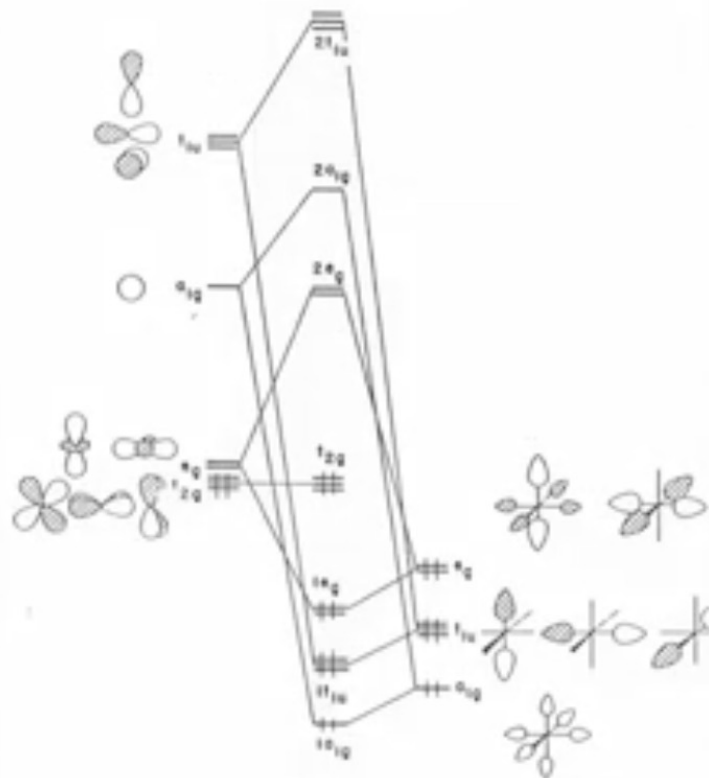


Learning Objectives

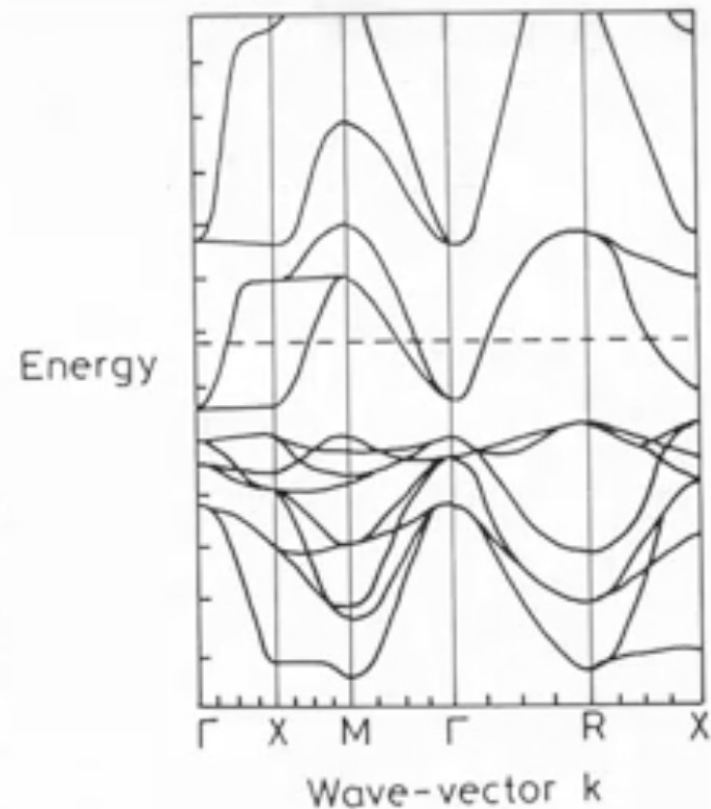
Band Structures of Transition Metal Oxides

- Describe the crystal structure of ReO_3 and its relationship to perovskite structures
- Construct band structure diagrams from molecular orbital diagrams for octahedral transition metal complexes
- Identify and interpret oxygen 2p bands and metal d bands (π^* and σ^*) at special k-points
- Extract key energetic parameters from band structures: octahedral ligand field splitting, charge transfer energy, and band gap
- Predict periodic trends in band structure when moving across the periodic table (changing electronegativity and covalency)
- Analyze the competing effects of spatial overlap versus energetic overlap when moving down the periodic table (3d vs 4d vs 5d)

Electronic Band Structure

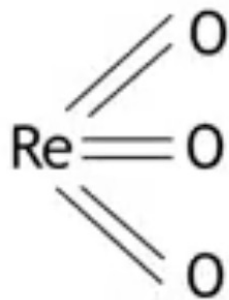
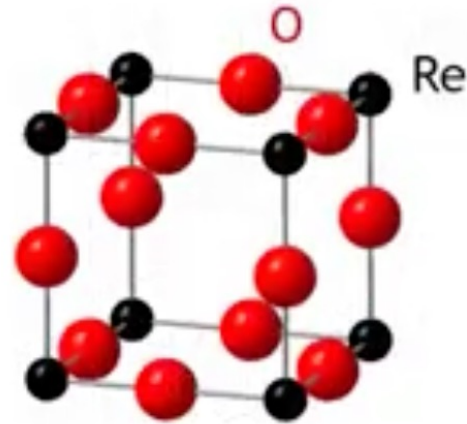
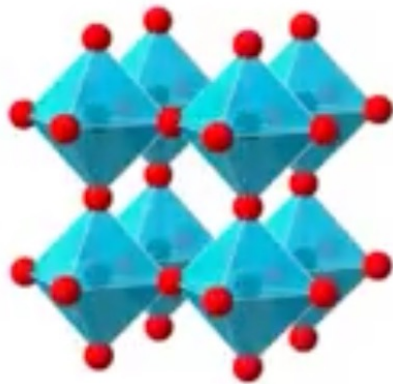


MO diagram for an octahedron



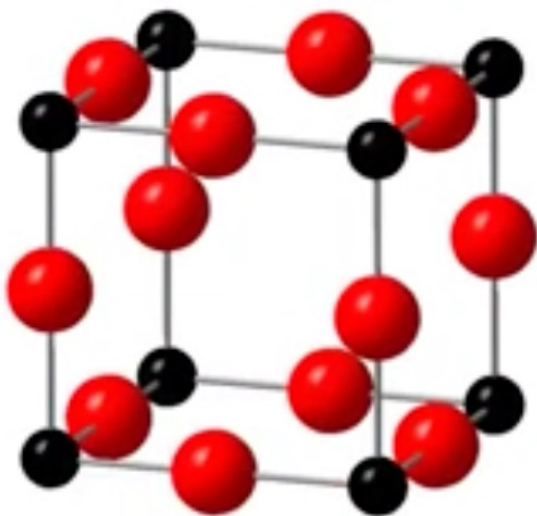
Band structure diagram for ReO_3

Rhenium Trioxide

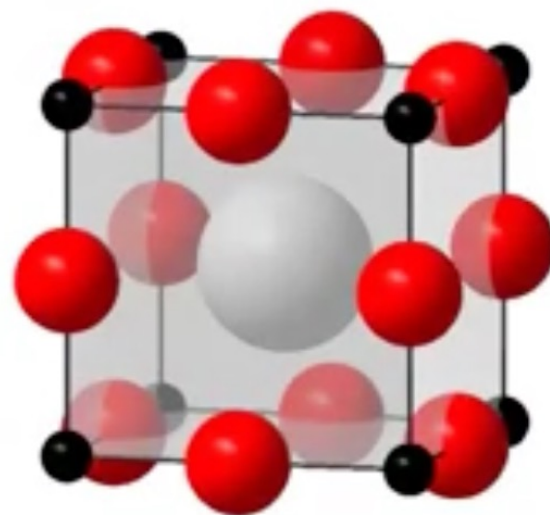


Substance	Conductivity (S/m)
Ag	62×10^6
Cu	59×10^6
Al	38×10^6
ReO ₃	11×10^6
Ti	2.5×10^6
Mn	0.62×10^6

Perovskites



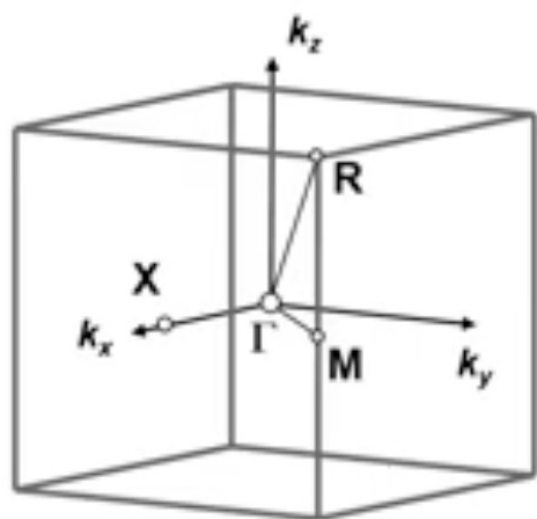
ReO₃



SrTiO₃
(Perovskite)

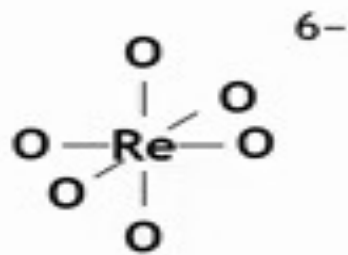
If we treat the large cation (e.g. Sr²⁺) as an electropositive electron donor, perovskites and ReO₃ are isostructural.

First Brillouin Zone - Primitive Cubic



label	coordinates
Γ	$0 a^* + 0 b^* + 0 c^*$
X	$(1/2) a^* + 0 b^* + 0 c^*$
M	$(1/2) a^* + (1/2) b^* + 0 c^*$
R	$(1/2) a^* + (1/2) b^* + (1/2) c^*$

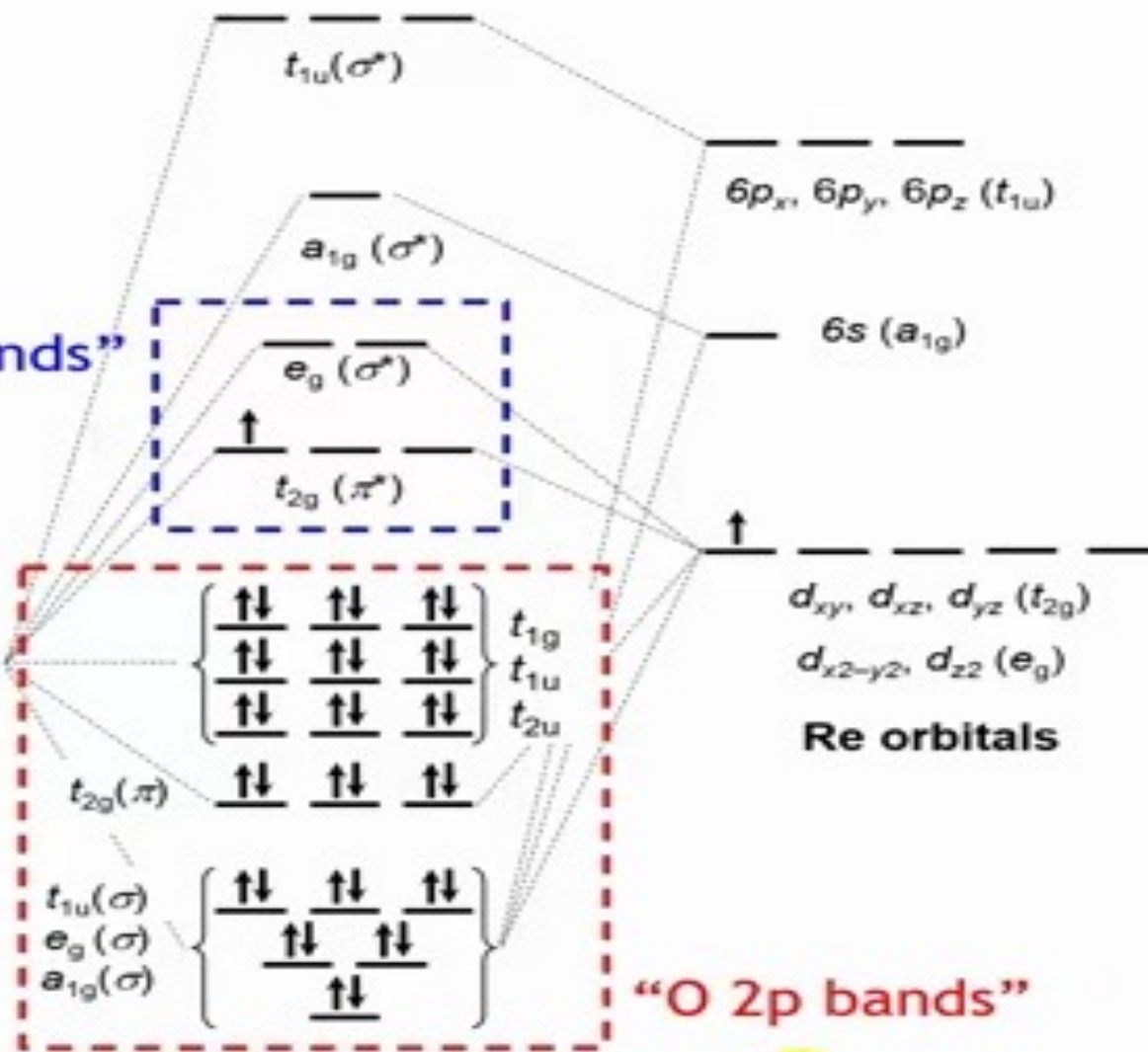
label	wave vector (Cartesian)
Γ	$0 k_x + 0 k_y + 0 k_z$
X	$(\pi/a) k_x + 0 k_y + 0 k_z$
M	$(\pi/a) k_x + (\pi/a) k_y + 0 k_z$
R	$(\pi/a) k_x + (\pi/a) k_y + (\pi/a) k_z$



“Re 5d bands”



O 2p orbitals



How many bands are there?

$$1 \text{ Rhenium} \times 1(6s \text{ orbitals}) = 1$$

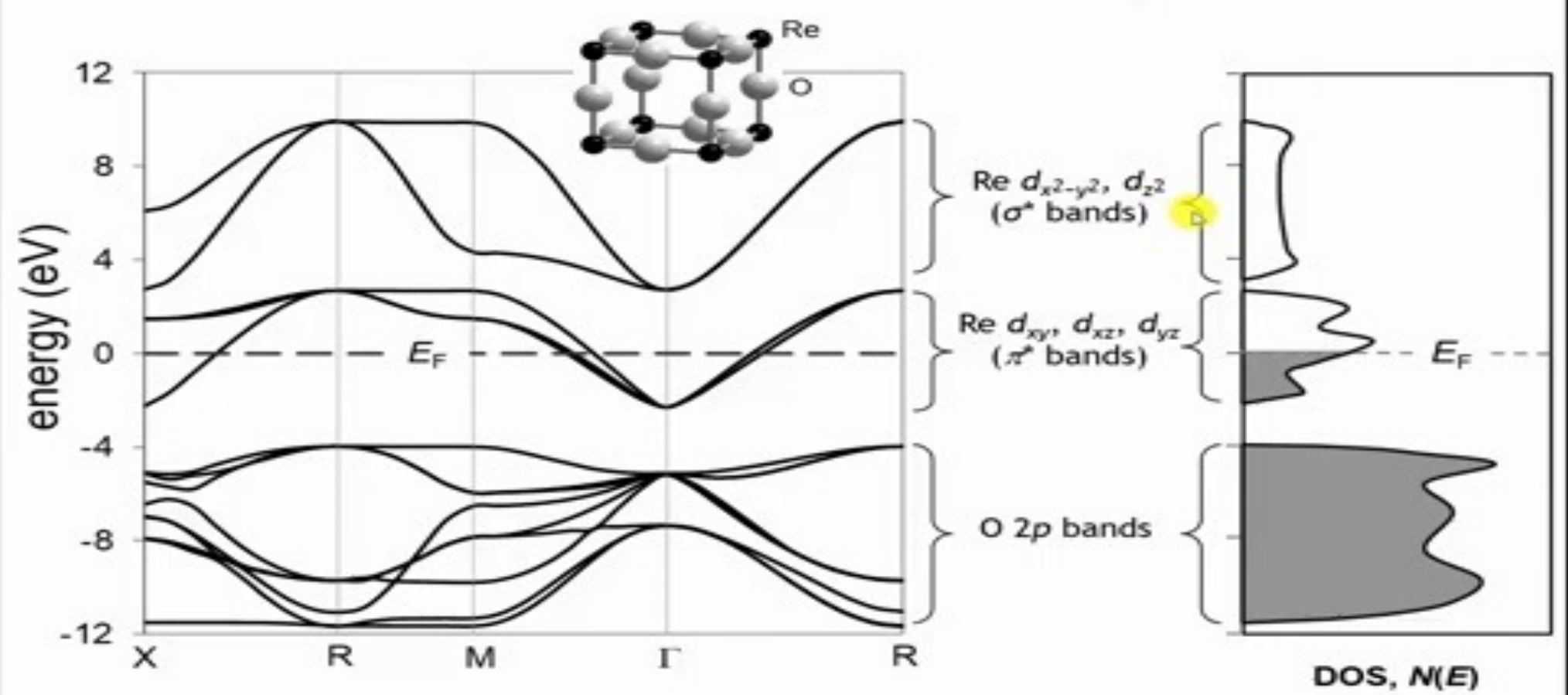
$$1 \text{ Rhenium} \times 3(6p \text{ orbitals}) = 3$$

$$1 \text{ Rhenium} \times 5(5d \text{ orbitals}) = 5$$

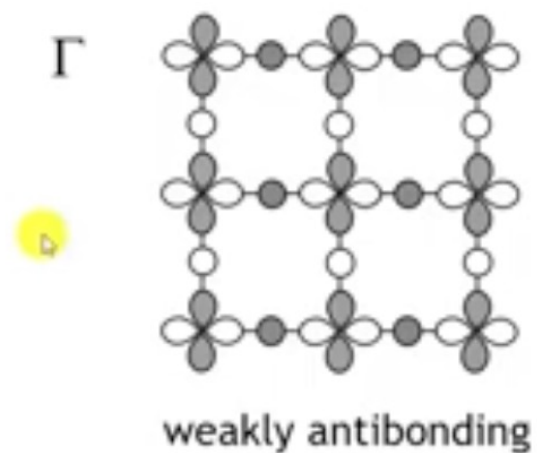
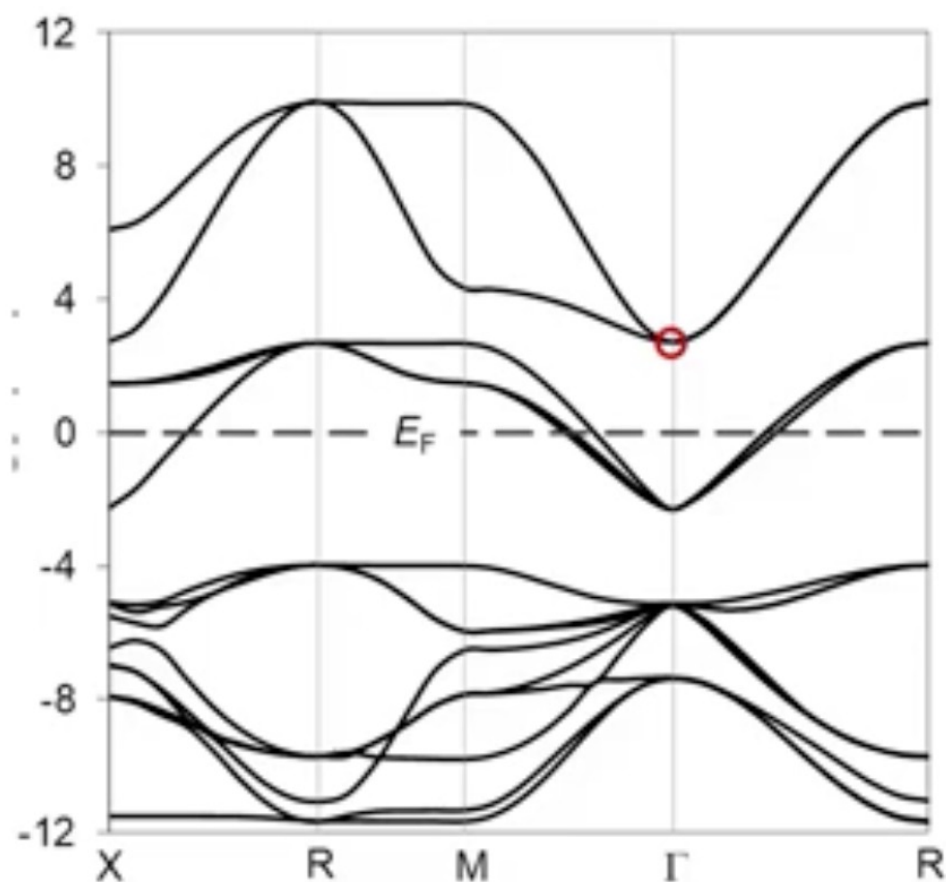
$$3 \text{ Oxygen} \times 3(2p \text{ orbitals}) = 9$$

$$3 \text{ Oxygen} \times 1(2s \text{ orbitals}) = 3$$

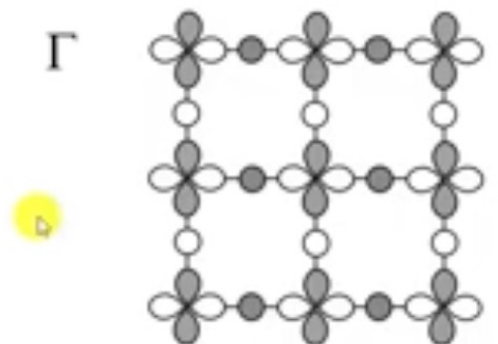
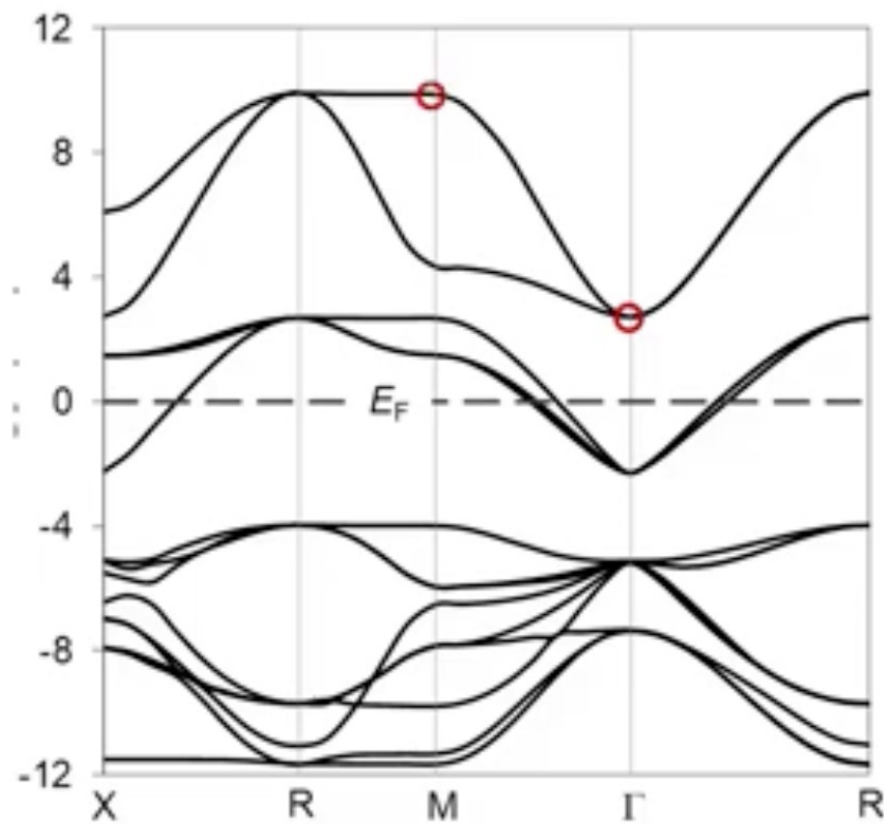
Band Structure of ReO_3



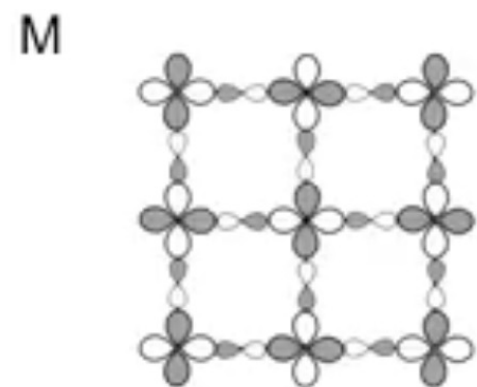
Orbital Overlap Re 5d (e_g) σ^* Bands



Orbital Overlap Re 5d (e_g) σ^* Bands

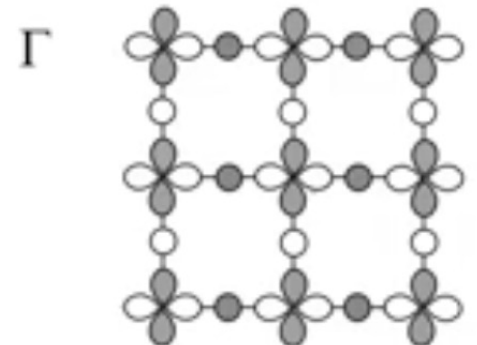
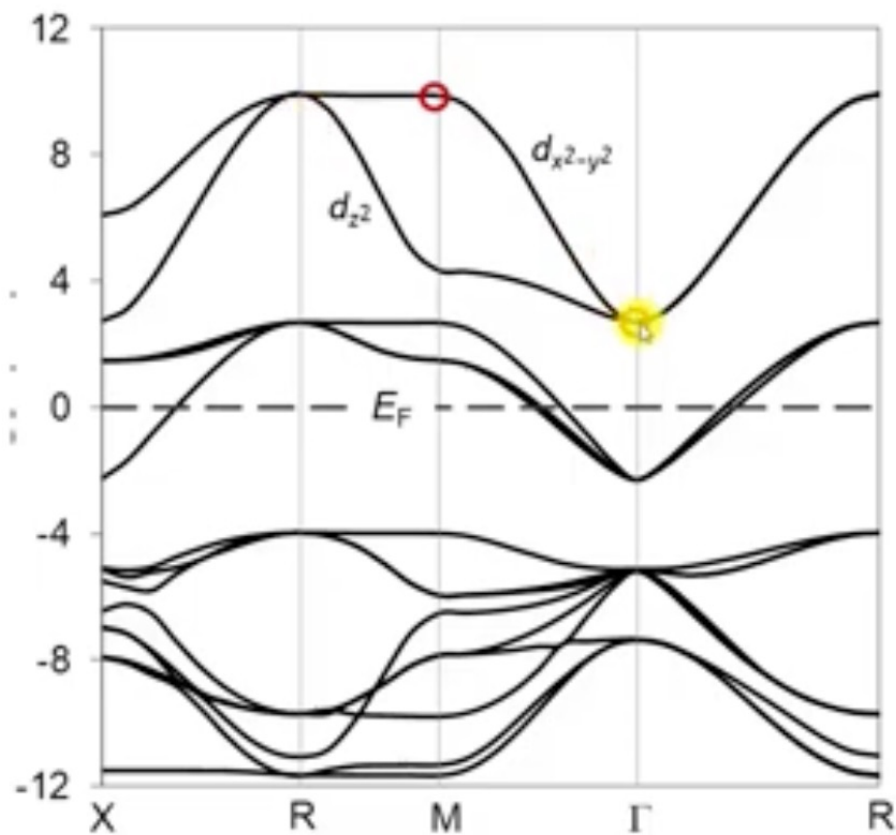


weakly antibonding

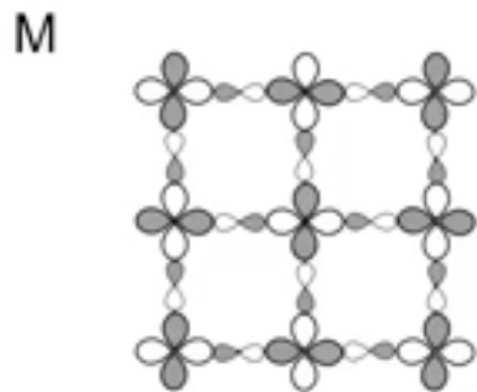


strongly antibonding

Orbital Overlap Re 5d (e_g) σ^* Bands

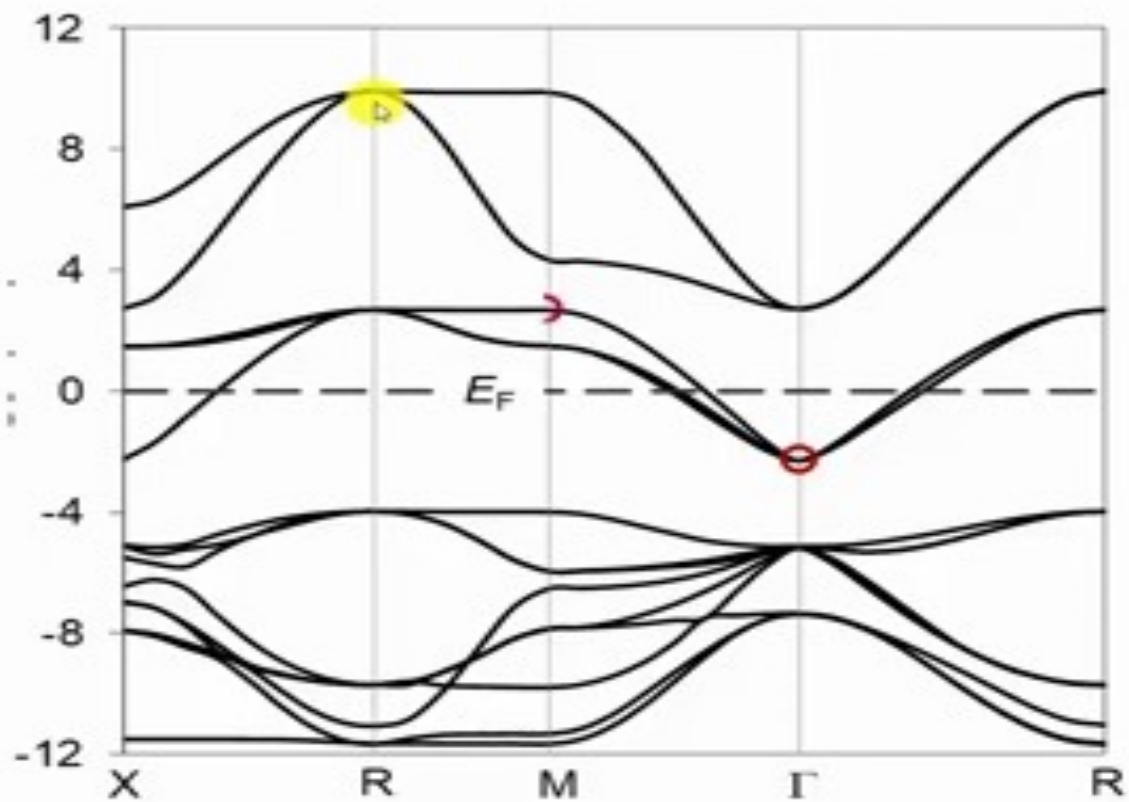


weakly antibonding

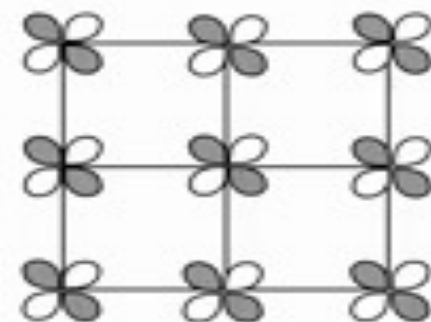


strongly antibonding

Orbital Overlap Re 5d (t_{2g}) π^* Bands

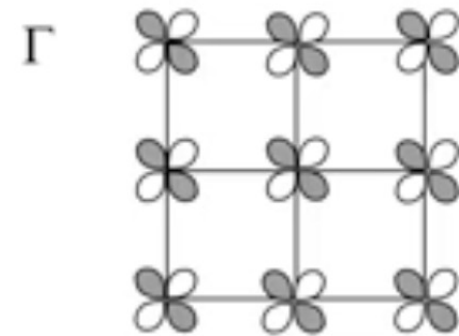
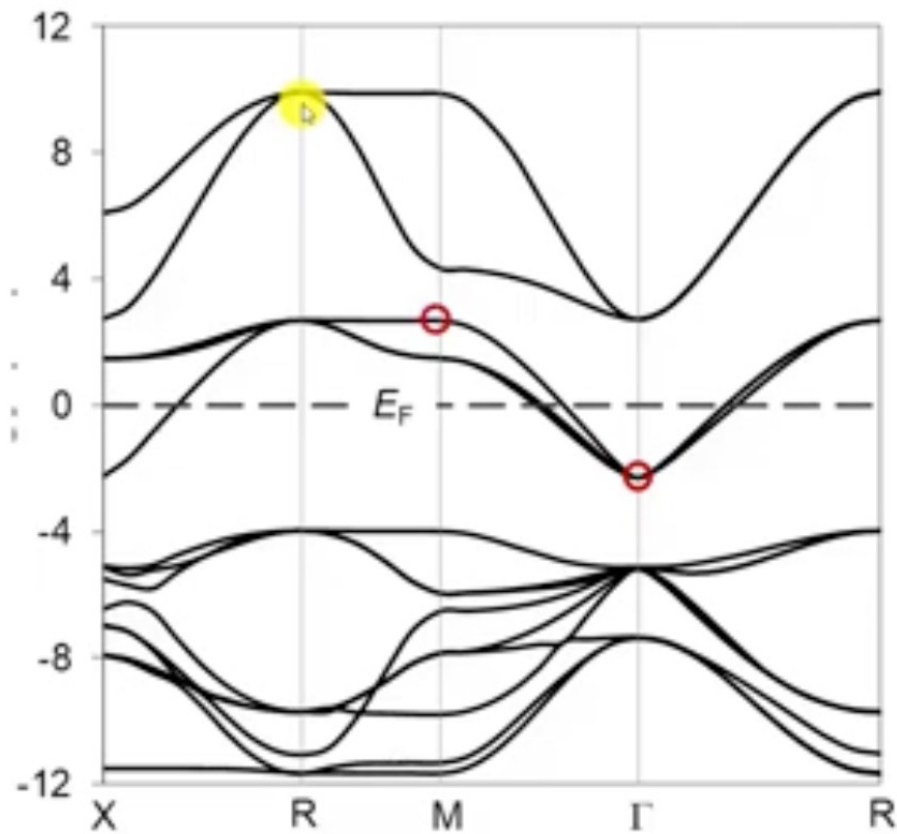


Γ

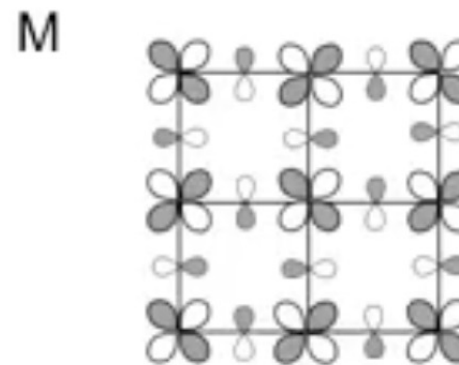


nonbonding

Orbital Overlap Re 5d (t_{2g}) π^* Bands

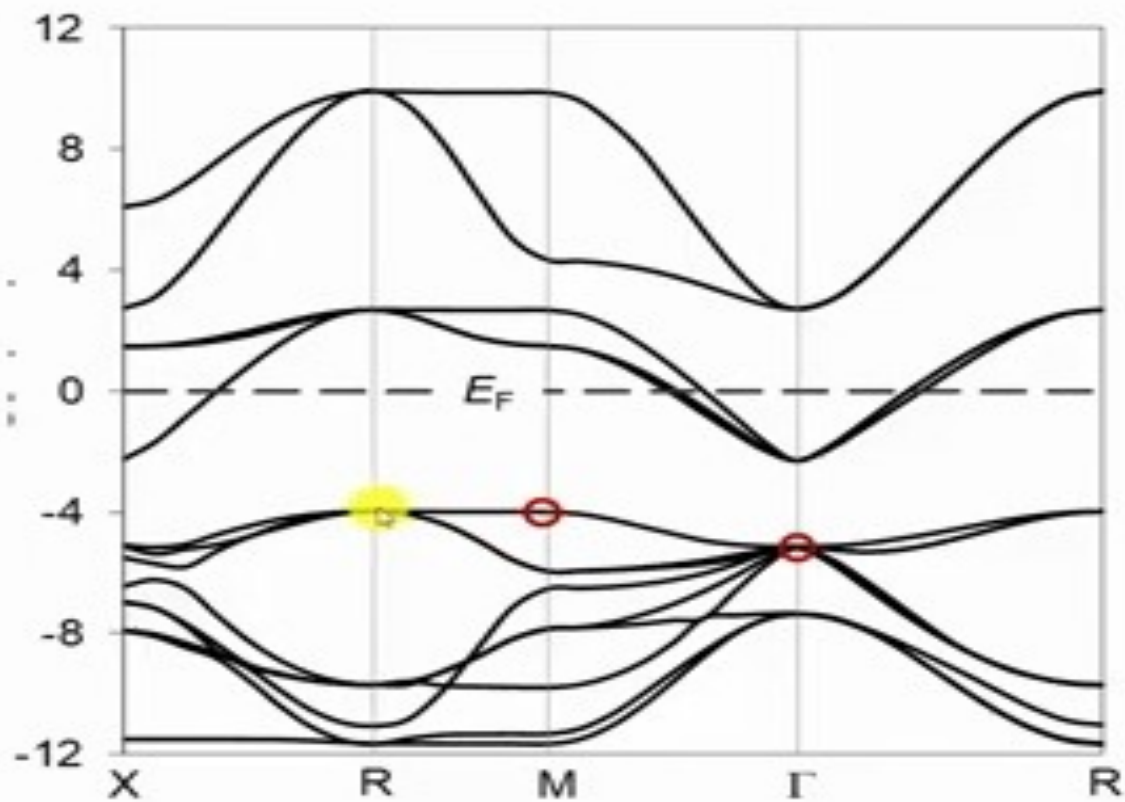


nonbonding

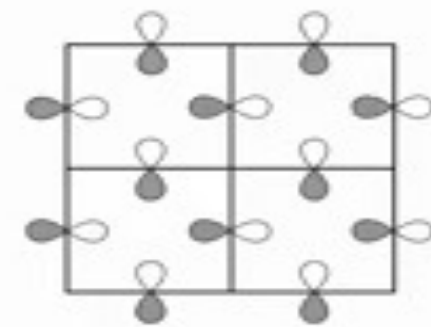


antibonding

Orbital Overlap O 2p Nonbonding Bands

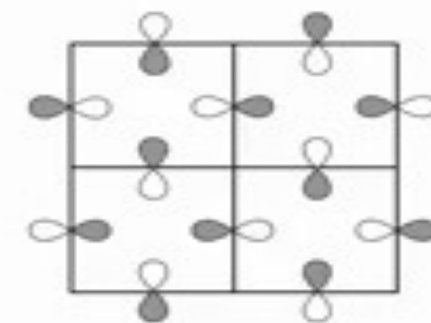


Γ



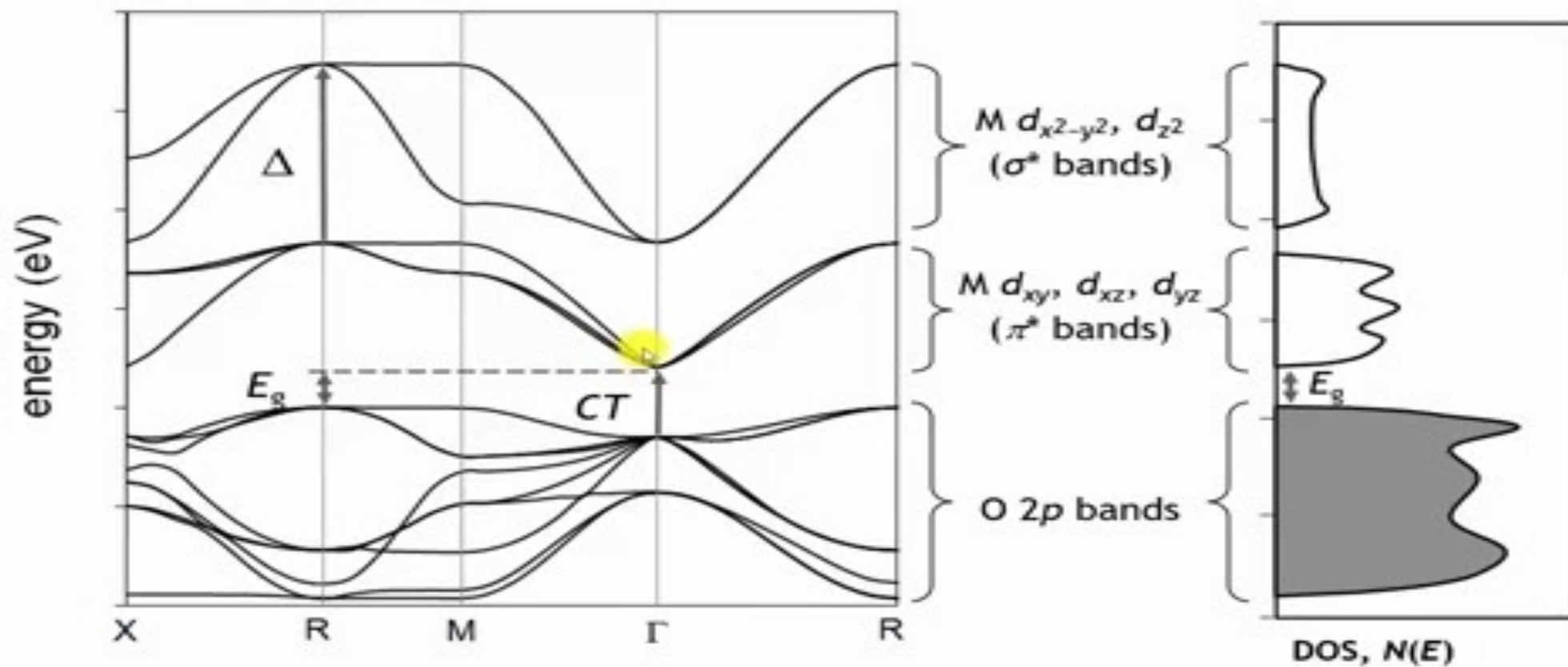
nonbonding

M



nonbonding

ReO₃ Band Structure - Key Features



Periodic Trends

	ReO ₃	WO ₃	KTaO ₃	BaHfO ₃
M-O distance (Å)*	1.87	1.95	1.99	2.09
e ⁻ configuration	5d ¹	5d ⁰	5d ⁰	5d ⁰
σ* bandwidth (eV)	7.2	6.4	6.2	5.1
π* bandwidth (eV)	5.0	4.3	4.2	3.5
Δ (eV)	7.2	6.3	6.1	5.5
CT (eV)	2.3	3.4	3.8	5.3
Band gap (eV)*	---	2.4	3.5	5.5

*All parameters calculated except M-O distance and band gap, which are experimental values.

Moving right-to-left (Re → Hf) the effective nuclear charge decreases

- Metal-oxygen bond distance increases
- Bandwidth decreases (less energetic and spatial overlap)
- Δ decreases
- Charge transfer energy increases
- Band gap increases

Periodic Table of the Elements

																					18 VIII A 8A		
1 IA 1A																	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.003	
3 Li Lithium 6.941	4 Be Beryllium 9.012																	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948						
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798						
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294						
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018						
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]						

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Periodic Trends

	SrTiO ₃	BaHfO ₃
M-O distance (Å)*	1.95	2.09
e ⁻ configuration	3d ⁰	5d ⁰
σ* bandwidth (eV)	4.1	5.1
π* bandwidth (eV)	2.4	3.5
Δ (eV)	3.9	5.5
CT (eV)	4.1	5.3
Band gap (eV)*	3.1	5.5

*All parameters calculated except M-O distance and band gap, which are experimental values.

Moving down a column (Ti → Hf)

- Metal-oxygen bond distance increases
- Bandwidth **increases** (more spatial overlap)
- Δ **increases** (more spatial overlap)
- Charge transfer increases
- Band gap increases

3. The unit cell of ReO_3 contains one Rhenium and three Oxygen atoms. Based on this, how many bands are expected to arise from the Oxygen 2p orbitals?

A. 6 bands

B. 9 bands

C. 3 bands

D. 5 bands

B. 9 bands

✓ **That's right!**

There are three oxygen atoms, and each has three p-orbitals (px, py, pz), leading to $3 \times 3 = 9$ bands.

5. At the Gamma (Γ) point ($k=0,0,0$) of the Brillouin zone, what is the bonding character of the Rhenium 5d t_{2g} (d_{xy} , d_{xz} , d_{yz}) orbitals?

A. Strongly sigma anti-bonding (σ^*) with Oxygen 2p

B. Weakly anti-bonding with Oxygen 2s

C. Strongly pi anti-bonding (π^*) with Oxygen 2p

D. Non-bonding, due to symmetry constraints with Oxygen 2p and 2s orbitals.

D. Non-bonding, due to symmetry constraints with Oxygen 2p and 2s orbitals.

✓ **Right answer**

The lecture explicitly states that at Gamma, the t_{2g} orbitals 'cannot overlap at all' with the oxygen orbitals, making them purely non-bonding.

6. Why does the energy of the σ^* (eg, dx^2-y^2) band increase significantly when moving from the Gamma (Γ) point to the M point?

A. At M, the crystal field splitting energy (Δ_o) disappears, causing the band to rise.

B. The orbital becomes non-bonding at M.

C. At M, it hybridizes with the Rhenium 6s orbital, pushing it up in energy.

D. At M, it gains strong σ^* anti-bonding character from interacting with Oxygen 2p orbitals.

D. At M, it gains strong σ^* anti-bonding character from interacting with Oxygen 2p orbitals.

✓ **That's right!**

At Gamma, it can't mix with O 2p, but at M, symmetry allows strong σ^* interaction with the O 2p orbitals (which have good energy overlap), raising the energy.

7. In the perovskite band structure, the energy splitting between the t_{2g} and e_g bands at the R point is said to be equivalent to what important chemical parameter?

A. The width of the Oxygen 2p bands

B. The charge transfer energy

C. The band gap energy

D. The octahedral ligand field splitting energy (Δ_o)

D. The octahedral ligand field splitting energy (Δ_o)

✓ **That's right!**

At R, both sets of orbitals are fully anti-bonding, and their energy difference directly reflects the ligand field splitting, just as in the MO diagram.

9. When moving left across the periodic table (e.g., from Re to Hf), the metal-oxygen bonds become more ionic. What effect does this have on the d-band widths and the charge transfer energy?

A. Bandwidths decrease and charge transfer energy increases.

B. Bandwidths increase and charge transfer energy decreases.

C. Bandwidths increase and charge transfer energy increases.

D. Bandwidths decrease and charge transfer energy decreases.

A. Bandwidths decrease and charge transfer energy increases.

✓ **That's right!**

Correct. Less covalency narrows the bands, and the less electronegative metal (Hf) raises the d-orbital energy, increasing the O 2p \rightarrow M 5d gap.

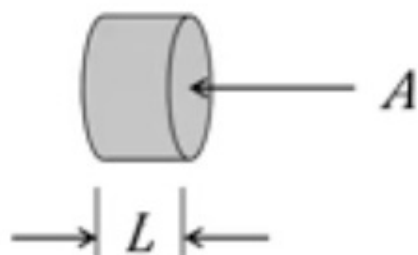
Learning Objectives

Electrical Conductivity and the Drude Model

- Distinguish between extrinsic (I , V , R) and intrinsic (J , E , σ , ρ) electrical properties
- Apply the Drude model to describe electron behavior as an ideal gas in metals
- Calculate key parameters: drift velocity, electron mobility, mean free path, and relaxation time
- Derive the relationship between conductivity, carrier concentration, and mobility ($\sigma = ne\mu$)
- Estimate conductivity parameters for simple metals using the Drude model
- Recognize the limitations and failures of the Drude model in predicting temperature dependence and trends across different metals

Ohm's Law

Ohm's Law (Extrinsic) $I = \frac{V}{R}$



Current density, $J = I/A$

Electric field intensity, $E = V/L$

Resistivity, $\rho = RA/L$

Intrinsic Properties

Conductivity

Ohm's Law (Extrinsic) $I = \frac{V}{R}$

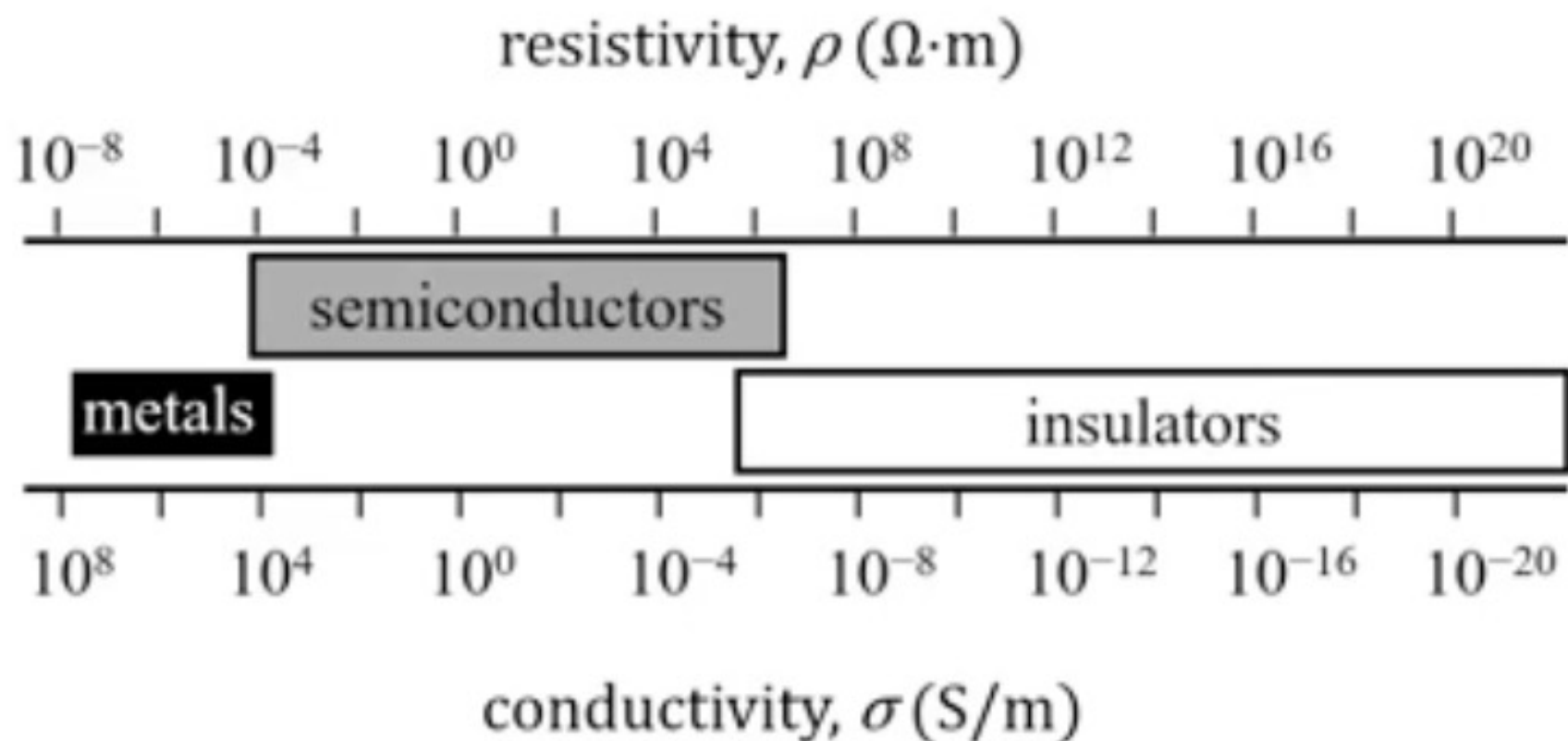
Ohm's Law (Intrinsic)

$$I = \frac{V}{R} \longrightarrow JA = \frac{(EL)}{(L\rho/A)} = \frac{EA}{\rho}$$

$$J = \frac{E}{\rho} \quad \text{Resistivity, } \rho \text{ } (\Omega \cdot \text{m})$$

$$J = \sigma E \quad \text{Conductivity, } \sigma = 1/\rho \text{ } (\Omega^{-1}\text{m}^{-1} = \text{S/m})$$

Conductivity of Materials



Conductivity of Select Materials

<i>Substance</i>	σ (S/m)	<i>Substance</i>	σ (S/m)
Ag	6.2×10^7	$\text{Bi}_2\text{Ru}_2\text{O}_7$	2×10^5
Cu	5.9×10^7	LaNiO_3	1×10^5
Al	3.8×10^7	doped polyacetylene	8×10^4
Na	2.1×10^7	Fe_3O_4	2×10^4
ReO_3	1.1×10^7	$\text{YBa}_2\text{Cu}_3\text{O}_7^*$	1×10^2
Ti	2.5×10^6	Ge	2×10^0
La	1.6×10^6	Si	10^{-3}
SrMoO_3	1.0×10^6	NiO	10^{-8}
Bi	7.7×10^5	Al_2O_3	10^{-12}
Mn	6.2×10^5	S	10^{-15}
NbN	4×10^5	SiO_2 (Quartz)	10^{-16}
TiO	3×10^5	Teflon	10^{-22}