

# Bonding in crystals: Covalent and van der Waals



bond lengths and polyhedra


















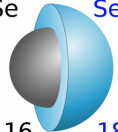


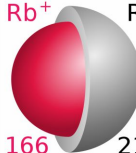


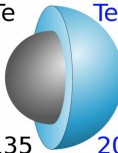
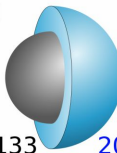
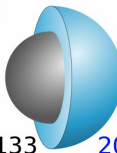
tin (Sn)



Johannes van der Waals



# Ionic vs. atomic radii

Group 1		Group 2		Group 13		Group 16		Group 17	
$\text{Li}^+$  90 Li 134	$\text{Be}^{2+}$  59 Be 90	$\text{B}^{3+}$  41 B 82	 73 O 126	$\text{O}^{2-}$  126 F 71	$\text{F}^-$  119				
$\text{Na}^+$  116 Na 154	$\text{Mg}^{2+}$  86 Mg 130	$\text{Al}^{3+}$  68 Al 118	 102 S 170	$\text{S}^{2-}$  170 Cl 99	$\text{Cl}^-$  167				
$\text{K}^+$  152 K 196	$\text{Ca}^{2+}$  114 Ca 174	$\text{Ga}^{3+}$  76 Ga 126	 116 Se 184	$\text{Se}^{2-}$  184 Br 114	$\text{Br}^-$  182				
$\text{Rb}^+$  166 Rb 211	$\text{Sr}^{2+}$  132 Sr 192	$\text{In}^{3+}$  94 In 144	 135 Te 207	$\text{Te}^{2-}$  207 I 133	$\text{I}^-$  206				

values  
in pm!

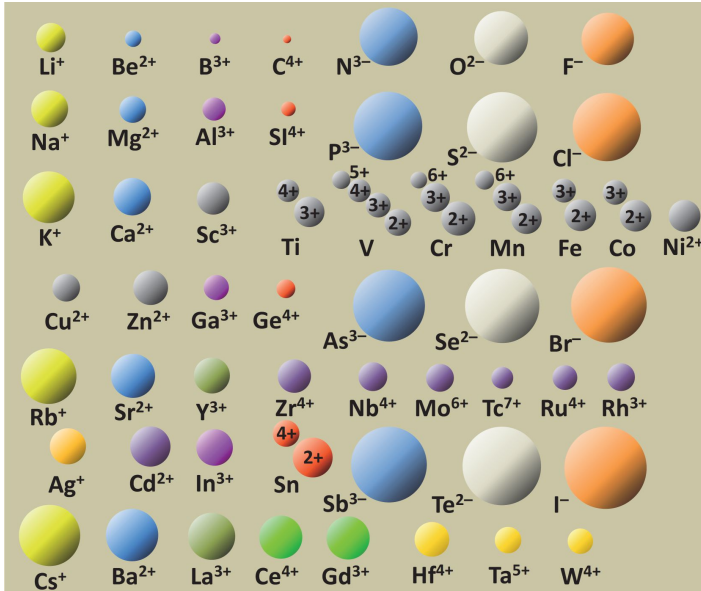


Image from Gross and Marx, Festkörperphysik

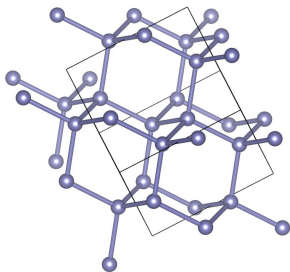
		coordination number		covalent (CR)	ionic (IR)	
NA+1	2P	6	IV	1.13	.99	
			V	1.14	1.00	
			VI	1.16	1.02	
			VII	1.26	1.12	
			VIII	1.32	1.18	
			IX	1.38	1.24	C
			XII	1.53	1.39	
NB+3	4D	2	VI	.86	.72	
			VIII	.93	.79	
NB+4	4D	1	VI	.82	.68	RE
			VIII	.93	.79	
NB+5	4P	6	IV	.62	.48	C
			VI	.78	.64	
			VII	.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)

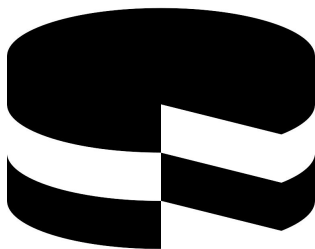
# Melting points, covalent crystals

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



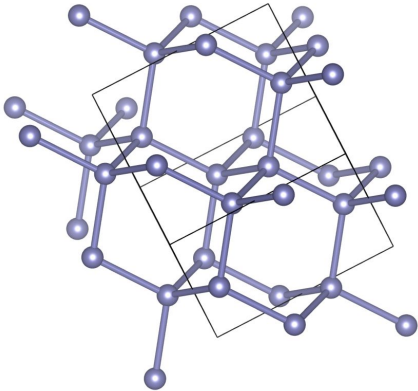
6	12.01*	<b>C</b> carbon
14	28.09*	<b>Si</b> silicon
32	72.63	<b>Ge</b> germanium
50	118.7	<b>Sn</b> tin

Data from CRC Handbook of Chemistry and Physics

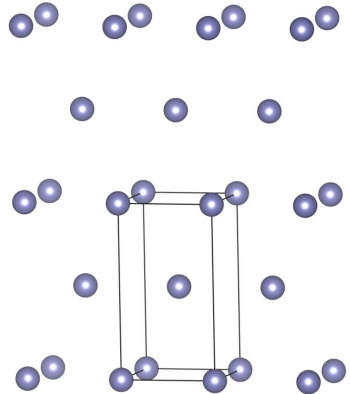


Material

*Tin (Sn)*



**gray tin** ( $\alpha$ -Sn)  
*covalent*



**white tin** ( $\beta$ -Sn)  
*metallic*

# Intermediate position of tin

metalloids

1 1.008* <b>H</b> hydrogen																	18 4.003 <b>He</b> helium
3 6.94* <b>Li</b> lithium	4 9.012 <b>Be</b> beryllium											5 10.81 <b>B</b> boron	6 12.01* <b>C</b> carbon	7 14.01* <b>N</b> nitrogen	8 16.00* <b>O</b> oxygen	9 19.00 <b>F</b> fluorine	10 20.18 <b>Ne</b> neon
11 22.99 <b>Na</b> sodium	12 24.31* <b>Mg</b> magnesium											13 26.98 <b>Al</b> aluminium	14 28.09 <b>Si</b> silicon	15 30.97 <b>P</b> phosphorus	16 32.06* <b>S</b> sulfur	17 35.45* <b>Cl</b> chlorine	18 39.95 <b>Ar</b> argon
19 39.10 <b>K</b> potassium	20 40.08 <b>Ca</b> calcium	21 44.96 <b>Sc</b> scandium	22 47.87 <b>Ti</b> titanium	23 50.94 <b>V</b> vanadium	24 52.00 <b>Cr</b> chromium	25 54.94 <b>Mn</b> manganese	26 55.85 <b>Fe</b> iron	27 58.93 <b>Co</b> cobalt	28 58.69 <b>Ni</b> nickel	29 63.55 <b>Cu</b> copper	30 65.38* <b>Zn</b> zinc	31 69.72 <b>Ga</b> gallium	32 72.63 <b>Ge</b> germanium	33 74.92 <b>As</b> arsenic	34 78.97* <b>Se</b> selenium	35 79.90* <b>Br</b> bromine	36 83.80 <b>Kr</b> krypton
37 85.47 <b>Rb</b> rubidium	38 87.62 <b>Sr</b> strontium	39 88.91 <b>Y</b> yttrium	40 91.22 <b>Zr</b> zirconium	41 92.91 <b>Nb</b> niobium	42 95.95* <b>Mo</b> molybdenum	43 [98] <b>Tc</b> technetium	44 101.1 <b>Ru</b> ruthenium	45 102.9 <b>Rh</b> rhodium	46 106.4 <b>Pd</b> palladium	47 107.9 <b>Ag</b> silver	48 112.4 <b>Cd</b> cadmium	49 114.8 <b>In</b> indium	50 118.7 <b>Sn</b> tin	51 121.8 <b>Sb</b> antimony	52 127.6 <b>Te</b> tellurium	53 126.9 <b>I</b> iodine	54 131.3 <b>Xe</b> xenon
55 132.9 <b>Cs</b> caesium	56 137.3 <b>Ba</b> barium	57-71 <b>La</b> lanthanum	72 178.5 <b>Hf</b> hafnium	73 180.9 <b>Ta</b> tantalum	74 183.8 <b>W</b> tungsten	75 186.2 <b>Re</b> rhenium	76 190.2 <b>Os</b> osmium	77 192.2 <b>Ir</b> iridium	78 195.1 <b>Pt</b> platinum	79 197.0 <b>Au</b> gold	80 200.6 <b>Hg</b> mercury	81 204.4* <b>Tl</b> thallium	82 207.2 <b>Pb</b> lead	83 209.0 <b>Bi</b> bismuth	84 [209] <b>Po</b> polonium	85 [210] <b>At</b> astatine	86 [222] <b>Rn</b> radon
87 [223] <b>Fr</b> francium	88 [226] <b>Ra</b> radium	89-103 <b>Ac</b> actinium	104 [267] <b>Rf</b> rutherfordium	105 [268] <b>Db</b> dubnium	106 [269] <b>Sg</b> seaborgium	107 [270] <b>Bh</b> bohrium	108 [277] <b>Hs</b> hassium	109 [278] <b>Mt</b> meitnerium	110 [281] <b>Ds</b> darmstadtium	111 [282] <b>Rg</b> roentgenium	112 [285] <b>Cn</b> copernicium	113 [286] <b>Nh</b> nihonium	114 [289] <b>Fl</b> flerovium	115 [290] <b>Mc</b> moscovium	116 [293] <b>Lv</b> livermorium	117 [294] <b>Ts</b> tennessine	118 [294] <b>Og</b> oganesesson
		57 138.9 <b>La</b> lanthanum		58 140.1 <b>Ce</b> cerium	59 140.9 <b>Pr</b> praseodymium	60 144.2 <b>Nd</b> neodymium	61 [145] <b>Pm</b> promethium	62 150.4 <b>Sm</b> samarium	63 152.0 <b>Eu</b> europium	64 157.3 <b>Gd</b> gadolinium	65 158.9 <b>Tb</b> terbium	66 162.5 <b>Dy</b> dysprosium	67 164.9 <b>Ho</b> holmium	68 167.3 <b>Er</b> erbium	69 168.9 <b>Tm</b> thulium	70 173.0 <b>Yb</b> ytterbium	71 175.0 <b>Lu</b> lutetium
		89 [227] <b>Ac</b> actinium		90 232.0 <b>Th</b> thorium	91 231.0 <b>Pa</b> protactinium	92 238.0 <b>U</b> uranium	93 [237] <b>Np</b> neptunium	94 [244] <b>Pu</b> plutonium	95 [243] <b>Am</b> americium	96 [247] <b>Cm</b> curium	97 [247] <b>Bk</b> berkelium	98 [251] <b>Cf</b> californium	99 [252] <b>Es</b> einsteinium	100 [257] <b>Fm</b> fermium	101 [258] <b>Md</b> mendelevium	102 [259] <b>No</b> nobelium	103 [266] <b>Lr</b> lawrencium

\*H: 1.00784, 1.00811]  
 Li: [6.938, 6.997]  
 B: [10.806, 10.821]  
 C: [12.0096, 12.0116]  
 N: [14.00643, 14.00728]  
 O: [15.99903, 15.99977]  
 Mg: [24.304, 24.307]  
 Si: [28.084, 28.086]  
 S: [32.059, 32.076]  
 Cl: [35.446, 35.457]  
 Br: [79.901, 79.907]  
 Ti: [204.382, 204.385]  
 Zn: [65.38(2)]  
 Se: [78.96(3)]  
 Mo: [95.96(2)]





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

Image credit: [periodictable.ru](http://periodictable.ru) (fair use)



$\beta \rightarrow \alpha$   
transformation  
below  $13.2^\circ\text{C}$

Image credit: [periodictable.ru](http://periodictable.ru) (fair use)



$\beta \rightarrow \alpha$   
transformation  
below  $13.2^\circ\text{C}$

Image credit: [periodictable.ru](http://periodictable.ru) (fair use)



Napoleon's army  
in Russia (1812)  
*tin buttons*

$\beta \rightarrow \alpha$   
transformation  
below  $13.2^\circ\text{C}$

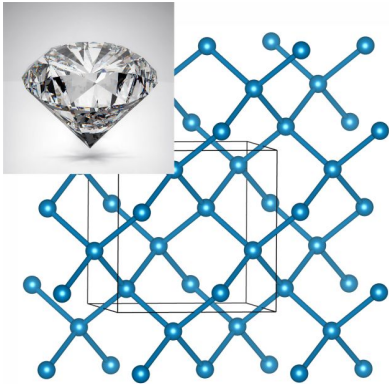
Image credit: periodictable.ru (fair use)  
British Museum (CC-BY-SA)



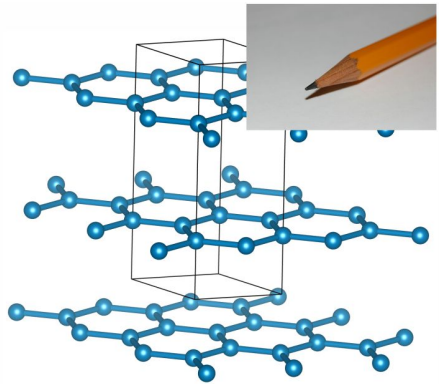
Robert Scott (1912)  
South Pole expedition  
*tin cans and pots*

$\beta \rightarrow \alpha$   
transformation  
below  $13.2^\circ\text{C}$

Image credit: periodictable.ru (fair use)  
Sun Ladder and T. Müller (CC-BY-SA)

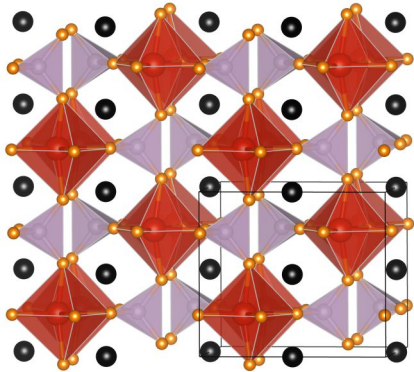


**Diamond**

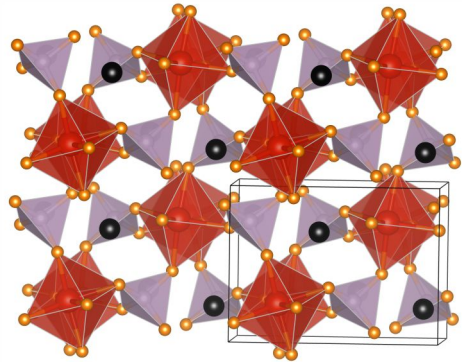


**Graphite**

Same chemical composition, but very different bonds and properties

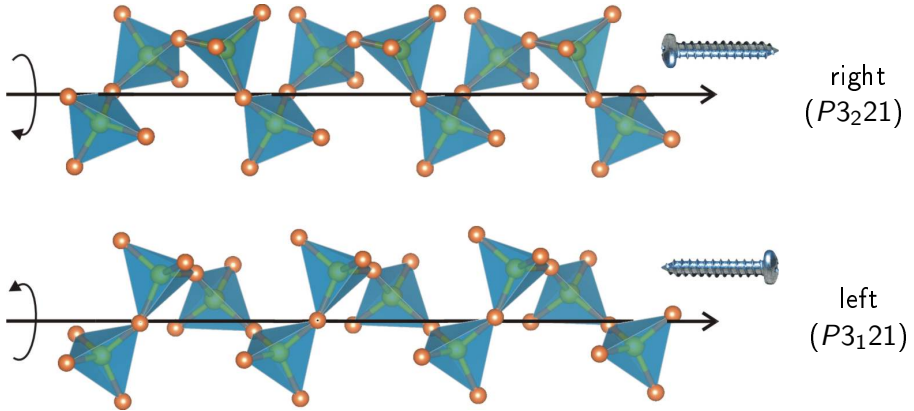


$\alpha$ -LiVOPO<sub>4</sub> ( $Pnma$ )



$\epsilon$ -LiVOPO<sub>4</sub> ( $P\bar{1}$ )

Similar chemical bonds, different symmetry (space group)

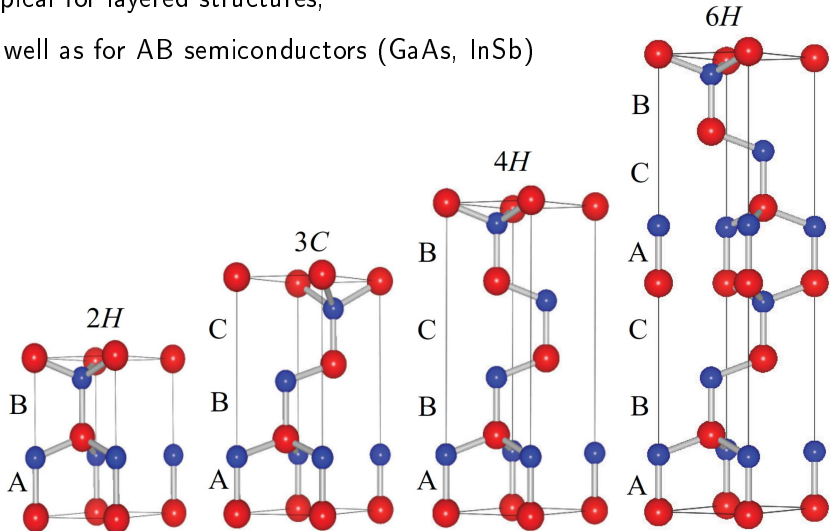


Two forms related by the mirror operation  
(in chiral crystals)





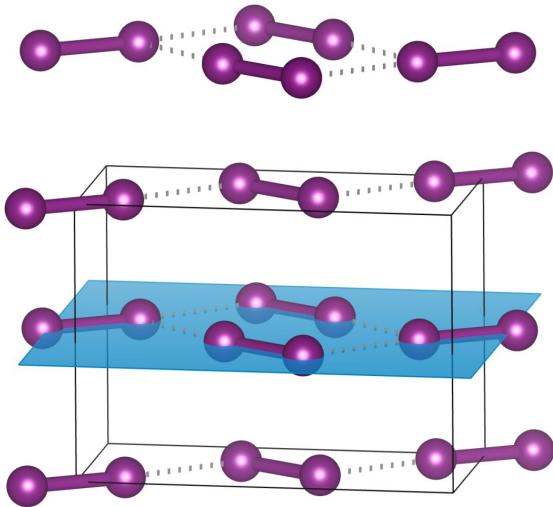
Typical for layered structures,  
as well as for AB semiconductors (GaAs, InSb)





# Experimental technique

*identifying bond lengths and polyhedra*

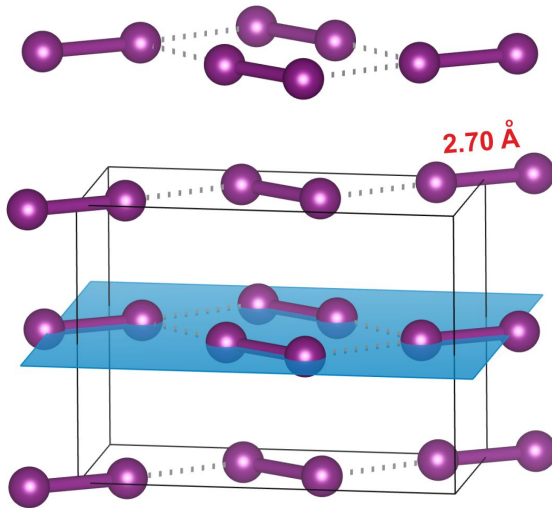


**Radius of iodine**

covalent: 1.39 Å

van der Waals: 1.98 Å

# Different bonds in iodine



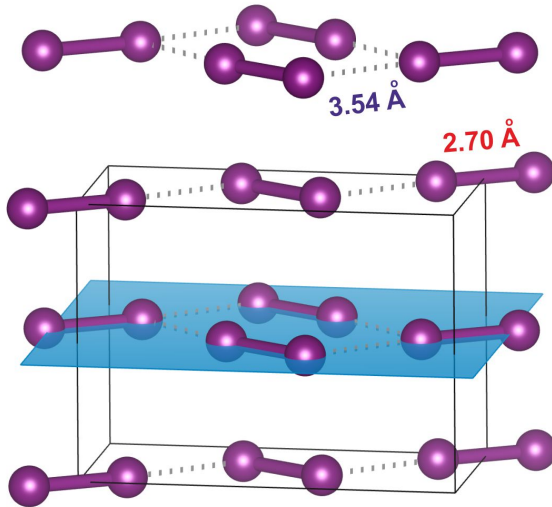
covalent

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van der Waals: 1.98 Å

# Different bonds in iodine



covalent

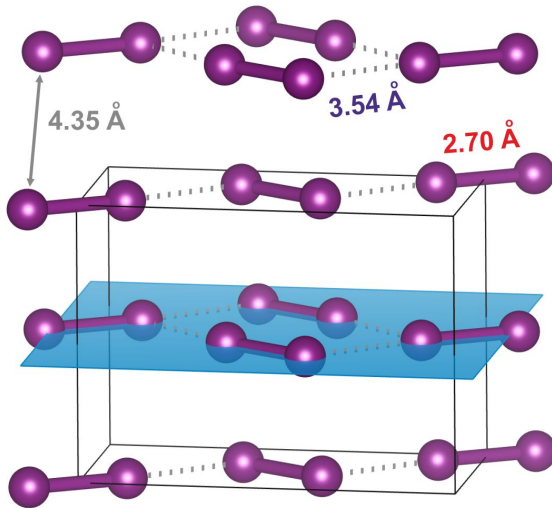
van der Waals

**Radius of iodine**

covalent: 1.39 Å

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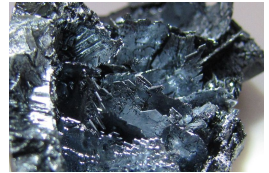
# Different bonds in iodine



covalent

van der Waals

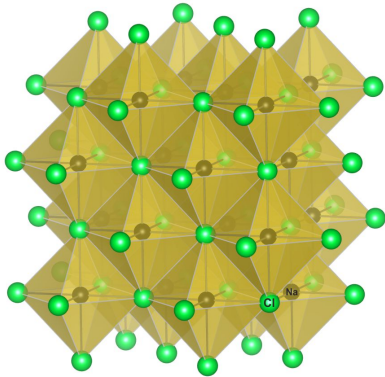
*interlayer bonding*  
vdW, very minute



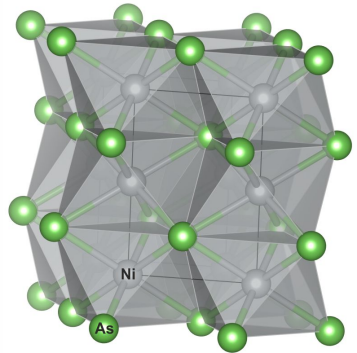
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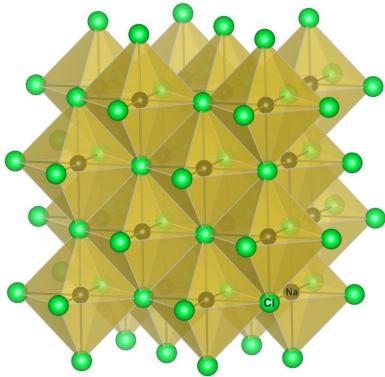
van der Waals: 1.98 Å



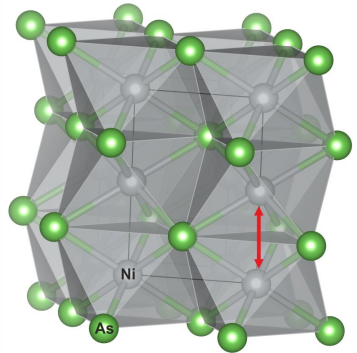
**NaCl-type** (ccp)  
octahedra share edges



**NiAs-type** (hcp)  
octahedra share faces



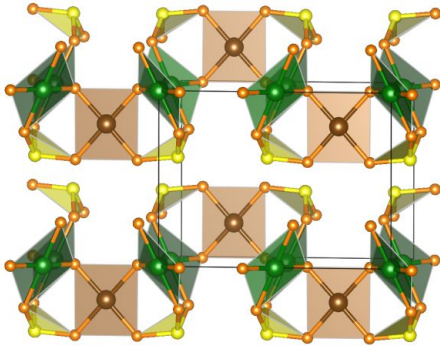
**NaCl-type** (ccp)  
octahedra share edges



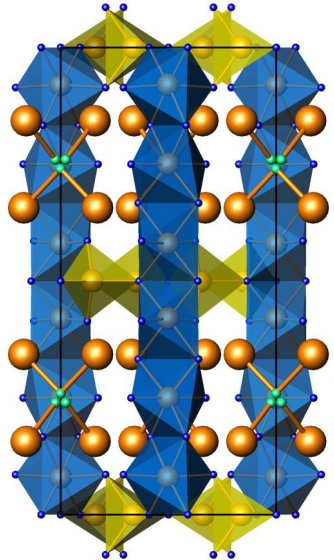
**NiAs-type** (hcp)  
octahedra share faces

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





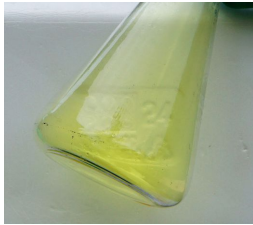
Structural features can be highlighted using the polyhedra



# Melting points, van der Waals crystals



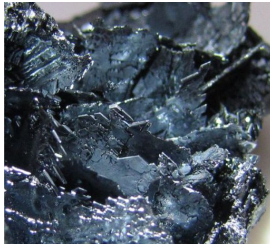
$F_2$  (53 K)



$Cl_2$  (172 K)



$Br_2$  (266 K)



$I_2$  (387 K)

9	19.00
<b>F</b>	
fluorine	
17	35.45*
<b>Cl</b>	
chlorine	
35	79.90*
<b>Br</b>	
bromine	
53	126.9
<b>I</b>	
iodine	

Image credits: Antek123, Jurii, Greenhorn1 (CC-BY-SA)



Person

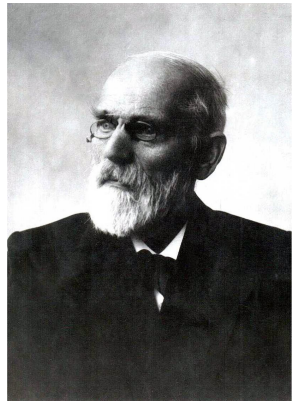
*Johannes van der Waals*

- 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

...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



Johannes Diderik  
van der Waals

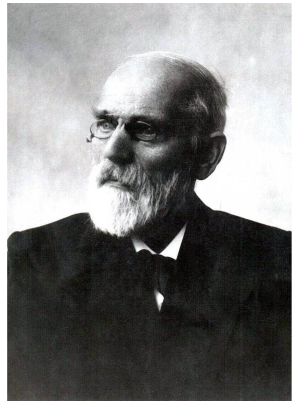
1837–1923

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James Maxwell



Johannes Diderik  
van der Waals

1837–1923



“Physics on the walls” (Leiden, Netherlands)

*ideal gas:  $pV = nRT$*

*van der Waals gas/liquid:*

*a – **interaction**  
between molecules*

*b – **size** of the molecule*