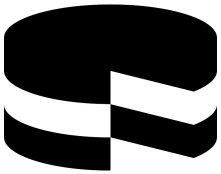
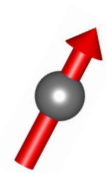
Bonding in crystals: Covalent and van der Waals

bond lengths and polyhedra



tin (Sn)

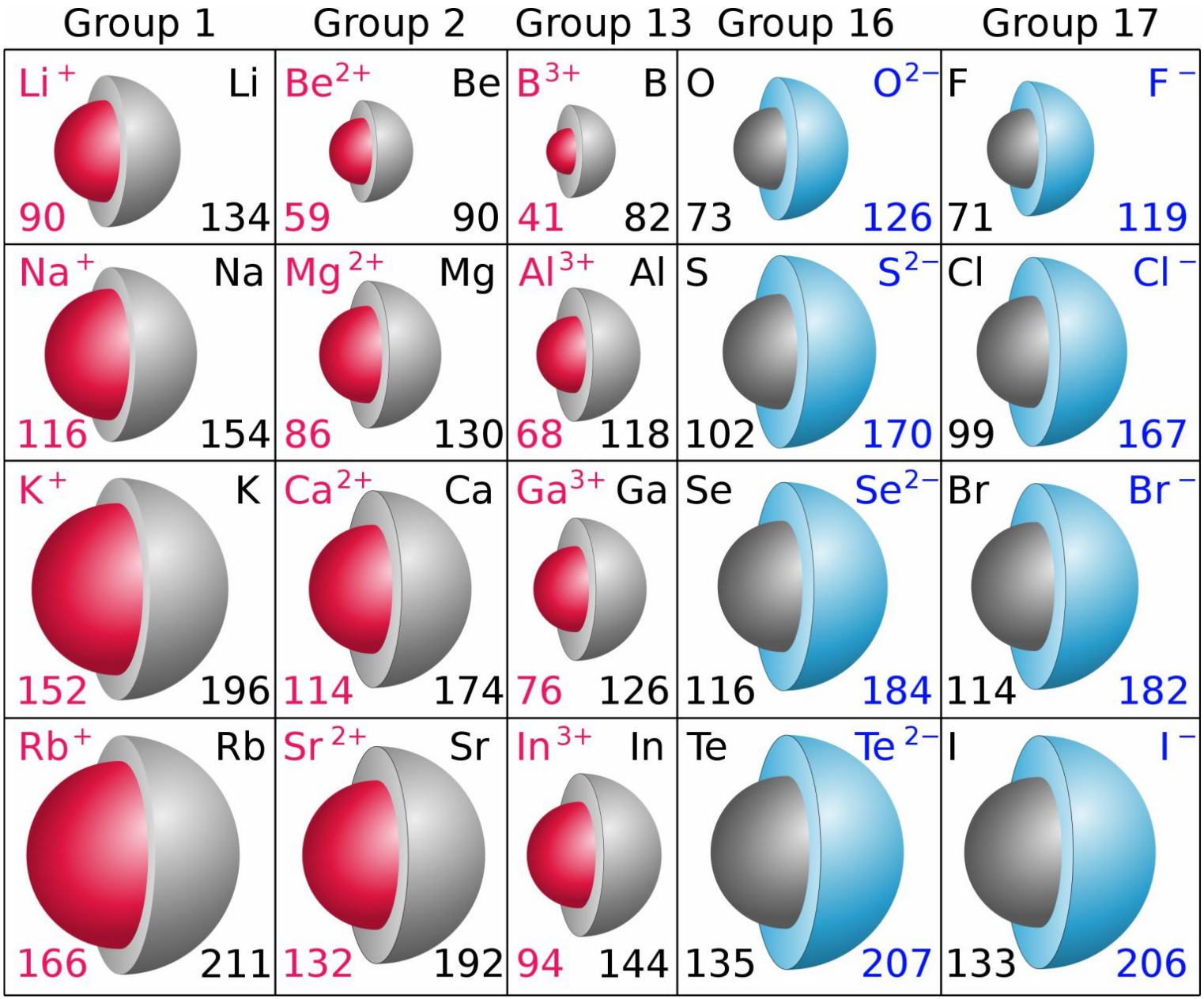
Johannes van der Waals



by Alexander Tsirlin, Leipzig University

Lecture 8: November 2, 2023

Ionic vs. atomic radii



values in pm!

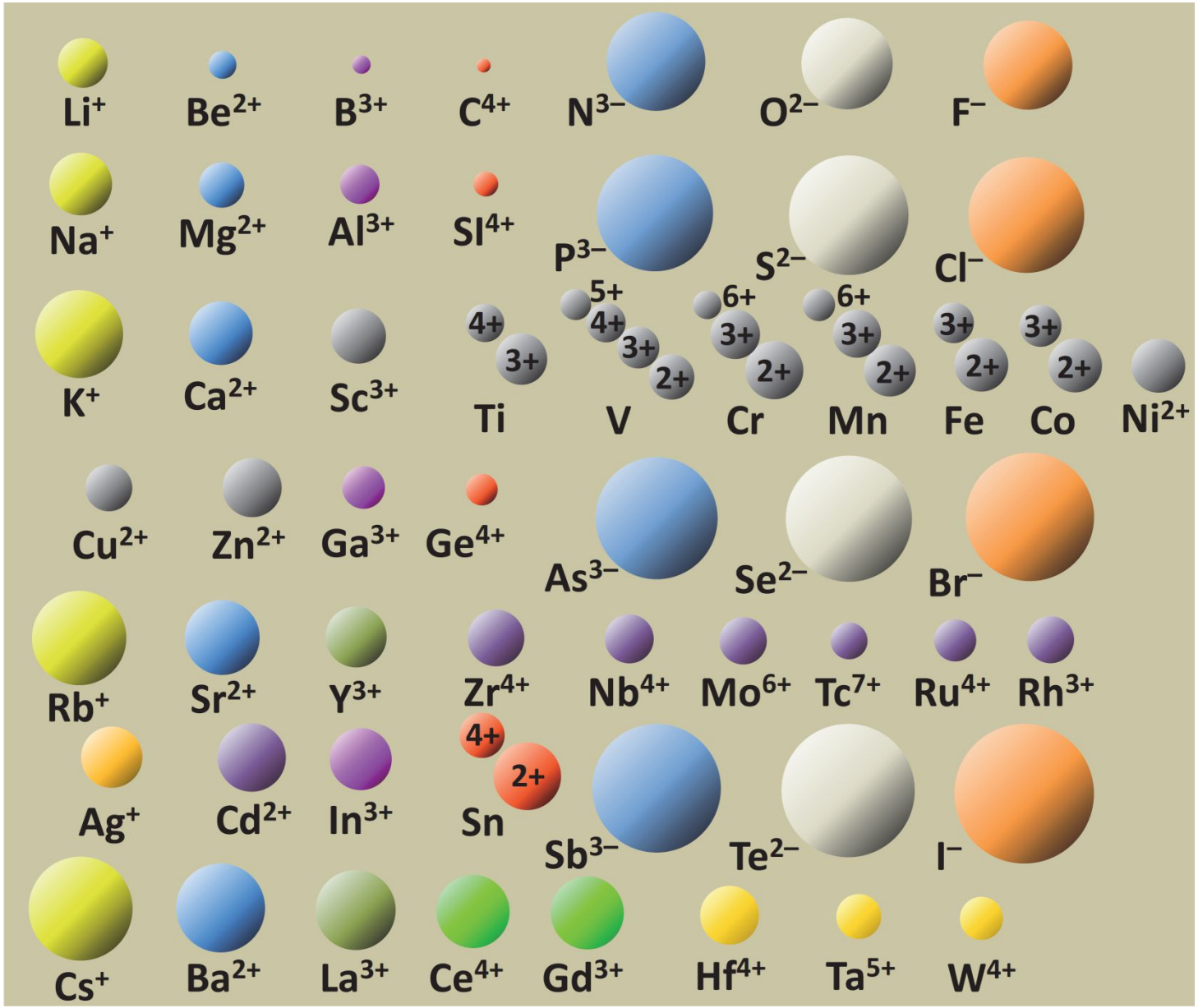


Image from Gross and Marx, Festkörperphysik

Ionic radii, more detailed

			coordination number	covalent (CR)	ionic (IR)	
NA+1	2P	6	IV	1.13	.99	
			V	1.14	1.00	
			VI	1.16	1.02	
			VII	1.26	1.12	
			VIII	1.32	1.18	
			IX	1.38	1.24	C
			XII	1.53	1.39	
NB+3	4D	2	VI	.86	.72	
NB+4	4D	1	VI	.82	.68	RE
			VIII	.93	.79	
NB+5	4P	6	IV	.62	.48	C
			VI	.78	.64	
			VII	.83	.69	C
			VIII	.88	.74	
ND+2	4F	4	VIII	1.43	1.29	
			IX	1.49	1.35	
ND+3	4F	3	VI	1.123	.983	R
			VIII	1.249	1.109	R*
			IX	1.303	1.163	R
			XII	1.41	1.27	E

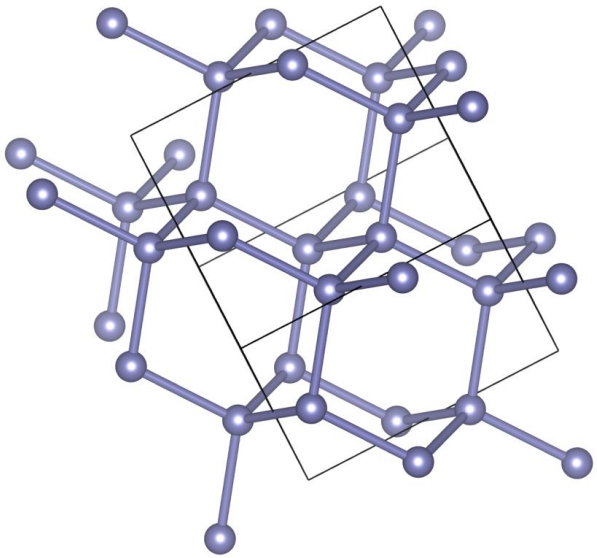
all values in Å !

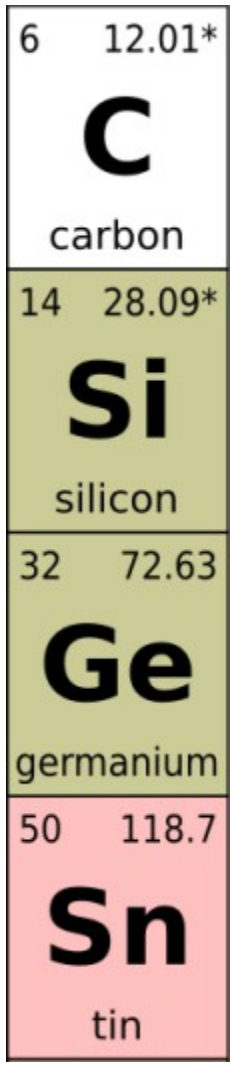
R.D. Shannon

Acta Cryst.
A32, 751 (1976)

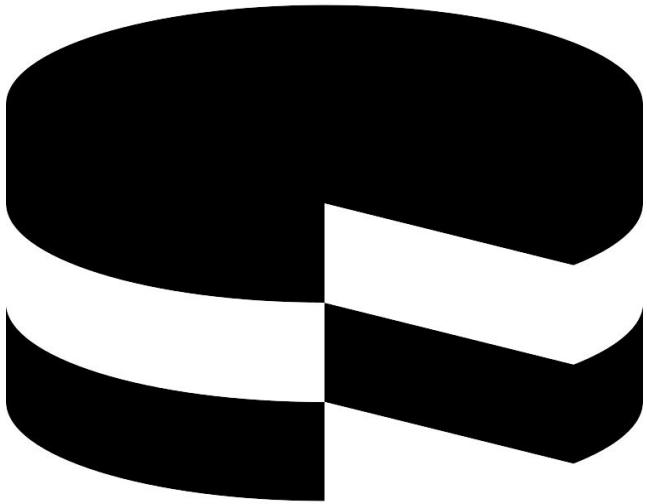
Melting points, covalent crystals

	r_0 (Å)	T_m (K)	E_{lat} (eV/atom)
diamond	1.54	∼4000	7.43
Si	2.35	1687	4.62
Ge	2.45	1211	3.80
Sn	2.81	–	3.14





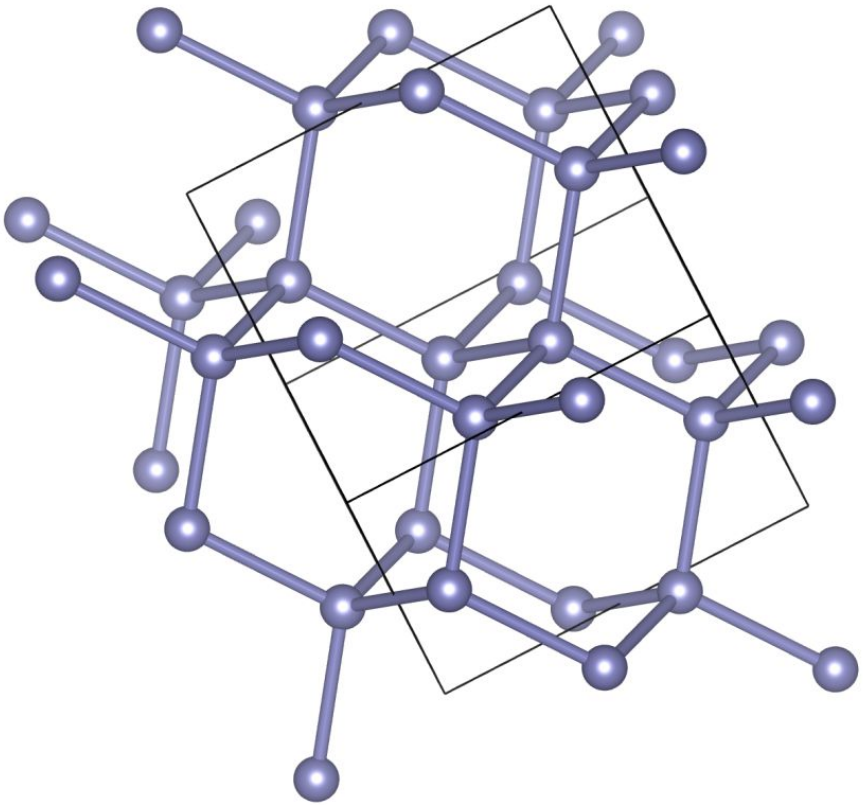
Data from CRC Handbook of Chemistry and Physics



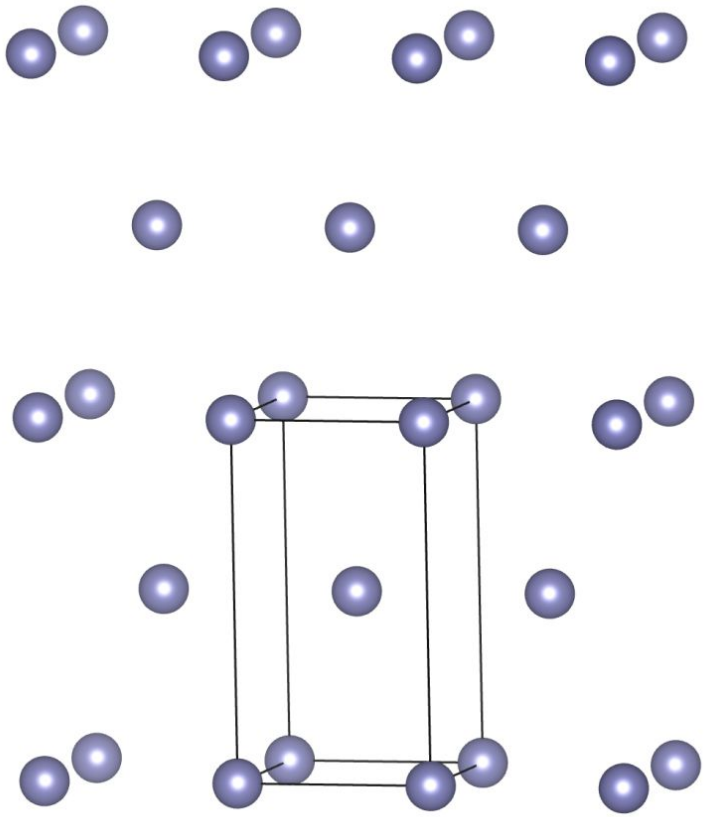
Material

Tin (Sn)

Two forms of tin

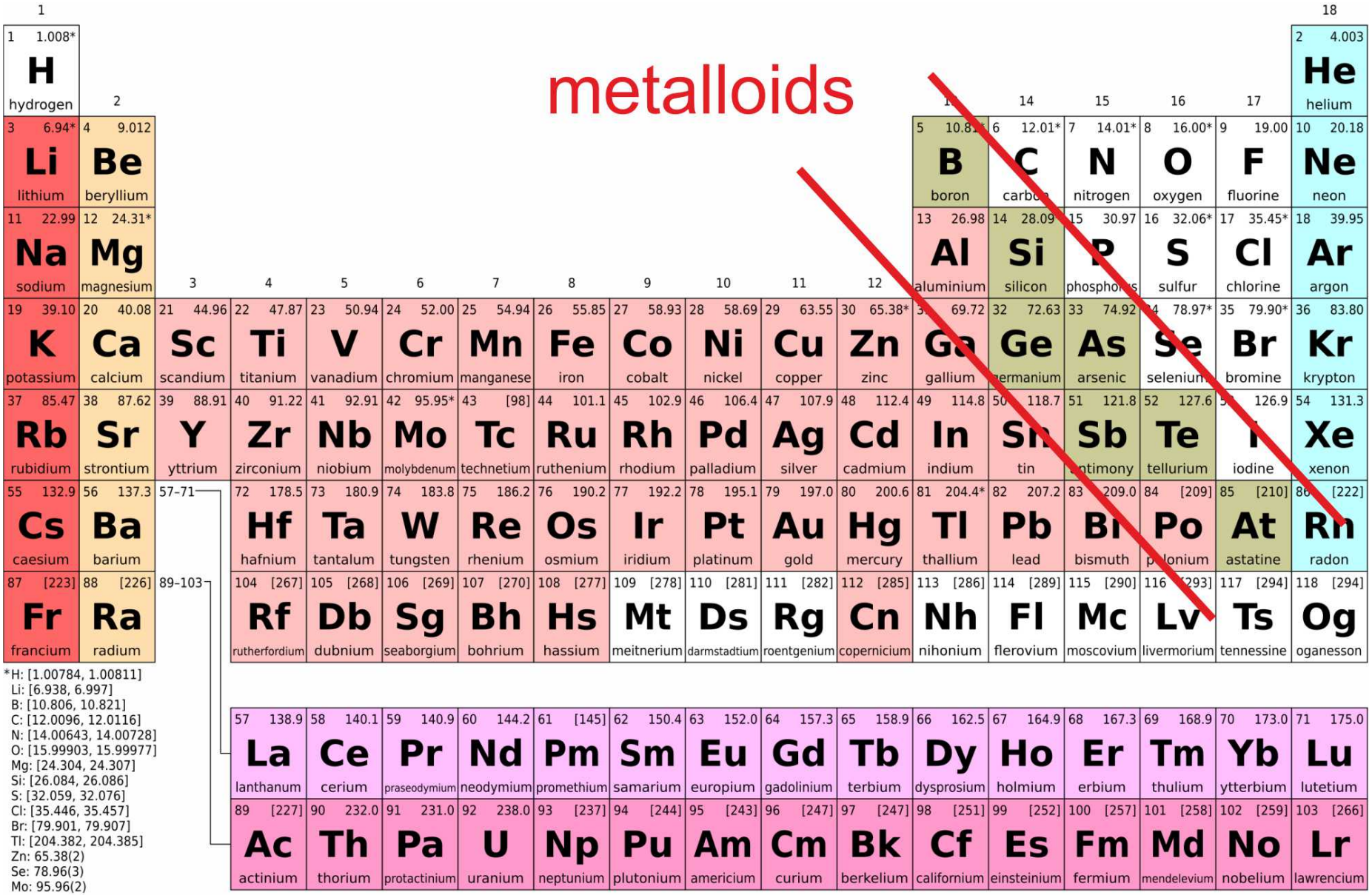


gray tin (α-Sn)
covalent



white tin (β-Sn)
metallic

Intermediate position of tin

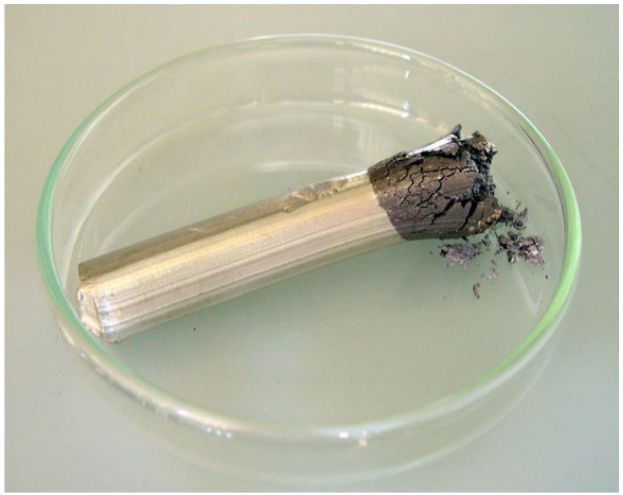


Tin pest

$\beta \rightarrow \alpha$
transformation
below 13.2 °C

Image credit: periodictable.ru (fair use)

Tin pest



$$\beta \rightarrow \alpha$$

transformation

below 13.2 °C

Image credit: periodictable.ru (fair use)

Tin pest

$$\beta \rightarrow \alpha$$

transformation

below 13.2 °C

Image credit: periodictable.ru (fair use)

Tin pest

Napoleon's army
in Russia (1812)

tin buttons

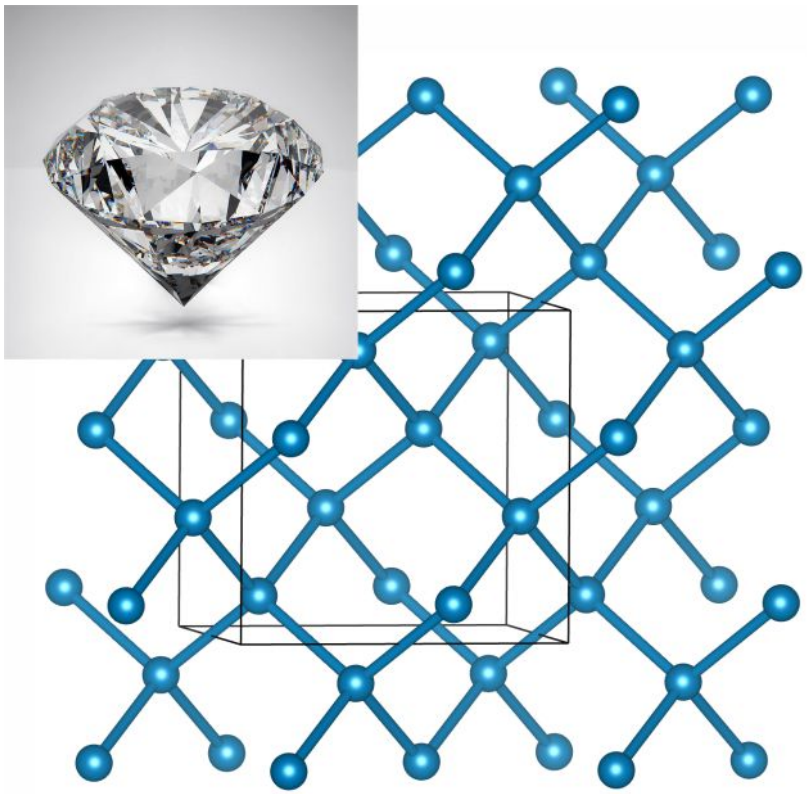
$\beta \rightarrow \alpha$
transformation
below 13.2 °C

Tin pest

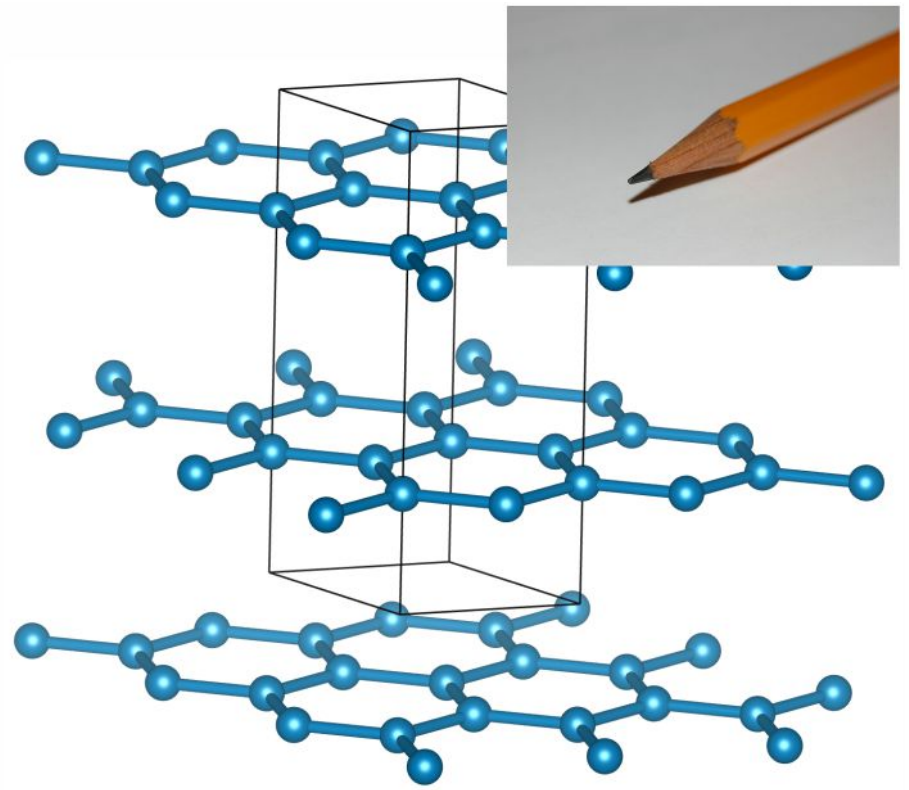
Robert Scott (1912)
South Pole expedition

tin cans and pots

$\beta \rightarrow \alpha$
transformation
below 13.2 °C

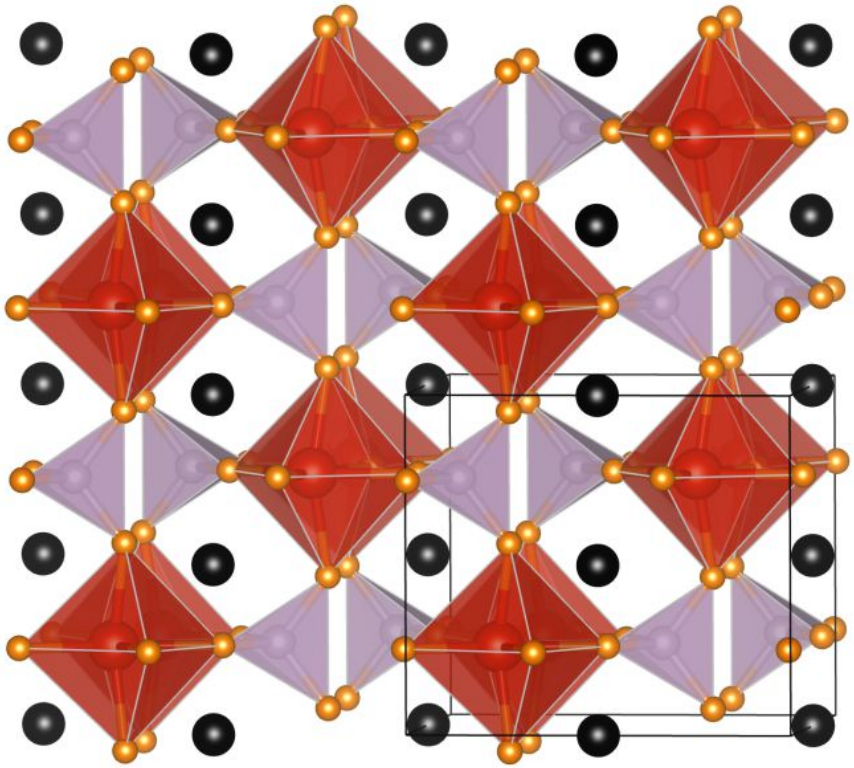


Diamond

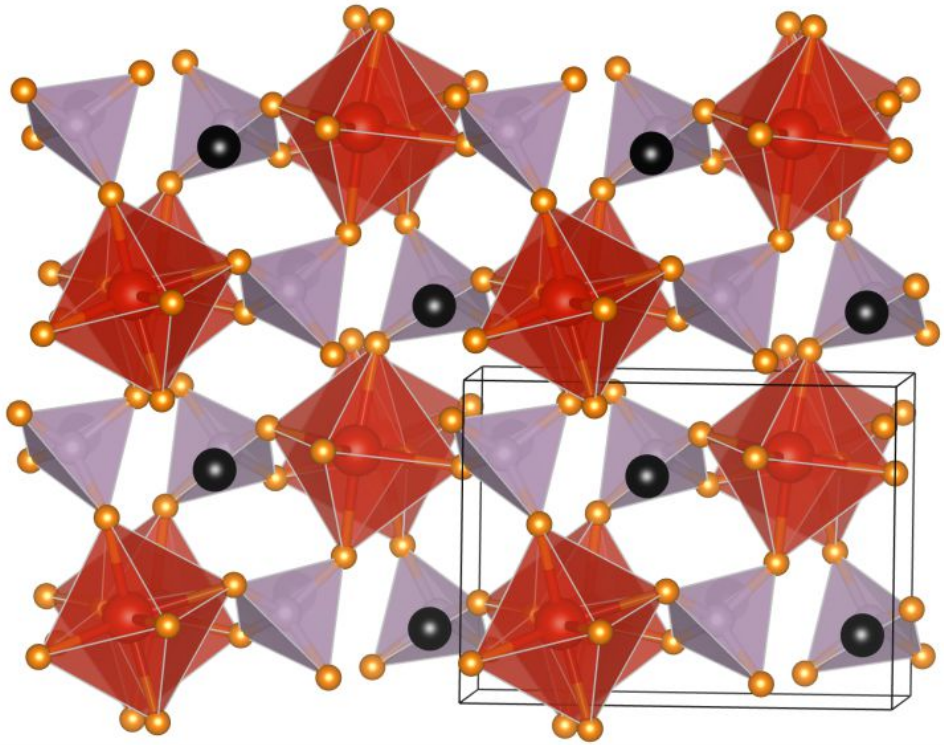


Graphite

Same chemical composition, but very different bonds and properties



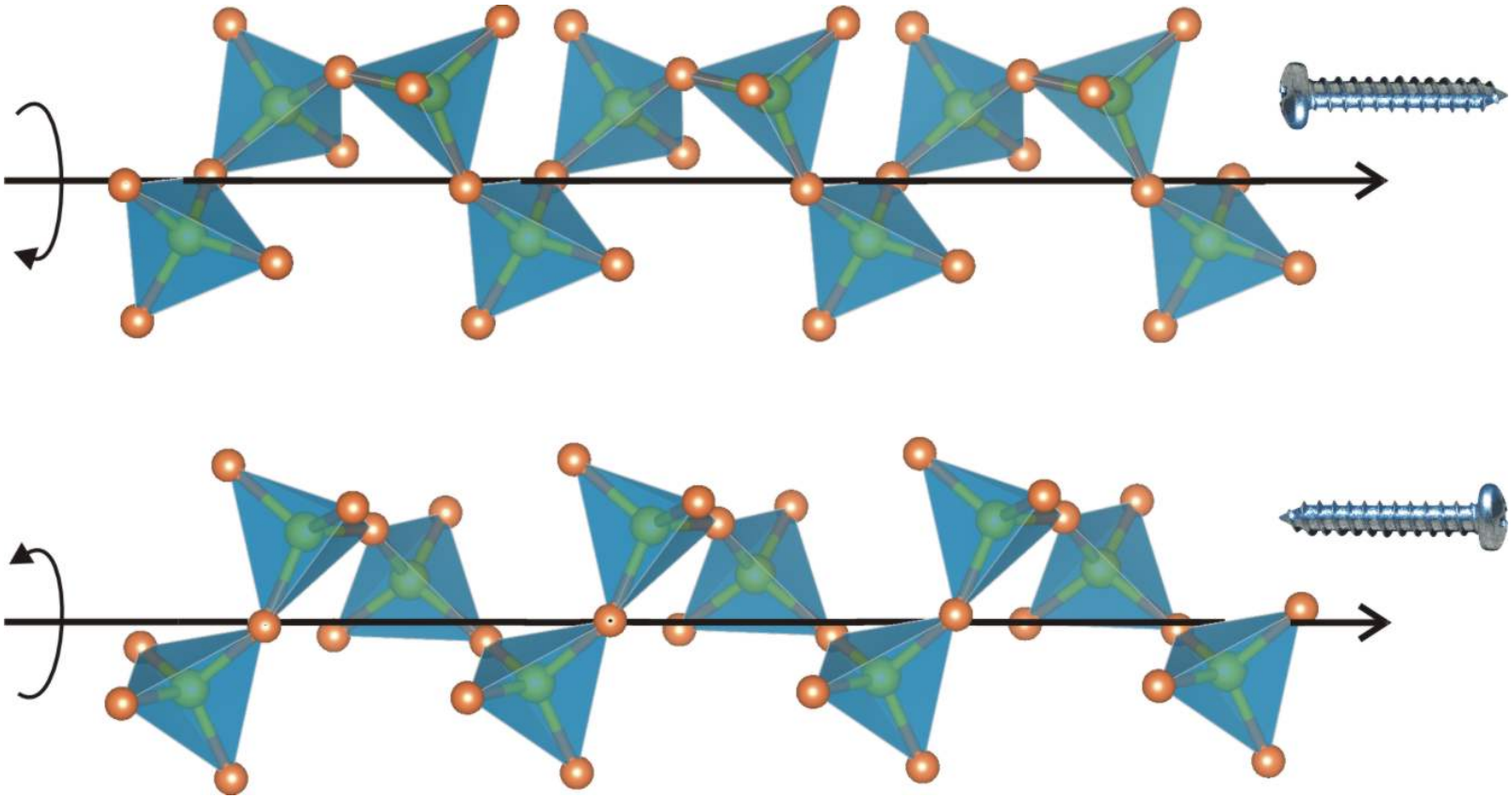
α-**LiVOPO$_4$** (*Pnma*)



ε-**LiVOPO$_4$** ($P\bar{1}$)

Similar chemical bonds, different symmetry (space group)

Enantiomorphs



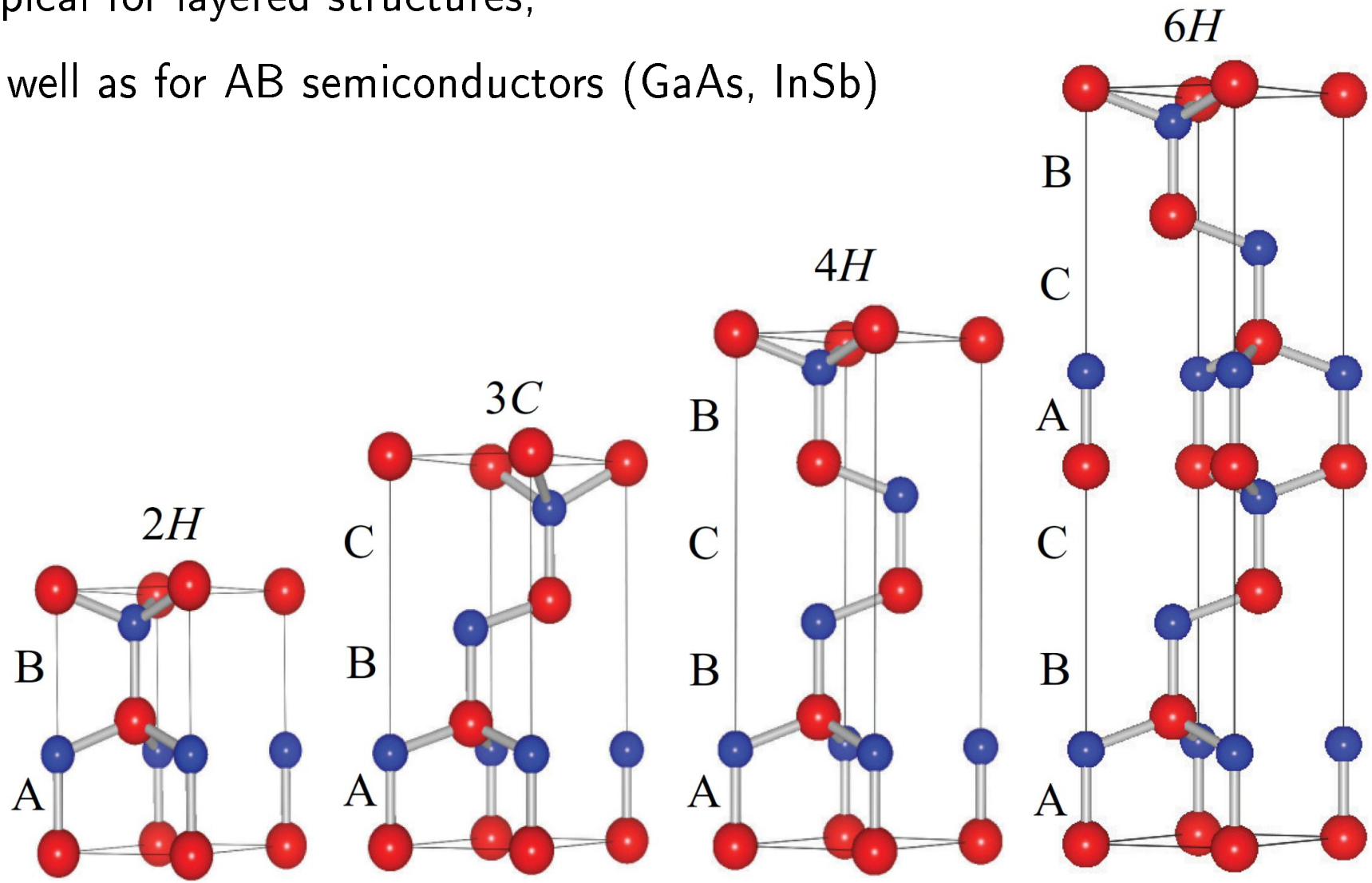
right
($P3_221$)

left
($P3_121$)

Two forms related by the mirror operation
(in chiral crystals)

Typical for layered structures,

as well as for AB semiconductors (GaAs, InSb)

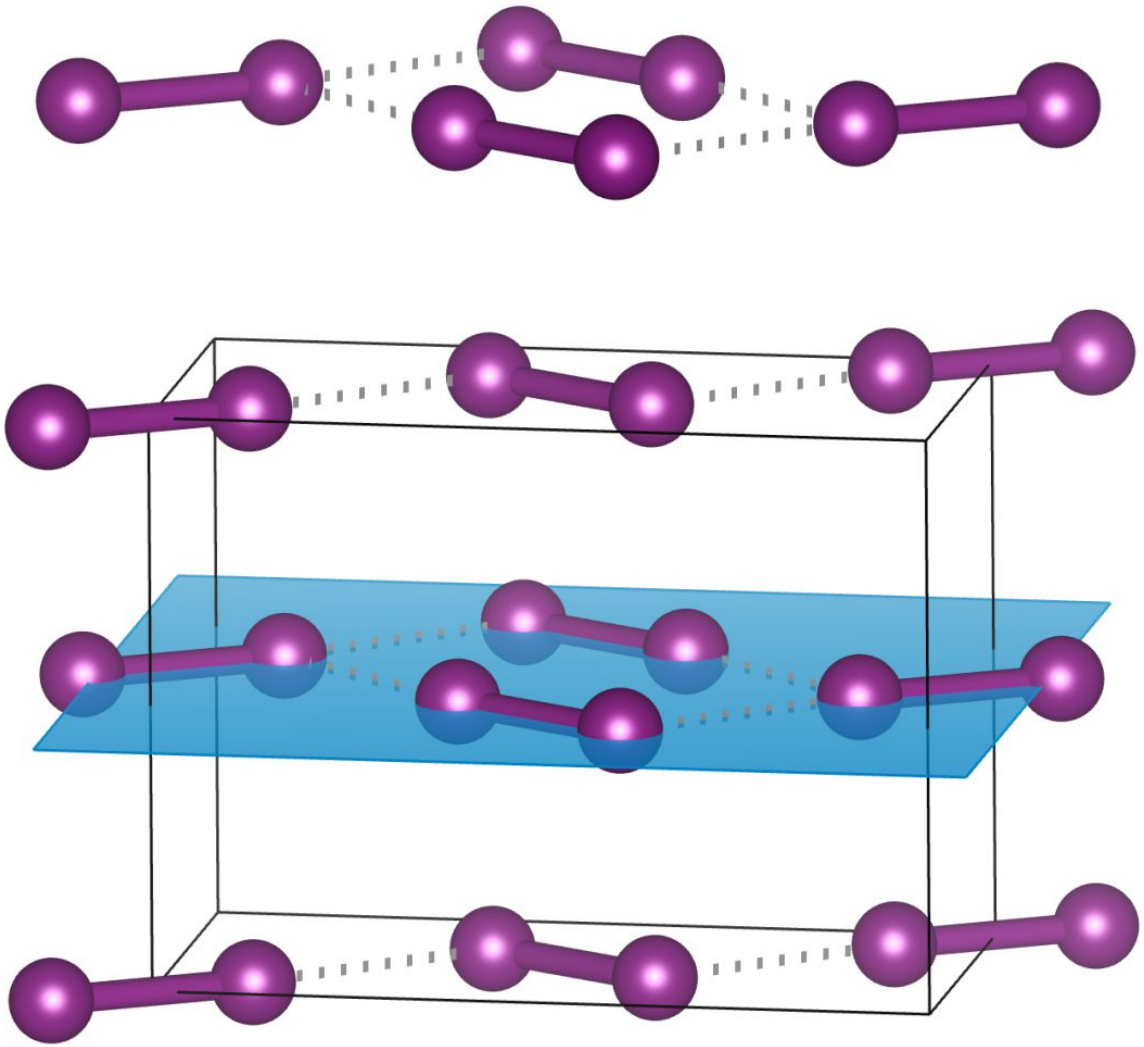


Phys. Rev. B 86, 075208 (2012)

Experimental technique

identifying bond lengths and polyhedra

Different bonds in iodine

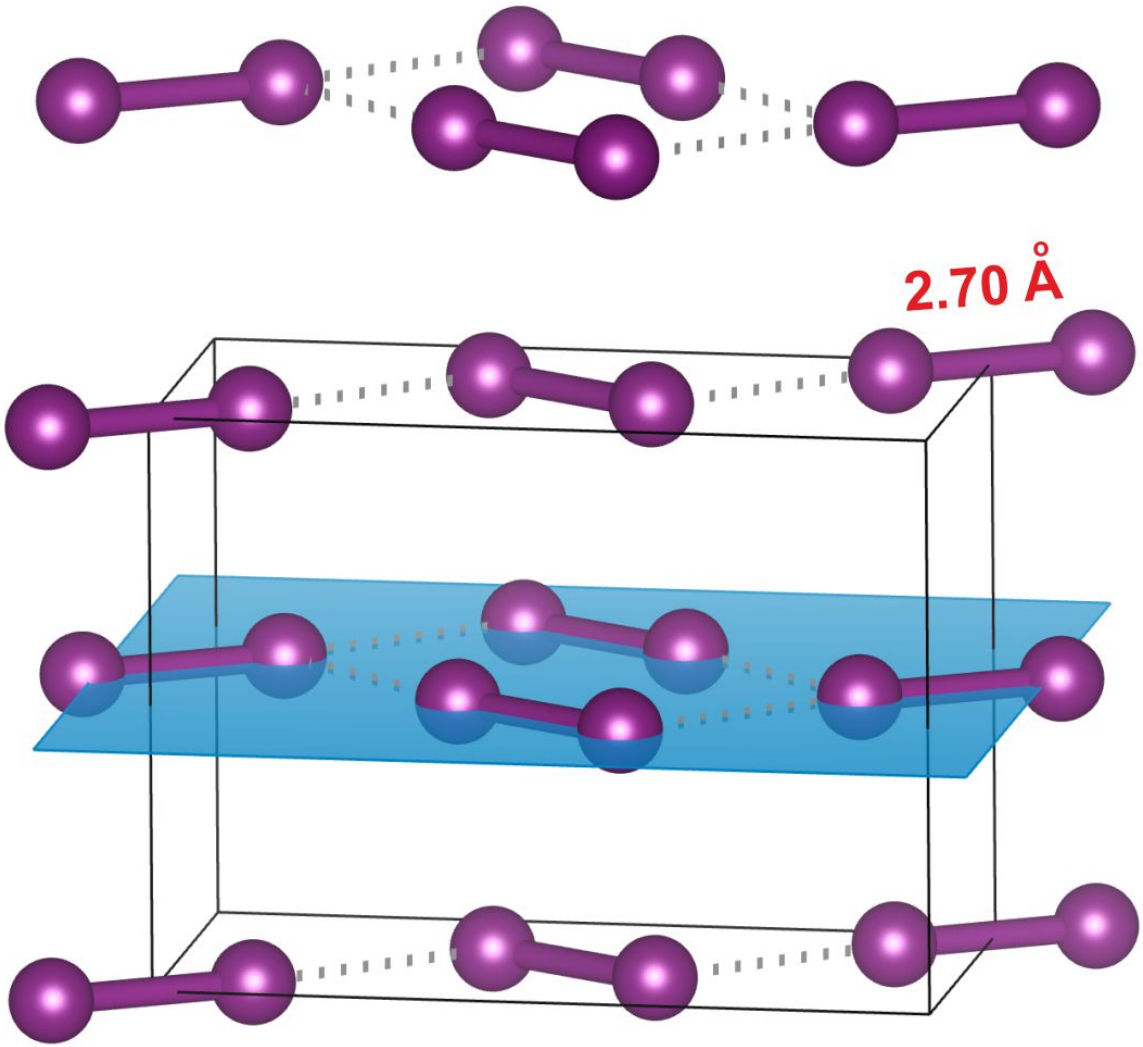


Radius of iodine

covalent: 1.39 Å

van der Waals: 1.98 Å

Different bonds in iodine



covalent

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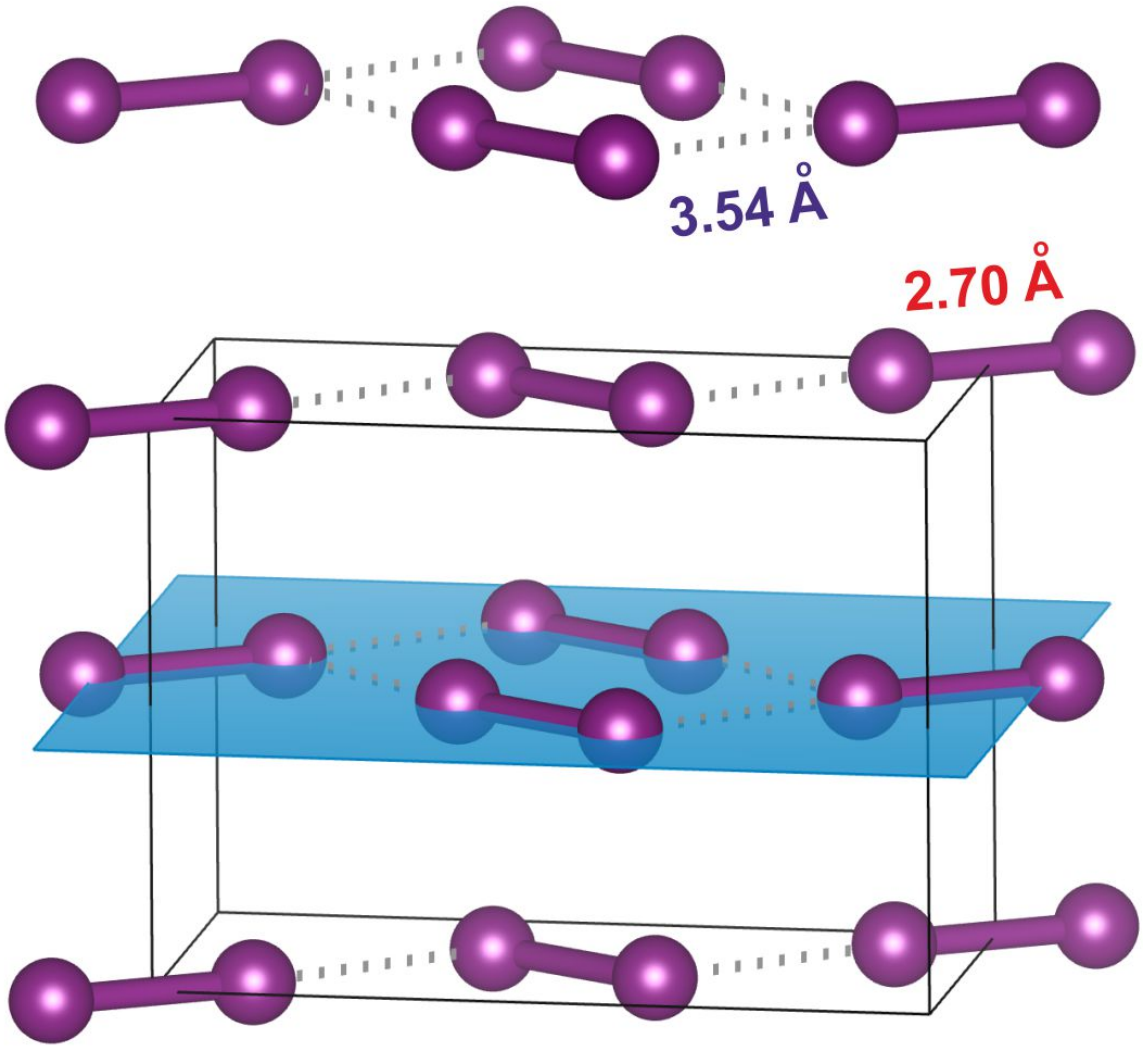
Different bonds in iodine



covalent

van der Waals

Radius of iodine

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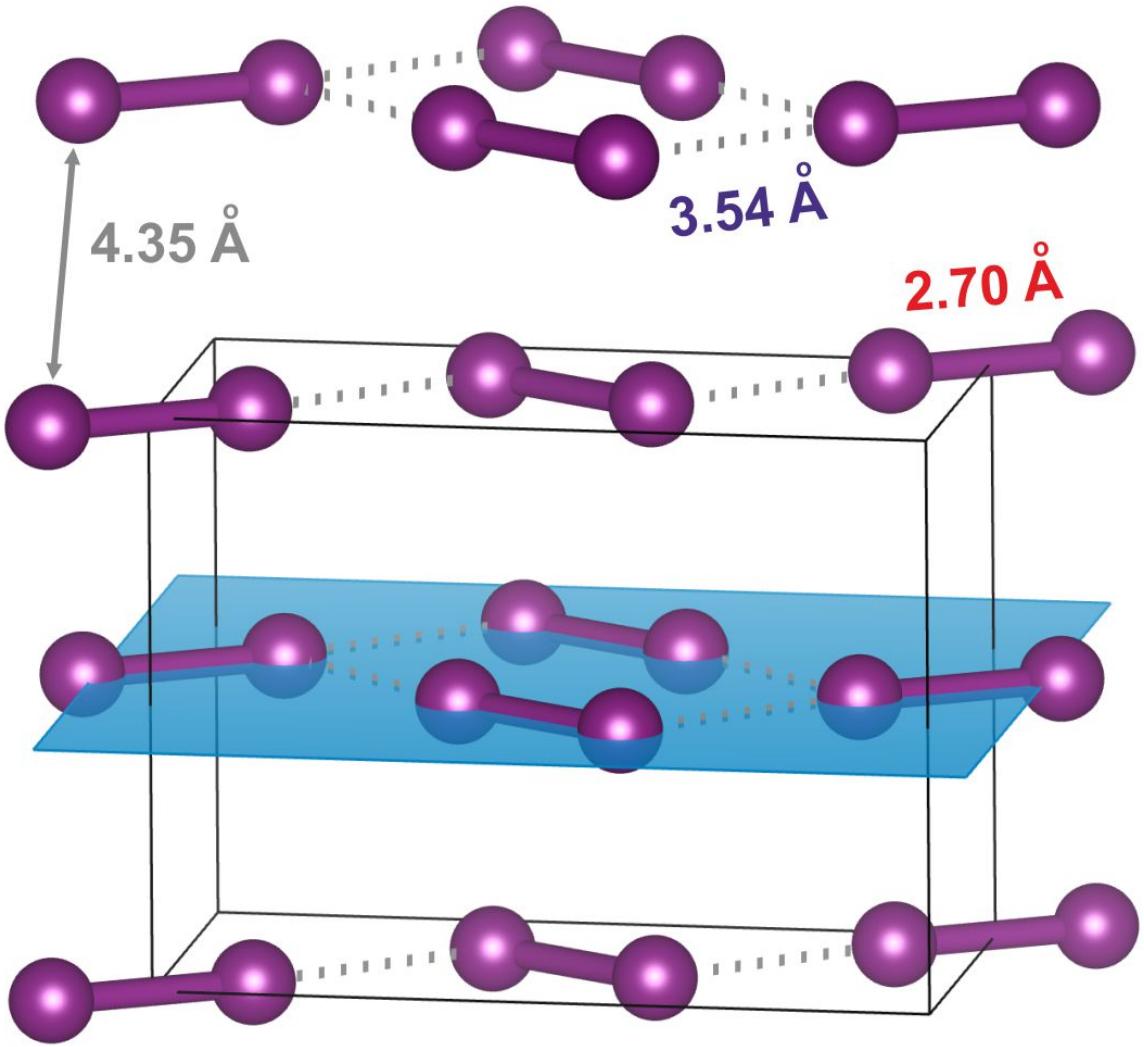
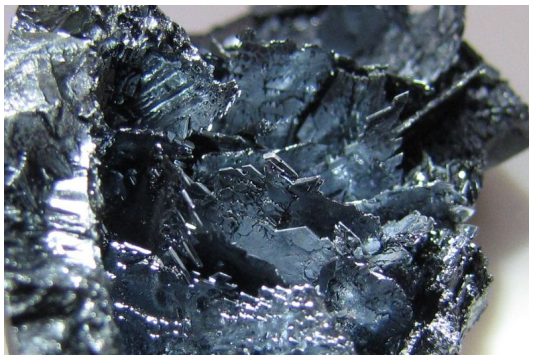
Different bonds in iodine



covalent

van der Waals

interlayer bonding
vdW, very minute



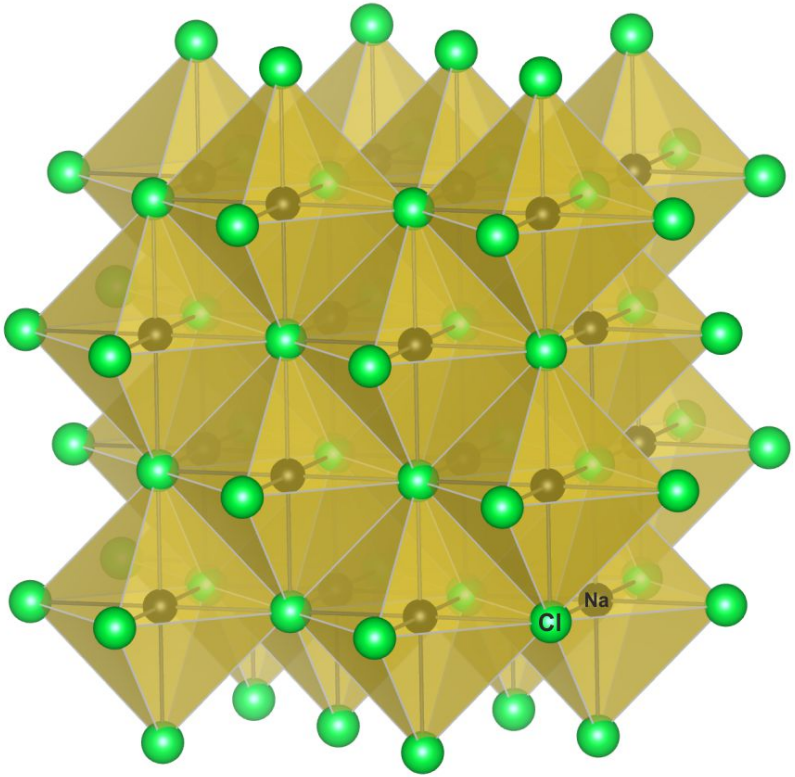
Radius of iodine

covalent: 1.39 Å

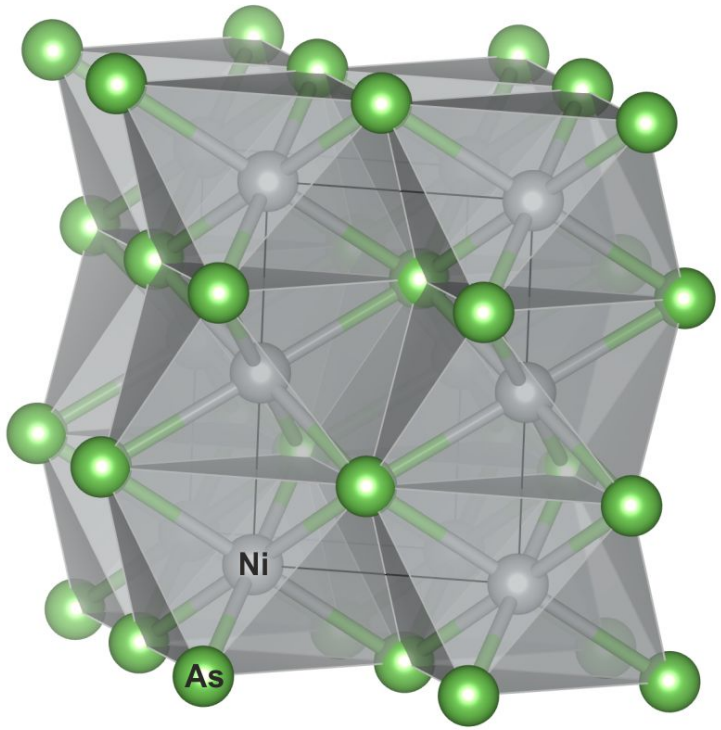
van der Waals: 1.98 Å

Image credit: Greenhorn1 (CC-BY-SA)

Polyhedral representation

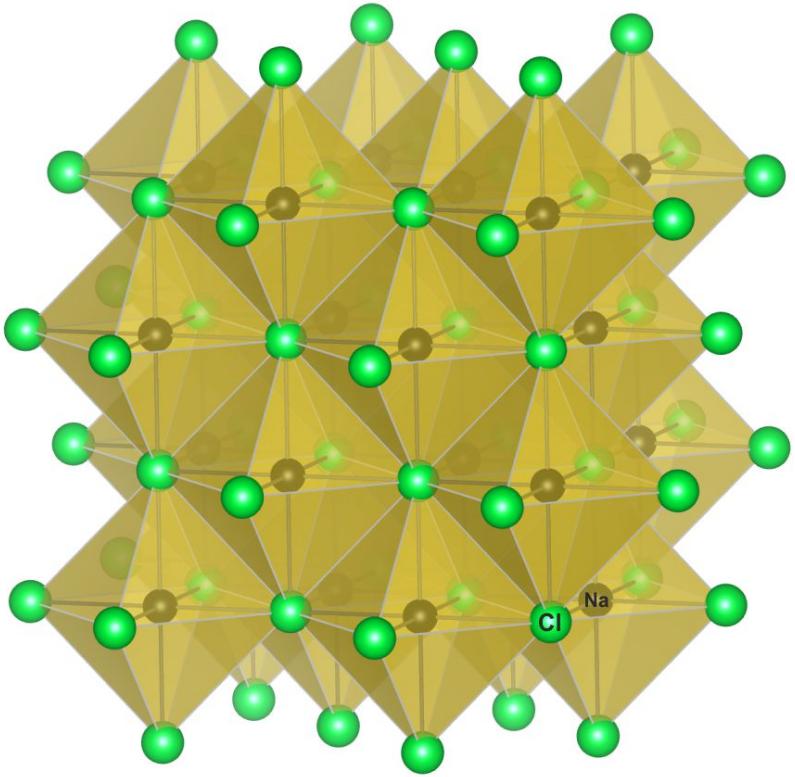


NaCl-type (ccp)
octahedra share edges

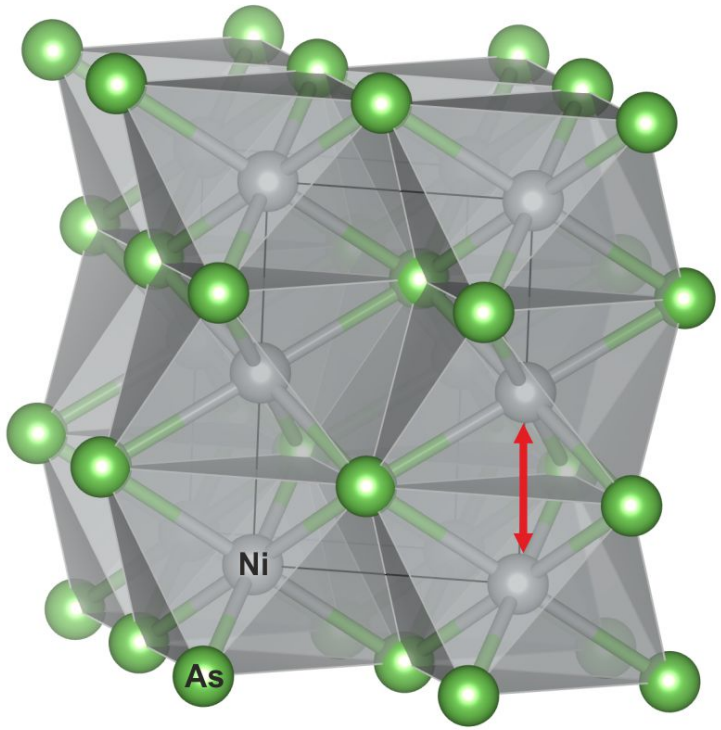


NiAs-type (hcp)
octahedra share faces

Polyhedral representation

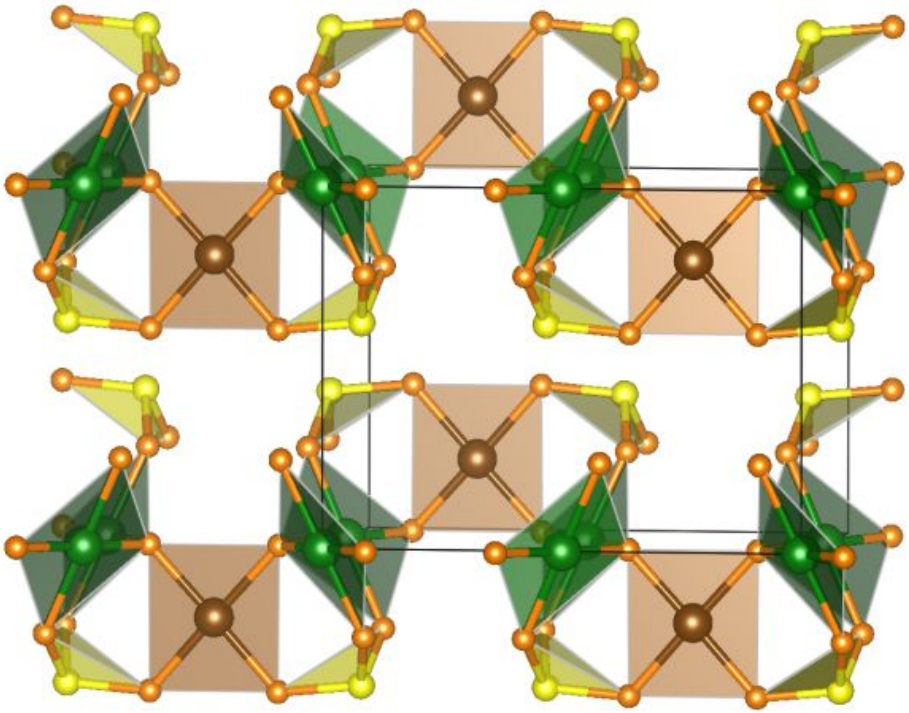


NaCl-type (ccp)
octahedra share edges

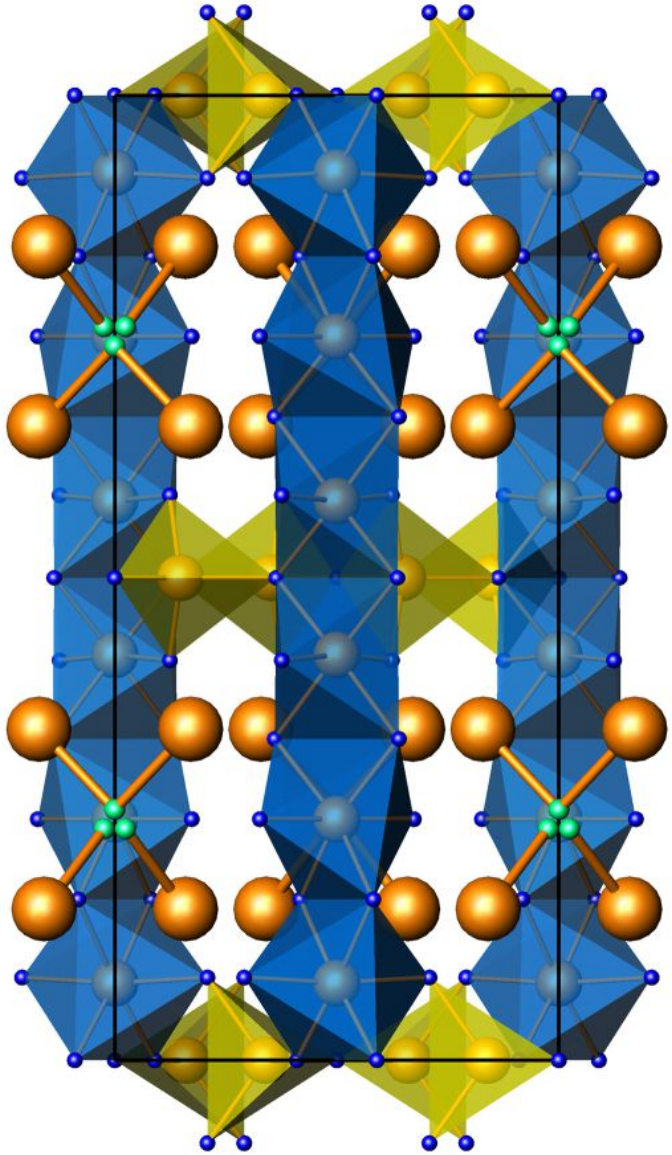


NiAs-type (hcp)
octahedra share faces

NaCl-type more likely in ionic crystals (third Pauling's rule)

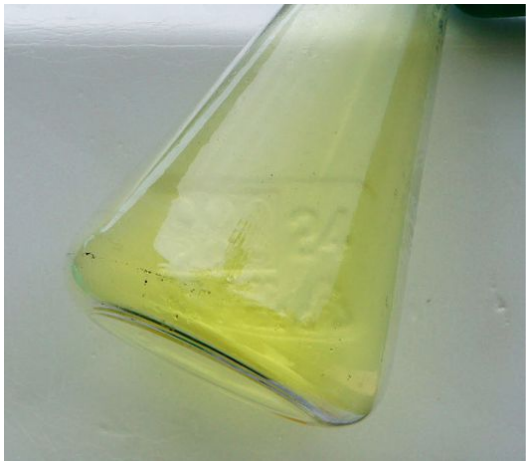


Structural features can be highlighted using the polyhedra



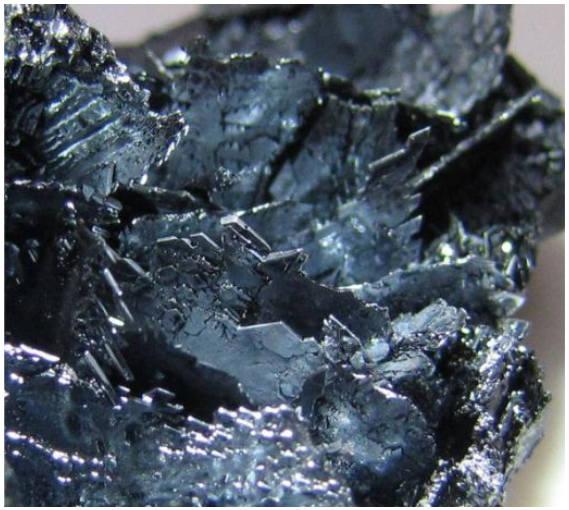
Melting points, van der Waals crystals

F_2 (53 K)

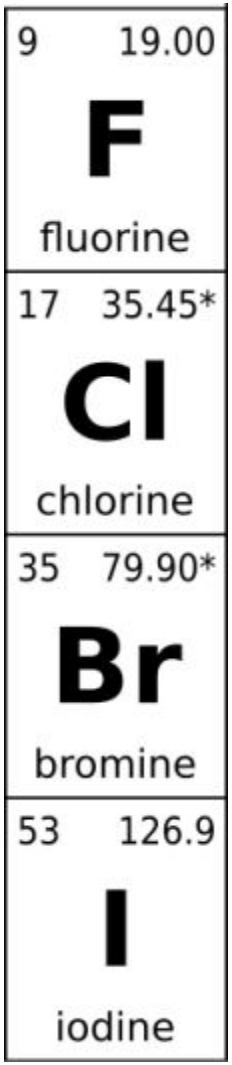


Cl_2 (172 K)

Br_2 (266 K)



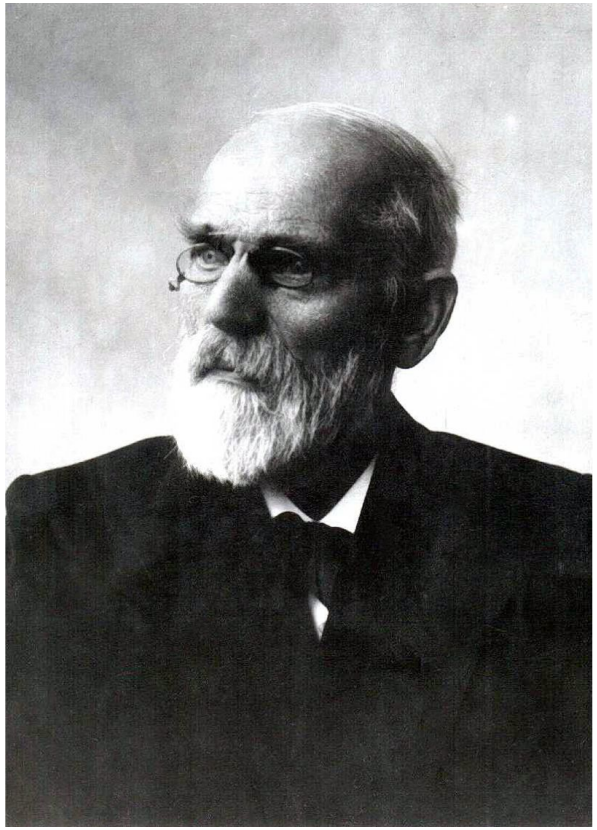
I_2 (387 K)



Person

Johannes van der Waals

- from 1865: worked as school teacher, could not enter university because he did not study classical languages
- 1873: PhD thesis **"On the continuity of the gaseous and liquid state"**
- from 1877: professor at Amsterdam University
- 1881: **law of corresponding states**
- 1910: Nobel prize in physics



Johannes Diderik van der Waals

1837–1923

...here can be no doubt that the name of Van der Waals will soon be among the foremost in molecular science

His thesis has certainly directed the attention of more than one inquirer to the **study of the Low-Dutch language** in which it is written

James Maxwell

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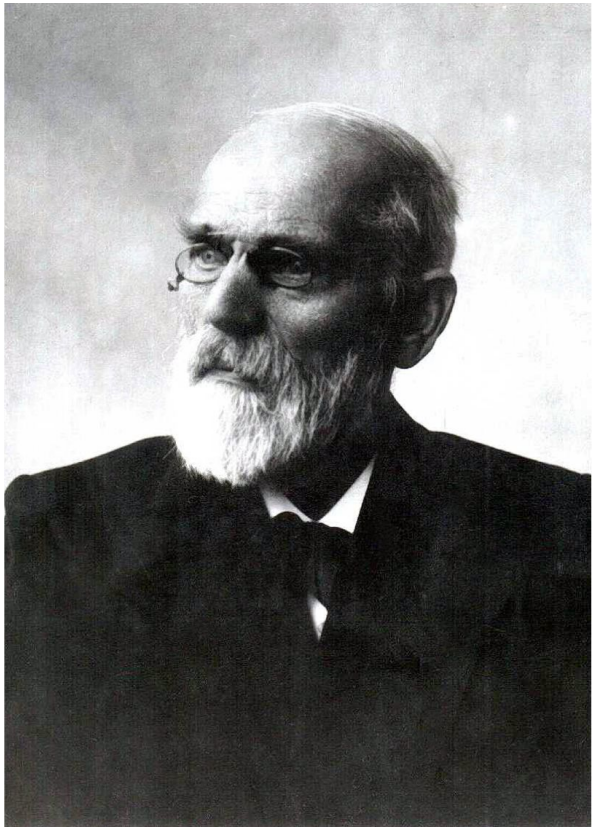
James Maxwell



Johannes Diderik van der Waals

1837–1923

Van der Waals equation

"Physics on the walls" (Leiden, Netherlands)

ideal gas: $pV = nRT$

van der Waals gas/liquid:

a – **interaction** between molecules

b – **size** of the molecule

Image credit: Wim van Saarloos (CC-BY-SA)