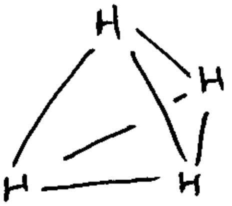
Second try on explaining metal structures.

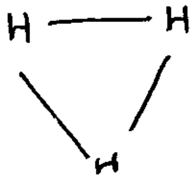
① Metal structures are best explained using MO theory (at least in this class) but we do not have the tools to calculate MO diagrams for fcc, hcp or bcc.

② Instead we will use an MO analysis for very simple (but hypothetical) H systems and then see that this simple analysis explains lots of features about the structures of different metals.

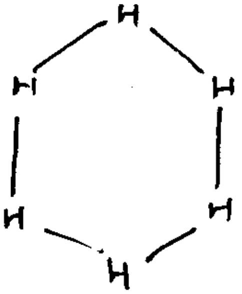
③ We consider the four H systems:



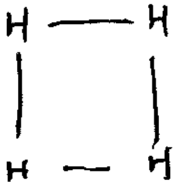
tetrahedra



triangle

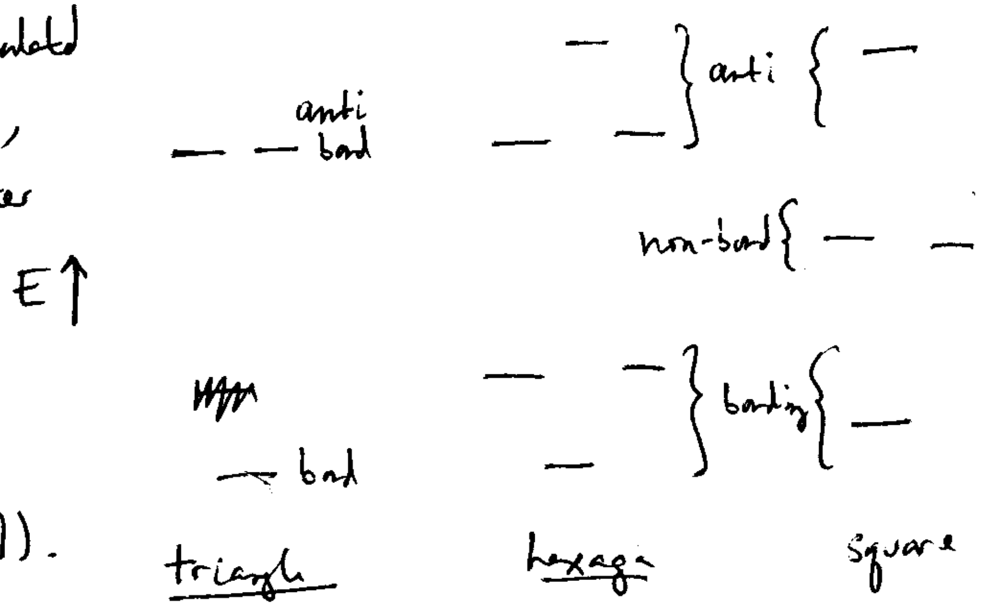


hexagon



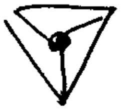
square

④ We have already calculated the MO diagram for ▽, ⬡ & □ (the latter two when we calculated π-MO diagrams of ⌬ & ▭ [the □ was an old prelim question]).

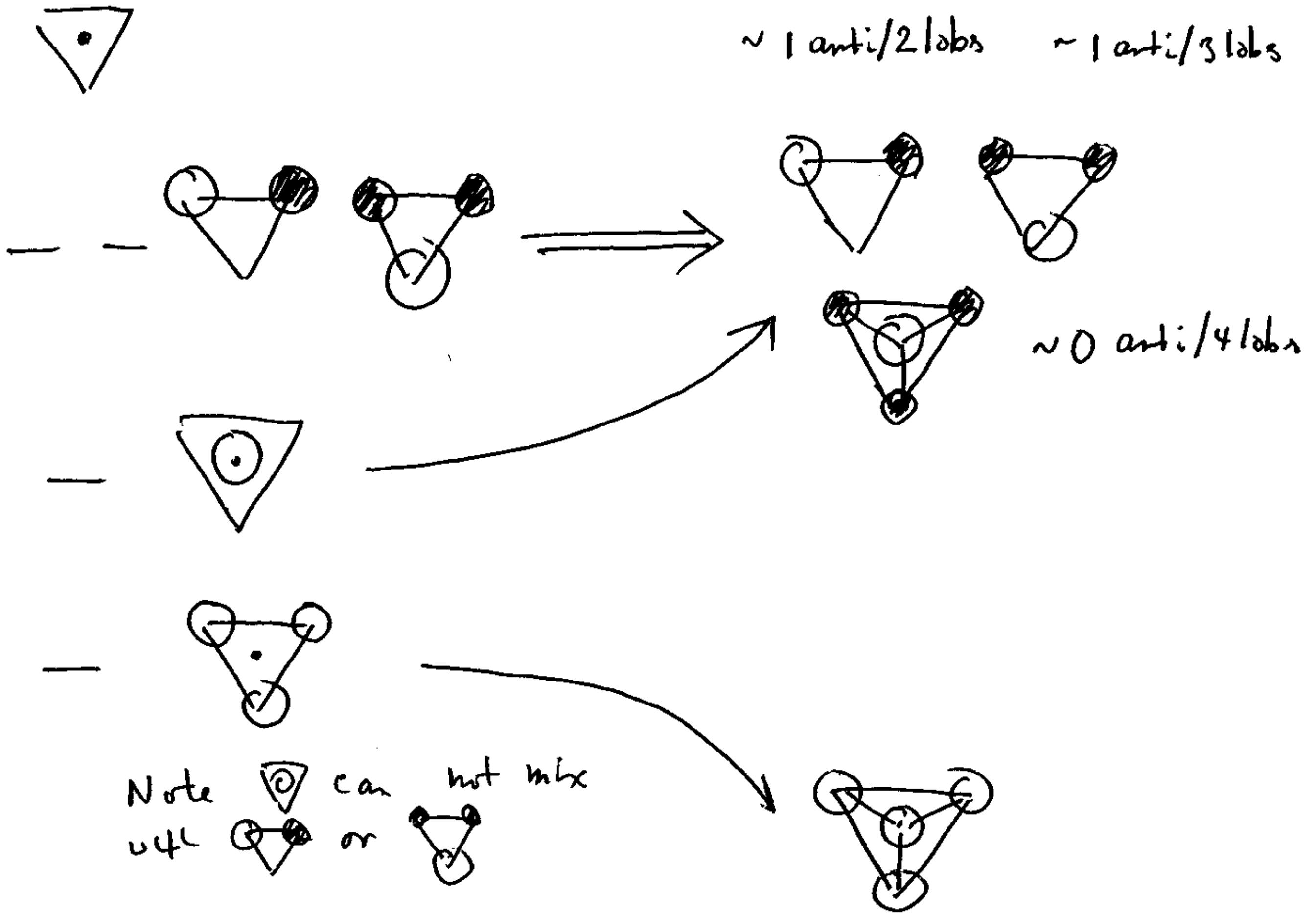


⑤ We only need calculate the MO diagram of  .

⑥ The easiest way to calculate the MO diagram of  turns out to be to calculate the MO diagram of a  & then add an atom on top  & then consider the interaction between the atom on top & the triangle .

Can you see  is a tetrahedron?

7)

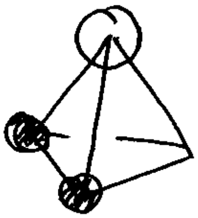


Note can not mix with or

⑧ At first glance  is a non-bonding orbital. But the antibonding interactions are much stronger than the bonding interactions ∴  is actually antibonding.

⑨ How antibonding is it?

Answer: Consider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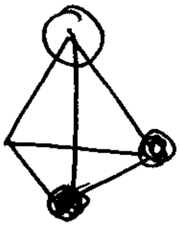
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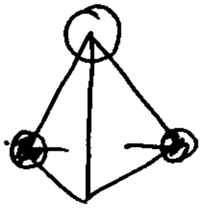
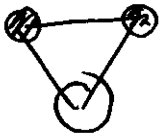
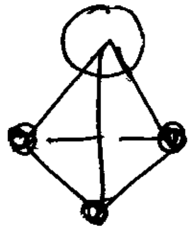

.

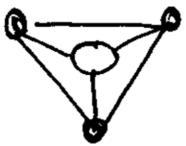
All have the same energy, the same energy as



. If we add the 3 above orbitals together we get

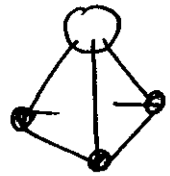


. This is just the

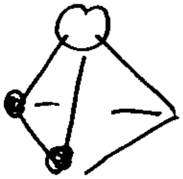


orbital from our MO diagram.

⑩ So

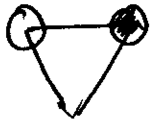


is the same energy as



and hence is the same energy as

⑪ Conclusion: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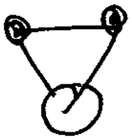
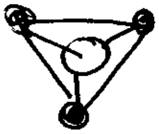
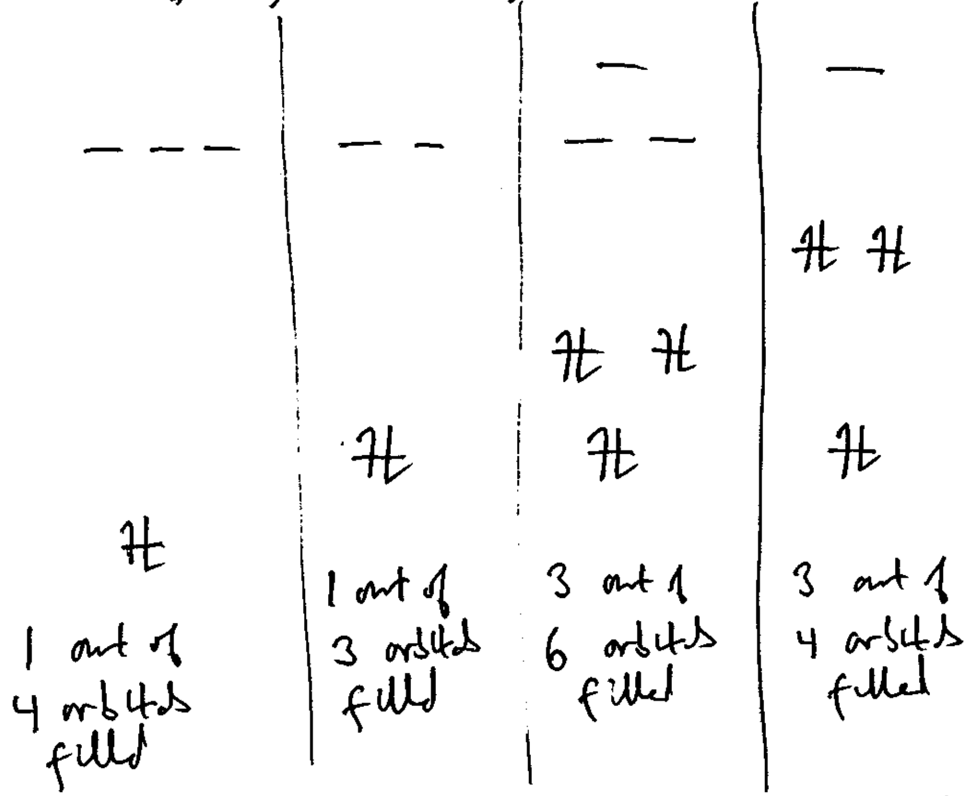

&


are all equal in energy.

This concludes our derivation of MO diagrams.

⑫ Now let's ask the question, if we only fill bonding & non-bonding states, ~~that~~ which orbitals are filled in , ▽, ⬡ & □ ?

Answer



¼ filled　⅓ filled　3/6 or ½ filled　¾ filled.

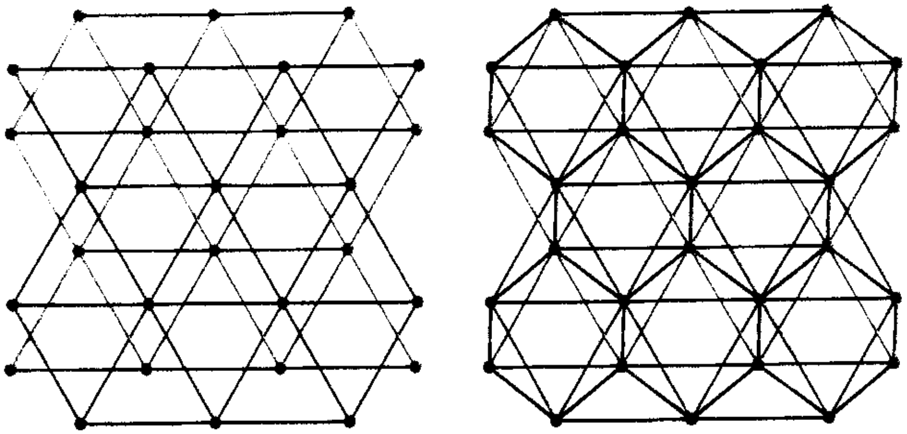
⑬ Conclusion: With half the orbitals filled the hexagon is the favored ring. With more than half the orbitals filled the square is most stable. With a little less than half the orbitals filled the ▽ is favored. With significantly less than half the orbitals filled the tetrahedra is favored.

⑭ Let's now look at the structures of the main group.

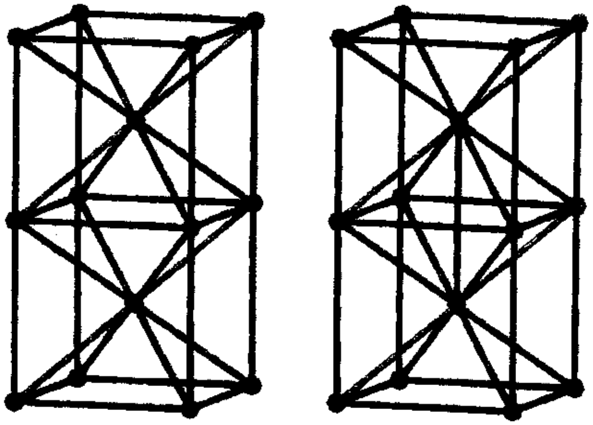
Main group structures

Li bcc	Be hcp	B R-12	C graphite, diamond	N molecule	O molecule	F molecule
Na bcc	Mg hcp	Al fcc	Si diamond	P P struc.	S S struc.	Cl {I struct. molecule
K bcc	Ca fcc	Ga Ga struct.	Ge diamond	As Bi struct	Se Te struct.	Br I · struct.
Rb bcc	Sr fcc	In dist. fcc	Sn diamond white-Sn	Sb Bi struct.	Te Te struct.	I I · struct.
Cs bcc	Ba bcc	Tl hcp	Pb fcc	Bi Bi struct.	Po simple cubic	(At)

Here ⑮ is a review of the structures we've seen so far.



hcp and fcc

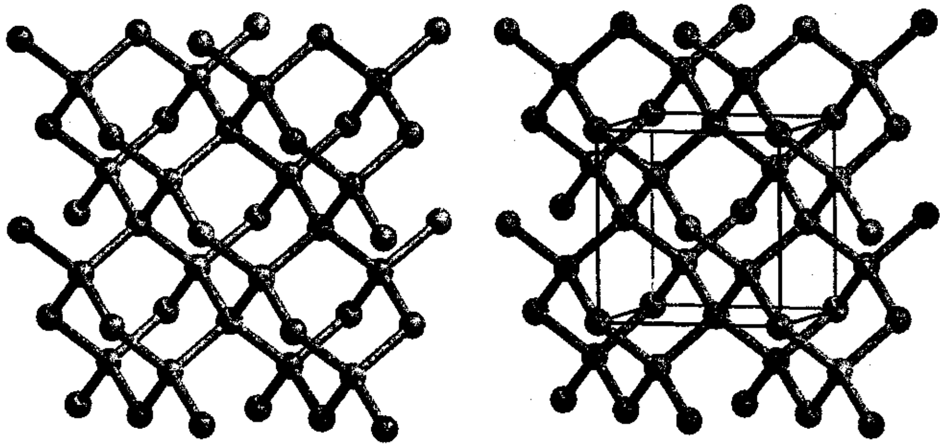


bcc

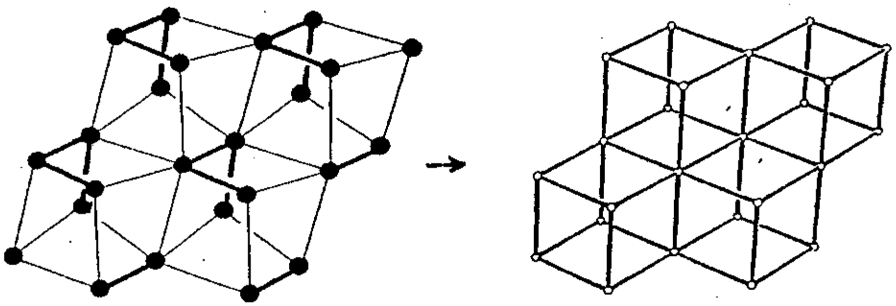
a little less closest packed than fcc or hcp

contains distorted tetrahedra and octahedra.

Carbon: cubic diamond



(also structure of Si, Ge & grey-Sn)

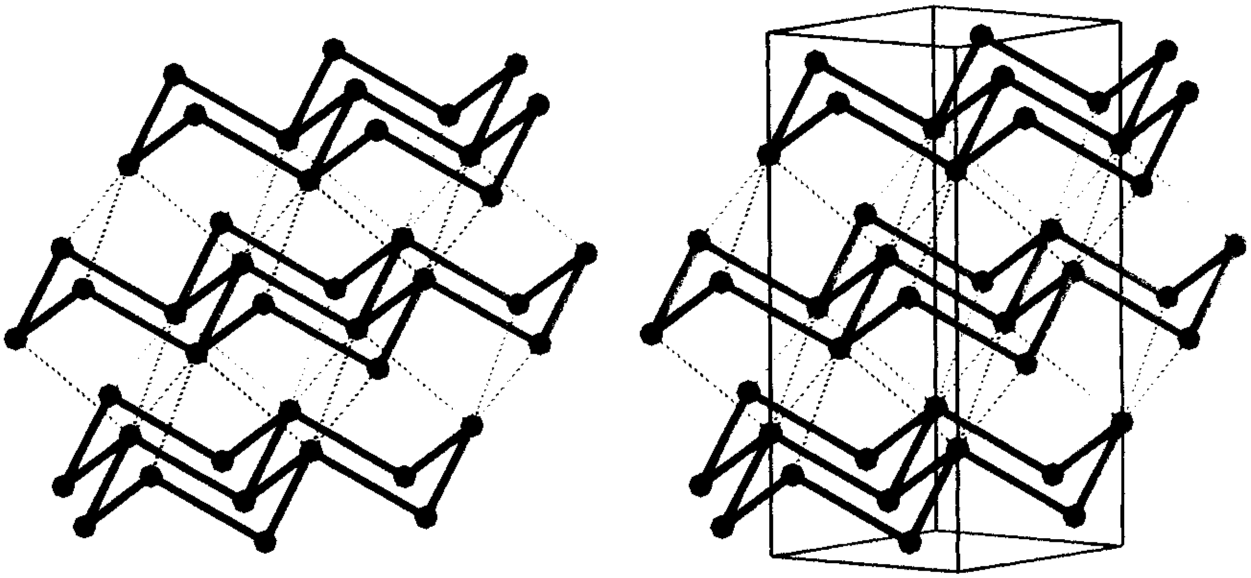


Se + Te → Po

Non-Metal

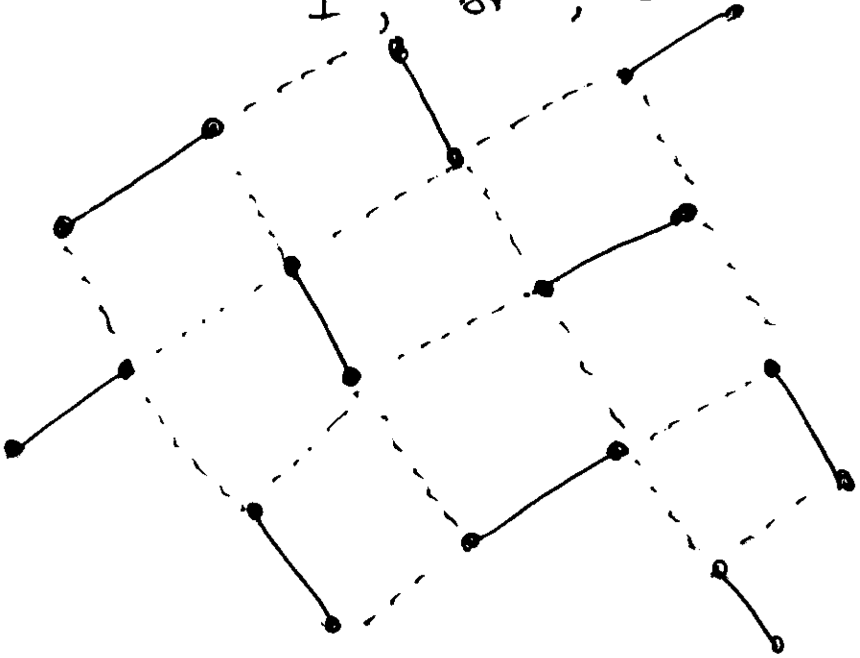
Metal

Structure of α–Bi

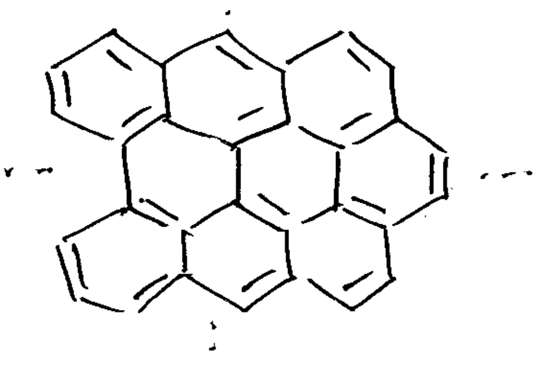


(also structure of As ~~&~~, Sb & one of P structures under pressure)

I, Br, Cl Structure



graphite



)
Questions based on the structures you already know [Use MO-model] S42 8

(i) Why do all the alkali metals & alkaline earths adopt fcc, hcp or bcc? $\frac{1}{4}$ tetrahedra

(ii) Why does Po adopt the Po structure? $\frac{3}{4}$ squares

(iii) Why does C, Si, Ge & grey-Sn adopt the diamond structure? $\frac{4}{8}$ hexagon

(iv) Why does Se & Te adopt their structure? 2 strong, 4 weak bonds make squares

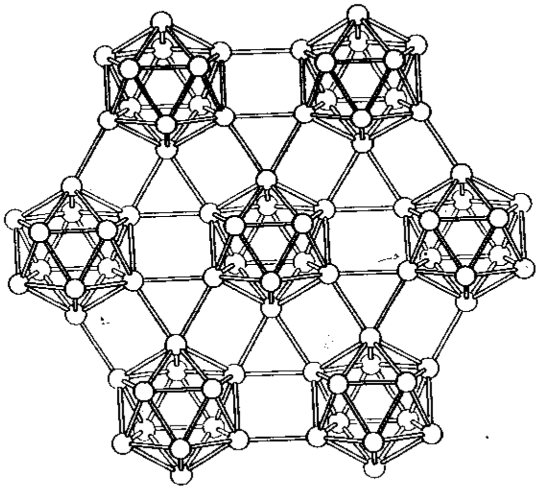
(v) Why does C adopt the graphite structure?

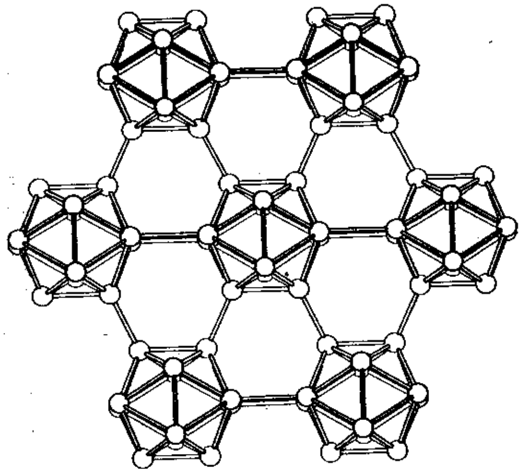
(vi) Why do Br & I adopt their structure?

(vii) Can Bi be thought of as a square structure? Can it be viewed as a hexagon structure?

⑰ Below are pictures of the B and Ge structures:

B:





fcc + hcp - tetrahedra

bcc - distorted Tetrahedra

Ga:

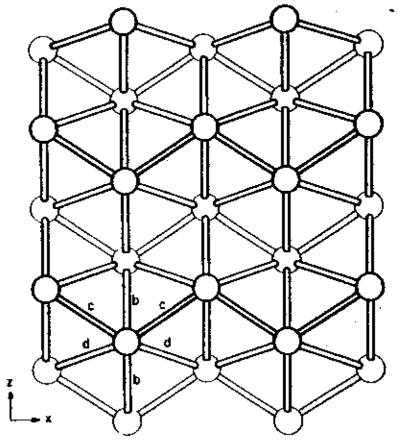


Fig. 31-1. One of the layers of the α-gallium structure viewed along the *y*-axis. The letters identify the bond types in the text. The interlayer bonds, which are down from the lower atoms and up from the upper atoms, are not shown.

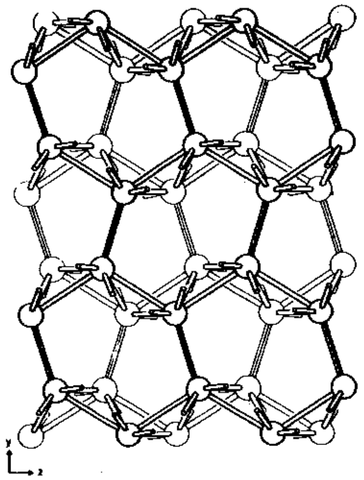


Fig. 31-2. The α-gallium structure viewed along the *x*-axis, or edgewise to the layers. The strong interlayer bonds of type *a* are shown as triple lines.

What portion of valence band is filled for B & Ga? Rationalize why B & Ga adopt the structures which they do & not fcc, hcp or bcc.

⑱ In, Tl & Pb adopt variants of closest packing (fcc & hcp) Rationalize why these elements adopt the structures which they do.

⑲ P.S. I can't rationalize the Al structure.