

Electronic Structure and Chemical Bonding

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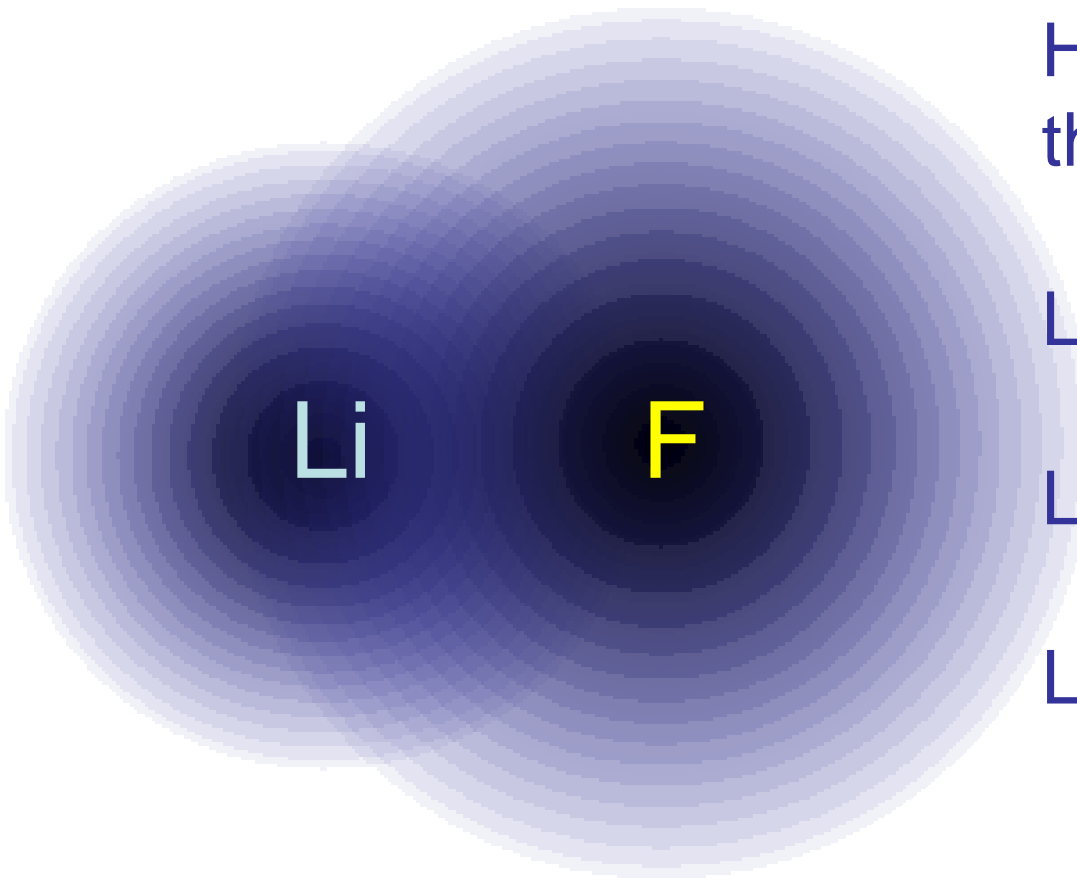


Chemical bonding is about the rearrangement of electrons due to the arrangement of the nuclei.

It is the source of the interesting properties of condensed matter.

But how do we characterize it?

How Do We Know What is What



How do we understand this in useful terms:

$\text{Li}^+ \text{F}^-$?

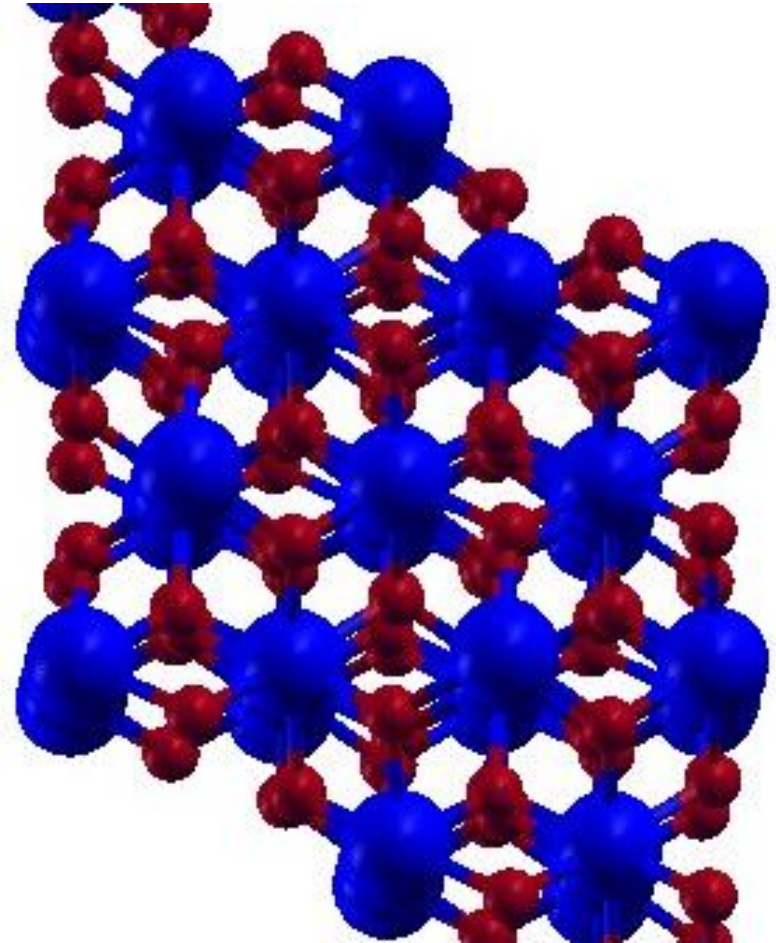
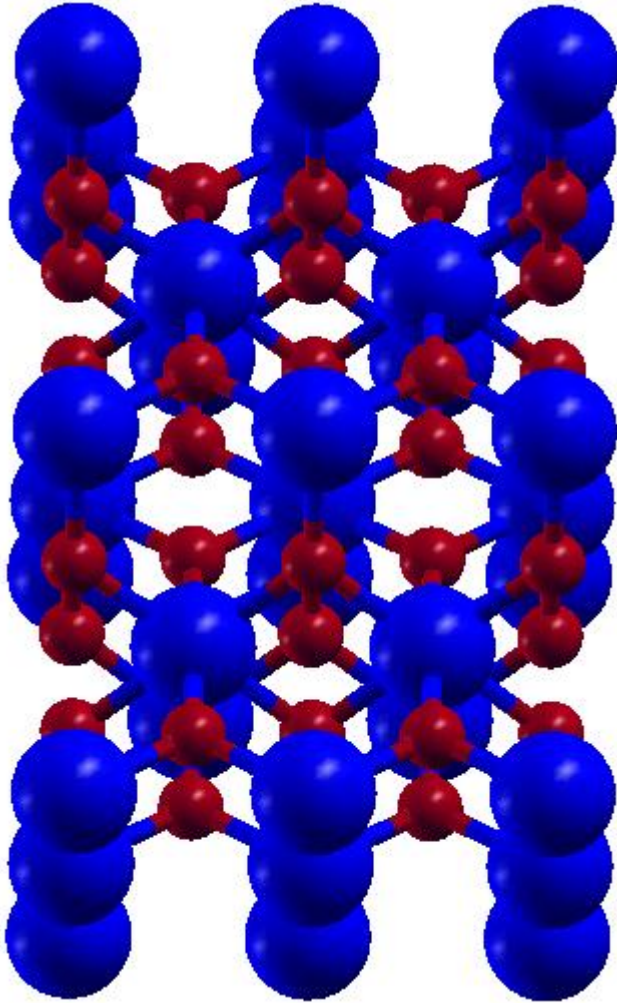
LiF (covalent)?

$\text{Li}^- \text{F}^+$?

Note: An expansion in radial functions times spherical harmonics is complete \rightarrow Expansion about more than one site is over-complete (ambiguous).

What Follows is Qualitative

An Example: Two Titanium Oxides



Both have Ti octahedrally coordinated by O.

A Chemist's View



Electronegativity:

Ti: 1.54 O: 3.44

Large difference means O is O^{2-} and therefore we have Ti^{4+} and Ti^{3+} respectively. These are known common valence states of Ti.

22	47.88
3560	4,3
1935	Ti
4.54	[Ar]3d ² 4s ²
	Titanium

Things are not always so simple:

- Smaller electronegativity differences (e.g. BaFe_2As_2).
- Metals (e.g. PdCoO_2).
- Multiple mixed valence ions (e.g. MnFe_2O_4 – $\text{Mn}^{2+}\text{Fe}^{3+}$; $\text{Mn}^{4+}\text{Fe}^{2+}$ etc.).

First Thought: Charges in Spheres

LAPW calculation with $r_{\text{Ti}}=2.0$ bohr, $r_{\text{O}}=1.6$ bohr.

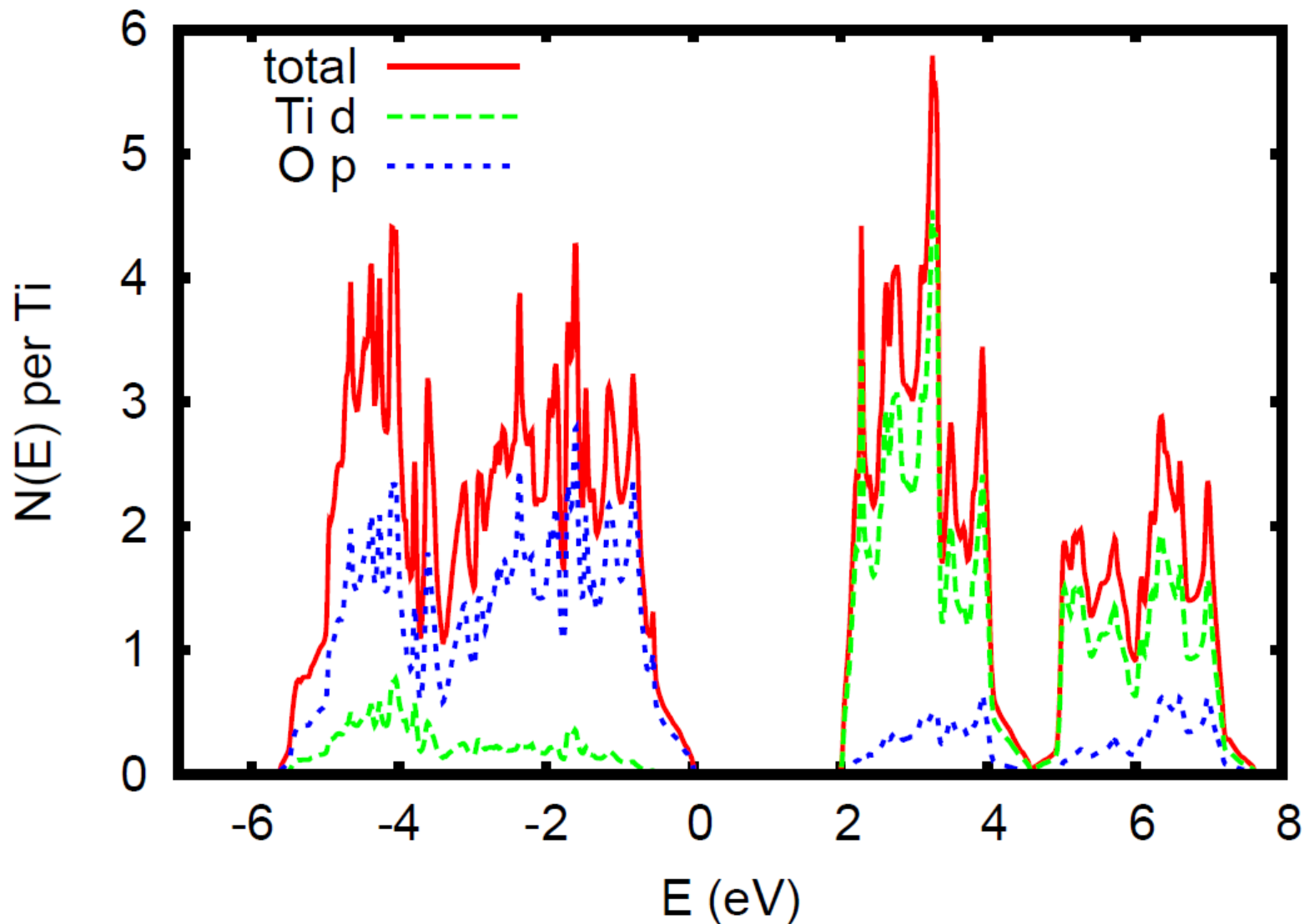
per Ti	TiO ₂	Ti ₂ O ₃
Ti	19.415 <i>e</i>	19.513 <i>e</i>
O	7.225 <i>e</i>	7.225 <i>e</i>
<i>Interstitial</i>	4.135 <i>e</i>	3.645 <i>e</i>

Difference in Ti sphere charge is less than 0.1 e !

Effect of “screening”, in other words orbitals breath as the occupation is changed due to effect of e-e Coulomb repulsion. Also, *sp* charge moves due to changes in covalency.

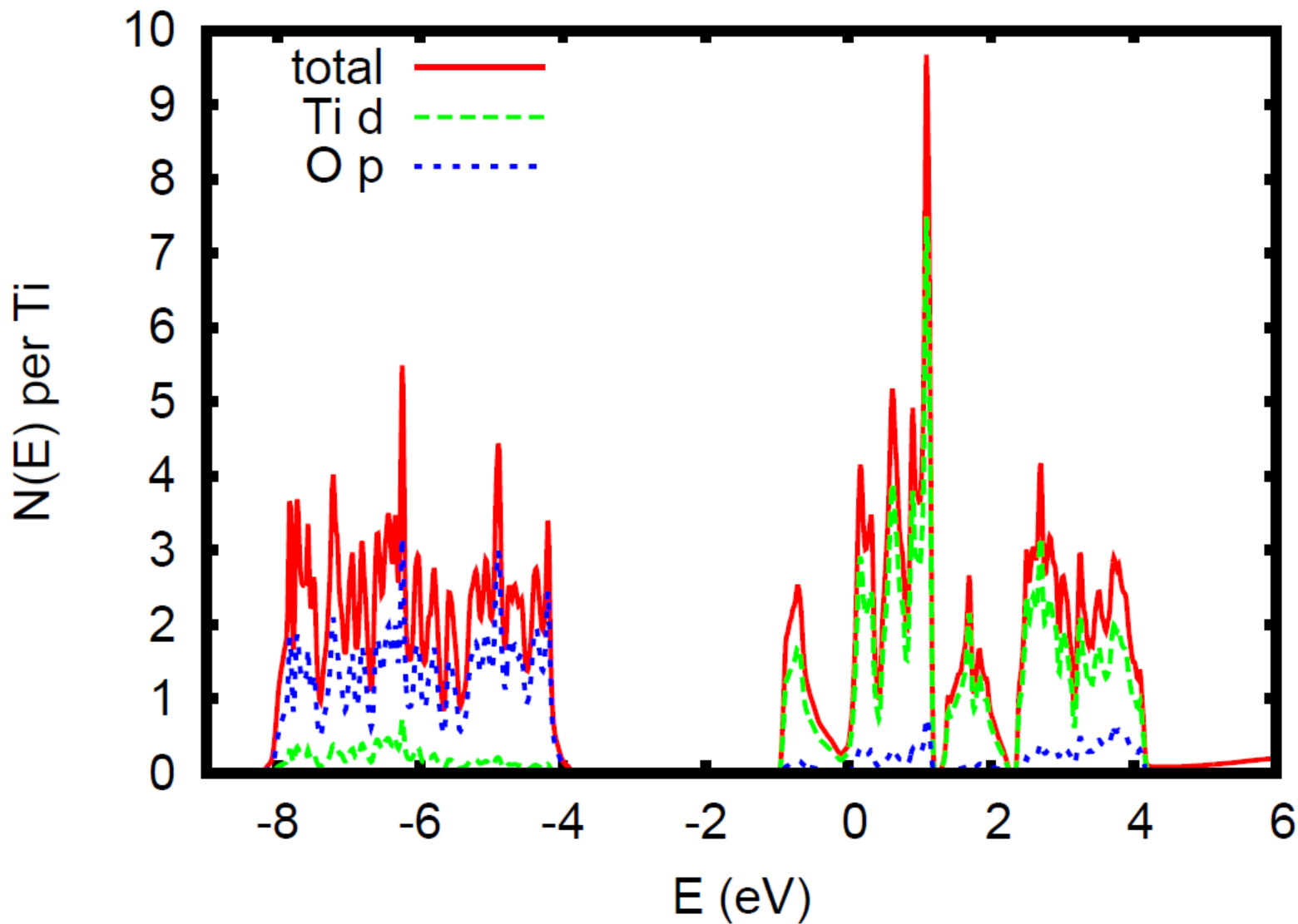
Density of States for TiO₂

LAPW calculation with $r_{\text{Ti}}=2.0$ bohr, $r_{\text{O}}=1.6$ bohr

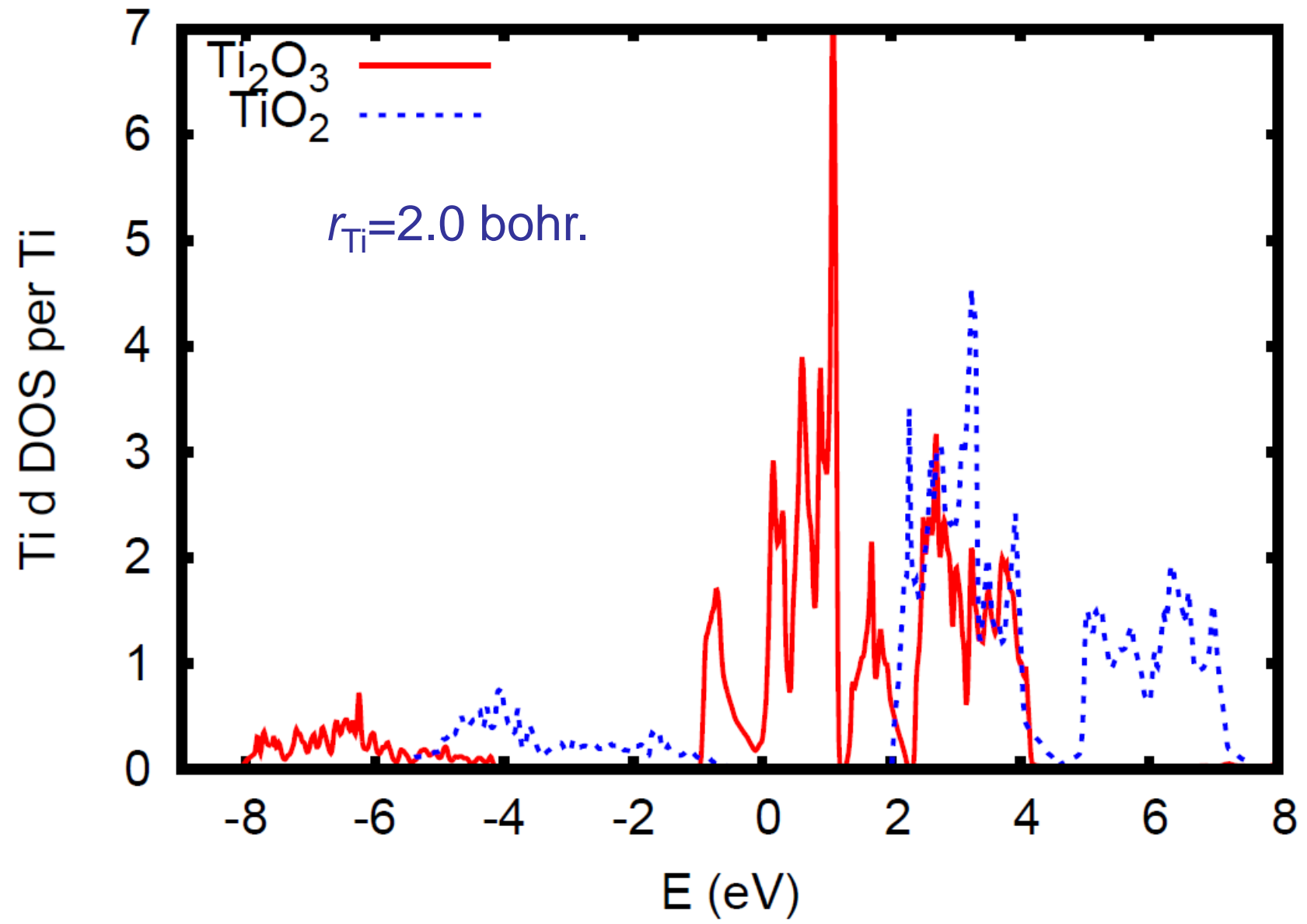


Density of States for Ti_2O_3

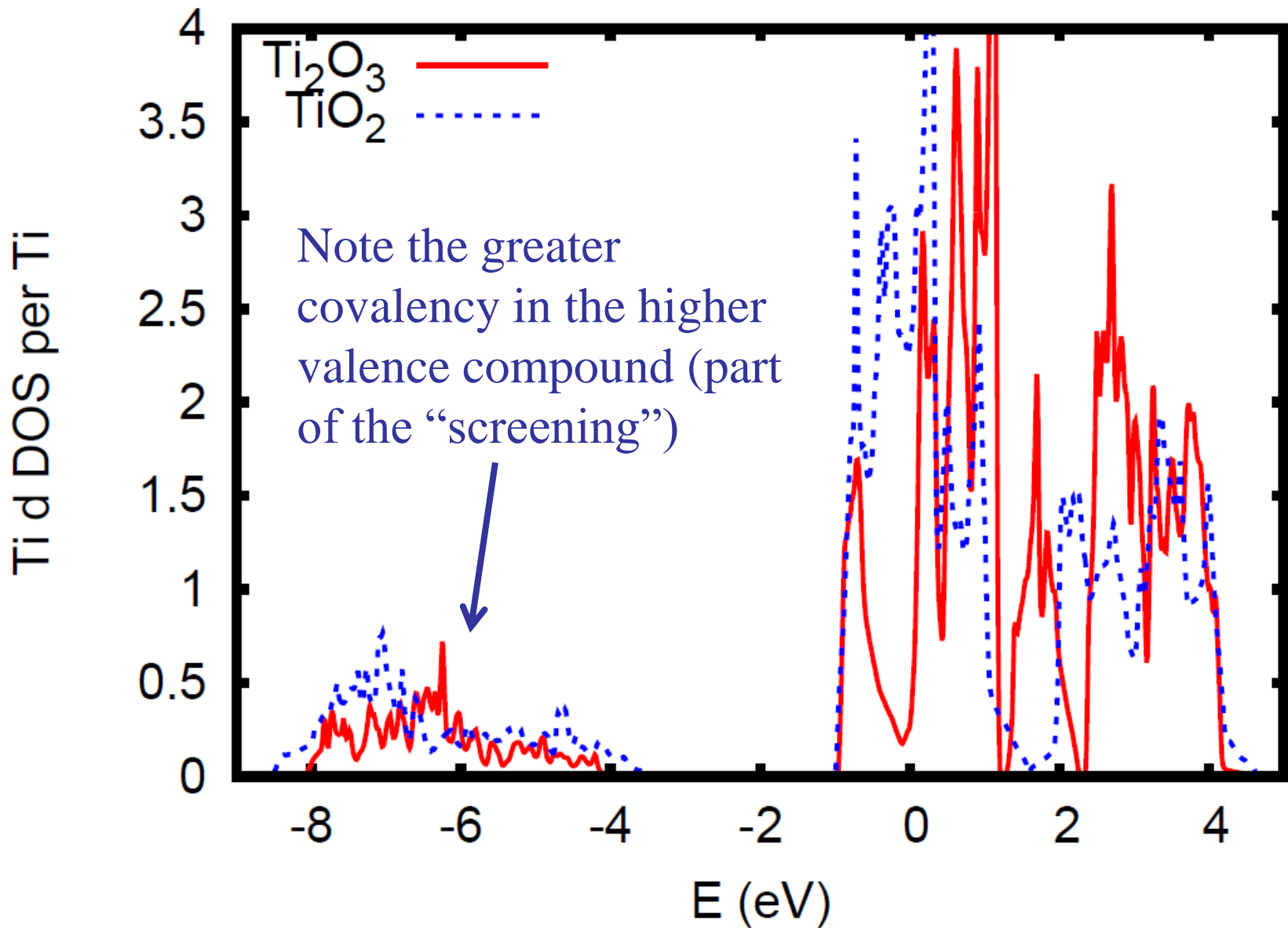
LAPW calculation with $r_{\text{Ti}}=2.0$ bohr, $r_{\text{O}}=1.6$ bohr



Comparison of Ti d Projections



Ti d Projections with 3 eV Shift



Deep Core Level Positions

- Reflect the Coulomb potential, which should vary with valence.
- Experimentally accessible quantities.
- Absolute position is arbitrary in a solid state calculation: Need to look either at differences or relative to some physical reference, e.g. Fermi level.

O $1s$ – Ti $1s$ (PBE GGA).

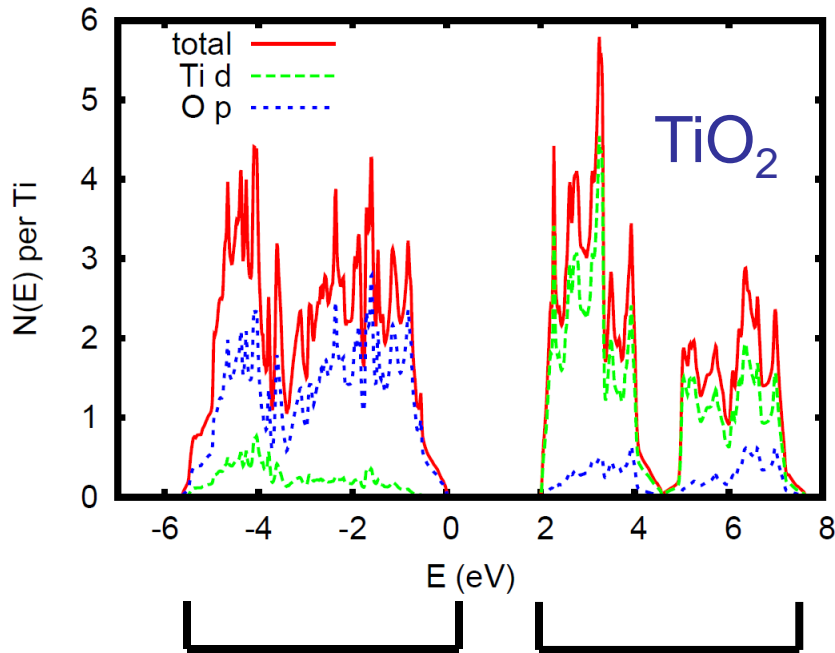
TiO₂: 4357.73 eV

Ti₂O₃: 4356.09 eV

- Difference is > 1 eV and can be used to characterize valence. However, the differences in non-oxides/halides are smaller, and this is indirect (relies on reference compounds).
- Higher binding energy for metal ion means higher valence.
- Can be misleading for hypothetical crystal structures.

What Can Be Done for TiO_2 / Ti_2O_3

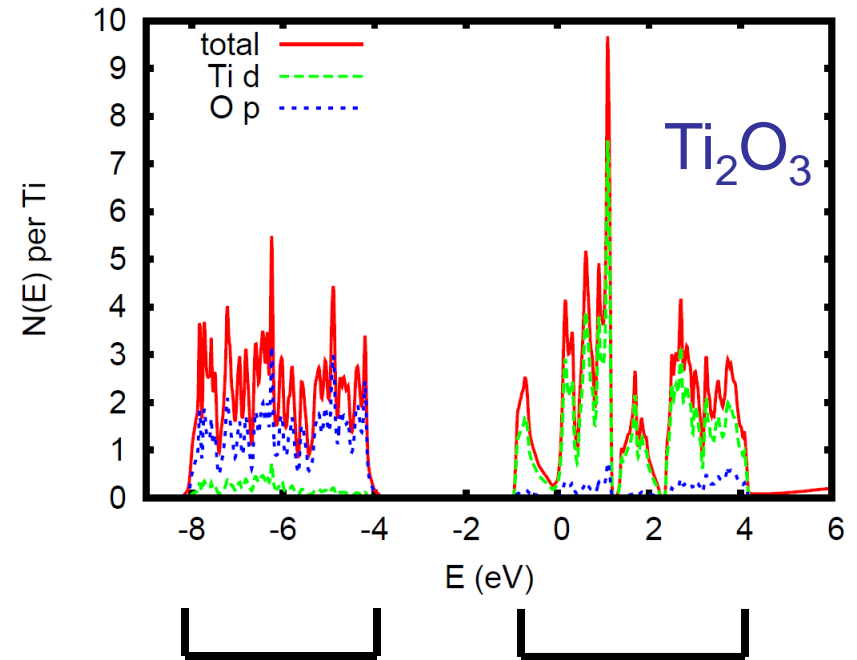
- Do DFT calculations; find band characters and then count.



O p

Ti d

12 O p bands occupied (24 e) per cell (Ti_2O_4), no occupied d bands \rightarrow Ti^{4+}



O p

Ti d

18 O p bands occupied (36 e) per cell (Ti_4O_6), 2 occupied d bands \rightarrow Ti^{3+}

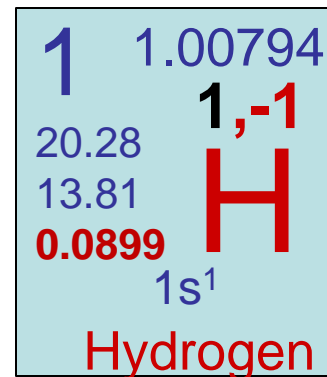
Another Example (Hydrides)

Hydrogen is exceptionally flexible and important.

- Cation: H^+ (proton, e.g. in fuel cells, acids).
- Anion: H^- (e.g. LiH).
- Metallic (PdH).
- Covalent: e.g. hydrocarbons.

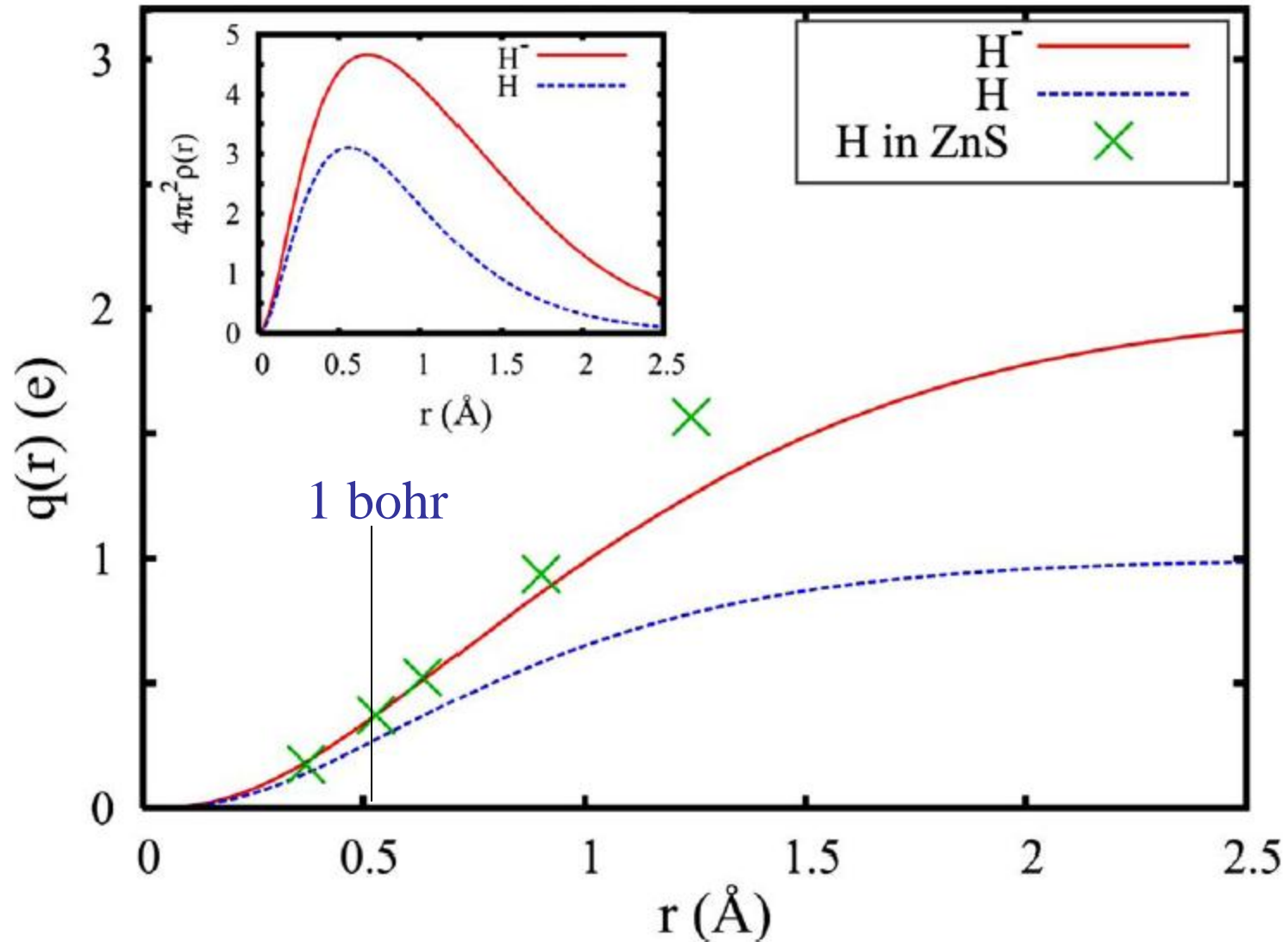
Can have very short bond-lengths:

- O-H $\sim 0.95 \text{ \AA}$, C-H $\sim 1.1 \text{ \AA}$.



Hydrogen powered lawn mower (K. Yvon).

Charge Density



Du et al., 2009 (H in anion vacancies of semiconductors)

Case Study



ELSEVIER

Journal of Alloys and Compounds 306 (2000) 127–132

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Trigonal SrAl_2H_2 : the first Zintl phase hydride

F. Gingl^a, T. Vogt^b, E. Akiba^{a,*}

Angewandte
Chemie

Semiconductor Materials

DOI: 10.1002/anie.200502090

SrAlSiH: A Polyanionic Semiconductor Hydride**

*Thomas Björling, Dag Noréus, Kjell Jansson,
Magnus Andersson, Ekaterina Leonova, Mattias Edé
Ulf Hålenius, and Ulrich Häussermann**

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Discovery of a family of new hydride compounds, possibly with very interesting bonding. *What does DFT say about it?*

J|A|C|S

A R T I C L E S

Published on Web 12/31/2005

**Polyanionic Hydrides from Polar Intermetallics AeE_2
(Ae = Ca, Sr, Ba; E = Al, Ga, In)**

Thomas Björling,[‡] Dag Noréus,[‡] and Ulrich Häussermann^{*,†,§}

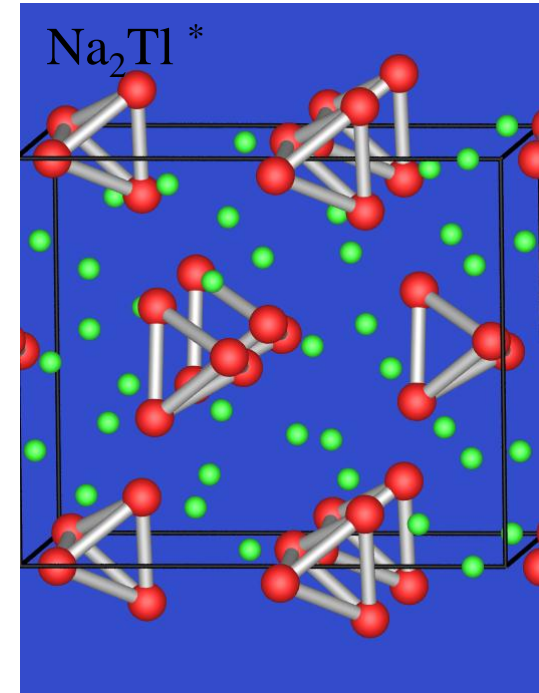
Zintl Compounds

Valence precise compounds based on:

- (1) electro-positive elements that donate charge.
- (2) polyanions, with bonding satisfied by the added charge.

Example: Na_2Tl

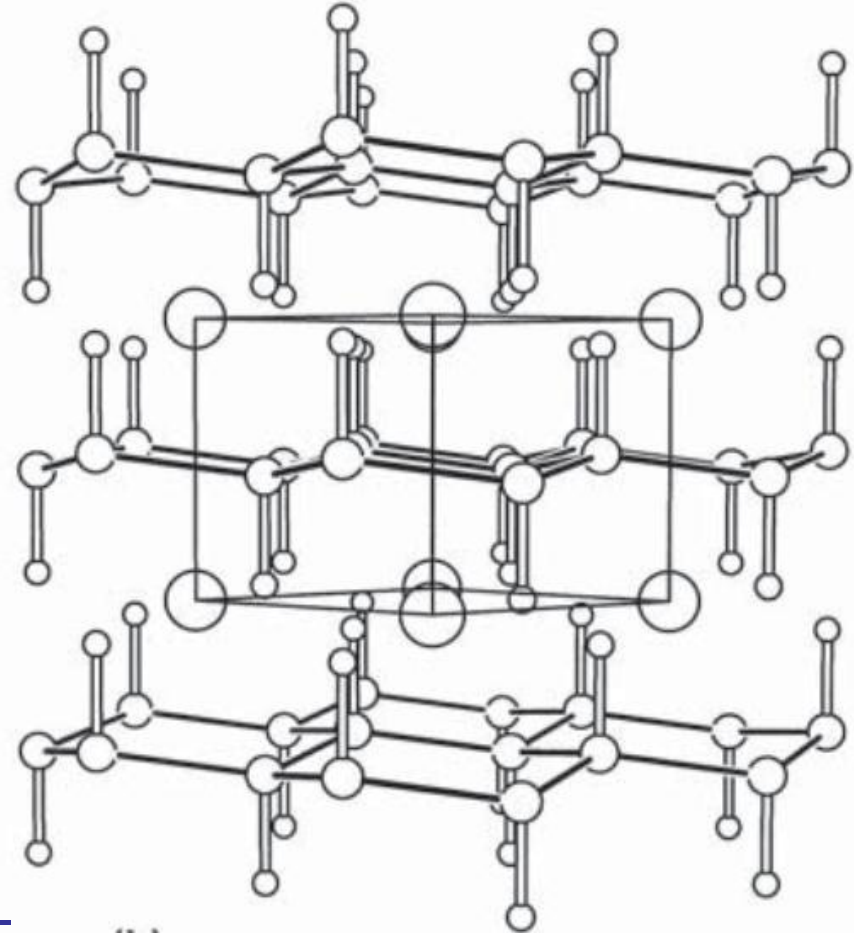
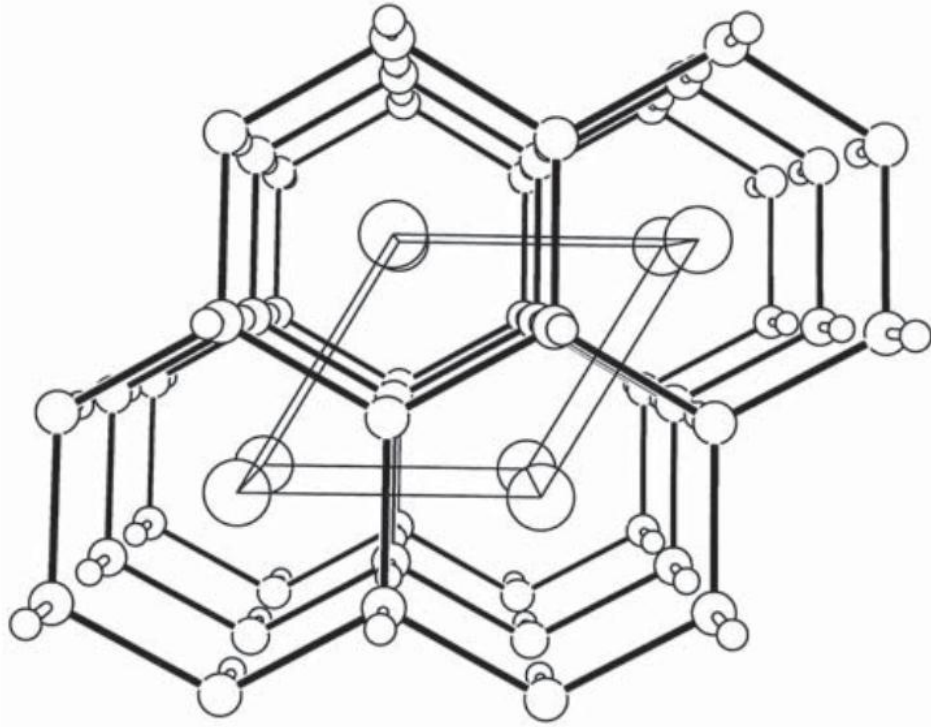
- Na donates charge to Tl.
- Structure based on $(\text{Tl}_4)^{8-}$ tetrahedral polyanions.
- Tl (group IIIB) then forms a bonding pattern characteristic of a group VB element such as P.



	5	6	7	8
	B	C	N	O
1B	13 Al	14 Si	15 P	16 S
30 Zn	31 Ga	32 Ge	33 As	34 Se
48 Cd	49 In	50 Sn	51 Sb	52 Te
80 Hg	81 Tl	82 Pb	83 Bi	84 Po

* Image from http://ruby.chemie.uni-freiburg.de/Vorlesung/intermetallische_0.html

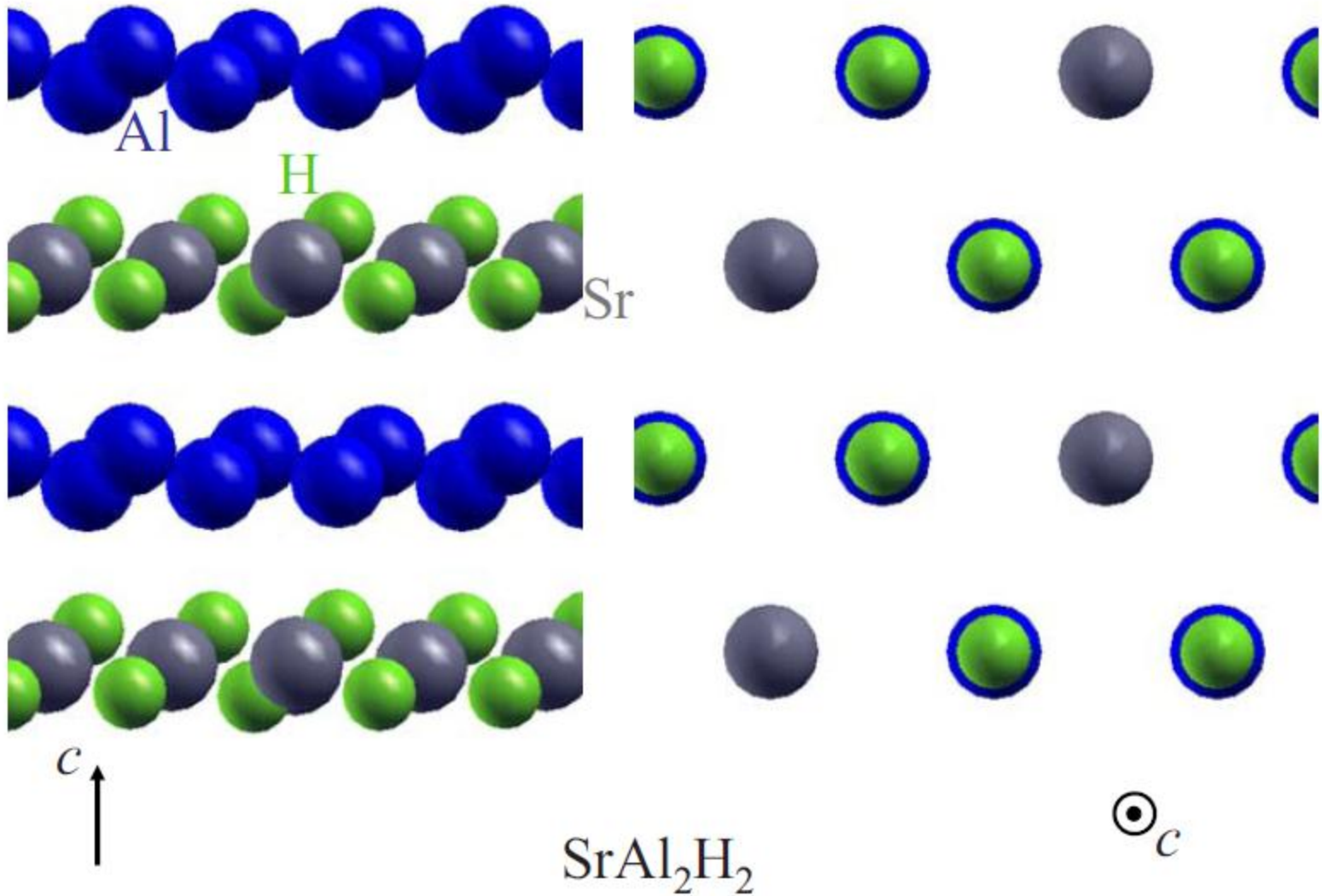
Structure – SrAl_2H_2



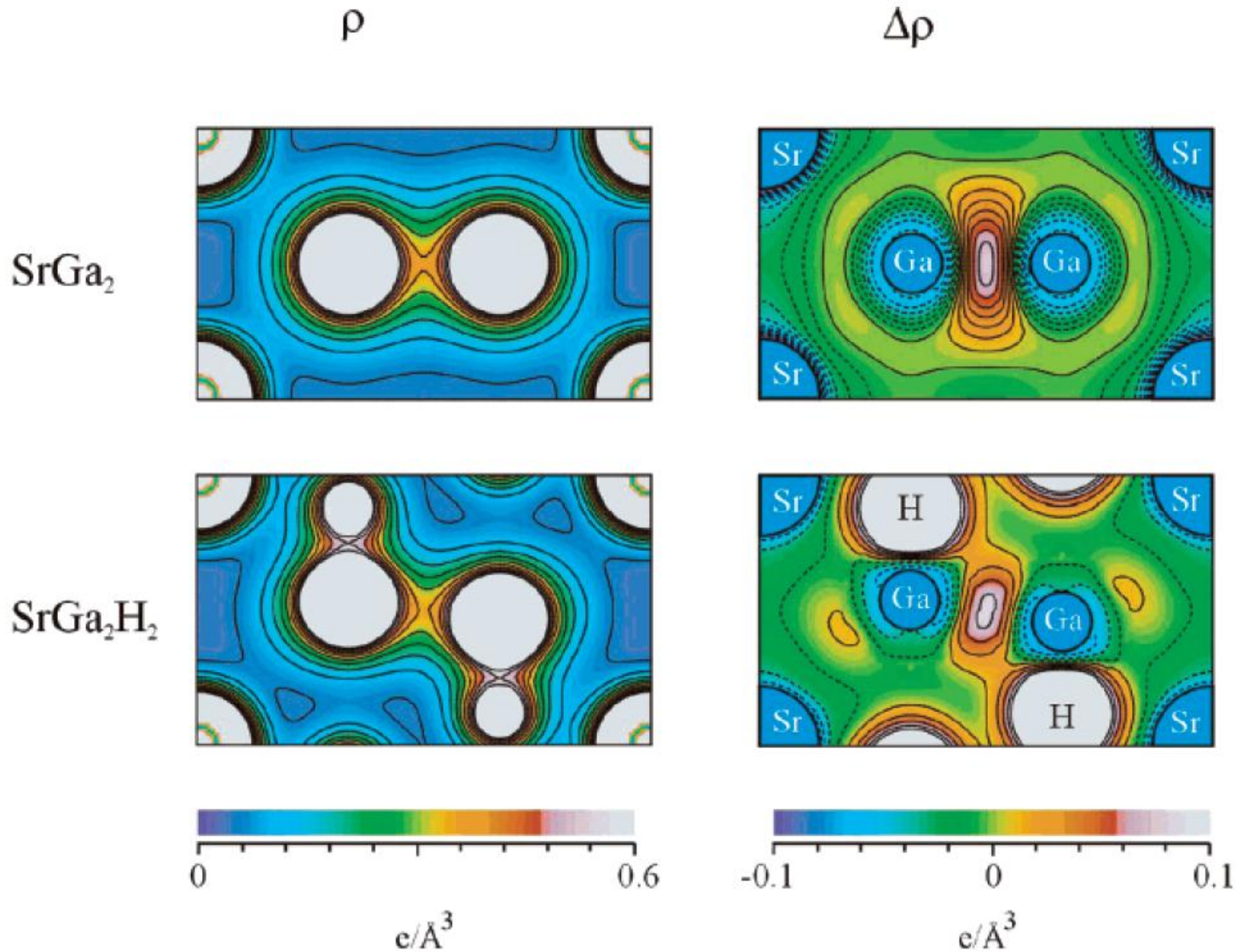
Sr^{2+} electropositive ion.

Al_2H_2 polyanionic framework (note Al-H bonds in drawing).

Structure (drawn without bonds)

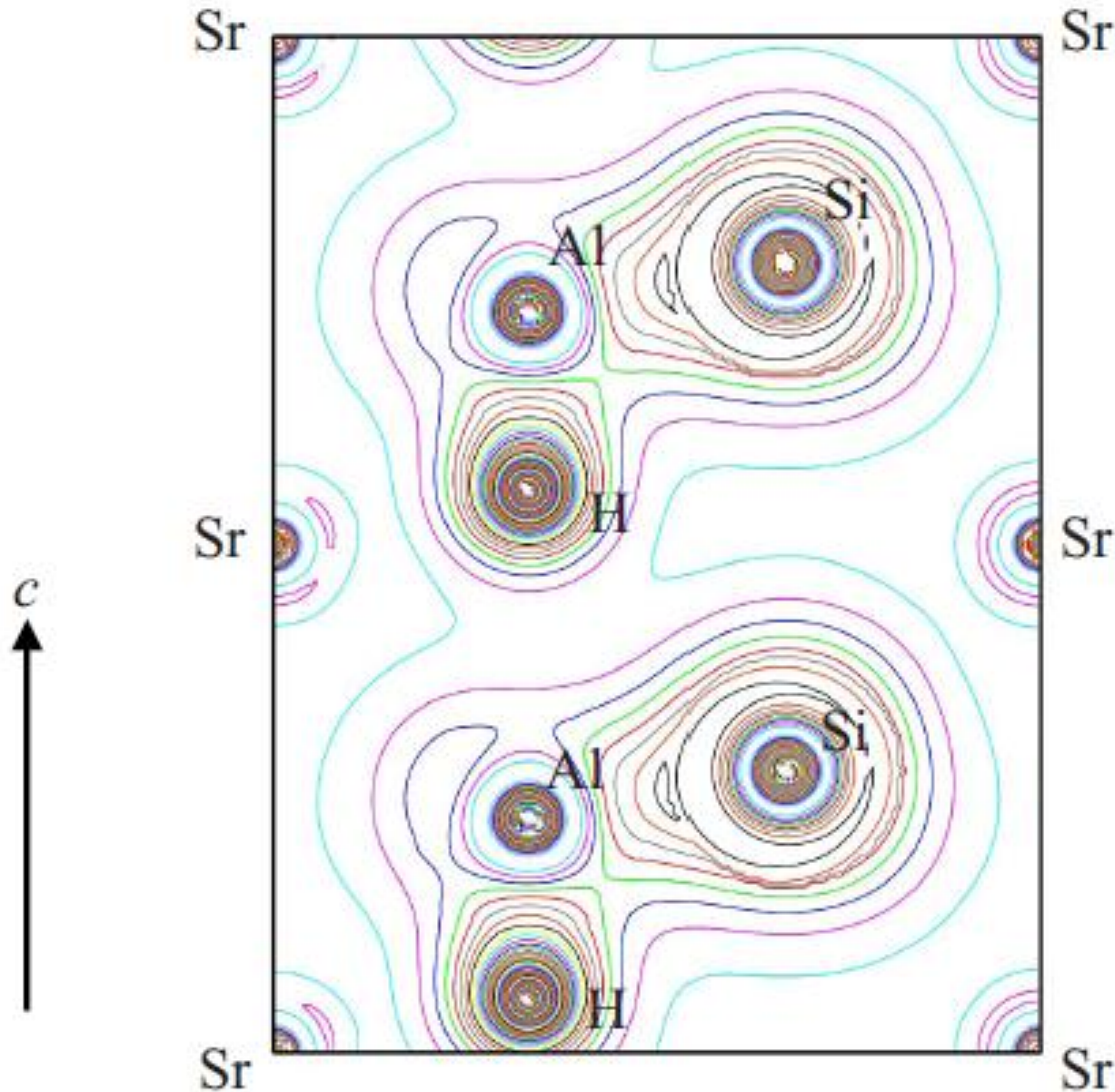


Charge Density



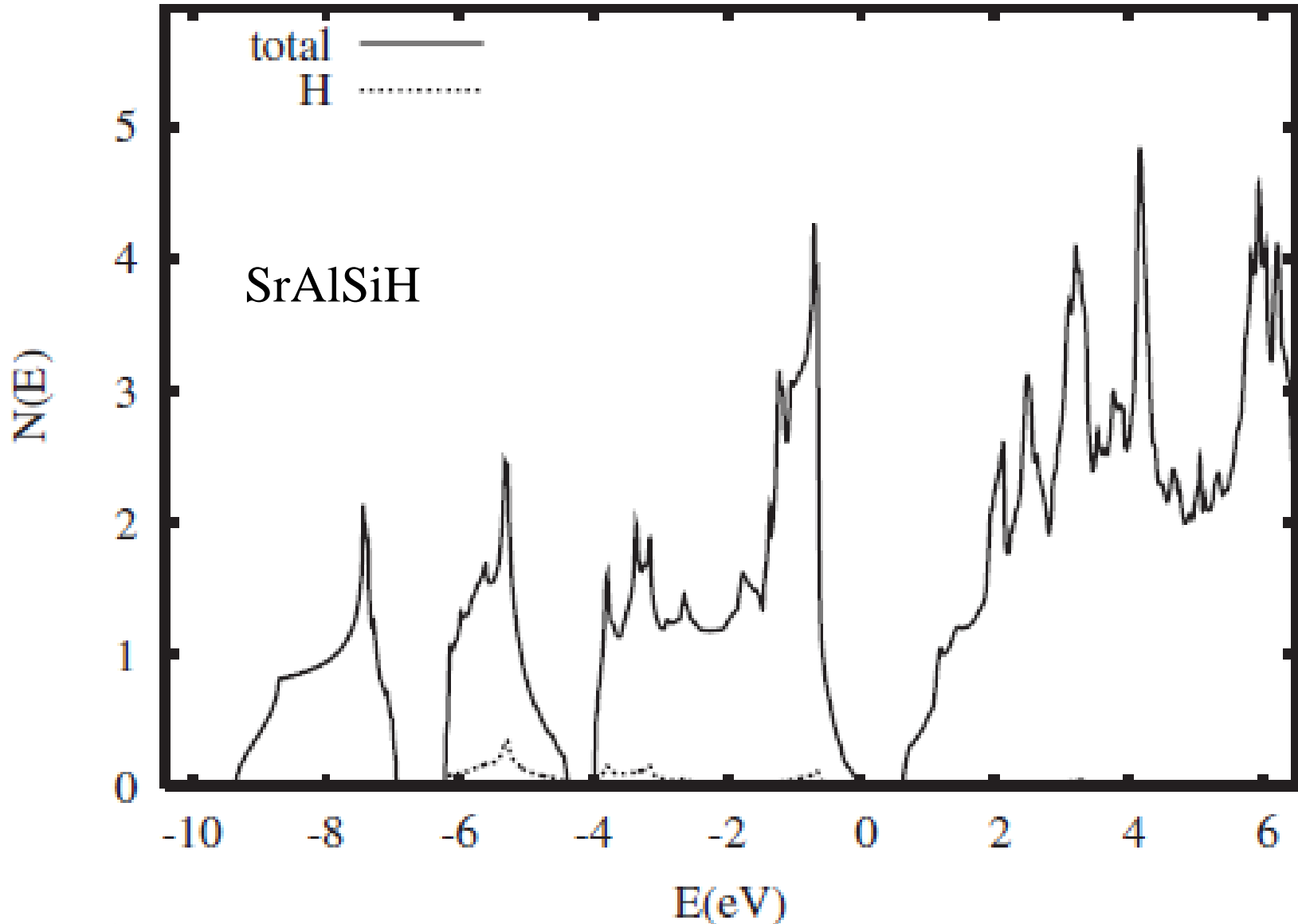
Bjorling, 2005 – interpreted this as covalency between H and Ga

Charge Density - SrAlSiH

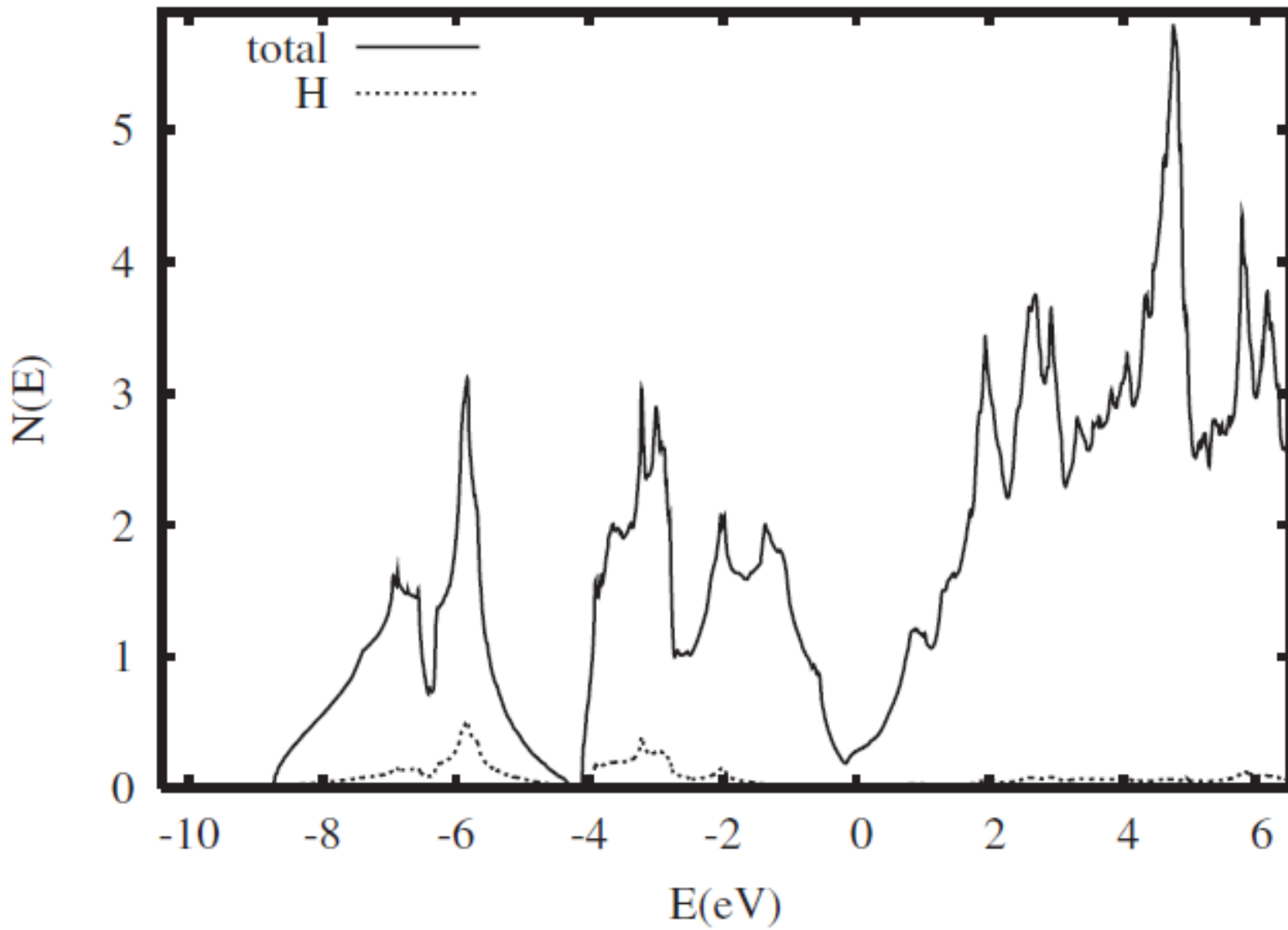


Subedi argued that this was covalent bonding of Si and Al, but ionic H⁻

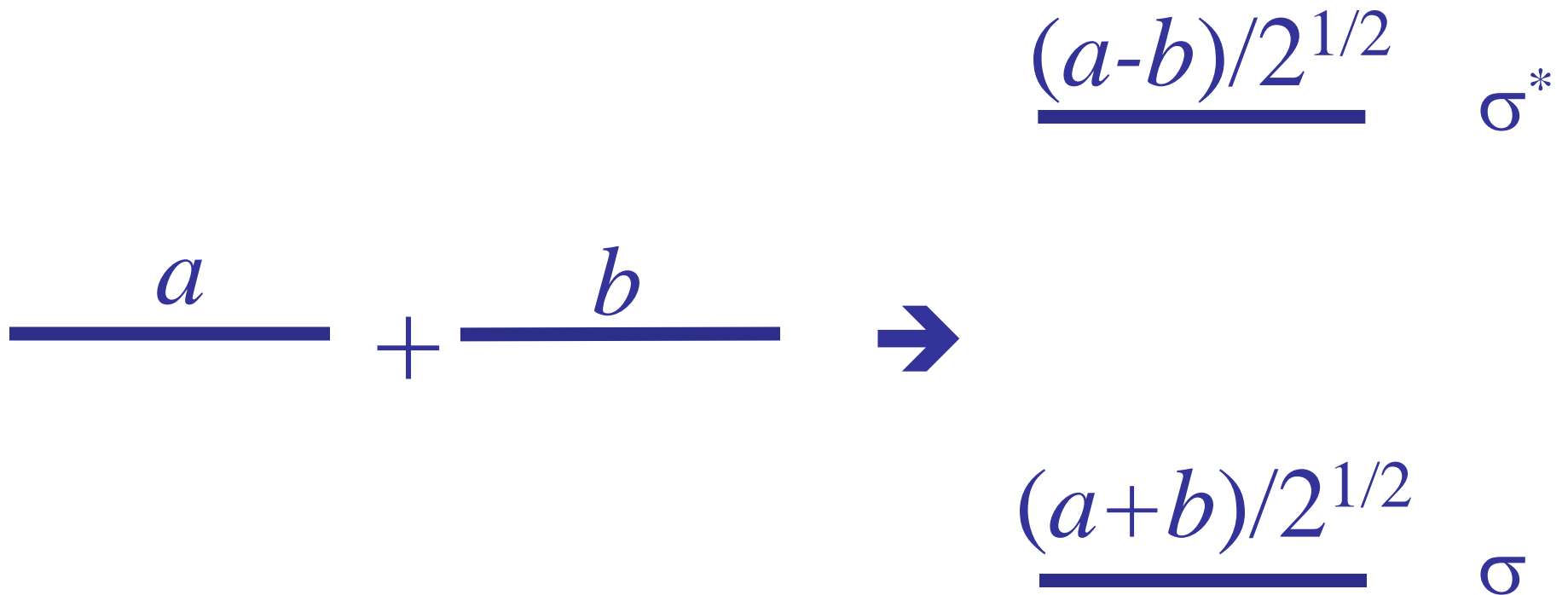
DOS: SrAlSiH (semiconductor)



SrAl₂H₂



Simplest Covalency



What is the Nature of Bonding of H

Charge

- DOS plot was based on LAPW calculations with a H sphere radius of 1 bohr.
- Charge inside H sphere for SrAlSiH was 0.46 e.
- Charge inside the same radius for a stabilized H⁻ is 0.48 e, which is similar.
- Charge inside sphere is at least consistent with anionic H, which therefore can be considered as a possible alternative to covalent Al-H bonding.

SrAlSiH and Hypothetical KAlSi

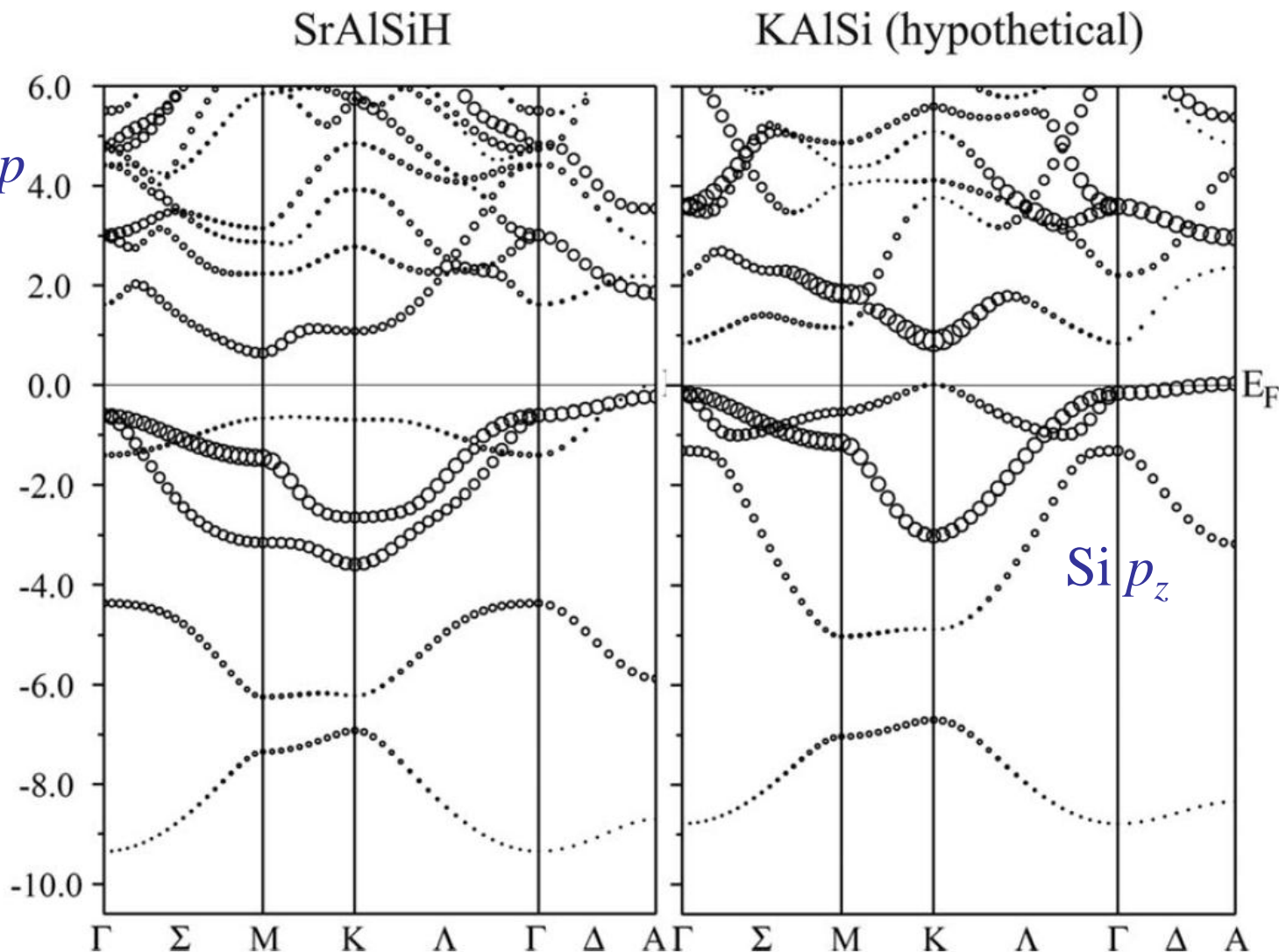
SrH layer \rightarrow K

Al s / Si p / Al p

2 Si p / Al p
+ Si p_z

H s
Si s

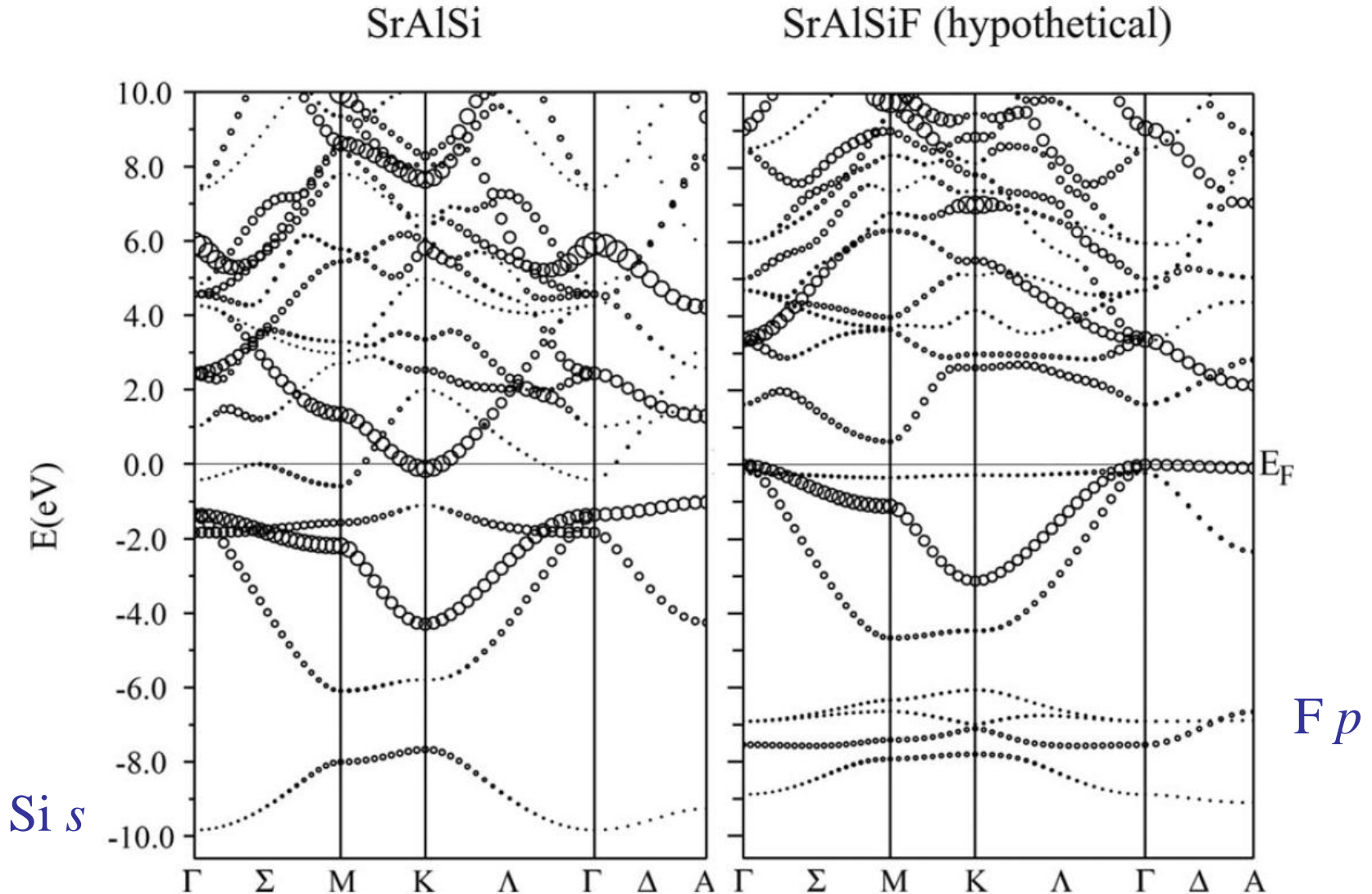
E(eV)



Symbol size proportional to Al p character

SrAlSi and Hypothetical SrAlSiF

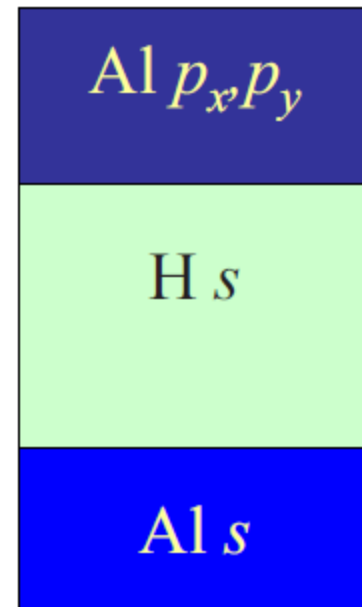
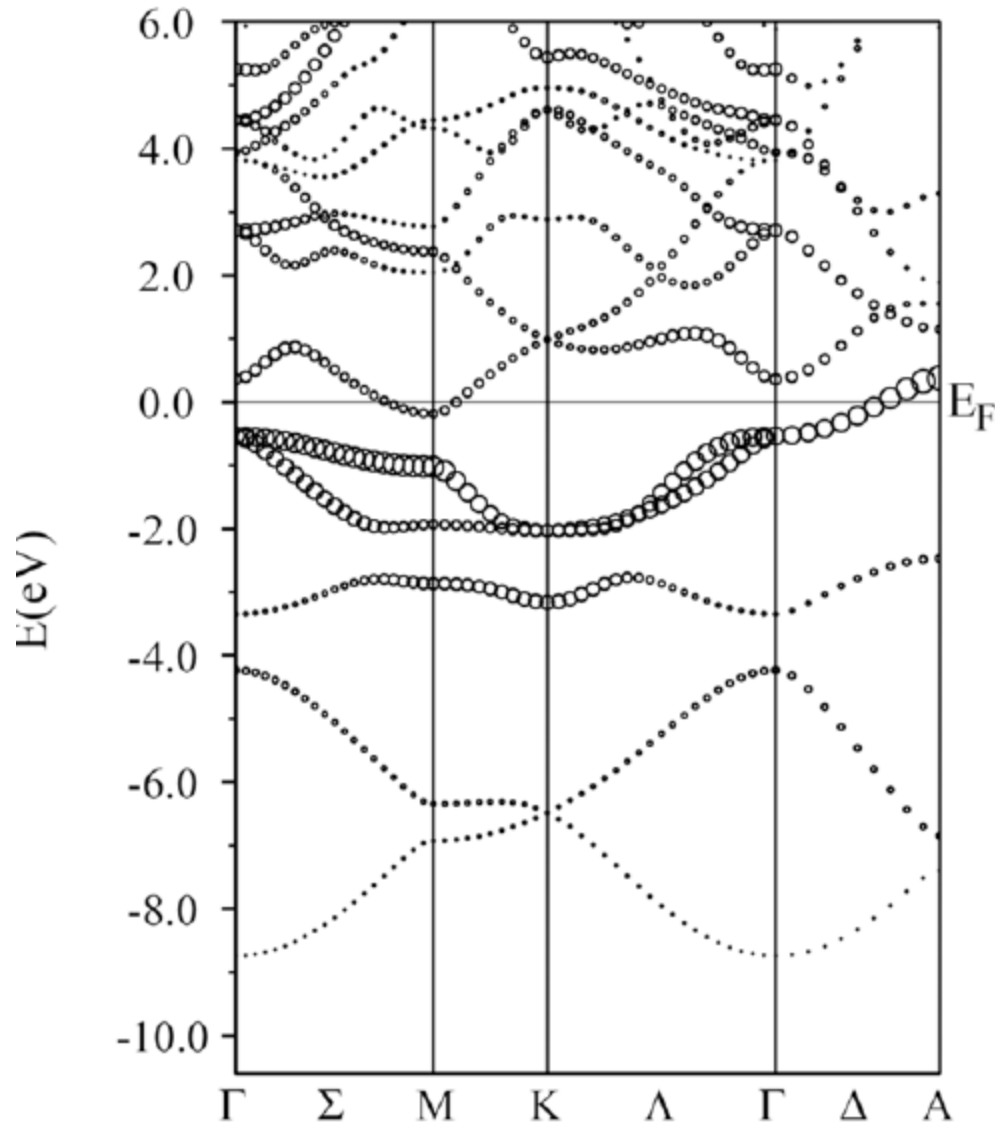
F has highest electronegativity of any element.



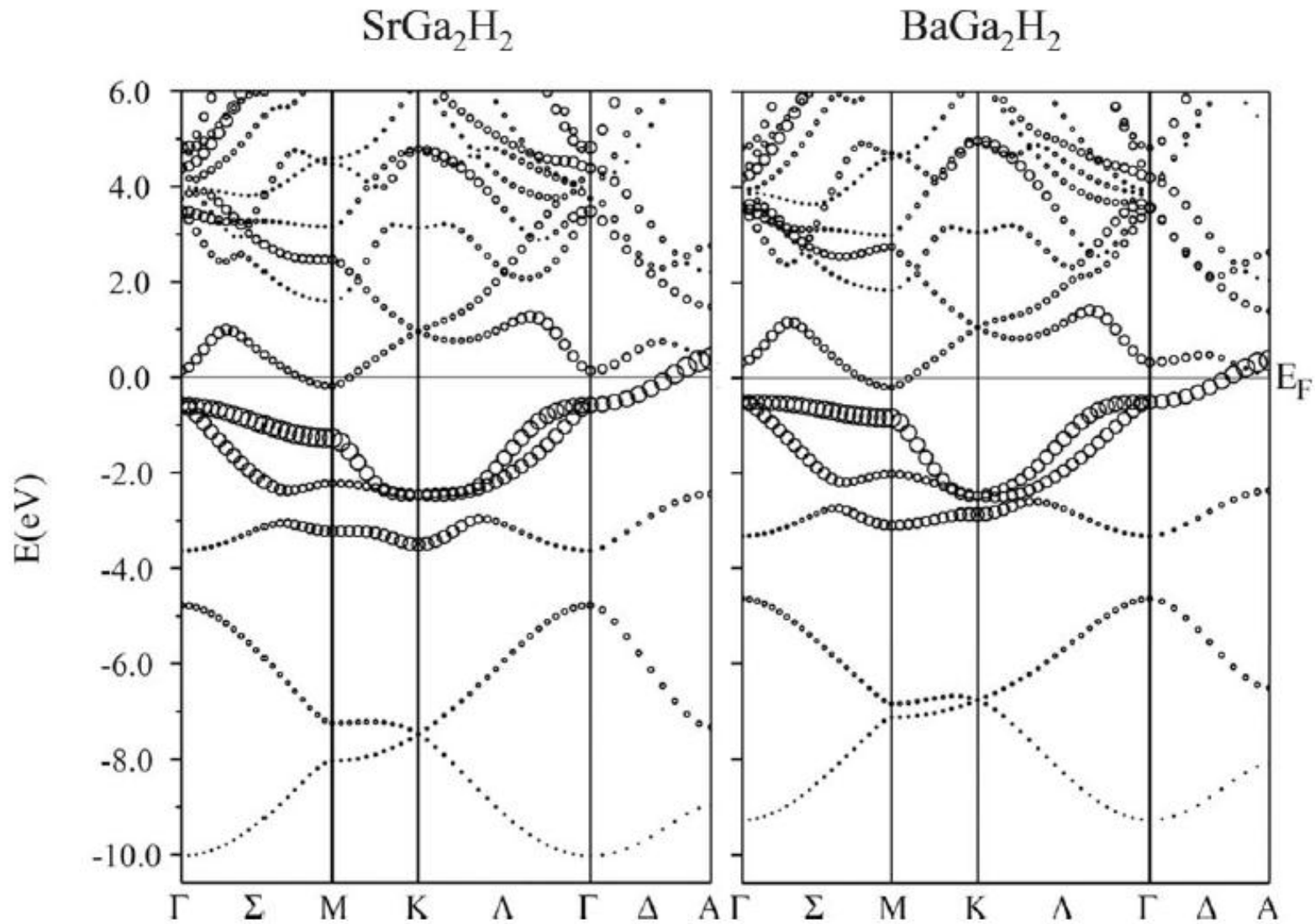
Symbol size proportional to Al p character

Interpretation

SrAl_2H_2



Ga Compounds



Plotting symbol size is based on Ga p contribution.

Qualitative Conclusion

- Sr, Ba are divalent cations (donate charge).
- H occurs as H^- (anion) in these compounds (takes charge, not covalent).
- Polyanionic framework is based on Si, Al, Ga – these behave like C in forming graphite like sheets with sp^2 bonding (Zintl concept).

Remarks

- Descriptions of bonding and charge state are invariably qualitative, but they are exceedingly useful in understanding materials.
- Sorting them out often requires a lot of “hand-work” and testing of different alternatives.