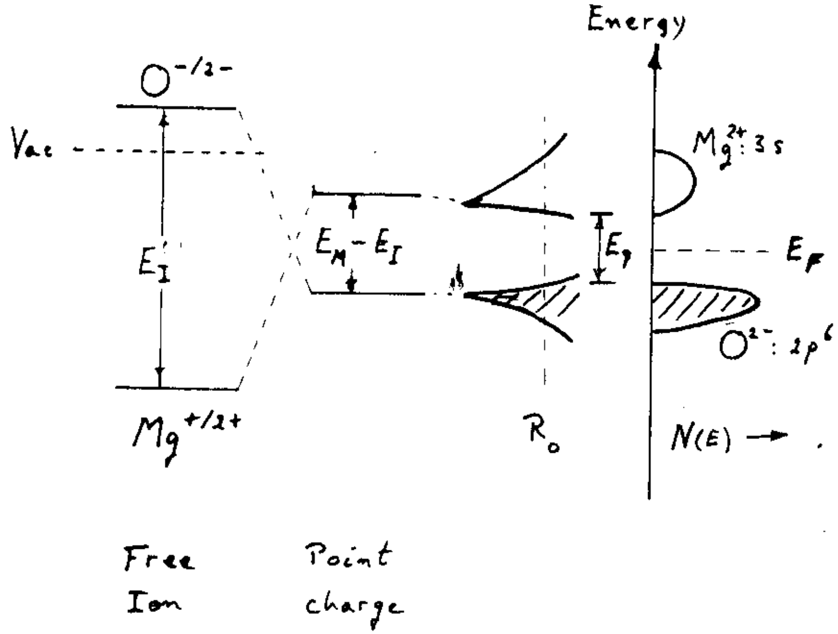


Group-A Metals: Oxides are insulators (large E_g). Conduction and valence bands inaccessible; introduction of native defects energetically favored.

Group-B Metals: 5s or 6s conduction bands are accessible to electrons (large Δ_{sp}), but disproportionation normally favored over metallic behavior.

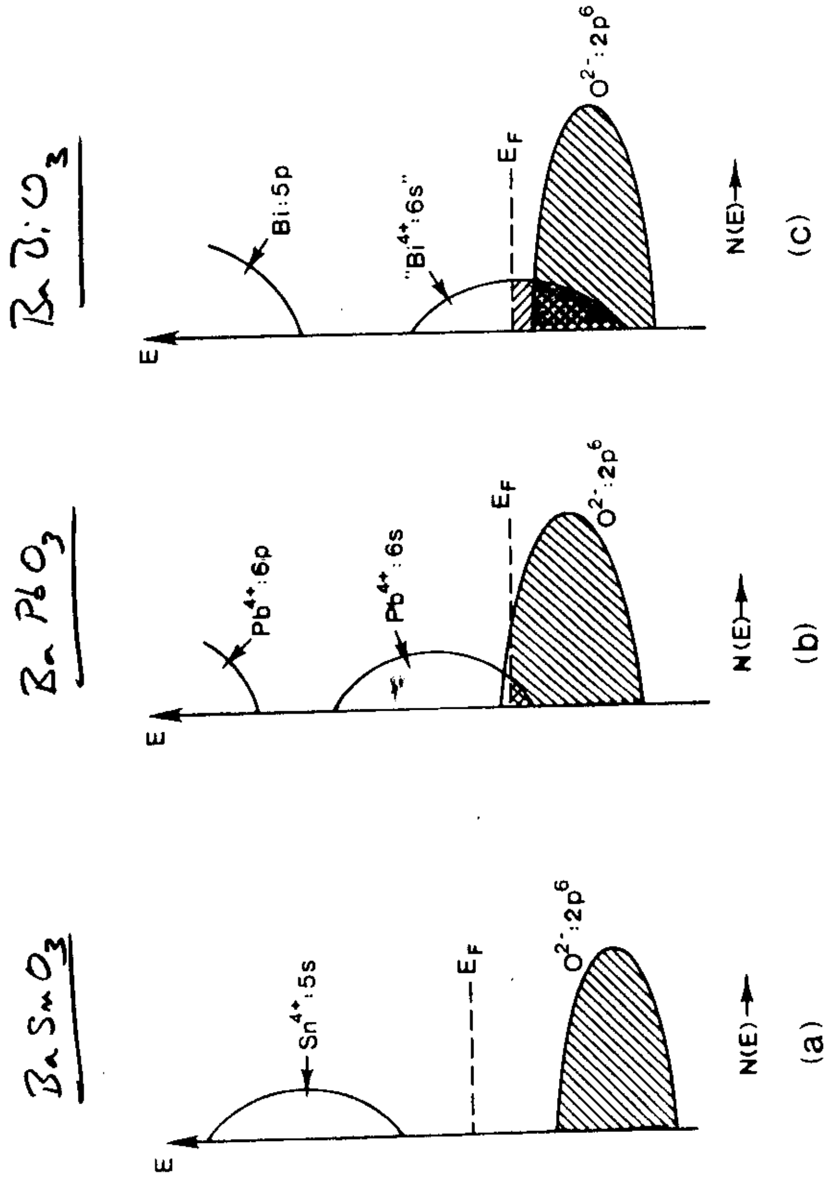
e.g. $2Bi^{4+} \longrightarrow Bi^{3+} + Bi^{5+}$

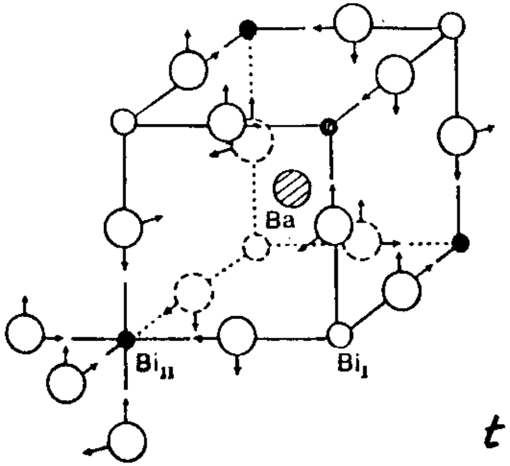
MgO



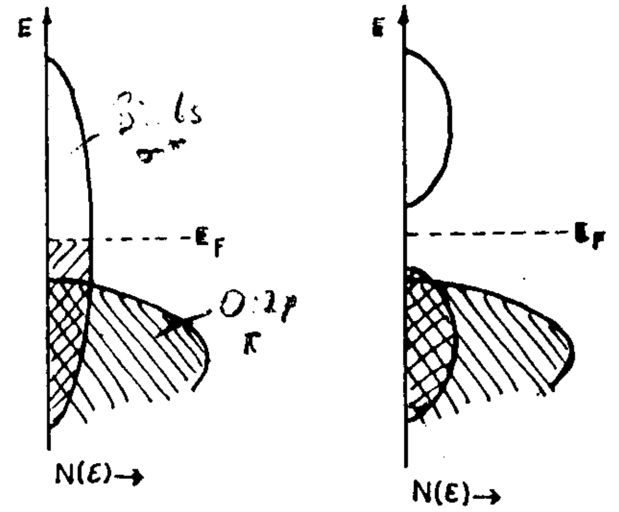
$E_M = N \sum_j \frac{\pm e^2}{r_j}$ = Madelung Energy

E_I - free-ion charge-transfer energy





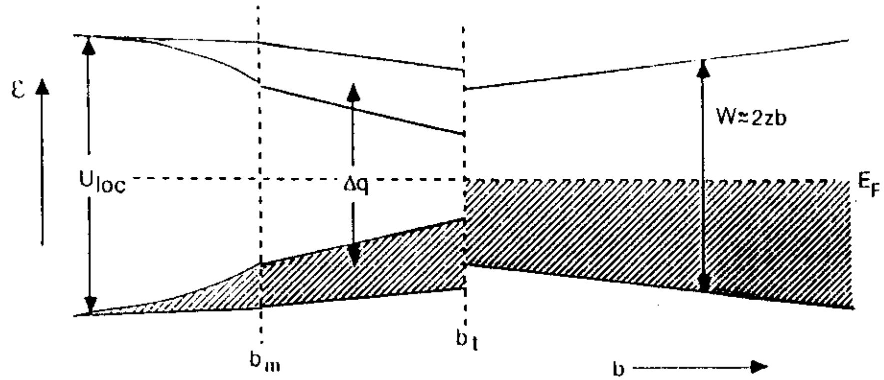
$$t = \frac{r_{Ba} + r_O}{\sqrt{2}(r_{Bi} + r_O)}$$

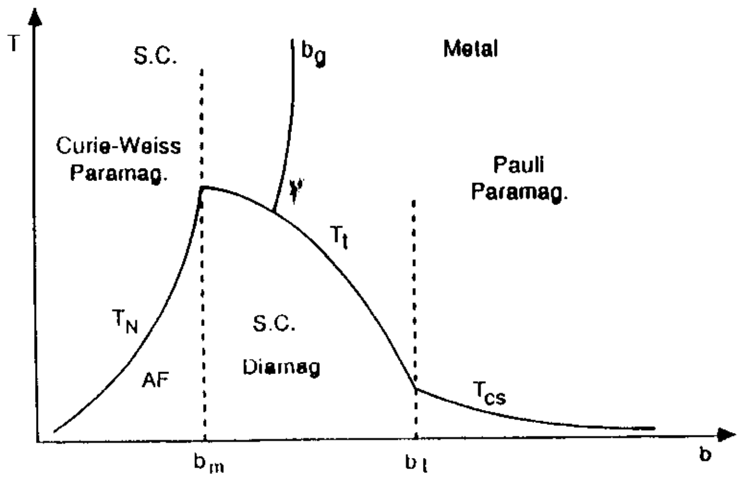


Cubic

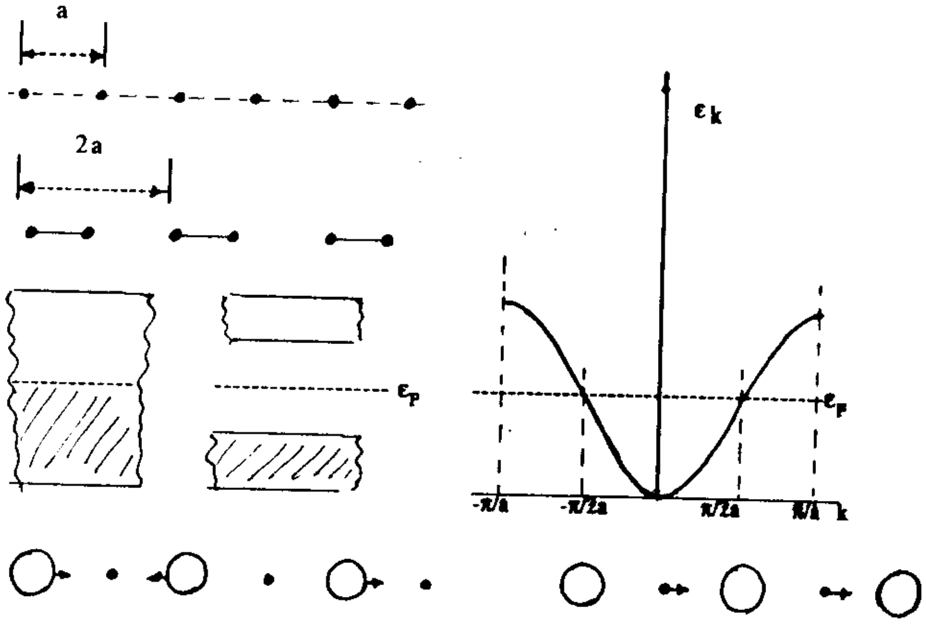
Monoclinic

$BaBiO_3$

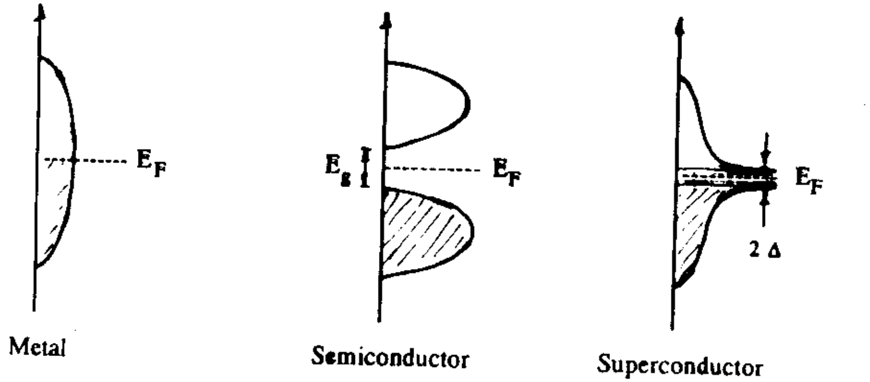


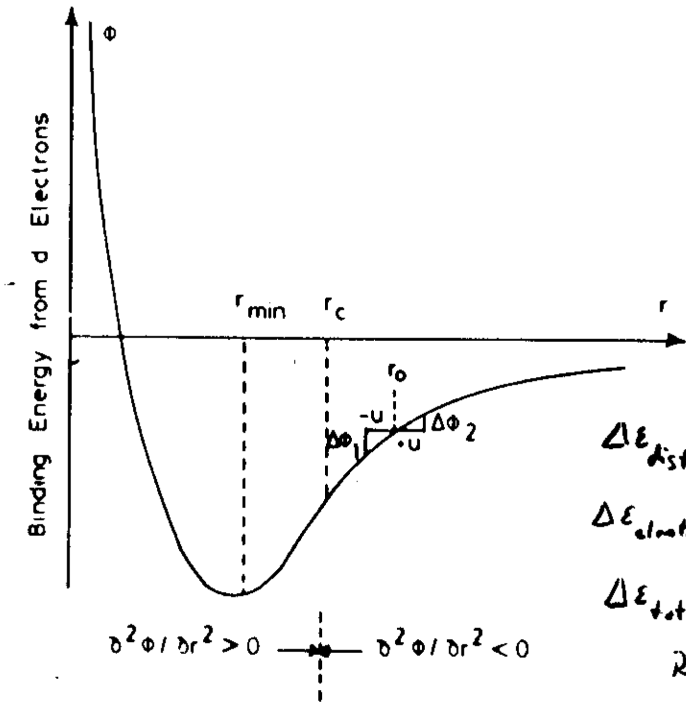


SOFT-MODE INSTABILITIES & SPIN-DENSITY WAVES



Note: May be Commensurate or Incommensurate



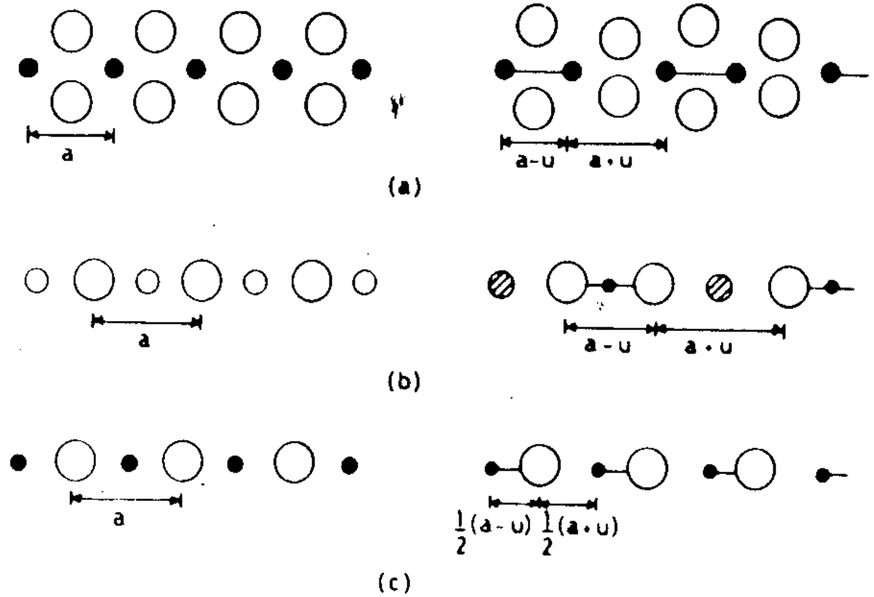


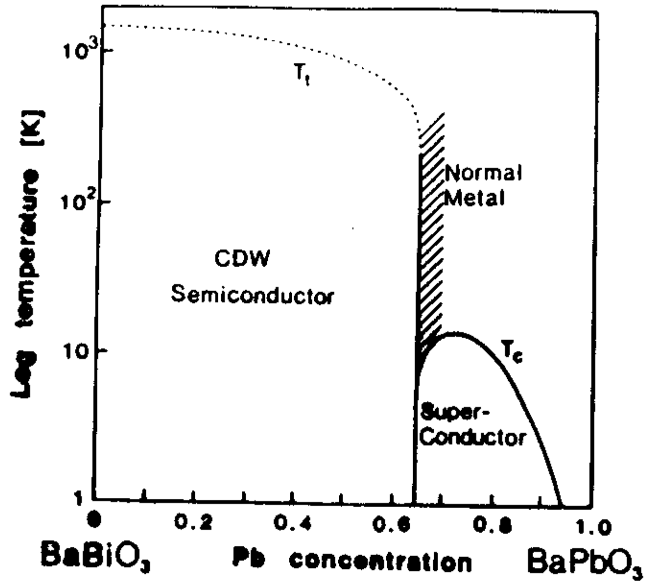
$$\Delta\varepsilon_{dist} = \frac{1}{2}\frac{\partial^2\phi}{\partial r^2}\cdot\delta^2 = -A\delta^2$$

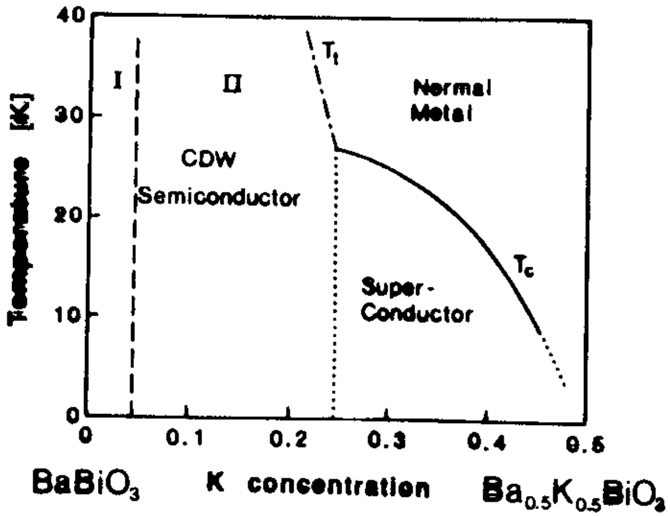
$$\Delta\varepsilon_{elastic} = B\delta^2$$

$$\Delta\varepsilon_{tot} = (B - A)\delta^2$$

Require $A > B$







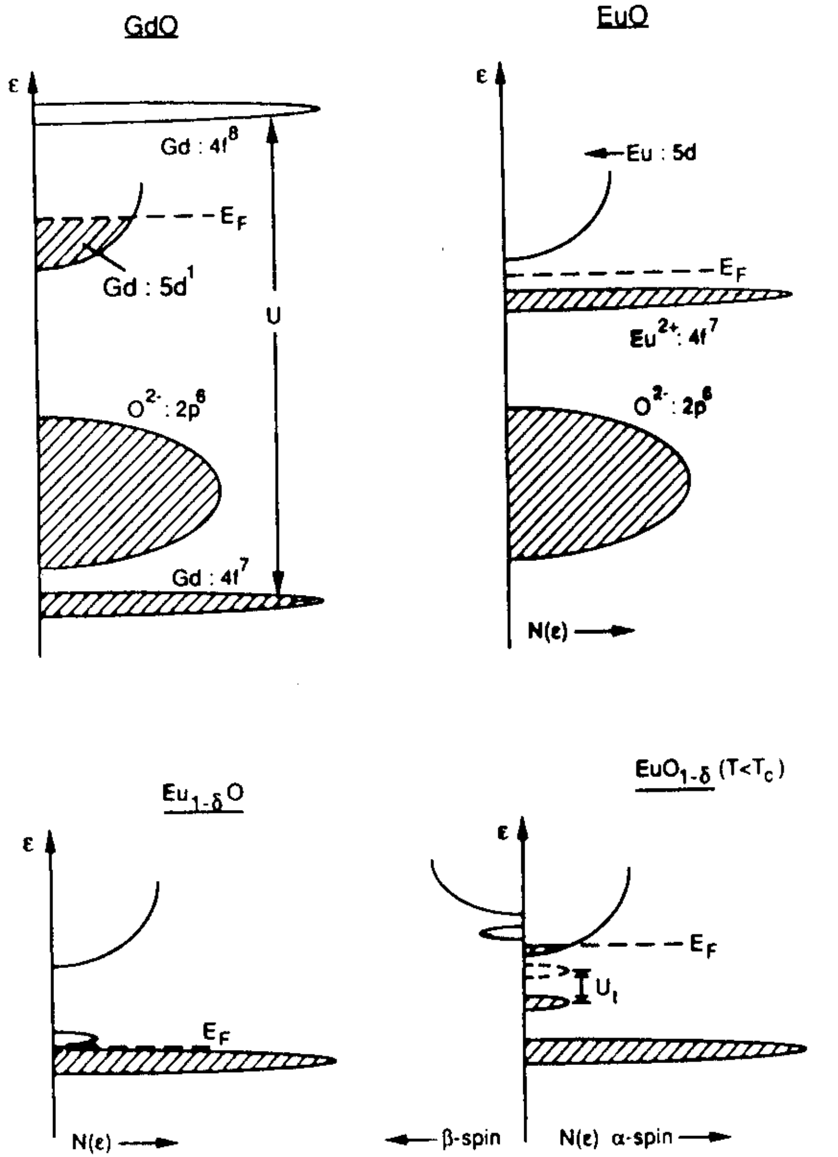
RARE-EARTH OXIDES

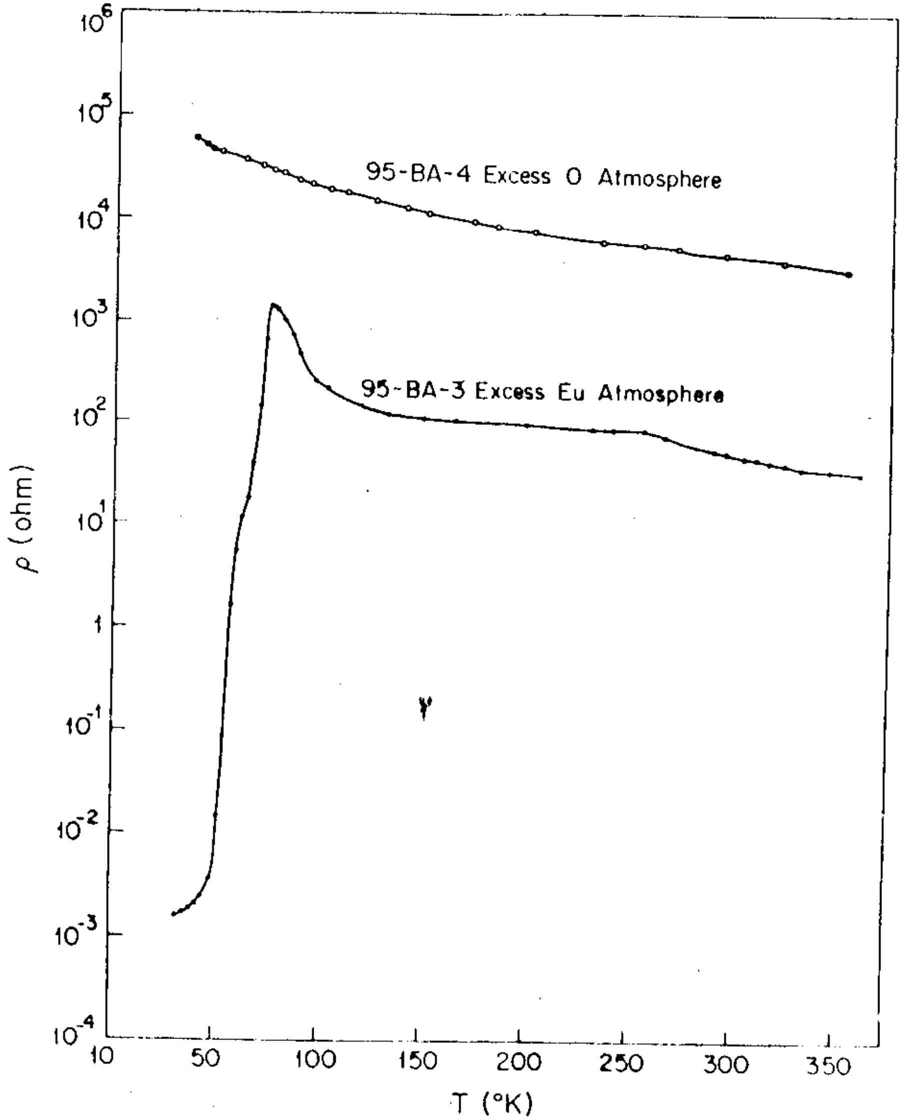
$4f^n$ Hamiltonian

$$H = H_O + V_{el} + \Delta_{LS} + \Delta_C + H_Z$$

$$\mu_J = gJ\mu_B \text{ with } g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$$V_{el} \rightarrow U > E_g$$


GdO
ε
Gd : 4f8
E_F
Gd : 5d1
U
O2- : 2p6
Gd : 4f7
EuO
ε
Eu : 5d
E_F
Eu2+ : 4f7
O2- : 2p6
N(ε)
$Eu_{1-\delta}O$
ε
E_F
N(ε)
$EuO_{1-\delta}$ ($T<T_c$)
ε
E_F
U_t
β-spin
N(ε) α-spin


95-BA-4 Excess O Atmosphere
95-BA-3 Excess Eu Atmosphere
ρ (ohm)
T (°K)
10
50
100
150
200
250
300
350
10^6
10^5
10^4
10^3
10^2
10^1
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}