

Lecture 43 Ionic Compounds

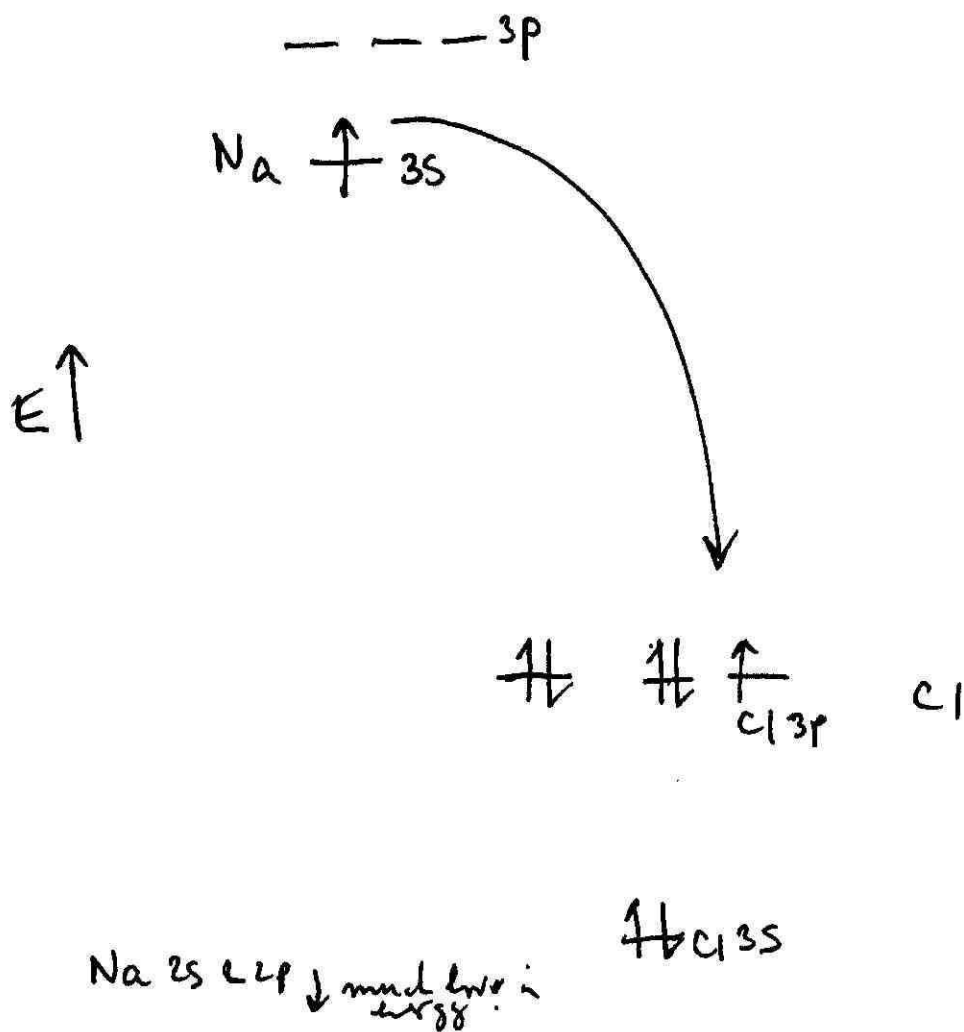
43.1

① Consider a compound such as NaCl.

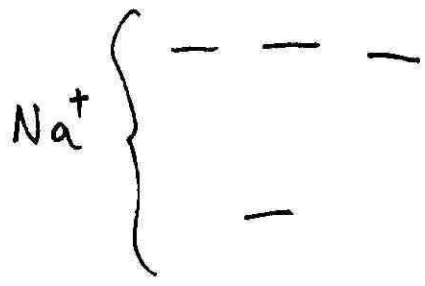
The Na is highly electropositive and loses an e^- to become Na^+ , which then has the very stable 10 core electron configuration of Ne.

The Cl gains one electron (Cl is highly electronegative) to become Cl^- , which has the 18 valence electrons like the electron configuration of Ar.

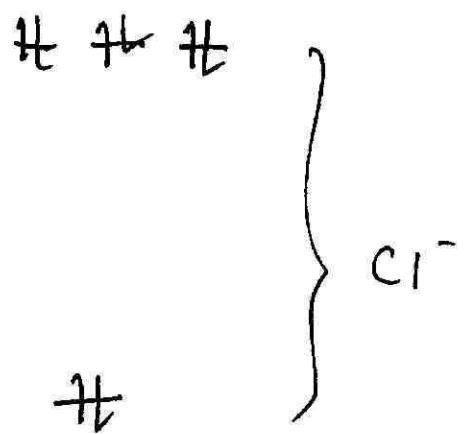
The orbital picture would be before e^- transfer



② After ~~in~~ oxidation of Na & reduction of Cl, the valence e^- orbitals of Na^+ & Cl^- look like this:



$E \uparrow$

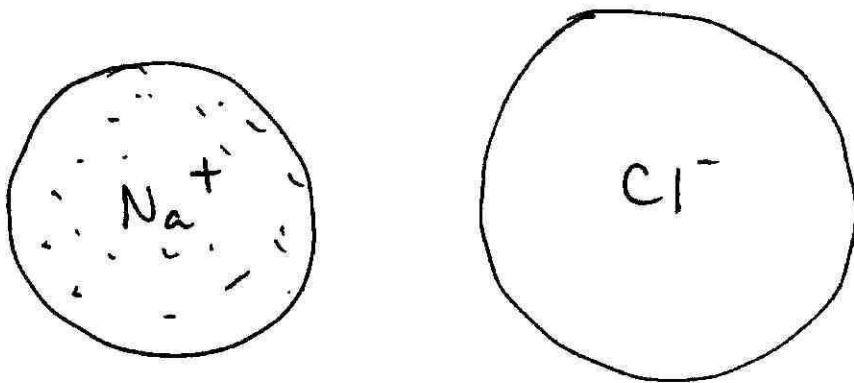


The gap between Na^+ & Cl^- orbitals is so large that any MO style interactions would be very weak (rule 3)

③ There are so little MO interactions between Na^+ & Cl^- , that for once, we can ignore them.

④ But as you know NaCl (table salt) is a pretty stable compound. (It melts at $\sim 700^\circ\text{C}$.)
What does the bonding in NaCl look like?

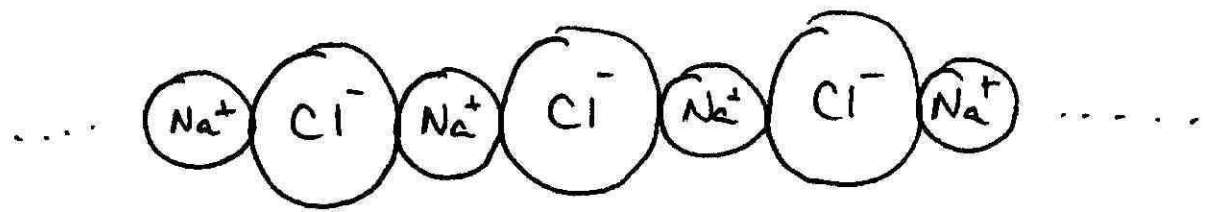
⑤ There are two parts to this NaCl bonding picture. On the one hand Na^+ & Cl^- both have noble gas e^- configurations. Thus both Na^+ & Cl^- have a certain fixed size.



(It turns out $(2s)^2 (2p)^6$ has a spherical charge distribution. Basically $\uparrow\downarrow + \uparrow\downarrow + \uparrow\downarrow$ comes out to a sphere of charge. The same is true for $(3s)^2 (3p)^6$.)

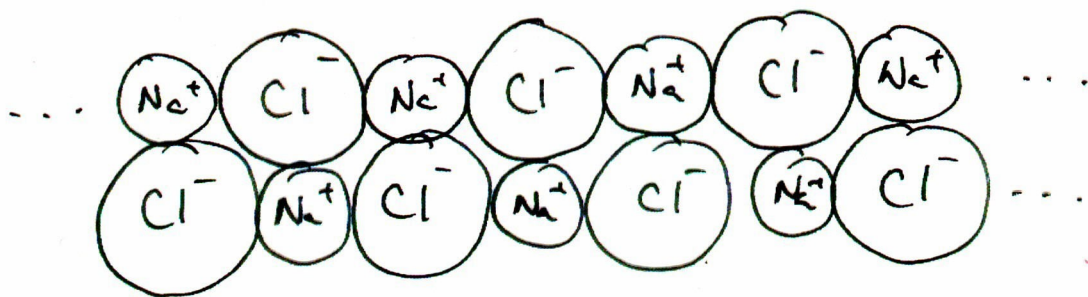
⑥ So Na^+ & Cl^- will both behave a bit like spheres. But these spheres are charged. As you know (+) - charge is attracted to (-) - charge but two (+) - ~~use~~ charges or two (-) charges are repelled.

⑦ How would these spheres of charge pack?
 To solve this problem, let's first consider a one-dimensional world? I hope you can see the most energy way of packing these spheres is as follows:

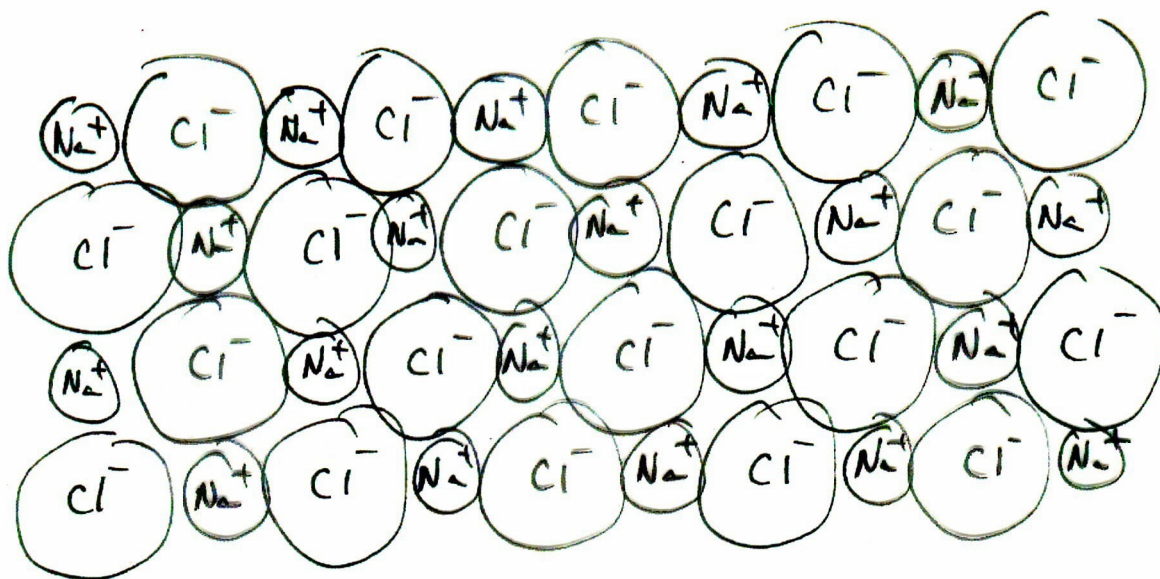


or
 $\text{Na}^+ \text{Cl}^- \text{Na}^+ \text{Cl}^- \text{Na}^+ \text{Cl}^- \text{Na}^+$

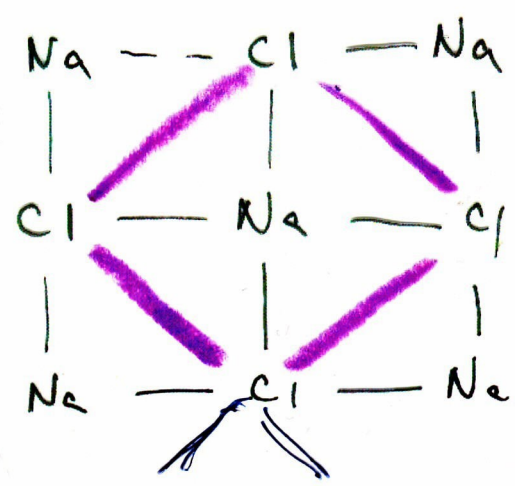
⑧ Let's move onto a 2-D world. We bring two 1-D chains together:



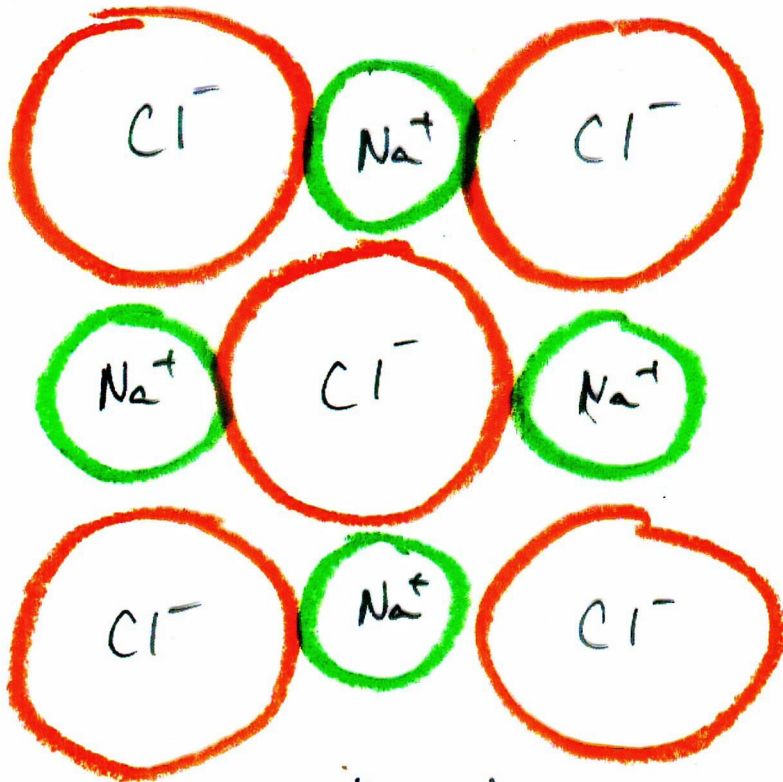
9 This continues to make the 2-D sheet



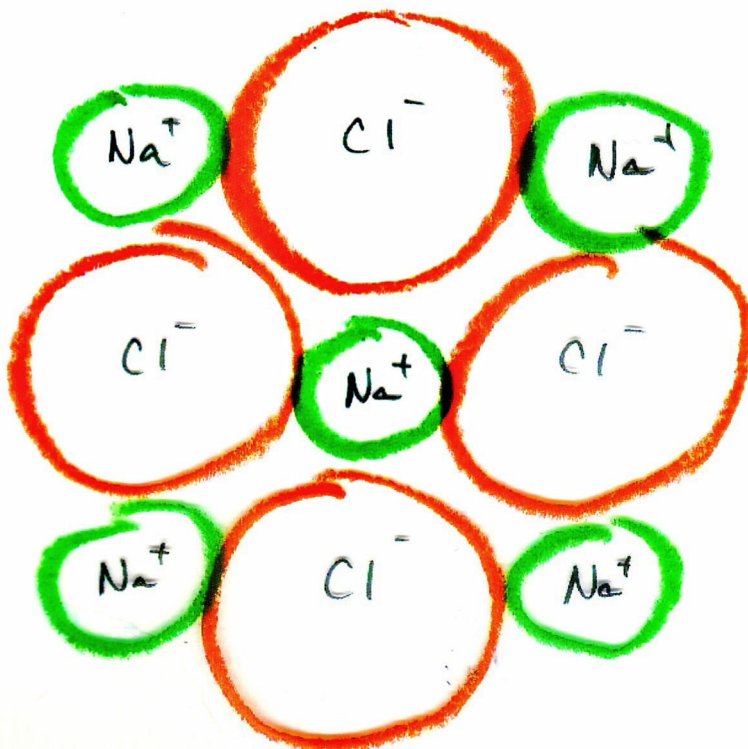
The 2-D unit cell is

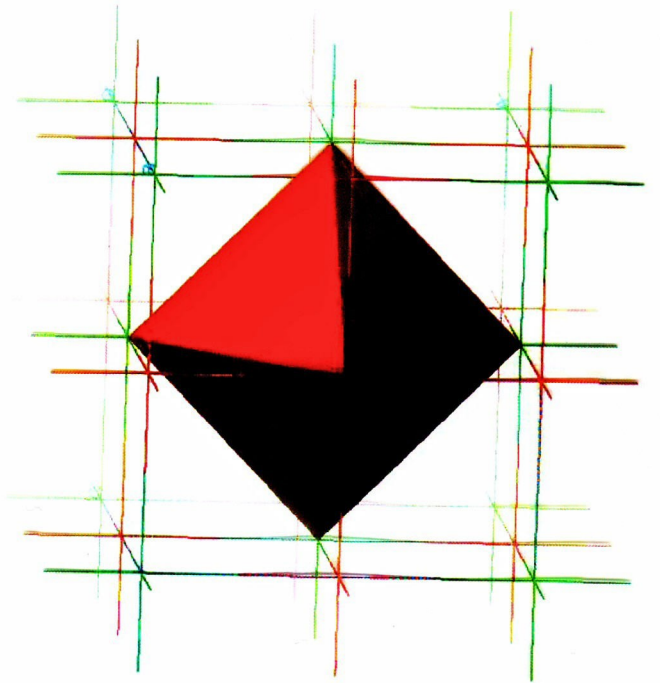
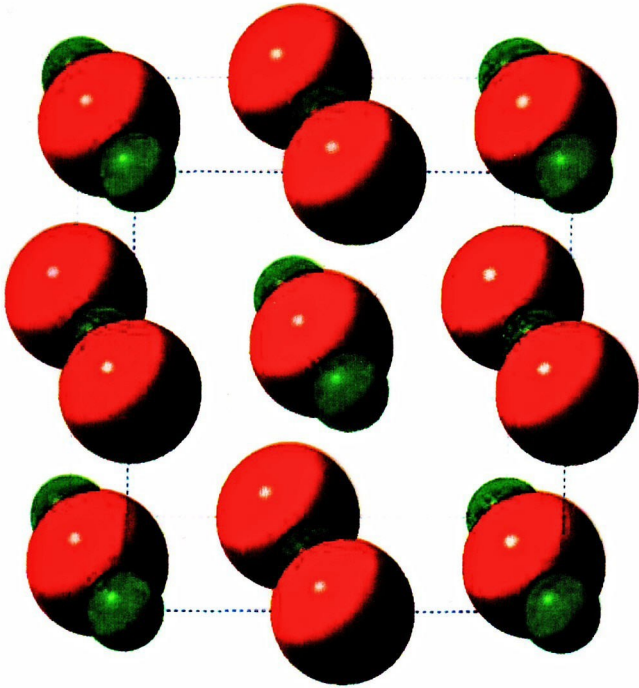
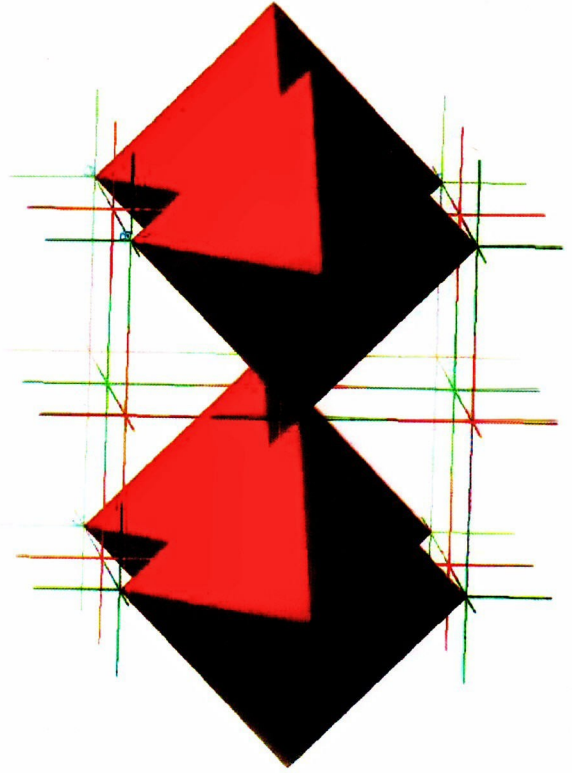
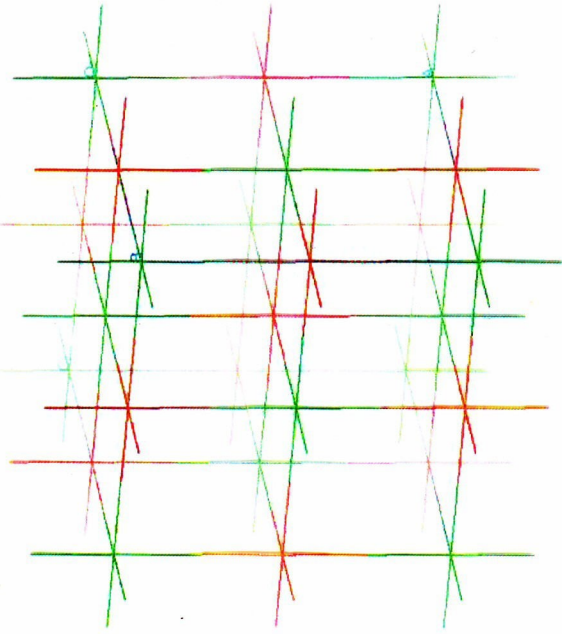


Finally the system can go 3-D.



Directly above this piece we can place:





NaCl

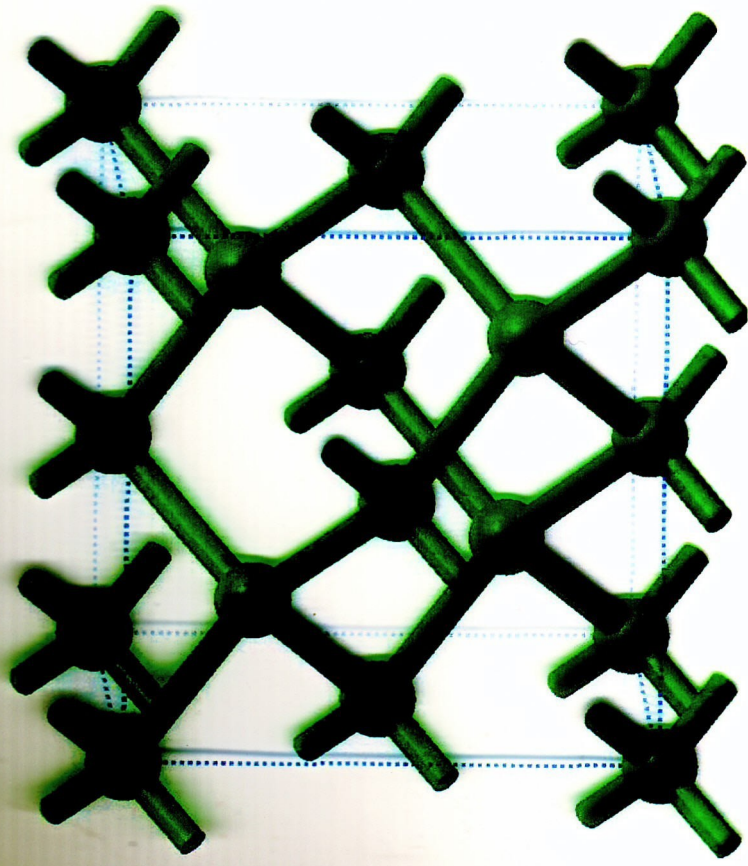
The NaCl, rock salt, structure is the best ionic structure. We would expect all really ionic compounds w/ a 1:1 mixture of cations:anions to adopt this structure. As we shall see this expectation is true.

But what about systems that are a little bit ionic, and a little bit MO-like in their energies?

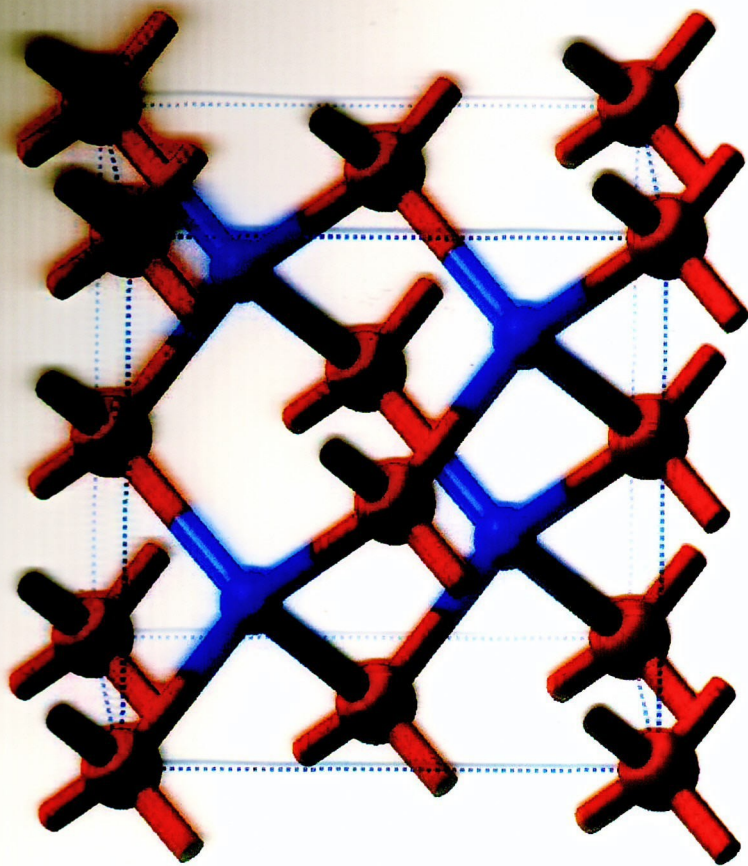
Let's consider five of the elemental structures which we have considered so far and consider 1:1 stoichiometries of two different elements placed into the structure.

Elemental structure	1:1 two element compounds related to the elemental structure
diamond (C)	ZnS (sphalerite)
fcc (Cu)	AuCu
hcp (Zn)	AuCd
bcc (W)	CsCl
Po (Po)	NaCl

diamond



sphalerite (ZnS)

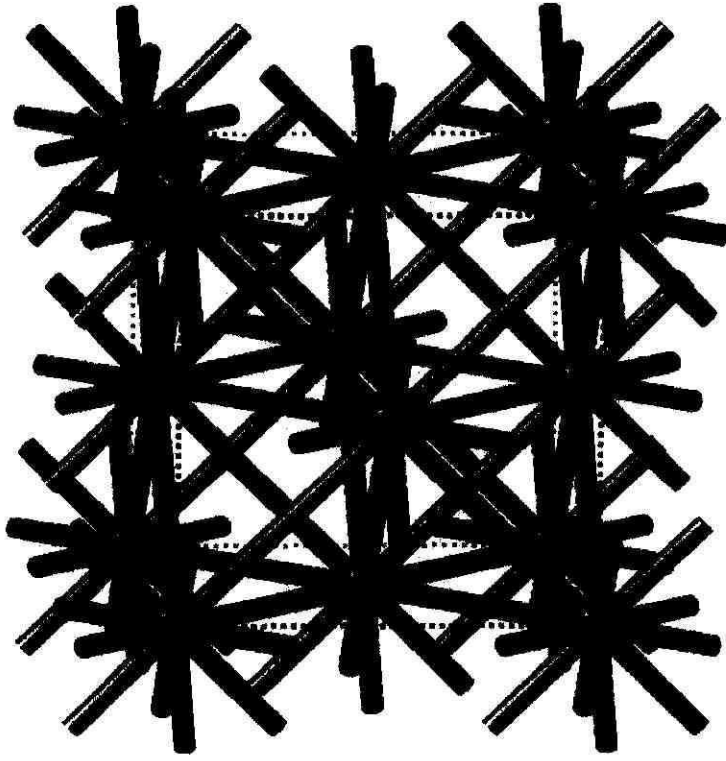


examples: C, Si, Ge, Sn

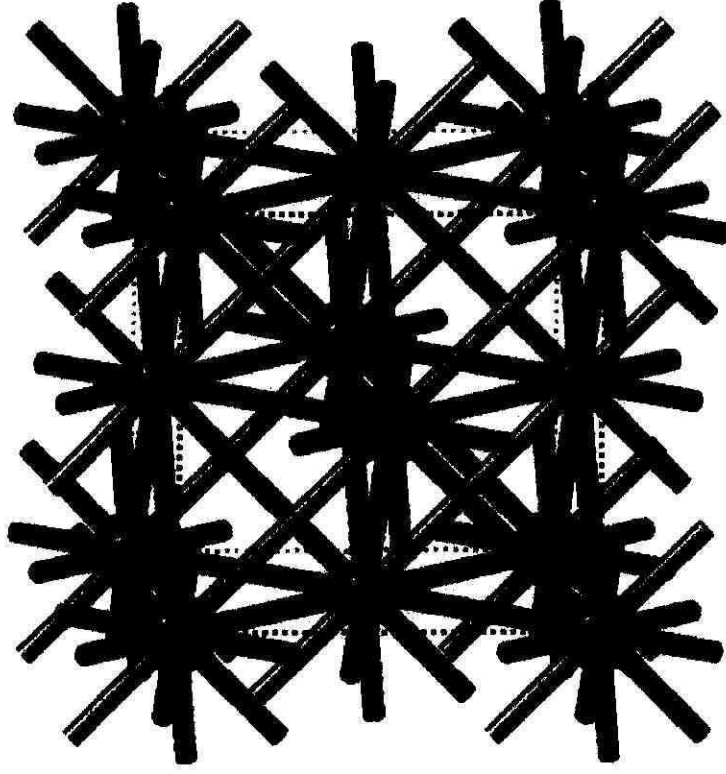
examples: InP, BP, AlSb, AgO
BAs, BeS, CdPo, SiC, AlAs, ...

In sphalerite all nearest neighbor contacts are between the "cation" and the anion". Sphalerite is a reasonable ionic solid.

fcc



AuCu

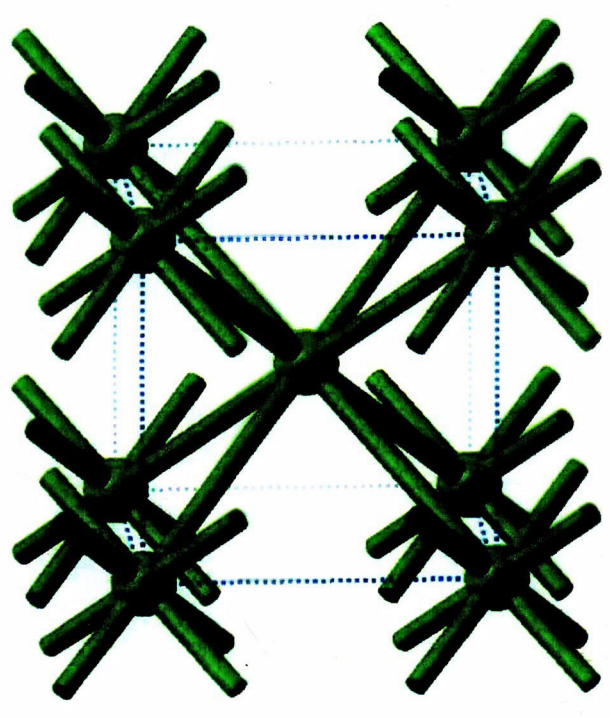


examples: Cu, Ag, Au, Ni ...

examples: AuCu, VPt, ZnPt,
TiRh, MnGa, NiHg, MnNi, ...

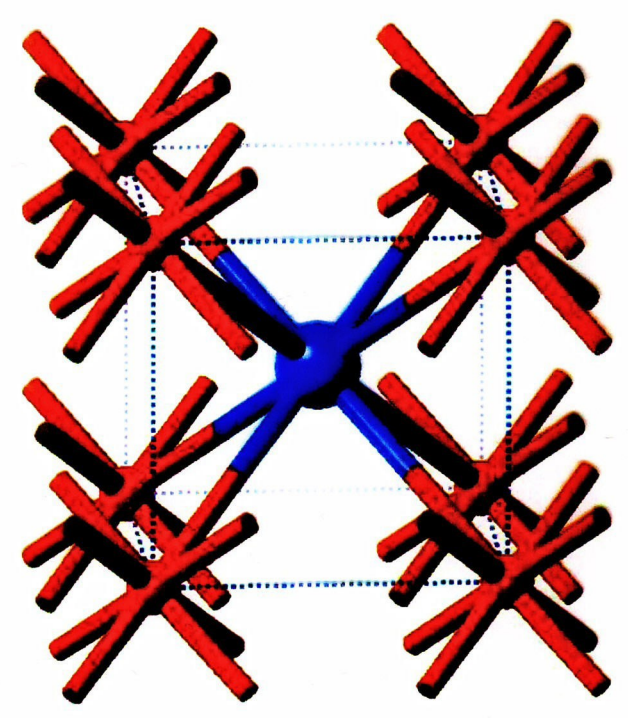
In AuCu all nearest neighbor contacts are not between the "cation" and the anion". AuCu is not a very good ionic solid.

bcc



examples: Cr, Ta, W, Na, K, Rb, Fe, ...

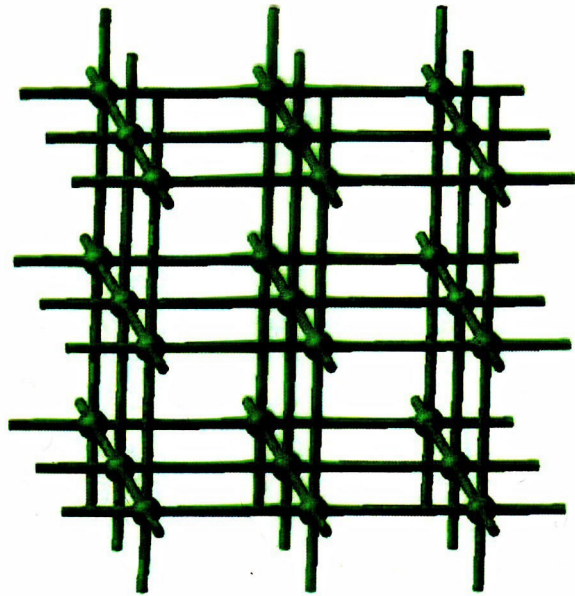
CsCl



examples: CsCl, CsBr, CsI, TiAu, LiPd, CaCd, LiTi, LaTi, MgPd, ...

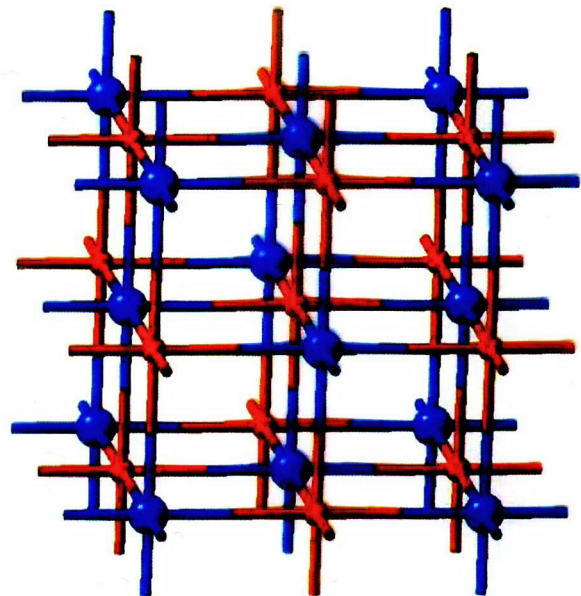
CsCl is a very reasonable ionic solid

Po



example: Po

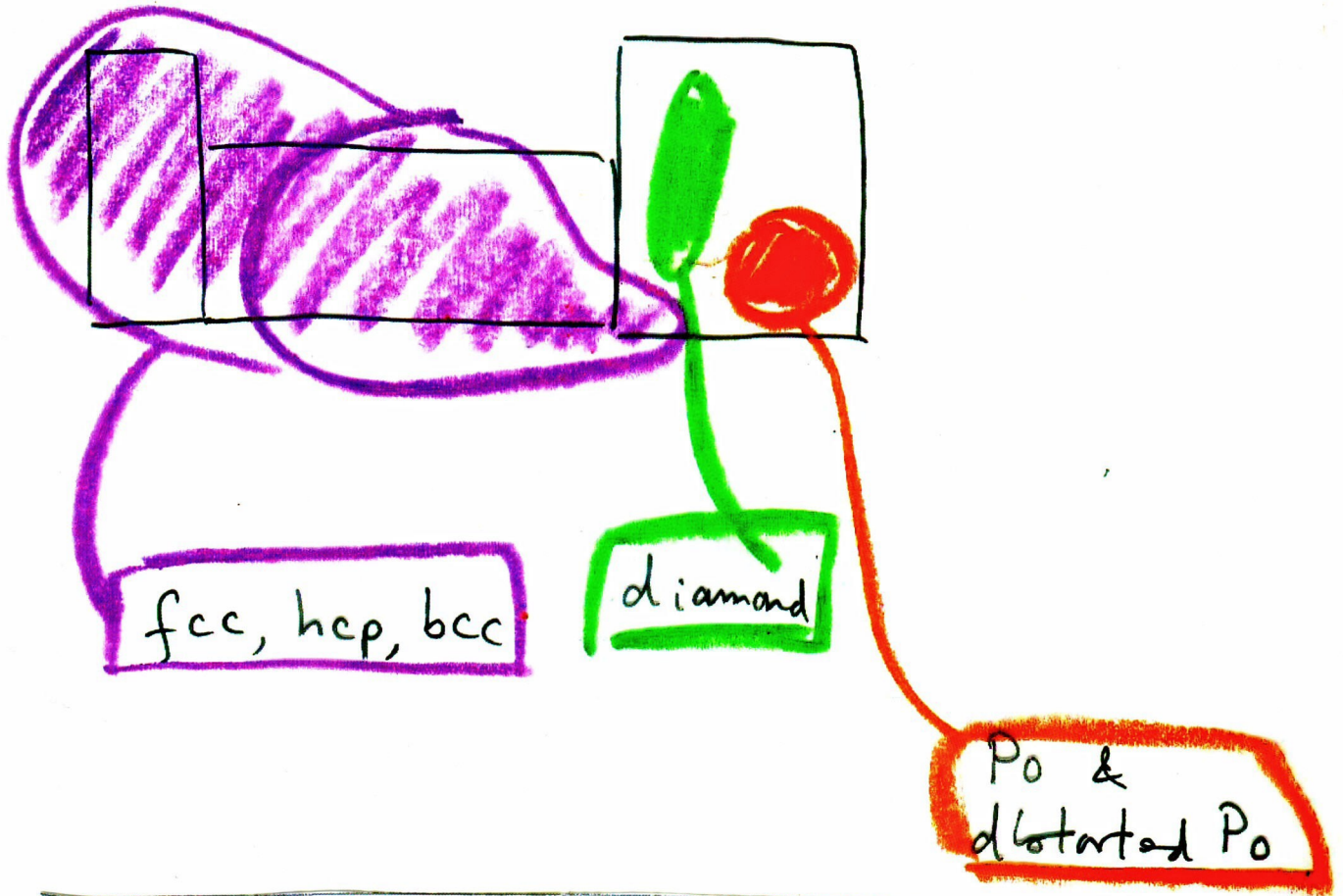
NaCl



examples: AgCl, MgO, PbS, TiC, CrN,
LiF, LiI, NaF, NaBr, CsF, RbI, InAs, BaTe,
CaS, VN, SrS, ZnTe, UN, ...

NaCl is a great ionic structure.

Summary of the 10 structures Elements



diamond : { 4 bonds , normal Lewis structure
insulators

Po : { 6 bonds , hypervalent. Found with
heavier main group. Metalloids.

fcc, hcp, bcc { 8-12-14 coordinate. Metallic
elements.

Five 1:1 structures

NaCl great ionic structure

ZnS (sphalerite) } reasonable ionic structure
CsCl }

AuCu } not so good ionic structure
AuCd }

Let's put all this info together and examine main group 1:1 compounds (all with an average of $4e^-$ /atom)

We plot two variables:

① \bar{n} : average principle quantum number

For \bar{n} small we have normal Lewis structures.

For \bar{n} large we have higher coordinate structures which are either (a) hypervalent (b) electron deficient.

② $\Delta\chi$: Difference in electronegativity between the two 1:1 elements

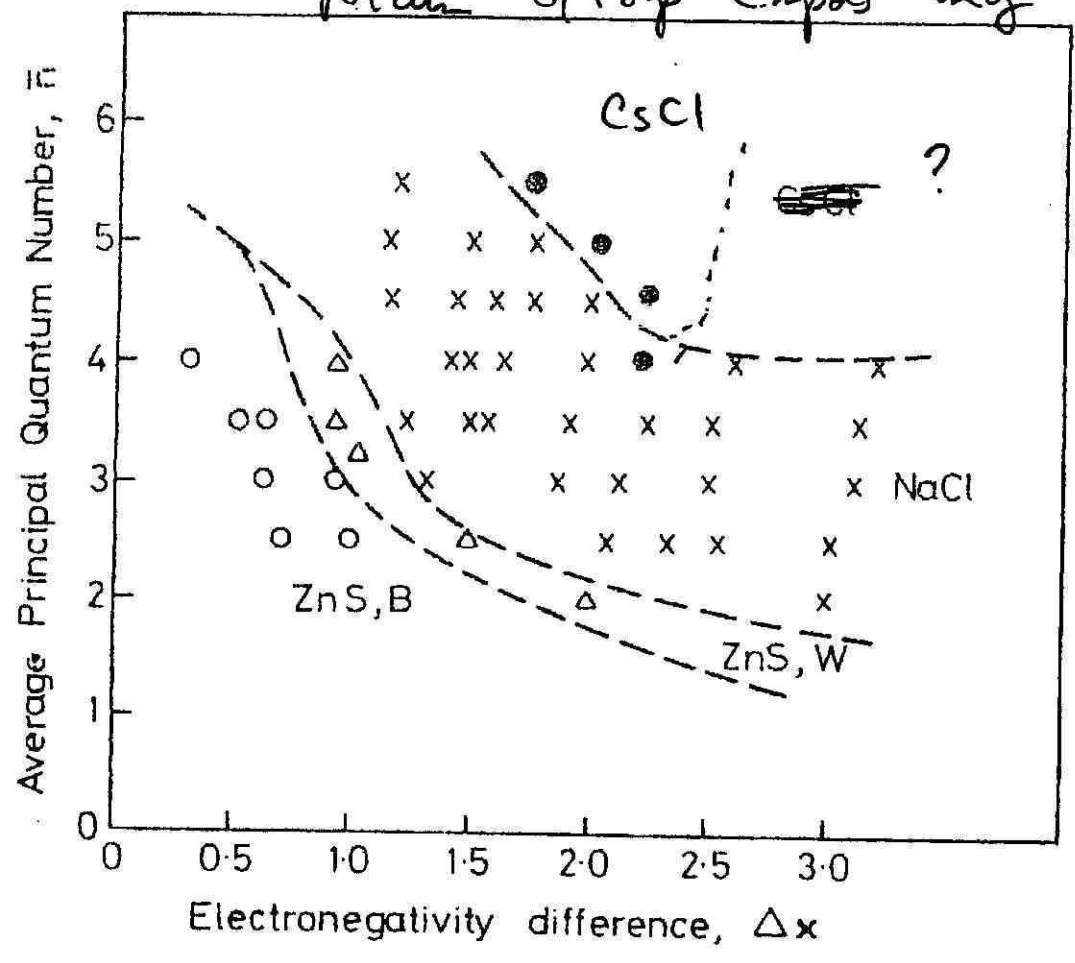
For $\Delta\chi$ small we shall get small ionic terms & the structure shall look a lot like elemental structures.

For $\Delta\chi$ reasonably strong NaCl, ZnS & CsCl shall form.

For $\Delta\chi$ very large only NaCl shall form.

The actual data (Moores-Pearson, 1959)

Main Group Compds only



ZnS, W is wurtzite, a close variant on diamond w/ 4 bonds in a tetrahedra per atom.

Problem 13.4

Addendum 43

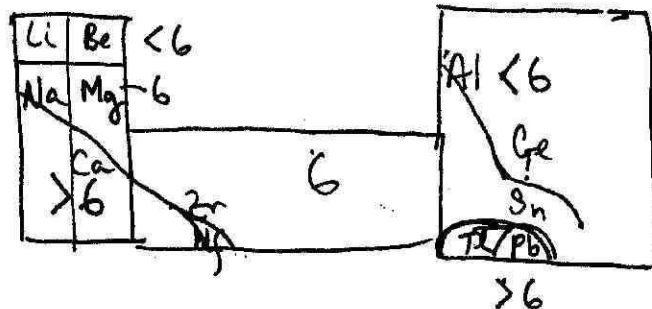
A43.1

There will be a problem on the final like Problem 13.4 i.e., there will be a picture of one or two ^(crs) crystals and you will be asked what compound could adopt the pictured structure. This addendum is to help you solve these problems. Also it will teach you some needed facts.

First the needed facts:

① In ionic compounds, the coordination number of the cation follows some simple general principles.

Cation Coordination #s:



Almost all the transition elements are octahedrally coordinated to O or F. Al is found both octahedrally coordinated & 4 coordinate. B is either 4 or 3 coordinate to O. Beside Mg, which is often 6 coordinate lots of alkali metals & alkaline earths are 8-12 coordinate with O, F. Tl & Pb can be found with large coordination numbers too.

The general rule is big cations can fit lots of oxygen & fluorine atoms around them. And remember, elements to the left of the periodic table are bigger (remember shielding!).

② Anions have very little to say to cSat H43.2 coordination. Take TiO_2 and TiF_4 . In both cases Ti is Ti^{4+} . In both cases the Ti atom is octahedral. In TiO_2 , the oxygen atom has 3 Ti bonds. In TiF_4 , the F atoms are 1 & 2 coordinate to Ti.

So remember (i.e., put on your index card) the common oxidation states. For groups 1-4 it's easy. Ti, Zr & Hf are all $4+$; alkaline earths are all $2+$ etc... But for the first row T.M. remember the numbers I gave you. Fe is Fe^{3+} most often & Fe^{2+} less often. Co is Co^{2+} most often & Co^{3+} less often. Cu is Cu^{2+} and Cu^{+} , Ni is Ni^{2+} most often.

③ Big anions take up more room than small anions.
eg. TiF_4 is Ti in octahedra but
 TiI_4 is Ti in tetrahedra.

④ Two metals when they mix together often make structures related to fcc, hcp or bcc.

⑤ Light main group elements often make structures which obey the octet rule. eg. BN is found in 2 forms: graphite-like & diamond-like with all B's only coordinated to N & vice-versa. Graphite is in the diamond structure

⑥ In ionic structures cations have their nearest neighbors & anions have their nearest neighbors.

So now how do you do problems like 13.4.

A 43.3

① Look at the structure. Is it metallic-like (fcc, hcp or bcc), ionic like (only different elements bound to each other, or covalent-like (sp^2 or sp^3 sites)).

② For covalent structures it's going to have to follow the octet-rule. For ionic structures, it will obey the ordinary rules of oxidation states. For metals, we have no uncertainty of what is a reasonable stoichiometry.

③ Establish the stoichiometry of the unit cell.

④ Use the rules I have given above. Also remember the structures we talked about in the course: fcc, hcp, bcc, diamond, NaCl, CsCl, α -Se, α -Bi & Po.

⑤ Remember the Moseley-Pearson diagram.
Here on the next pages are some practice problems.

