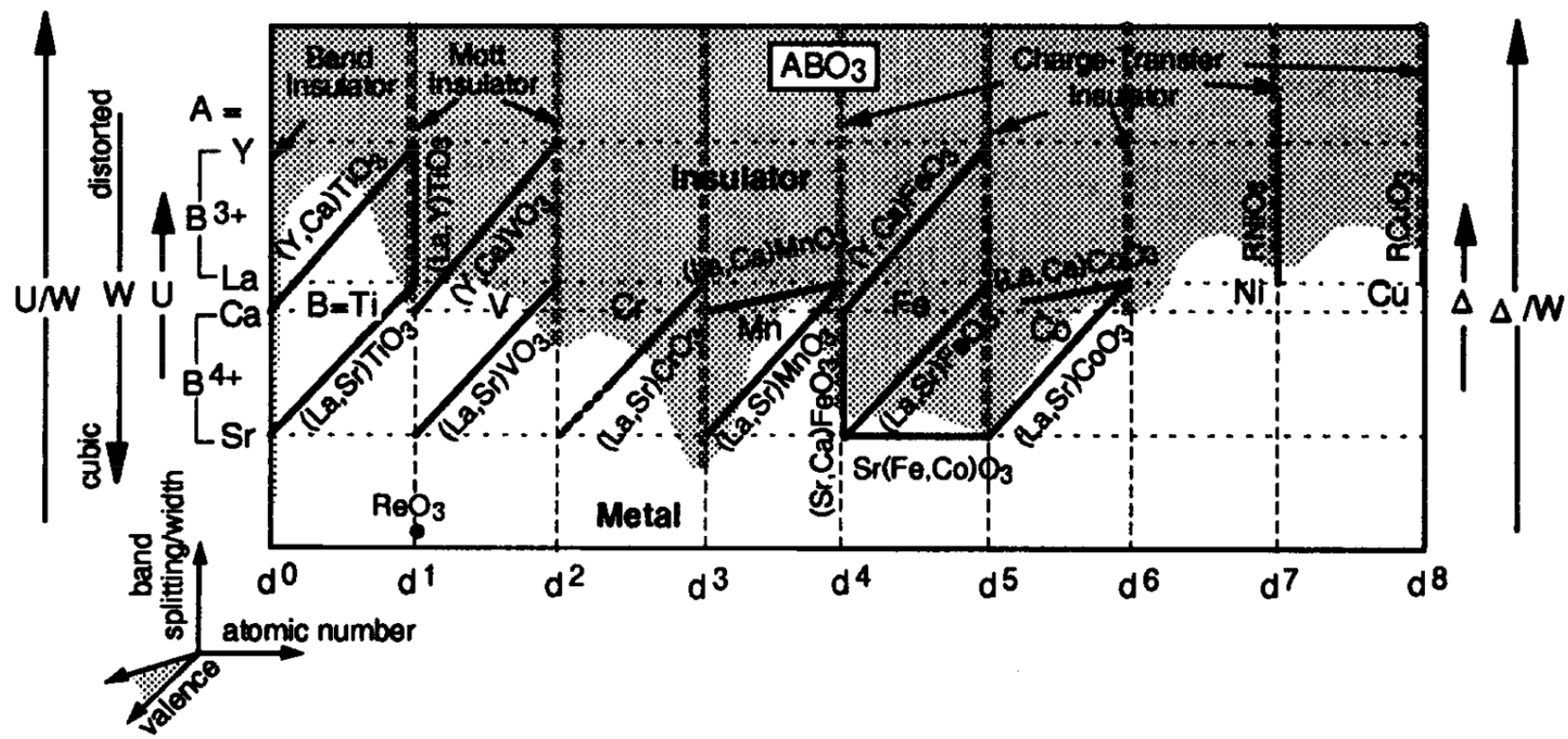


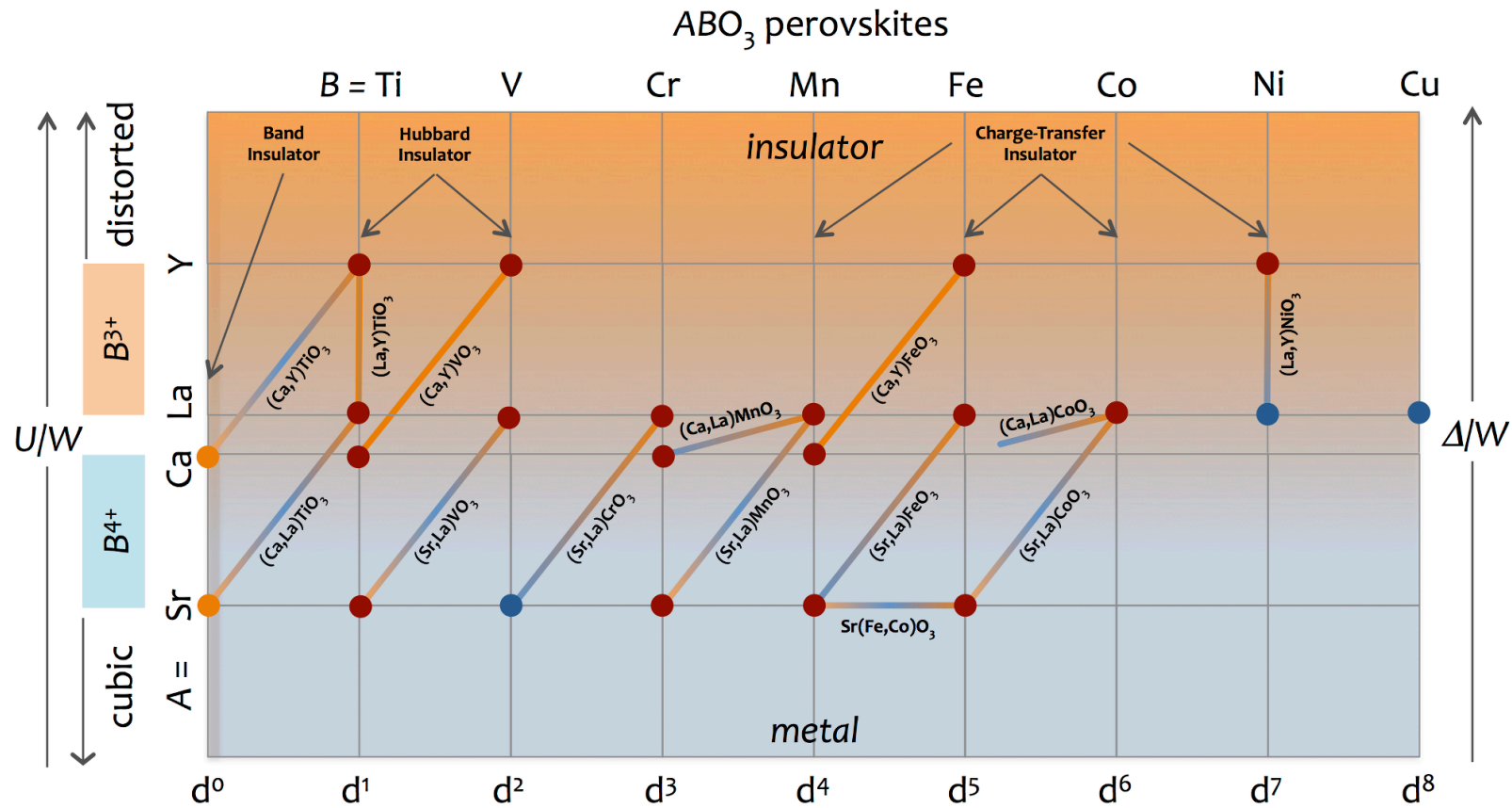
## Non-metal to Metal Transitions

Purpose of this materials – understanding the diagram below:



Fujimori, Electronic structure of metallic oxides: band-gap closure and valence control, *J. Phys. Chem. Solids* 53 (1992) 1595–1602.

# Purpose of this course – understanding the diagram below:



Fujimori, Electronic structure of metallic oxides: band-gap closure and valence control, *J. Phys. Chem. Solids* **53** (1992) 1595–1602.

See also: Imada, Fujimori, and Tokura, Metal-insulator transitions, *Rev. Mod. Phys.* **70** (1998) 1039–1263.

# An example of non-metal to metal transitions: The Periodic Table

## PERIODIC TABLE OF THE ELEMENTS

<http://www.periodni.com>

GROUP	PERIODIC TABLE OF THE ELEMENTS																18					
1	2		3										10	11	12	13	14	15	16	17	18	
1	2		3										10	11	12	13	14	15	16	17	18	
1	1.0079																				4.0026	
1	H																					He
2	3	4																				
2	Li	Be																				
3	11	12																				
3	Na	Mg																				
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36				
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54				
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
6	55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86				
6	Cs	Ba	La-Lu Lanthanide	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
7	87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118				
7	Fr	Ra	Ac-Lr Actinide	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo				

RELATIVE ATOMIC MASS (1)

GROUP IUPAC: 13 IIIA

GROUP CAS: 5

ATOMIC NUMBER: 5

SYMBOL: B

ELEMENT NAME: BORON

Legend:

- Metal (Blue)
- Semimetal (Orange)
- Nonmetal (Green)
- Alkali metal (Light Blue)
- Alkaline earth metal (Light Blue)
- Transition metals (Dark Blue)
- Lanthanide (Pink)
- Actinide (Purple)
- Chalcogens element (Light Green)
- Halogens element (Dark Green)
- Noble gas (Light Green)

STANDARD STATE (25 °C; 101 kPa)

- Ne - gas
- Hg - liquid
- Fe - solid
- Tc - synthetic

(1) Pure Appl. Chem., 81, No. 11, 2131-2156 (2009)  
 Relative atomic masses are expressed with five significant figures. For elements that have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element. However three such elements (Th, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

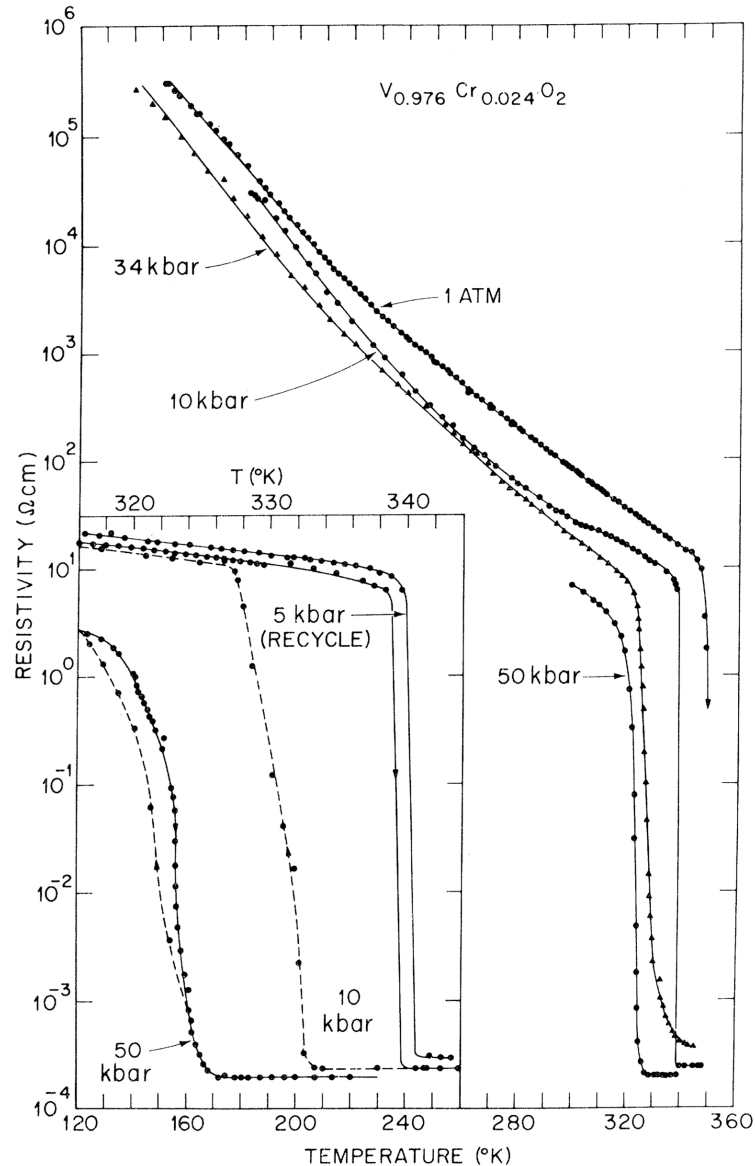
LANTHANIDE

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LANTHANUM	CERIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	YTTERBIUM	LUTETIUM

ACTINIDE

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
ACTINIUM	THORIUM	PROTACTINIUM	URANIUM	NEPTUNIUM	PLUTONIUM	AMERICIUM	CURIUM	BERKELIUM	CALIFORNIUM	EINSTEINIUM	FERMIUM	MENDELEVIUM	NOBELIUM	LAWRENCIUM

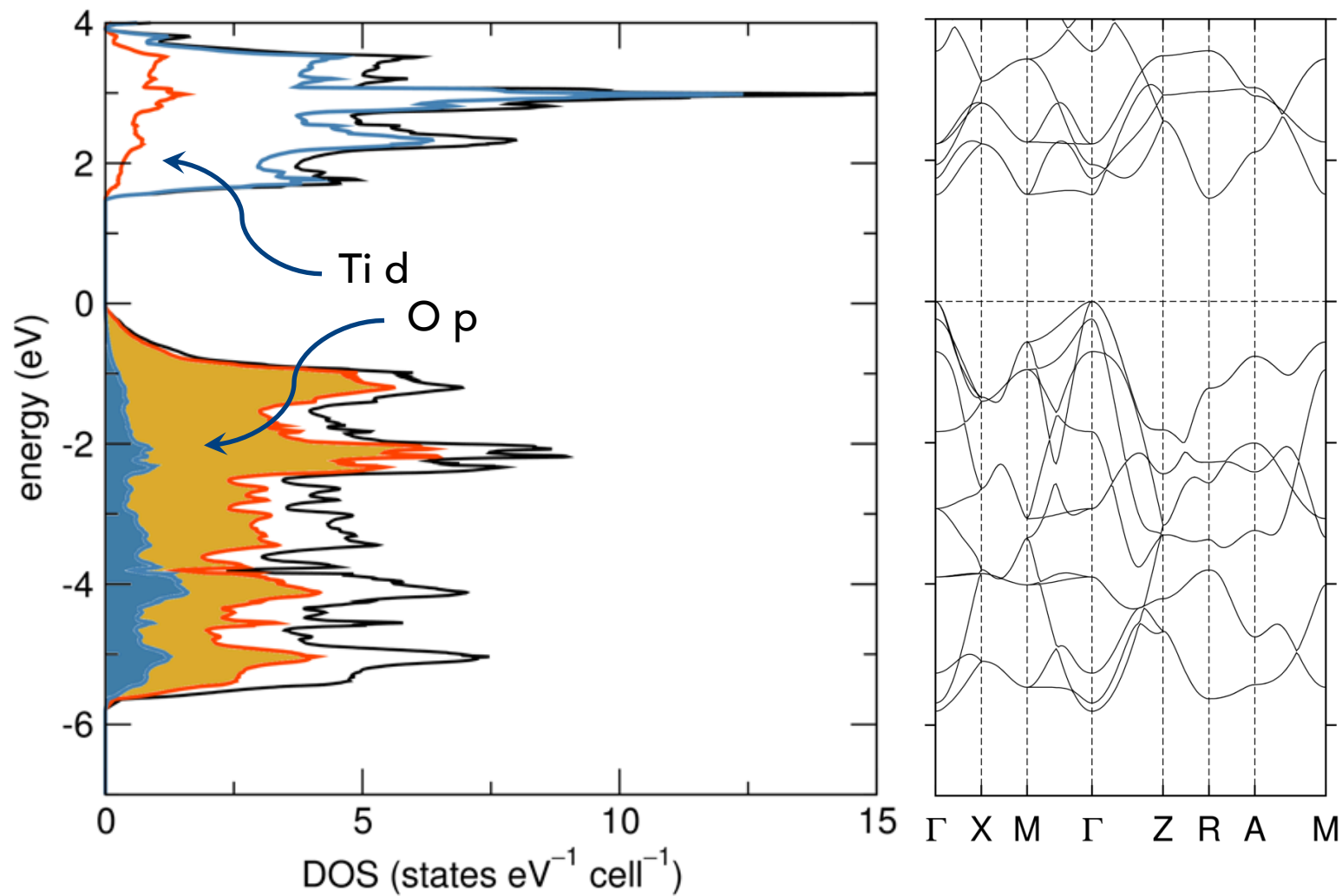
Why are most elements metallic, but not all?



6-order of magnitude resistivity change over a 10 K range in the vicinity of 340 K, in  $\text{V}_{0.976}\text{Cr}_{0.024}\text{O}_2$

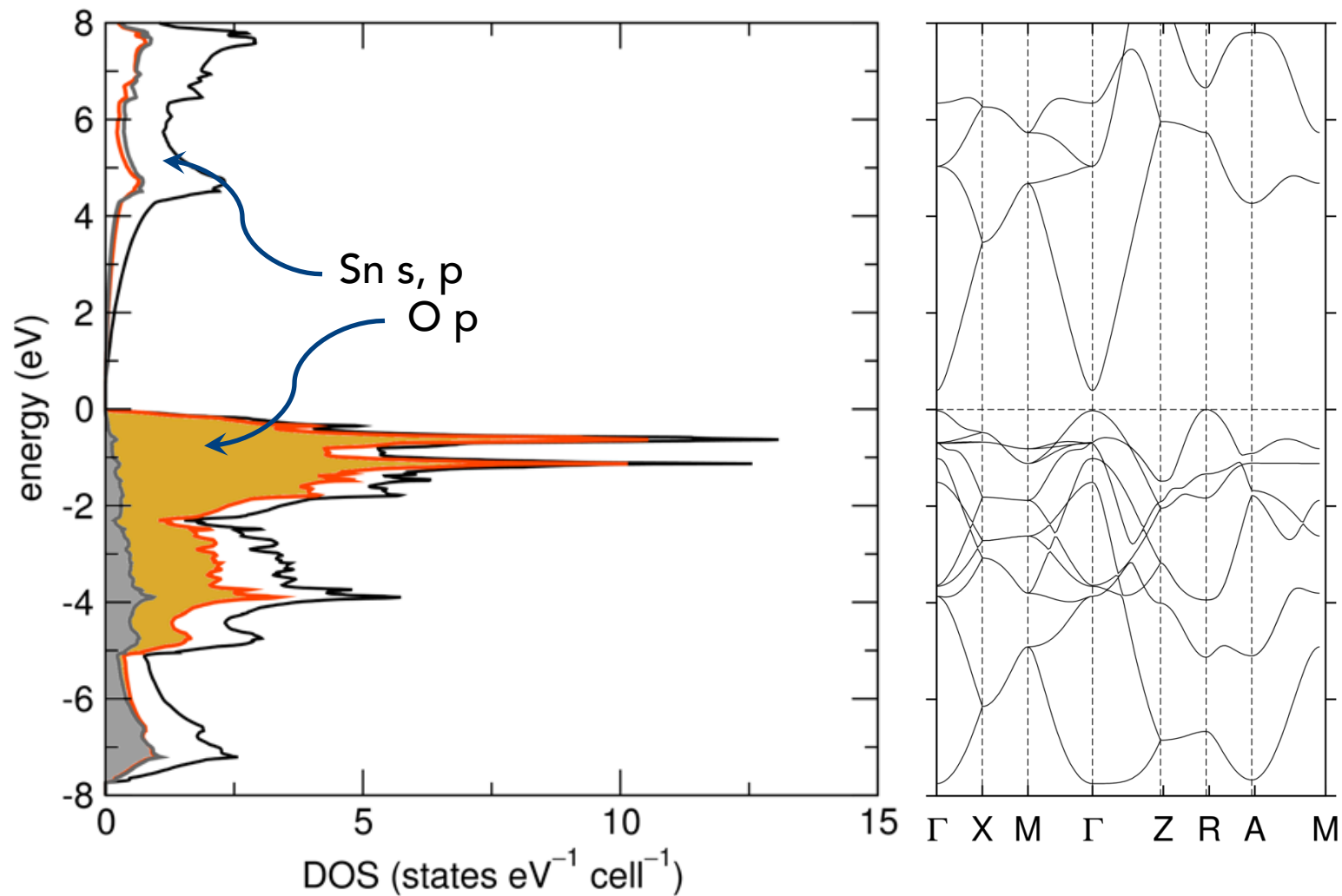
Marezio, McWhan, Remeika, Dernier, Structural aspects of the metal-insulator transitions in Cr-doped  $\text{VO}_2$ , *Phys. Rev. B* 5 (1972) 2541–2551.

# Valence-precise compounds. Counting electrons in $\text{TiO}_2$ : Assign as $\text{Ti}^{4+}$ and $\text{O}^{2-}$



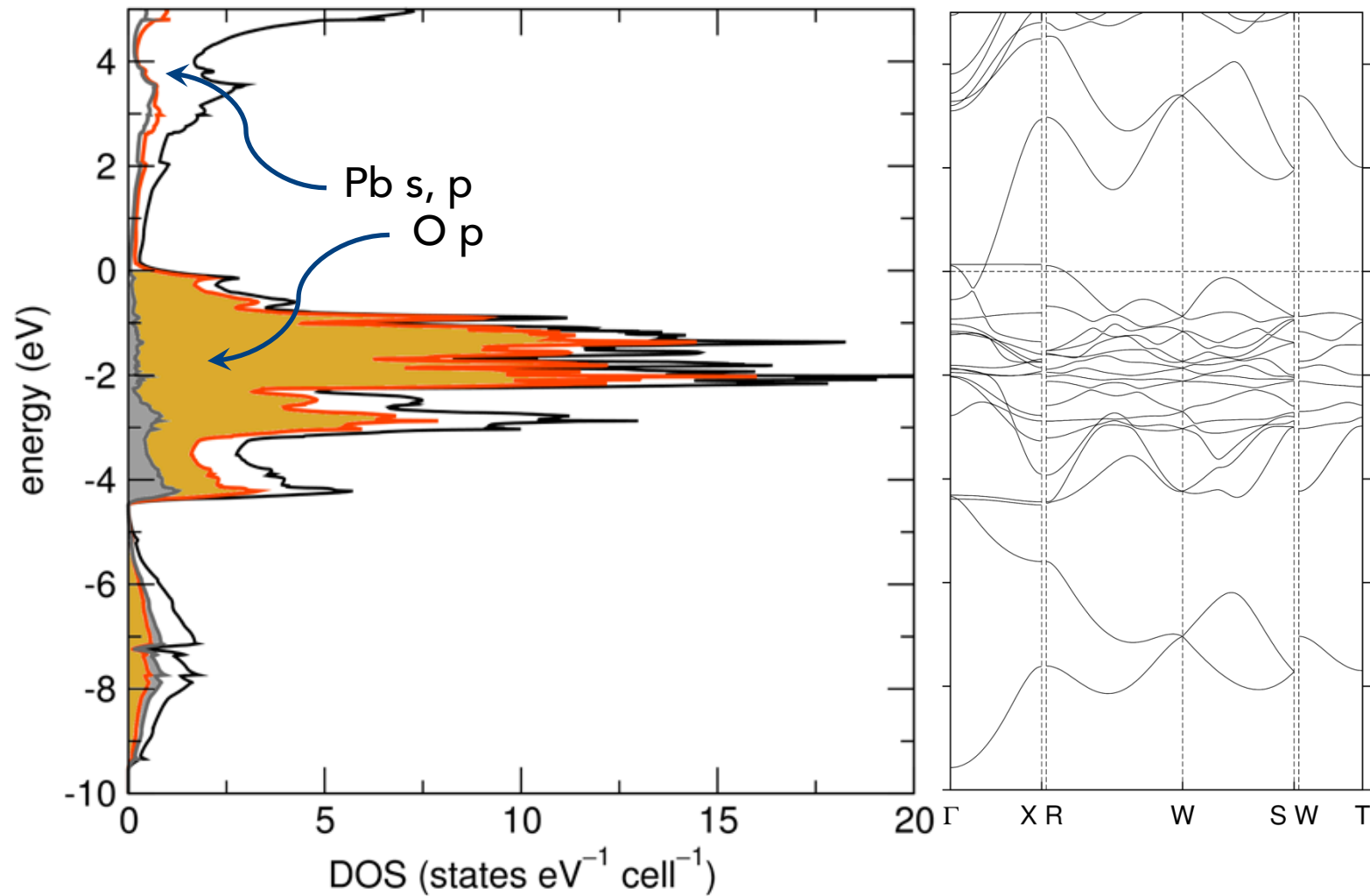
Insulator, not so easy to dope.

# Counting electrons in $\text{SnO}_2$ : Assign as $\text{Sn}^{4+}$ and $\text{O}^{2-}$ (more covalent than $\text{TiO}_2$ )



Semiconductor: Easier to dope. Used as a TCO material.

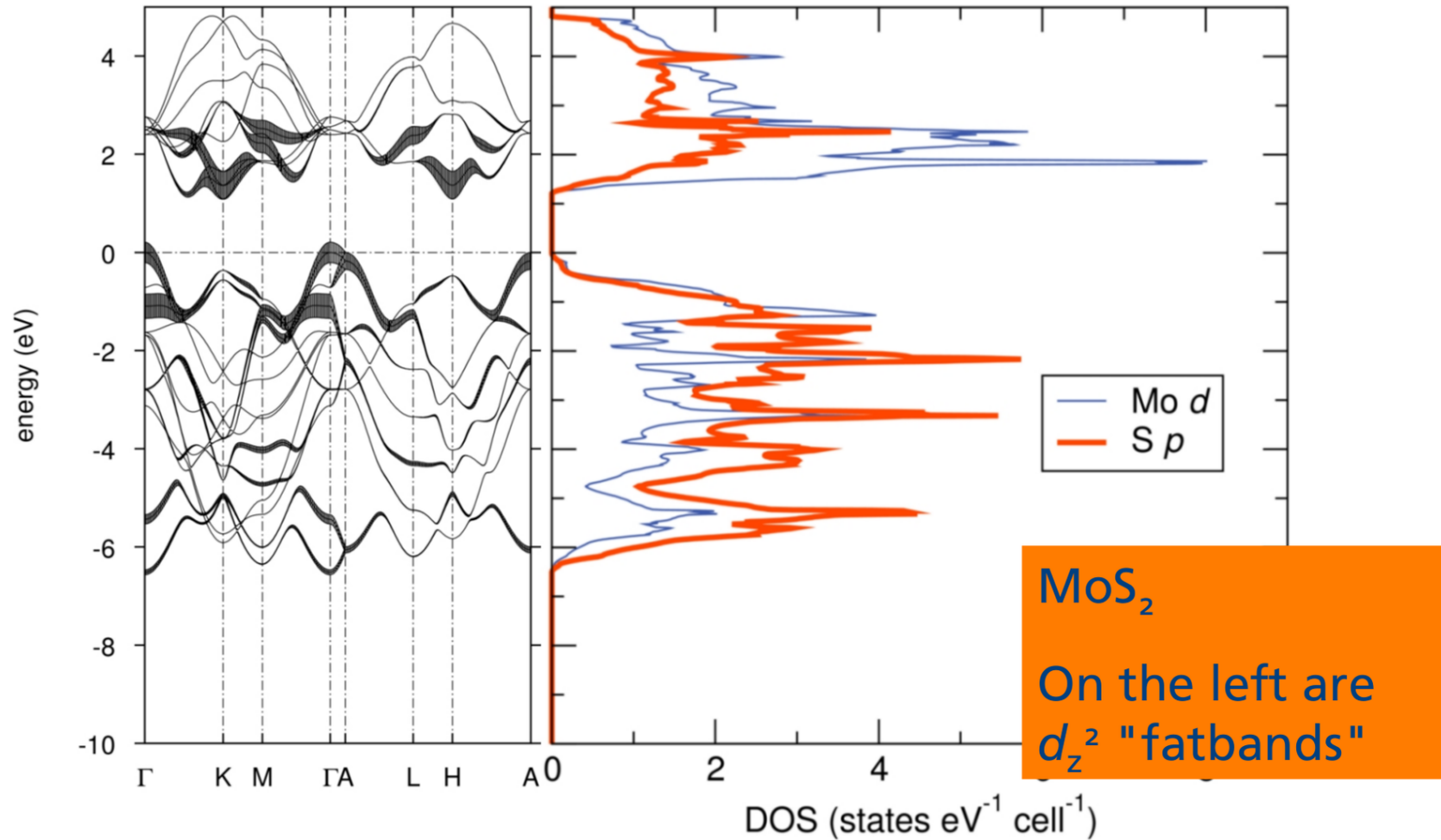
# Counting electrons in BaPbO<sub>3</sub>: Assign as Pb<sup>4+</sup> and O<sup>2-</sup>. An unexpected semi-metal



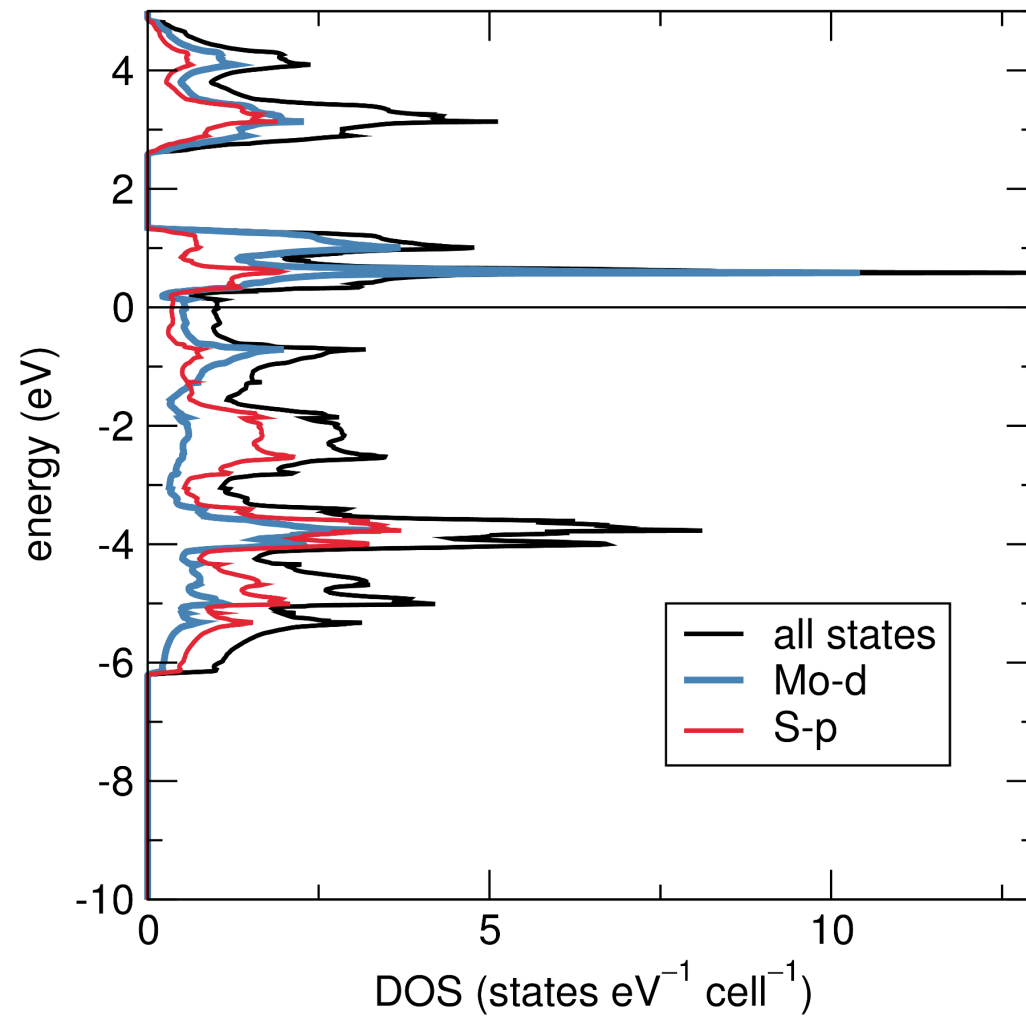
A surprise – it's a (semi)metal. The equivalent Sn<sup>4+</sup> compound is not.



# MoS<sub>2</sub>: Crystal-field effects are important (and therefore structure).

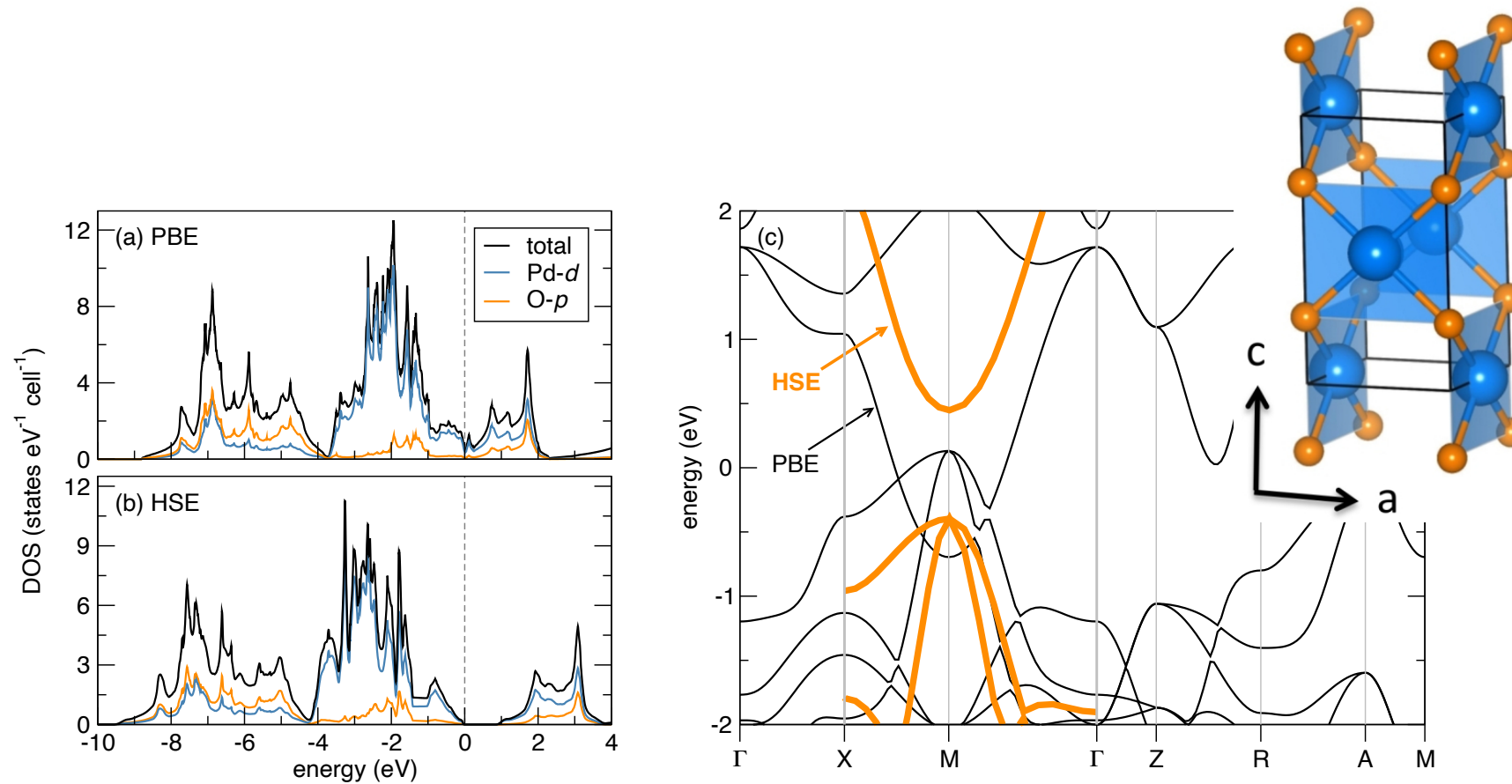


It's a semiconductor because the two d electrons occupy a (filled) *d*<sub>z<sup>2</sup></sub> orbital.



The two d electrons are now in a degenerate band.

# Another example of crystal-field effects: PdO



Square-planar  $d^8$  configuration allows a band insulator.

Kurzman, Miao, Seshadri, Hybrid functional electronic structure of  $\text{PbPdO}_2$ , a small-gap semiconductor, *J. Phys.: Condens. Matter* 23 (2011) 465501(1–7).

The Wilson (Arthur Herries Wilson) theory:

Partially filled bands allow electrons to move, and this increases the zero-point energy (the Heisenberg uncertainty principle).

If the band were filled, the Pauli exclusion principle would ensure that any movement (of electrons) is precisely compensated.

However: "... overlap of the wave functions gives rise to a half-filled band, and according to the Wilson picture, the system should be metallic-however far apart the atoms might be."

Wilson, *The Theory of Metals. I, Proc. R. Soc. London. Ser. A* **138** (1932) 594–606.

Quote from: Edwards and Sienko, *The transition to the metallic state, Acc. Chem. Res.* **15** (1982) 87–93.

## Thomas-Fermi screening:

Consider the density of electrons in a metal: These are of the order of  $10^{22} \text{ cm}^{-3}$ , which is as dense as a condensed (crystalline phase). If we expected these electrons to strongly repel, they should crystallize (like hard spheres do).

How is it that they go about their business like other electrons were not there.

Answer: They do NOT interact through the Coulomb ( $1/r$ ) potential !

The Screened Coulomb Potential (after Kittel):

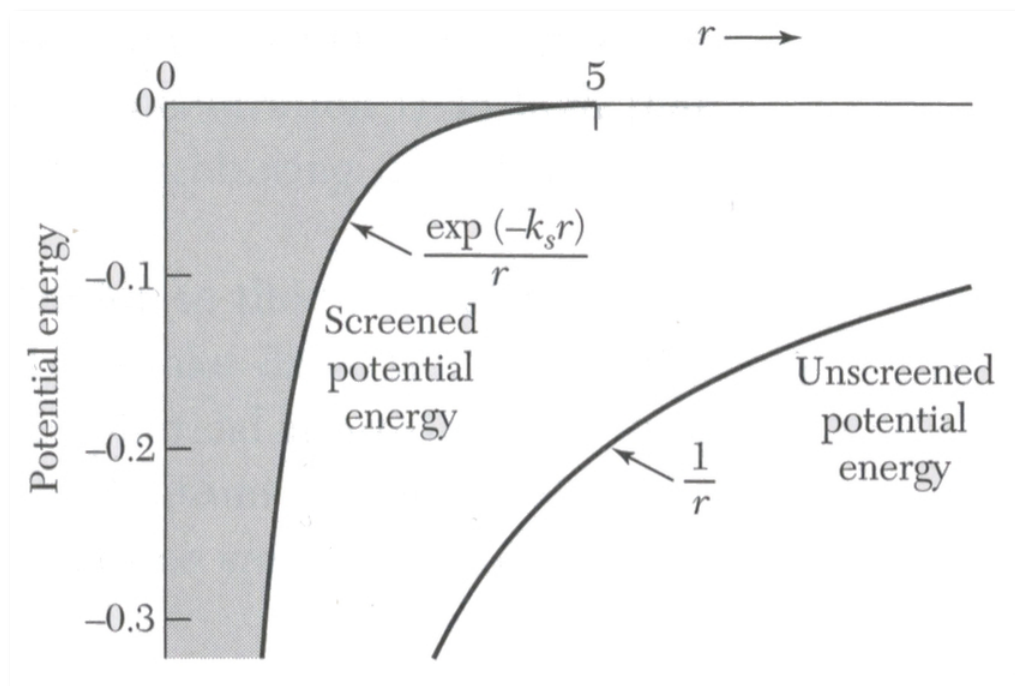
$$\varphi = \frac{q}{r} \exp(-k_s r)$$

$k_s$  is the Thomas-Fermi screening wavelength:

$$k_s = 4\pi e^2 D(\epsilon_F)$$

$$\varphi = \frac{q}{r} \exp(-k_s r) \quad \text{with} \quad k_s = 4\pi e^2 D(\epsilon_F)$$

The larger the densities of state, the more electrons are screened. See image below from Kittel (8<sup>th</sup> Edn. page 407).



Also:

$$k_s \propto \frac{n_0^{1/3}}{a_0}$$

where  $a_0$  is the Bohr radius and  $n_0$  is the concentration of charge carriers.

For Cu metal,  $n_0 = 8.5 \times 10^{22} \text{ cm}^{-3}$  and  $1/k_s = 0.55 \text{ \AA}$ . It is only below this distance that electrons "talk".

So more electrons in a limited volume means the less they "see" each other.

The Clausius-Mossotti equation relates the relative dielectric  $\epsilon_r$  constant of matter to the molar refractivity  $R_m$  in the gaseous state, and the molar volume  $V_m$  in condensed phase.

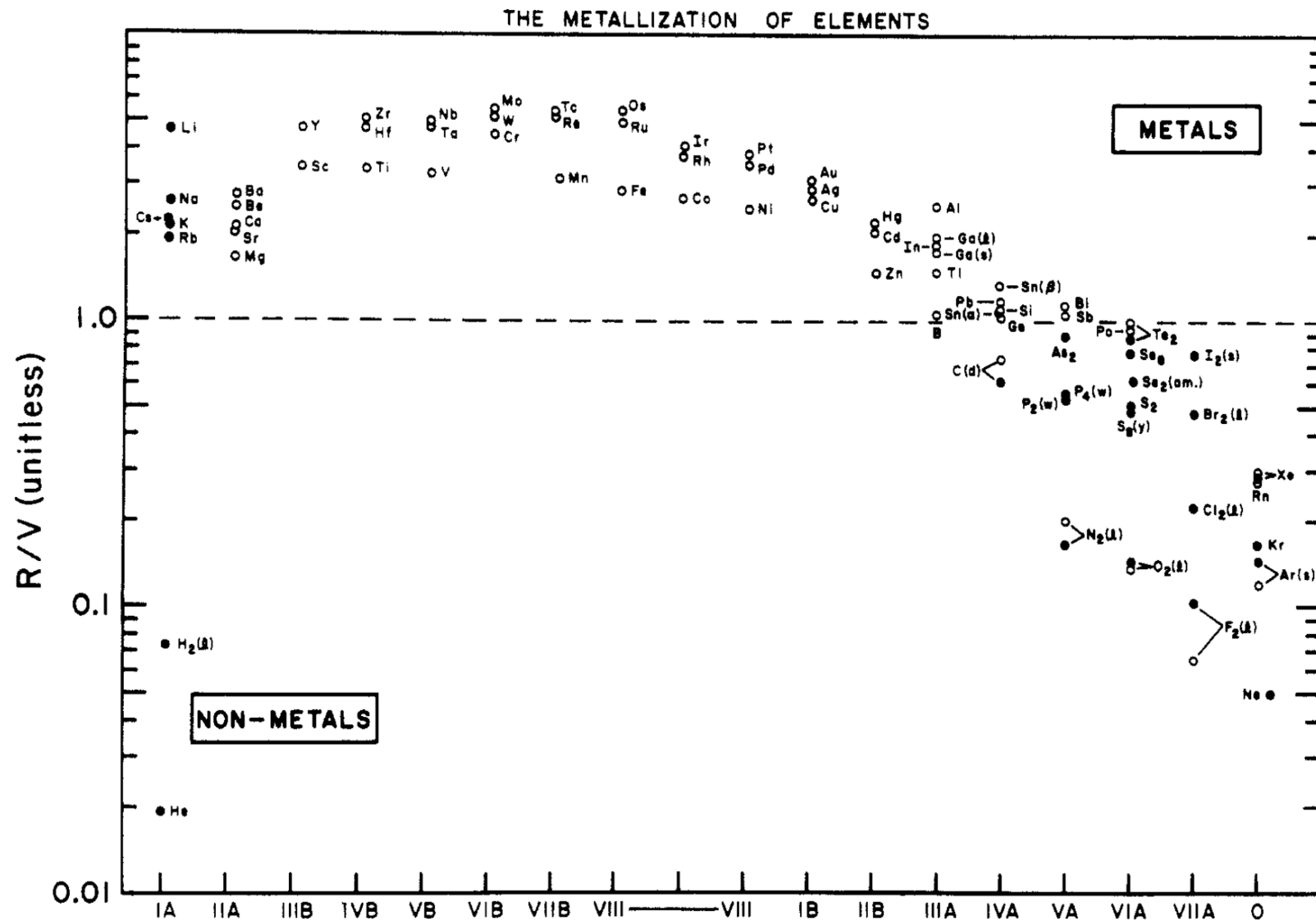
$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{R}{V} \text{ which means that } \frac{R}{V} = 1 \implies \epsilon_r = \infty$$

This is the condition of a metal (infinite dielectric screening).

Since  $R$  and  $V$  are properties of the atom, this allows the periodic table to be sorted (see next page).

Edwards and Sienko, The transition to the metallic state, *Acc. Chem. Res.* **15** (1982) 87–93.

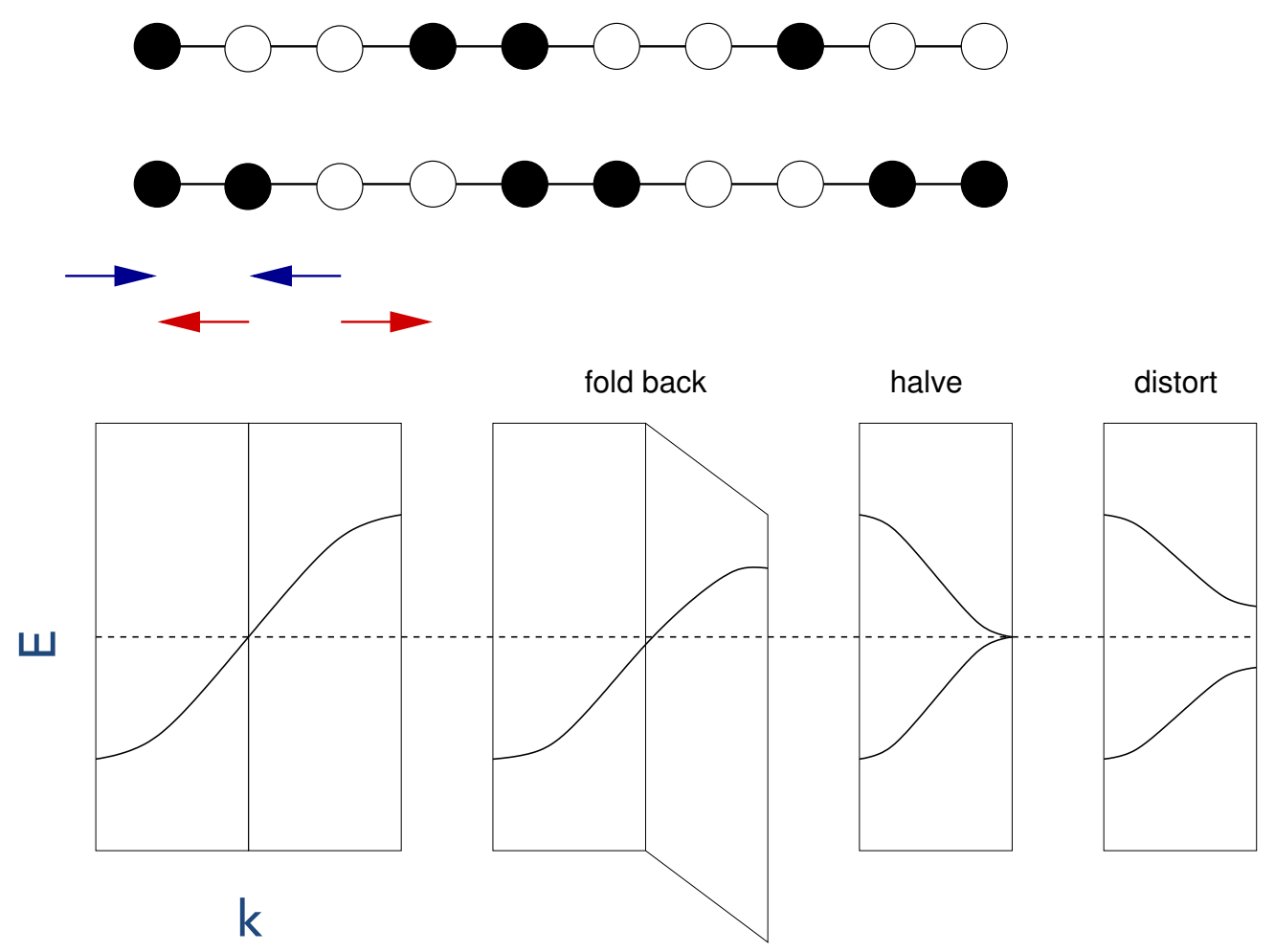
# The Herzfeld criterion and the periodic table



Edwards and Sienko, The transition to the metallic state, *Acc. Chem. Res.* 15 (1982) 87–93.

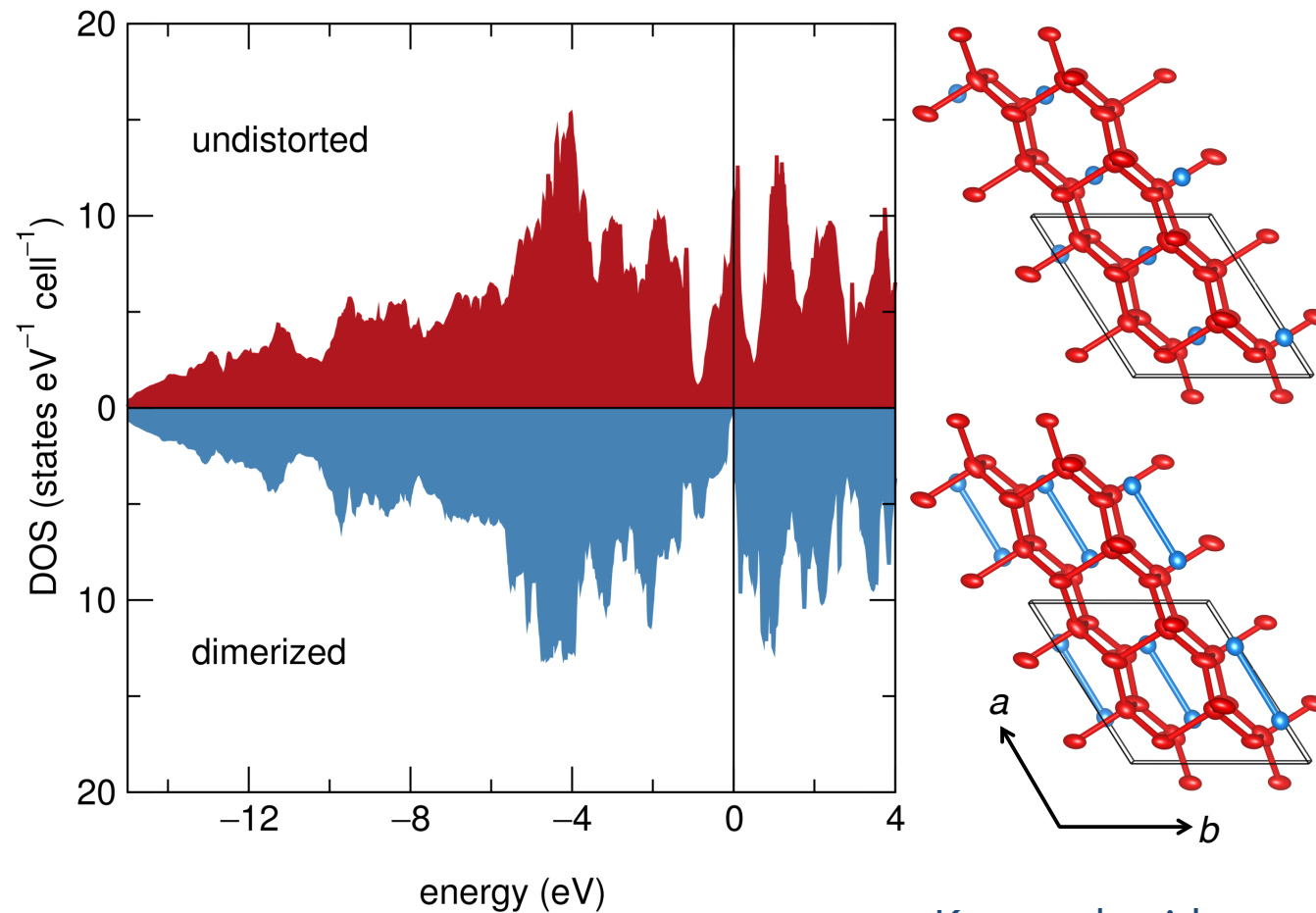


# The Peierls distortion seen in 1D chains: The simplest model for a gap.



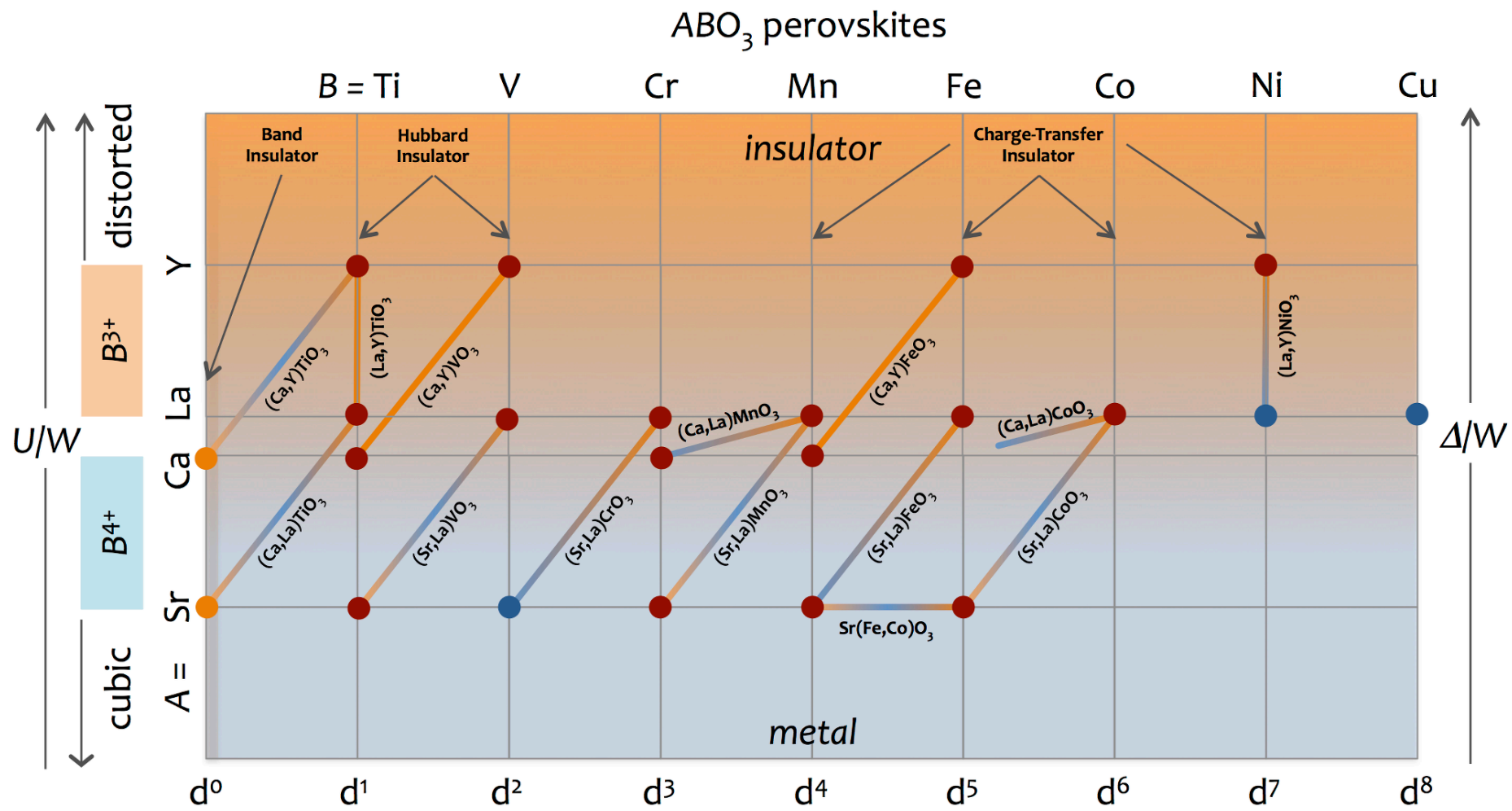
Note that we go from being valence-imprecise to being valence precise:  
Now two electrons per unit cell.

## A real-world example of Peierls:



Knappschneider *et al.*, Peierls-distorted monoclinic MnB<sub>4</sub> with a Mn-Mn bond, *Angew. Chem. Int. Ed.* **53** (2014) 1684–1688.

# Charge carrier concentration and the filling-driven Mott transition

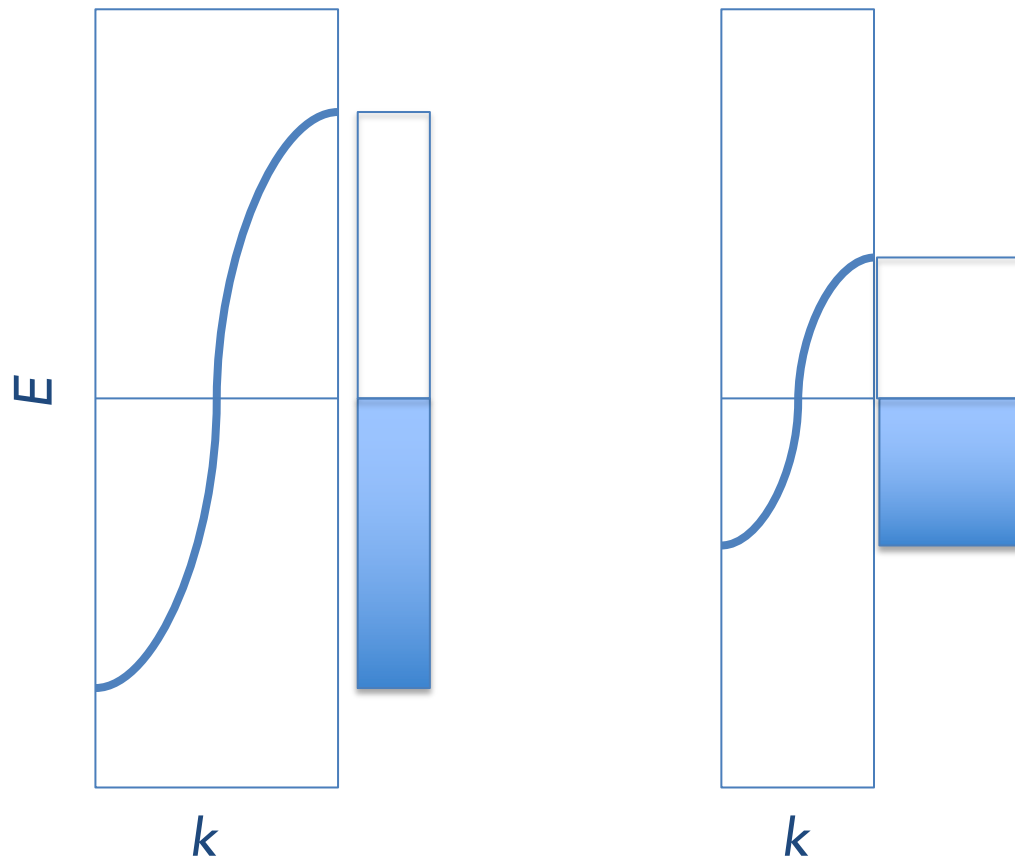


Band theory (Wilson theory) and DFT would suggest that any departure from a band insulator should give rise to metallic behavior. This is wrong. Look close to SrTiO<sub>3</sub> and CaTiO<sub>3</sub>.

# Charge carrier concentration and the filling-driven Mott transition

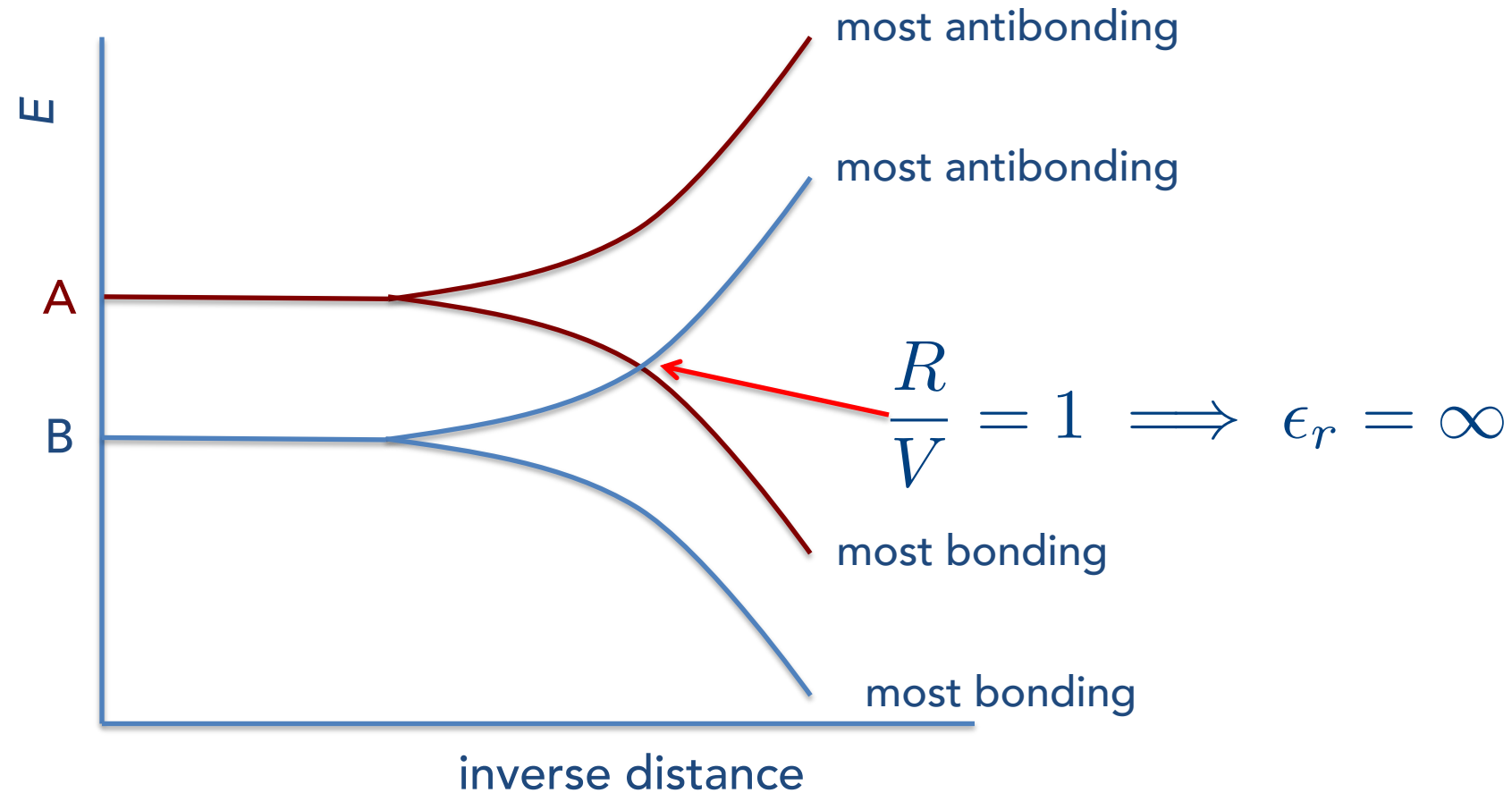
Consider the 1D chain again, at half-filling. Assume Peierls does not take place.

The system remains metallic no matter how far apart the atoms, which cannot be right. Mott: "... this is against common experience, and, one might say, common sense"



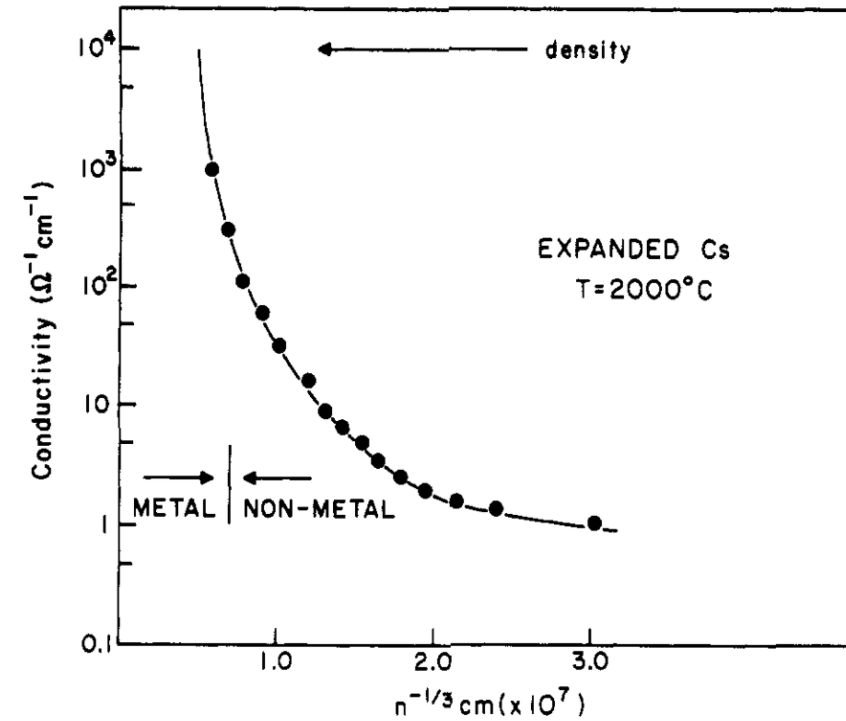
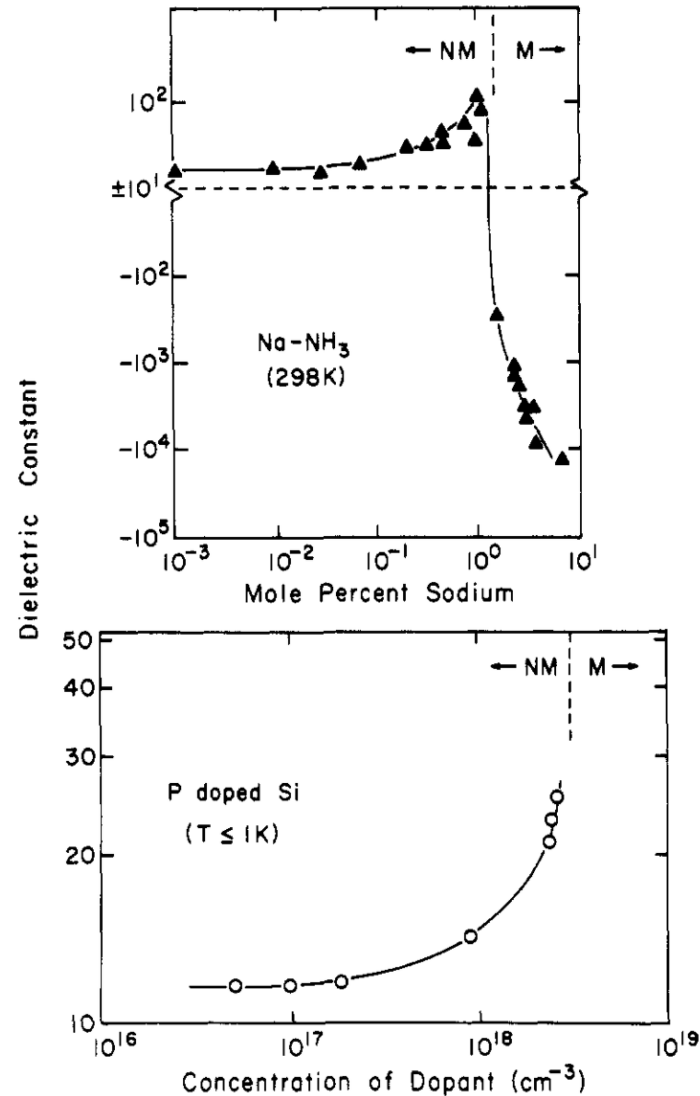
# Charge carrier concentration and the filling-driven Mott transition

This familiar picture of atomic orbital levels interacting and spreading out as they approach, is not a band-structure picture. This picture captures the Herzfeld criterion discussed previously.



# Charge carrier concentration and the filling-driven Mott transition

Examples of composition (band-filling) dependent non-metal to metal transitions:



Edwards and Sienko, *Acc. Chem. Res.*

Consider the case of expanded Cs, which for convenience, can be treated as a chain. When the atoms are infinitely separated, the energy required to remove an electron is the ionization energy  $IE = 3.89$ .

The energy required to place an electron on neutron Cs is the electron affinity  $EA = 0.47$  eV.

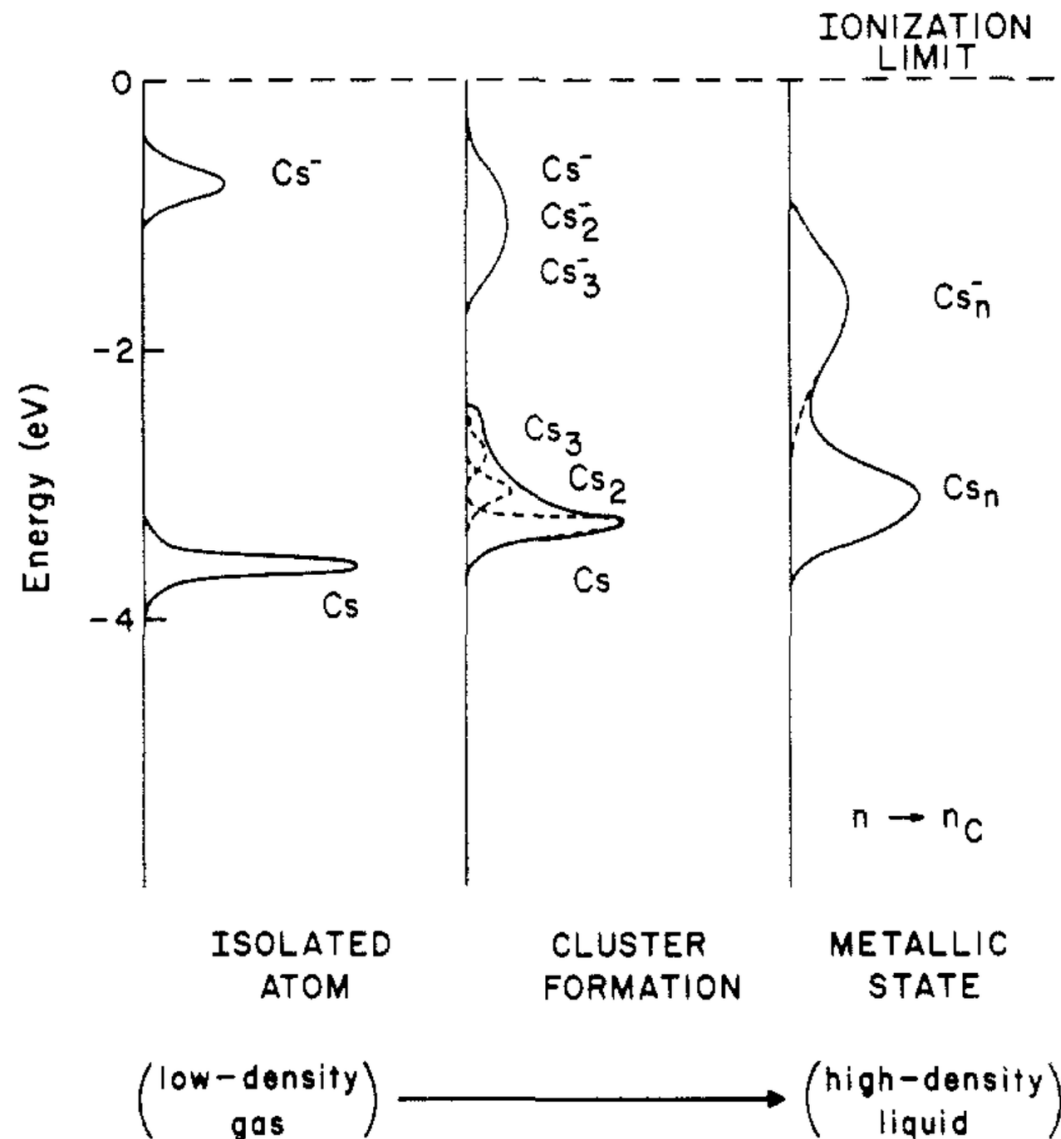
The energy cost to transfer an electron is the difference, referred to as the Hubbard  $U$ .

$$U = IE - EA = 3.42 \text{ eV}$$

This is the potential energy barrier required to be overcome, in order for electrons to hop.

Hopping is favored by the kinetic energy or bandwidth.

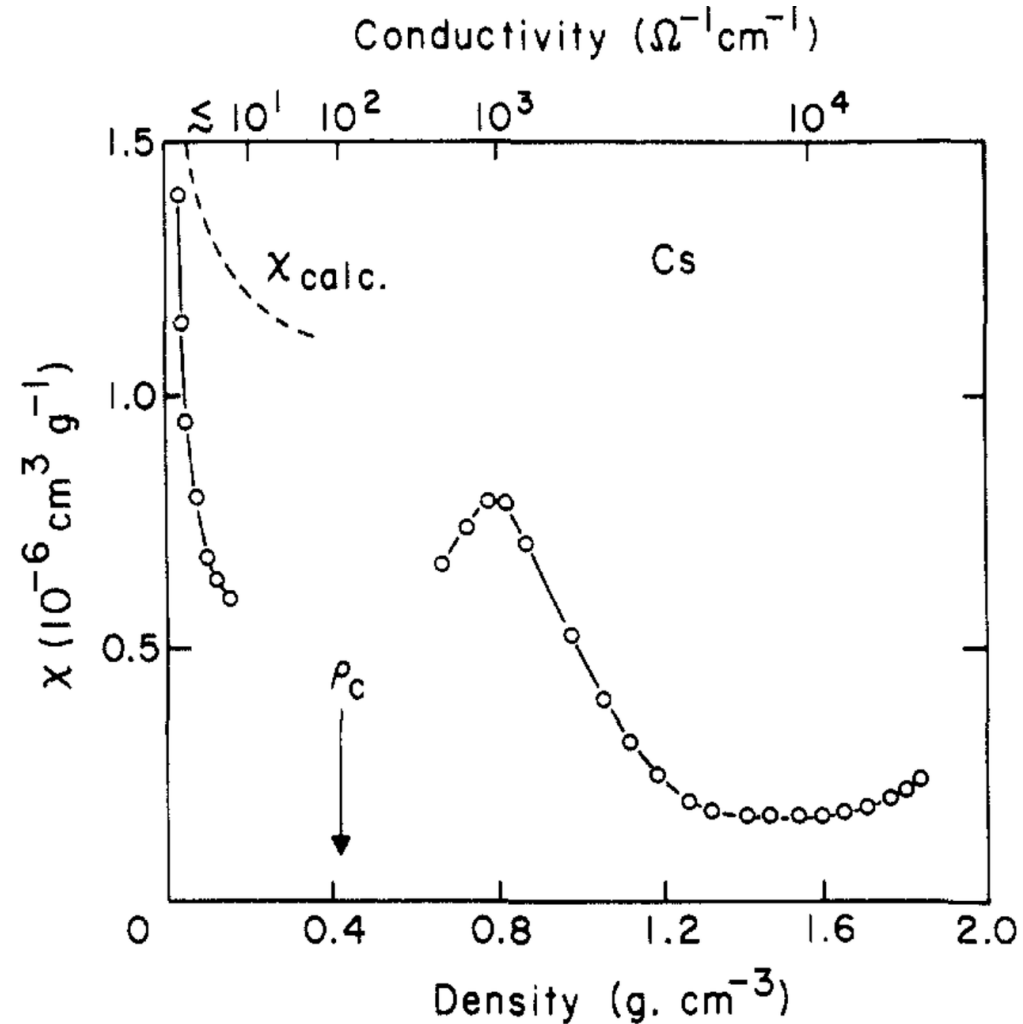
# Charge carrier concentration and the filling-driven Mott transition



Approximate energetics  
for the metallization of Cs.

Edwards and Sienko, *Acc. Chem. Res.*





Consequences for magnetism:  
When the charge carriers are localized, they can carry spin.

Magnetism is therefore frequently associated with non-metal to metal transitions.

Edwards and Sienko, *Acc. Chem. Res.*

The Mott treatment of when the threshold concentration is crossed, is based on Thomas-Fermi screening:

$$\varphi = \frac{q}{r} \exp(-k_s r) \quad \text{with} \quad k_s \propto \frac{n_0^{1/3}}{a_0}$$

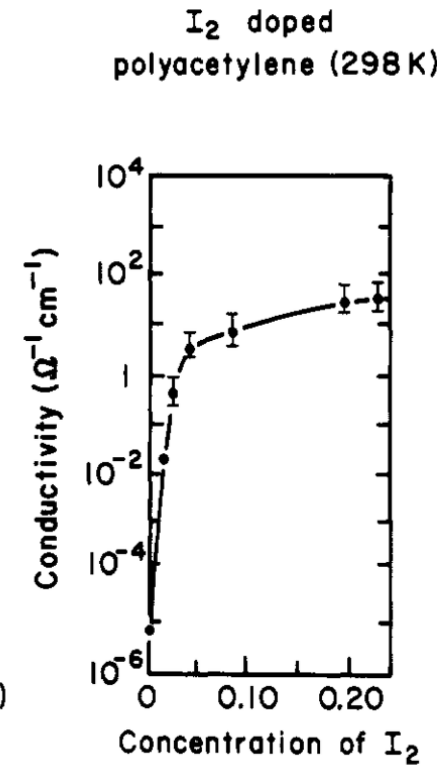
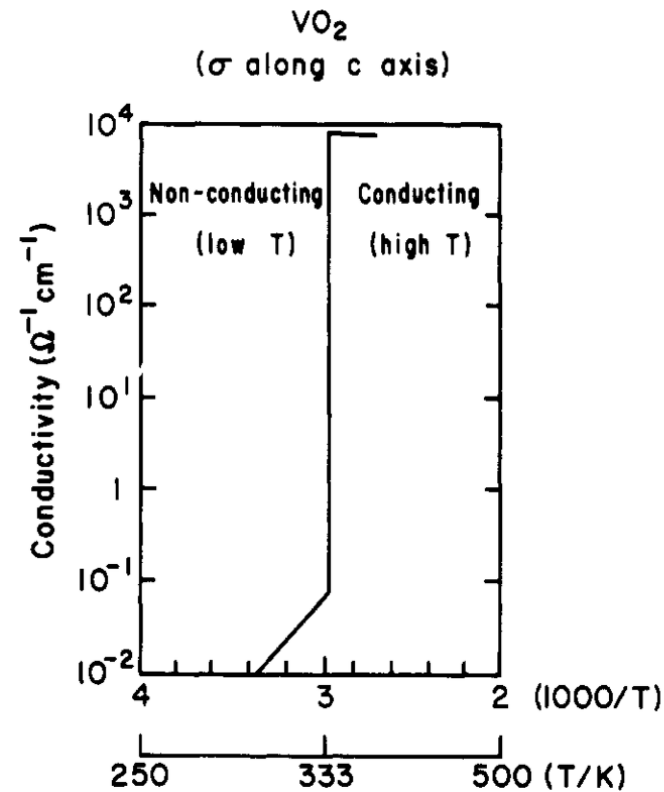
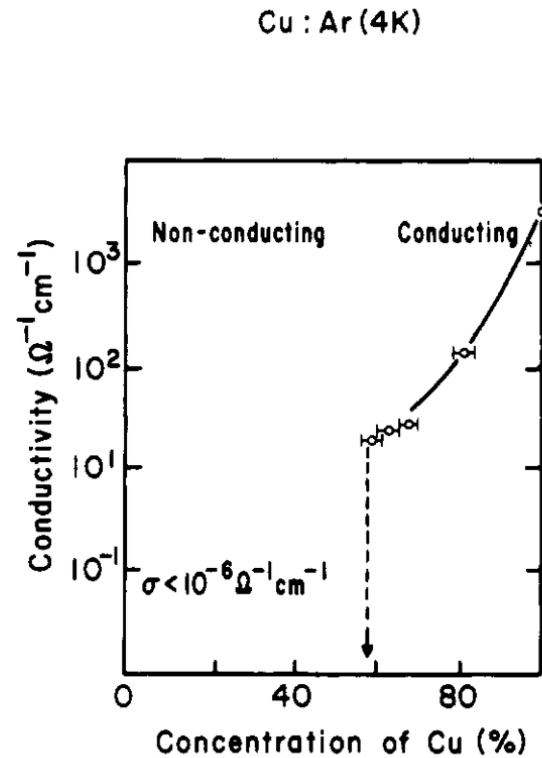
When the strength of the screening overcomes the Coulombic repulsion  $U$ , at a critical number density of carriers  $n_c$  and the Mott criterion is fulfilled:

$$n_c^{1/3} a_0 \approx 0.25$$

where  $a_0$  is the hydrogenic Bohr radius.

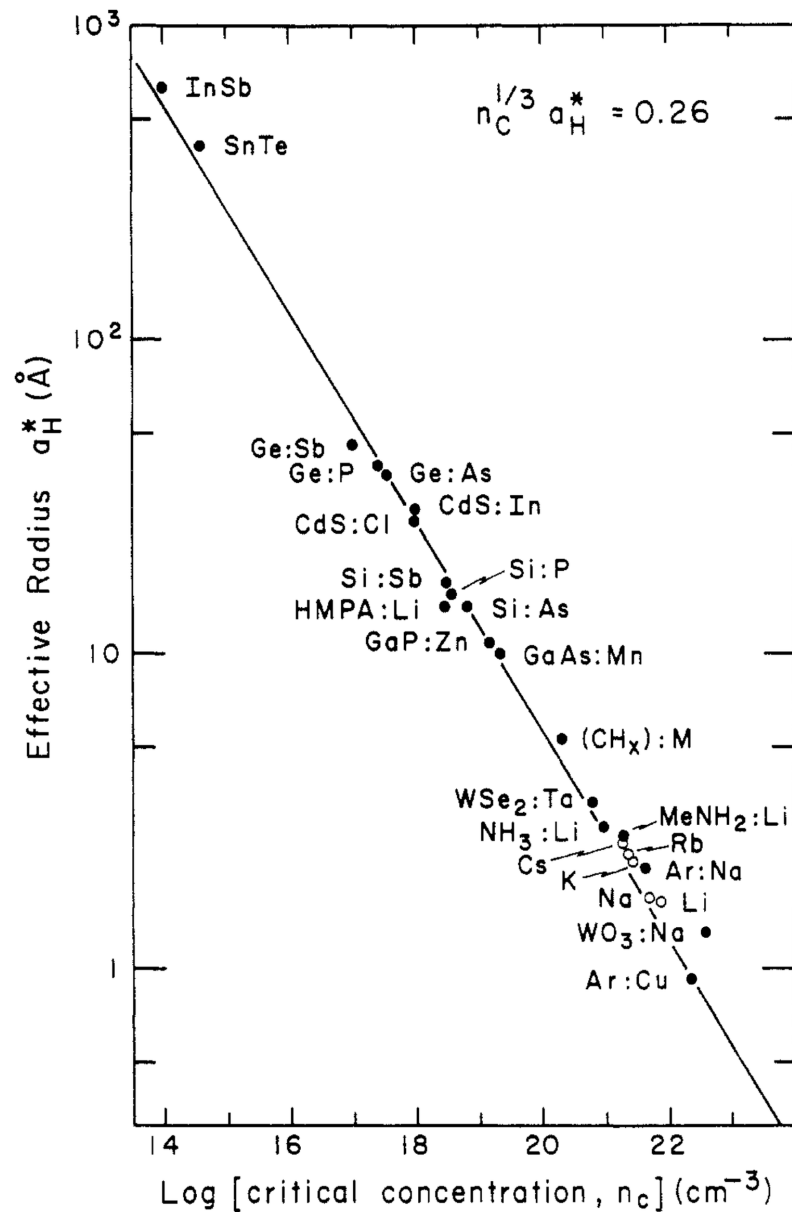
This should be a first-order phase transition, although that has not been easy to verify.

Some more examples:



Edwards and Sienko, *Acc. Chem. Res.*

# Charge carrier concentration and the filling-driven Mott transition



Manifestations of the Mott criterion.

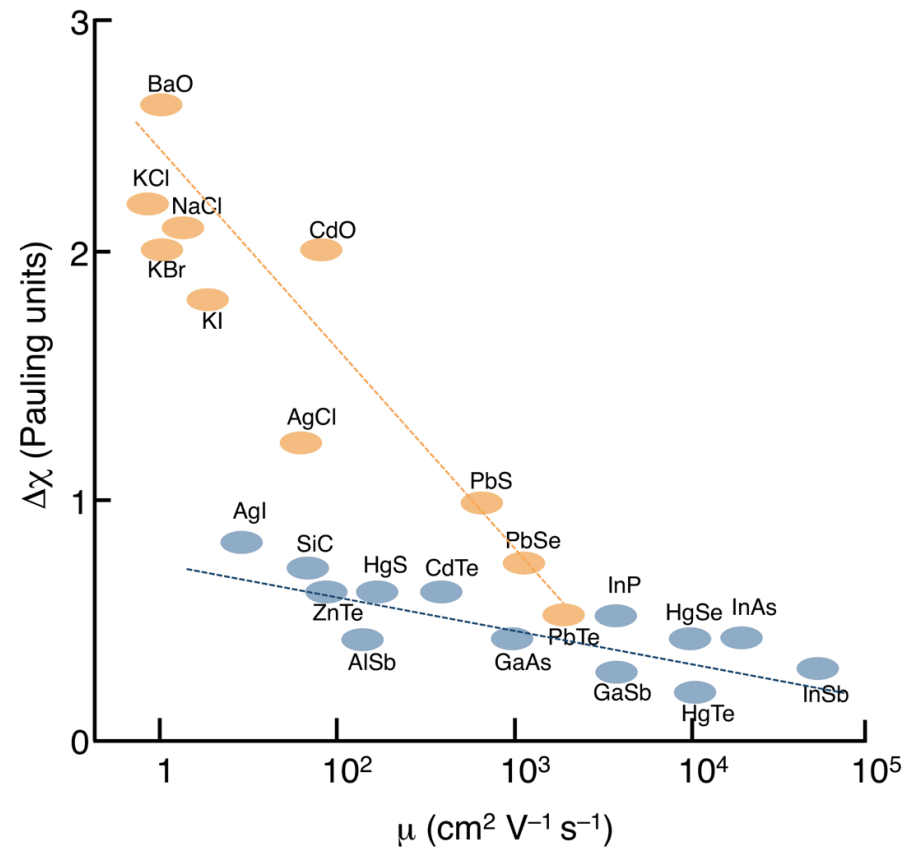
Note that a large Bohr radius should correspond to a high mobility.

Remember:

$$\sigma = ne\mu$$

Edwards and Sienko, *Acc. Chem. Res.*

# Charge carrier concentration and the filling-driven Mott transition



But large intrinsic  $\mu$  is associated with small electronegativity differences.

Adapted from R. E. Newnham,  
Properties of Materials

The Mott minimum metallic conductivity (originally argued for disordered systems):

$$n_c^{1/3} a_0 \approx 0.25$$

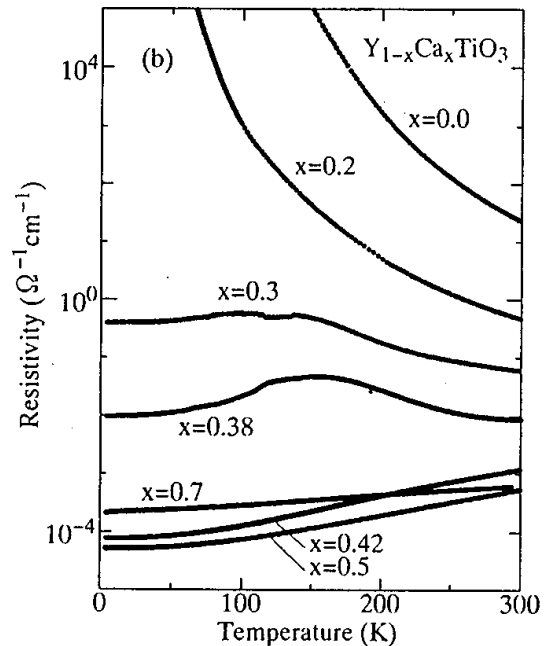
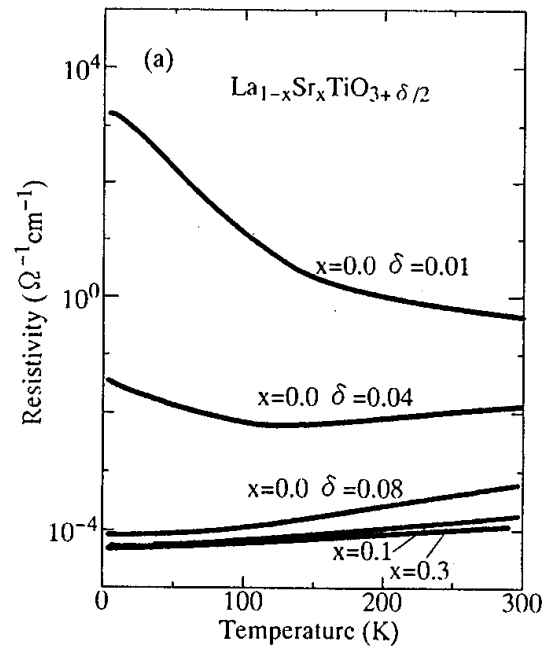
implies that at the transition:

$$\sigma_M = C e^2 / (\hbar a_0)$$

This is a fixed value of the conductivity, usually close to  $100 \text{ S cm}^{-1}$ , or correspondingly, there is a maximum metallic resistivity, close to  $0.01 \text{ } \Omega \text{ cm}$ .

Möbius, The metal-semiconductor transition in three-dimensional disordered systems-reanalysis of recent experiments for and against minimum metallic conductivity, *J. Phys. C: Solid State Phys.* **18** (1985) 4639–4670.

Examples:



From Imada, Fujimori, and Tokura, *Metal-insulator transitions*, *Rev. Mod. Phys.* **70** (1998) 1039–1263.

