Lecture 41 Heavy Main Group Elements and Diamond

① Today we will see some of the consequences of the electron orbitals in the heavy main group elements. We will use 3 concepts.

(i) Localized e^- picture

(ii) Hypervalent system (see previous lecture on I)

(iii) Inert pair effect.

② Inert pair effect. Let's observe the following chemical facts:

ⓐ Common oxidation state of Al & Si are Al^{3+} & Si^{4+}. But the common oxidation state of heavier group 13 & 14 elements are respectively 1+ and 2+. eg. Tl^{1+} and Pb^{2+}

Conclusion: One valence pair of e^- in Tl and Pb is hard to remove

ⓑ Hg which is $d^{10}s^2$ is a liquid (i.e., almost a gas) but Zn which is also $d^{10}s^2$ is a solid up $\sim 400^\circ C$.

Conclusion: Hg appears to almost have a filled shell noble gas type configuration.

© 

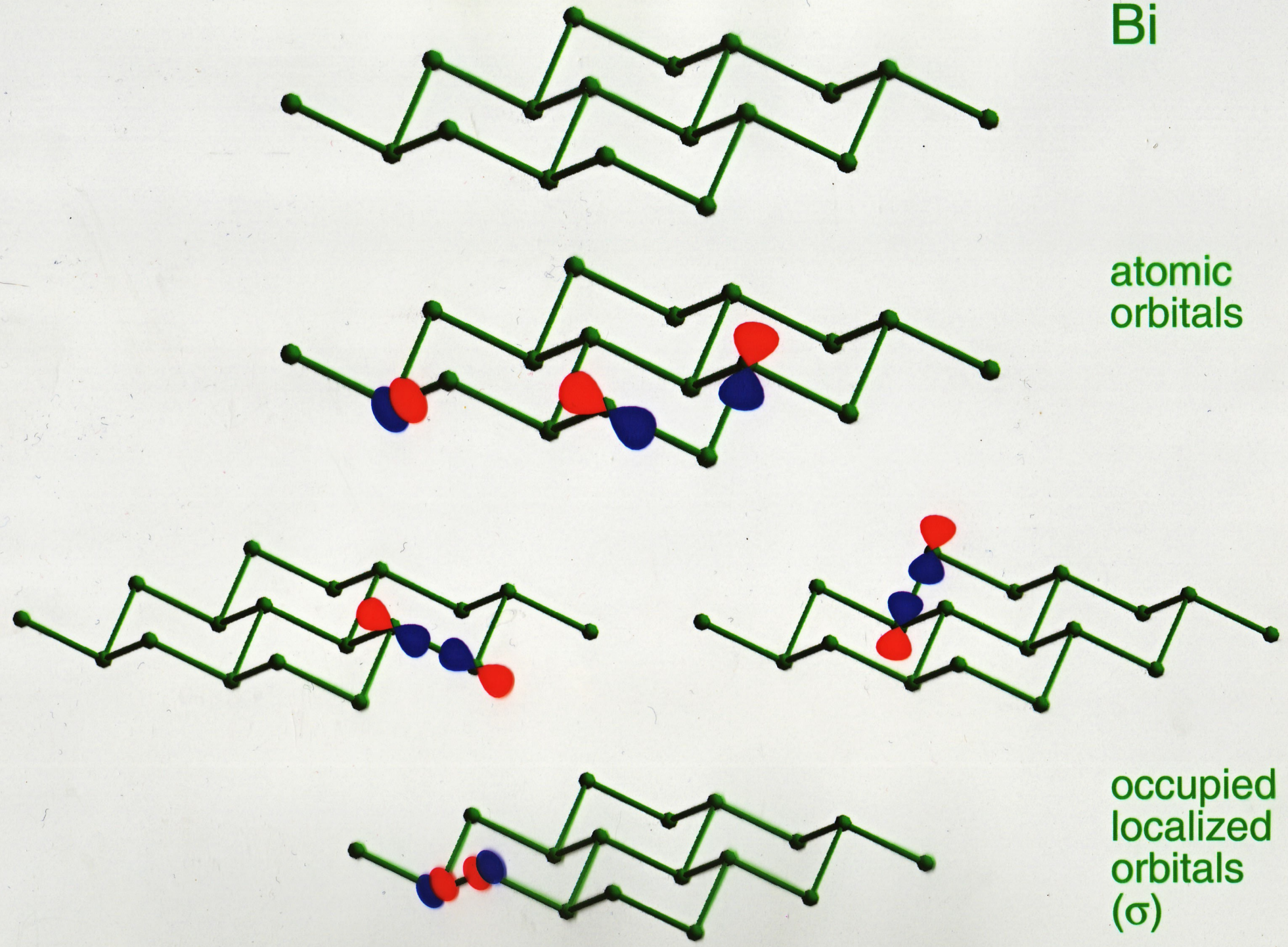
NH_3	PH_3	AsH_3	SbH_3	BiH_3
107.8°	93.6°	91.8°	91.3°	≈91°(?)

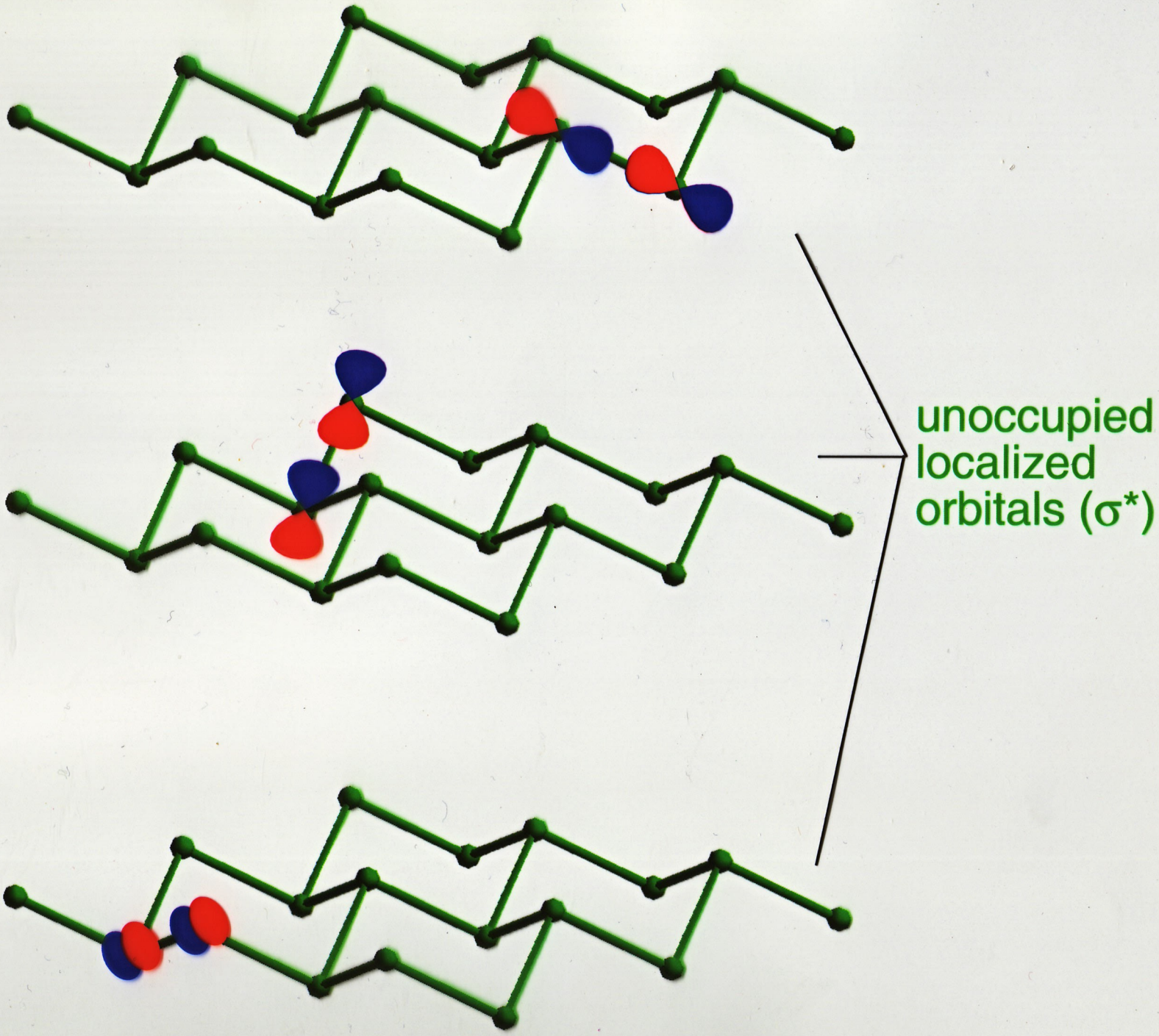
H_2O	H_2S	H_2Se	H_2Te	H_2Po
104.5°	92.1°	91°	90°	90°(?)

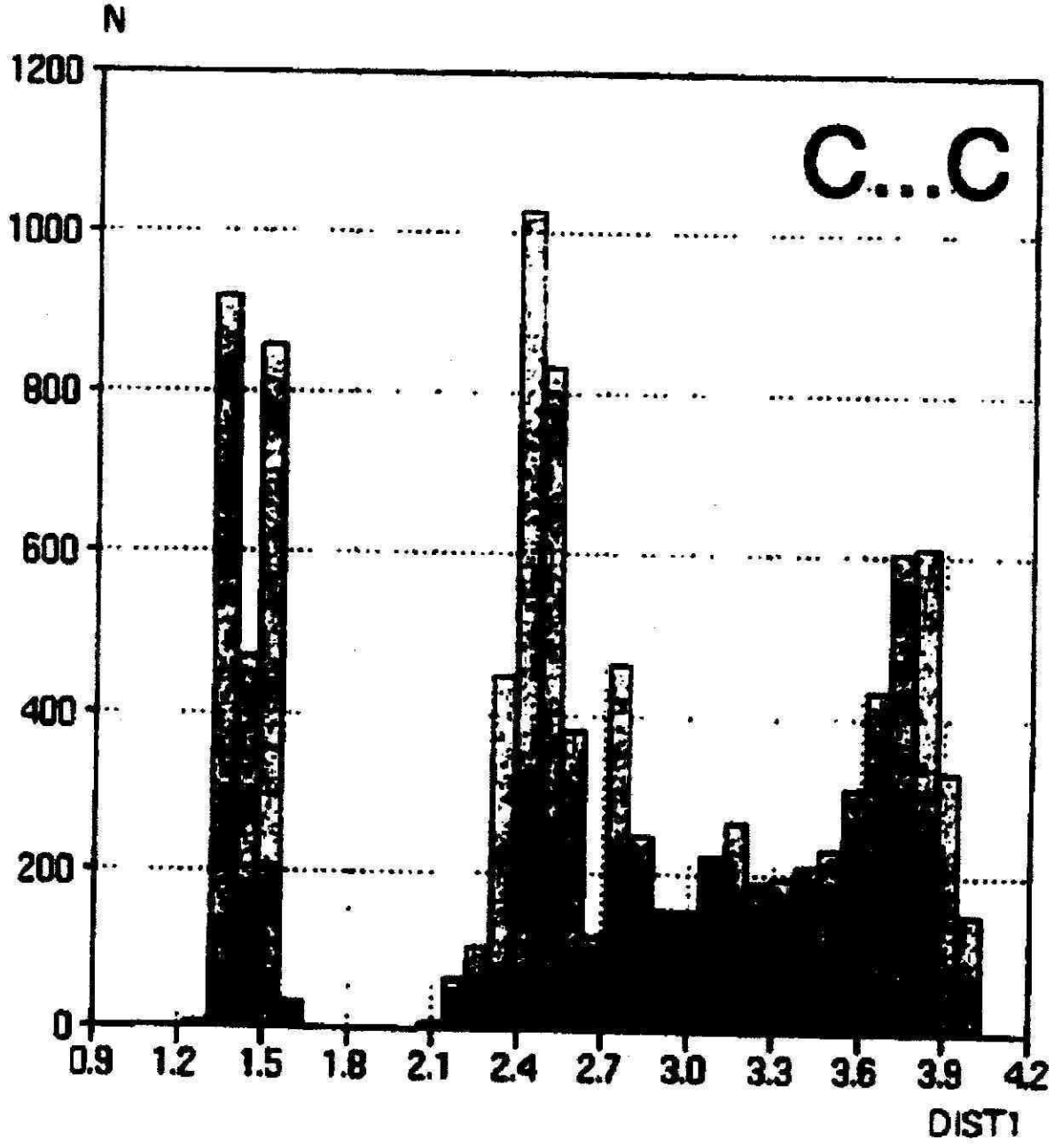
③ These three facts are all compatible with the idea that the so-called valence s pair for heavy main group elements is almost core-like in its properties. We call this pair of s e^- which are core-like the inert pair.

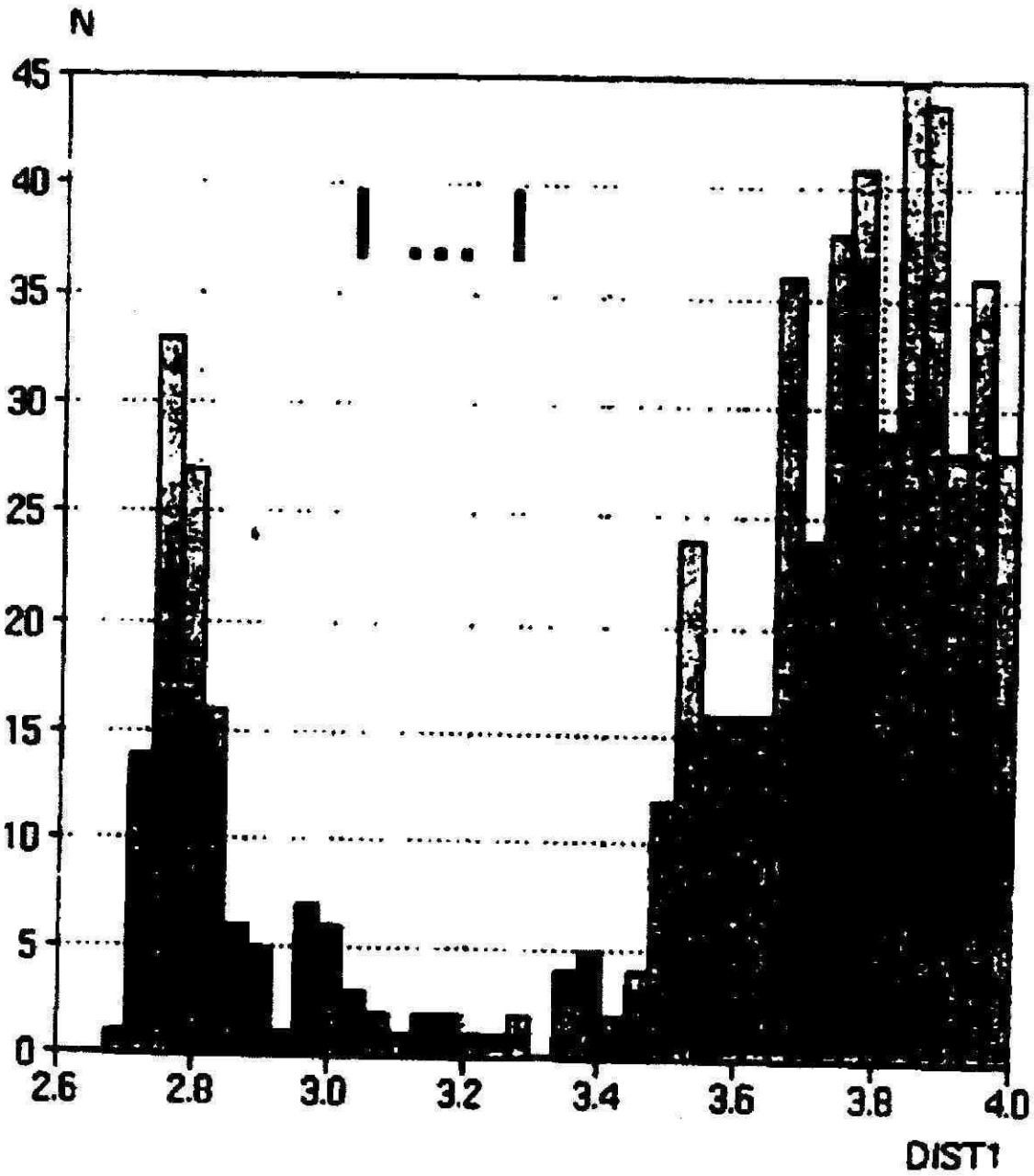
④ When considering the structure of Sb, Bi, Se, Te, Po and I to a very good extent we only need to consider the p electron as valence e^-.

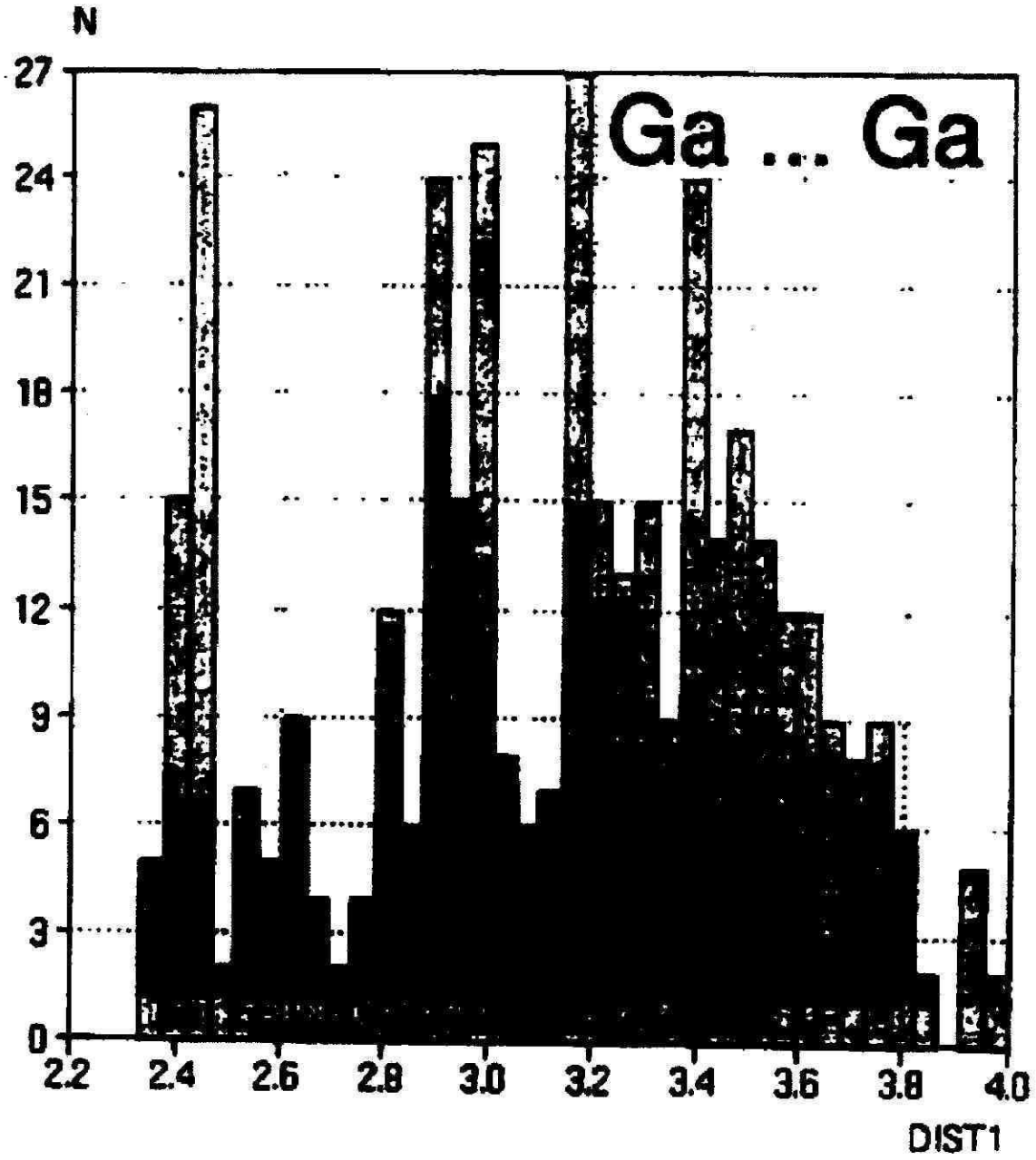
We can further use the idea of localization to draw an approximate scheme of the e^- configuration of these elements.


Bi
atomic
orbitals
occupied
localized
orbitals
(σ)

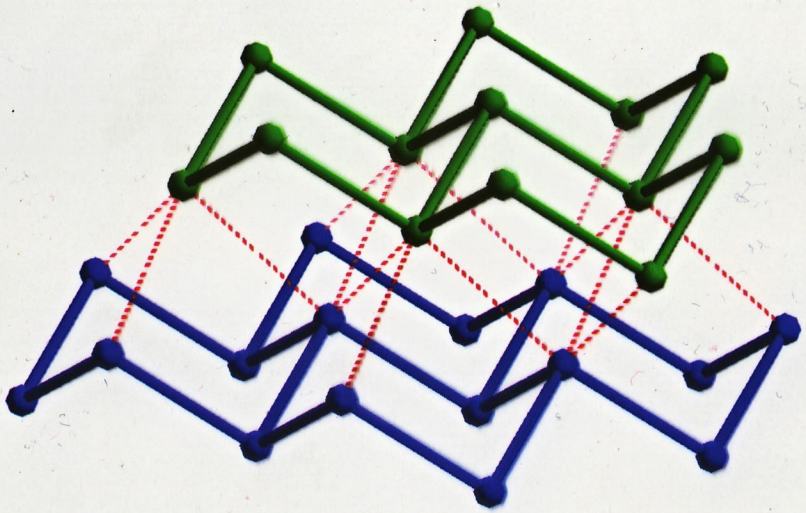

unoccupied
localized
orbitals (σ*)

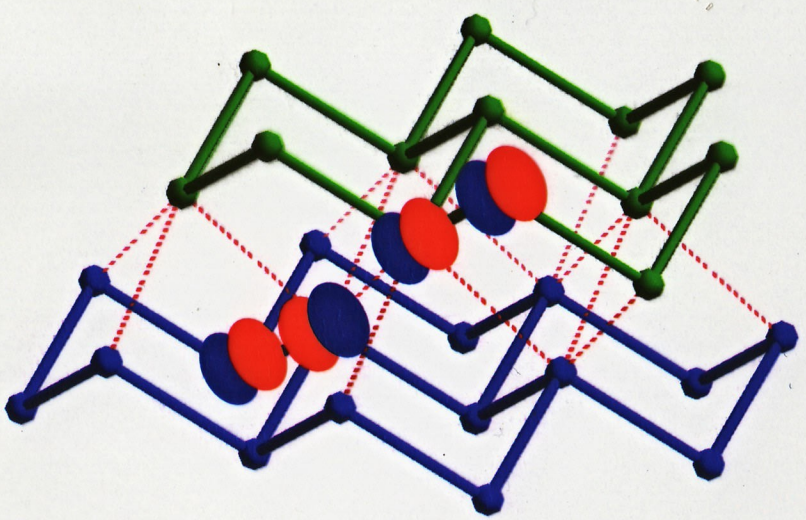

N
1200
1000
800
600
400
200
0
C...C
0.9
1.2
1.5
1.8
2.1
2.4
2.7
3.0
3.3
3.6
3.9
4.2
DIST1

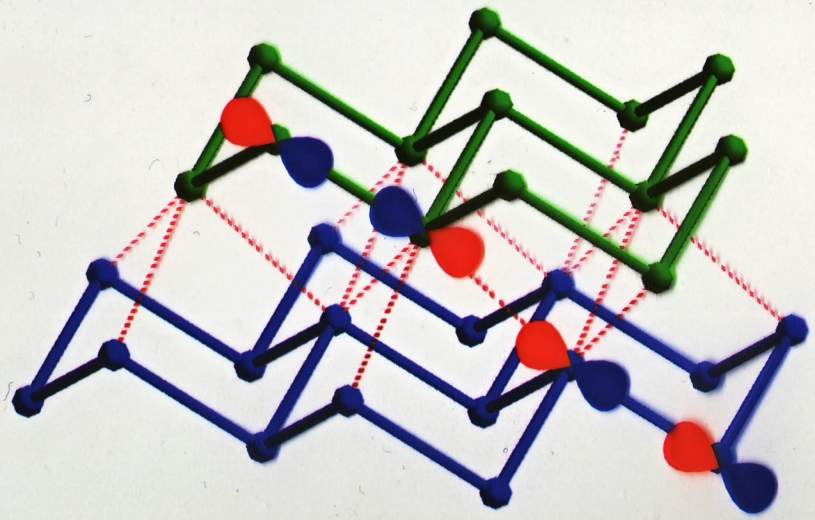

N
45
40
35
30
25
20
15
10
5
0
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
DIST1

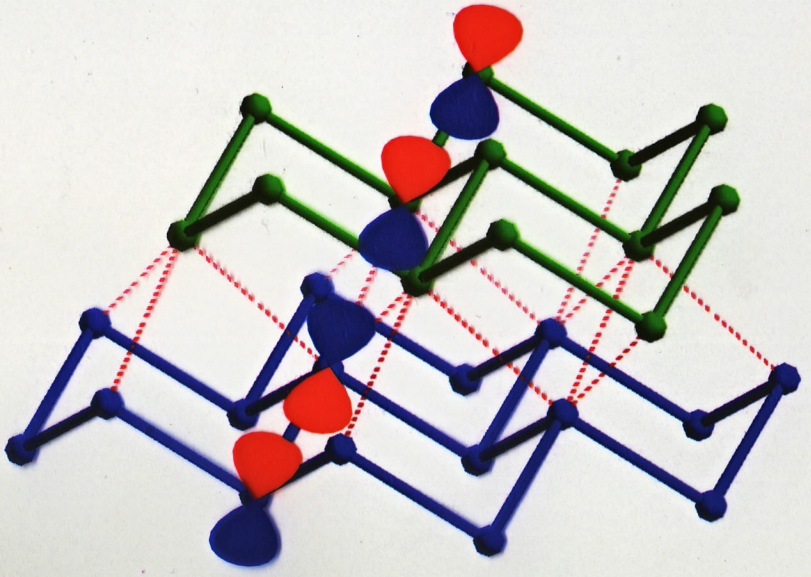

N
27
24
21
18
15
12
9
6
3
0
Ga ... Ga
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
DIST1

Lewis acid (σ*) and Lewis base (σ) interactions of localized orbitals

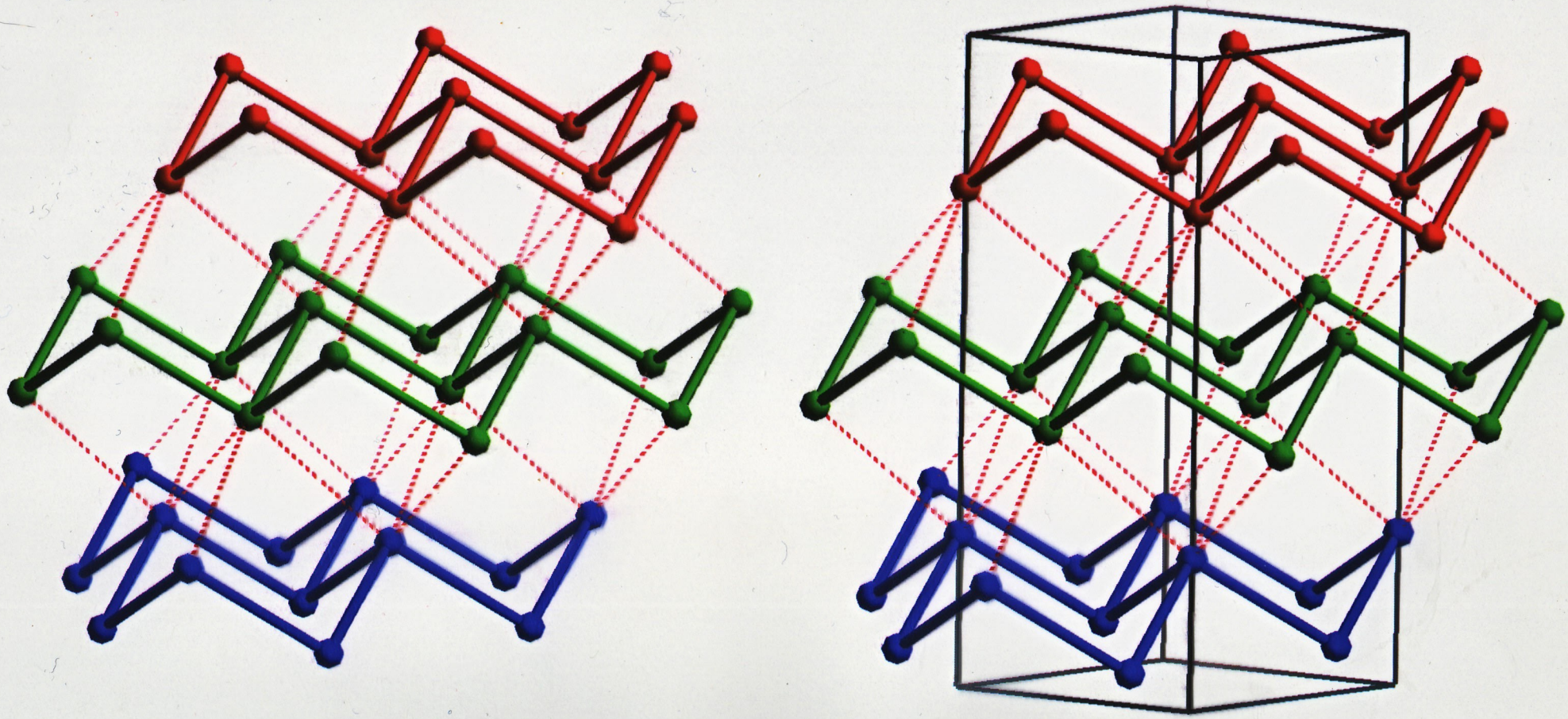


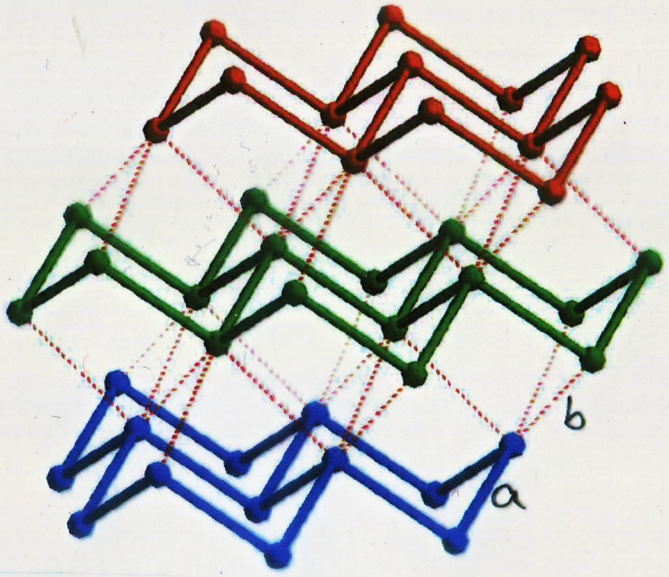






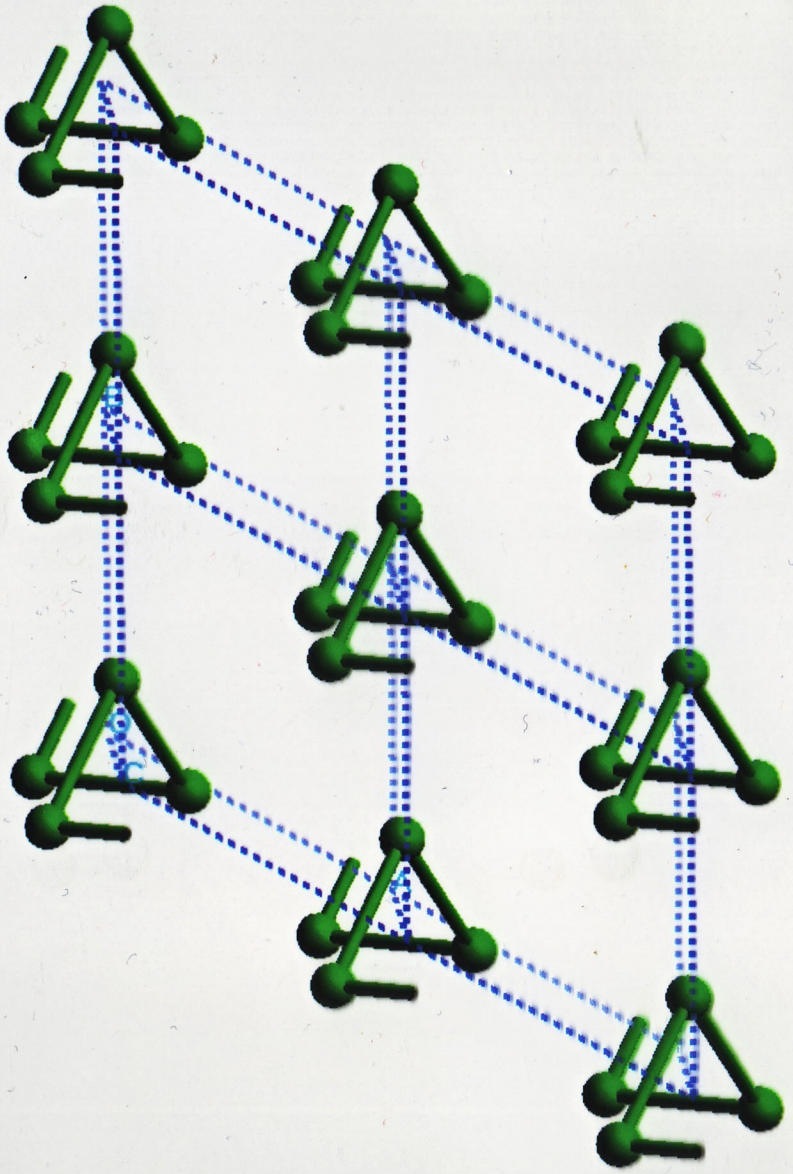
Structure of α–Bi



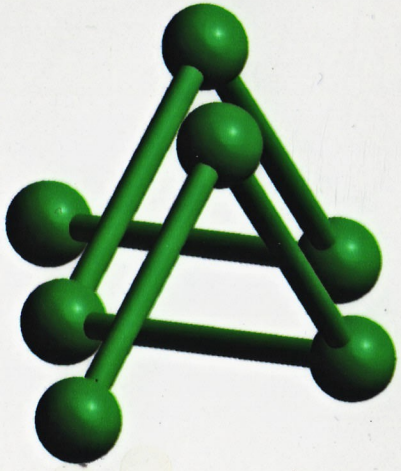


	a	b	b/a
As	2.517 Å	3.120 Å	1.240
Sb	2.908 Å	3.355 Å	1.154
Bi	3.072 Å	3.529 Å	1.149

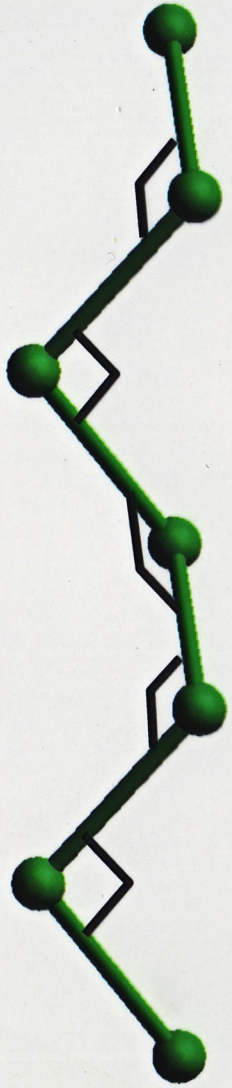
As, Sb, Bi are all non-metals



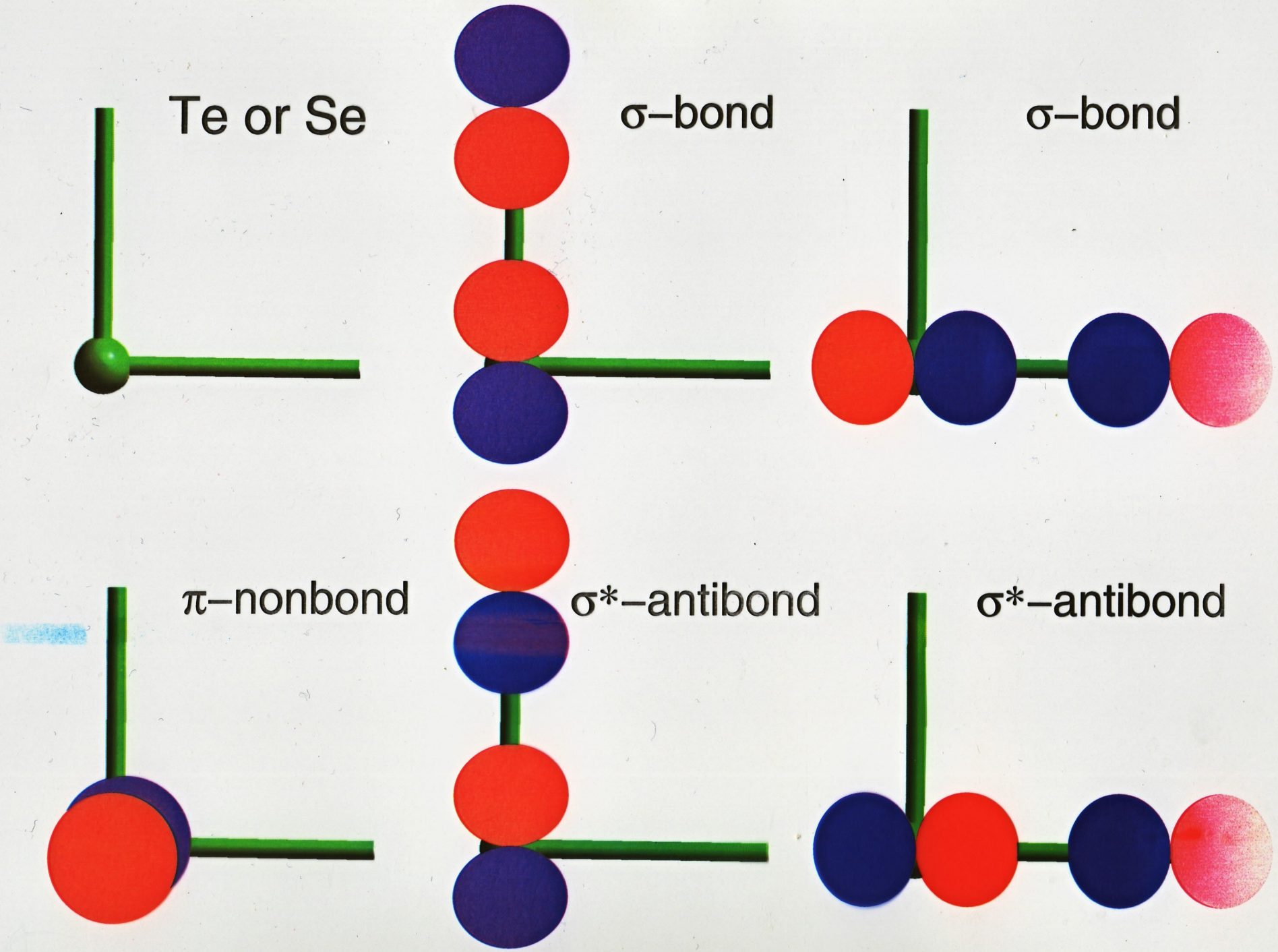
α–Se and α–Te

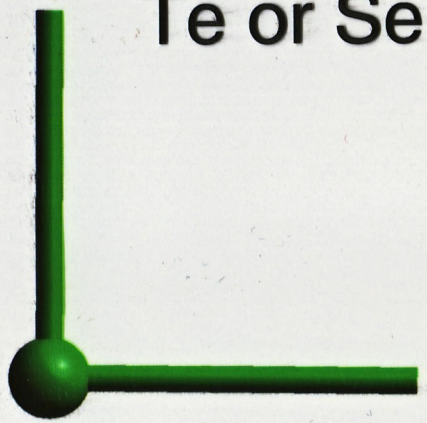


top view



side view

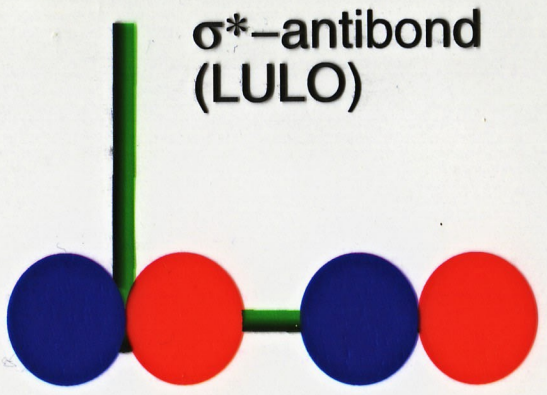

Te or Se
σ–bond
σ–bond
π–nonbond
σ*–antibond
σ*–antibond

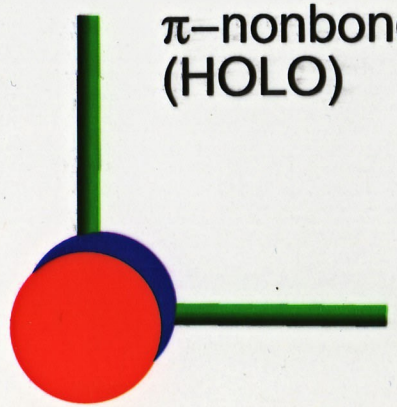


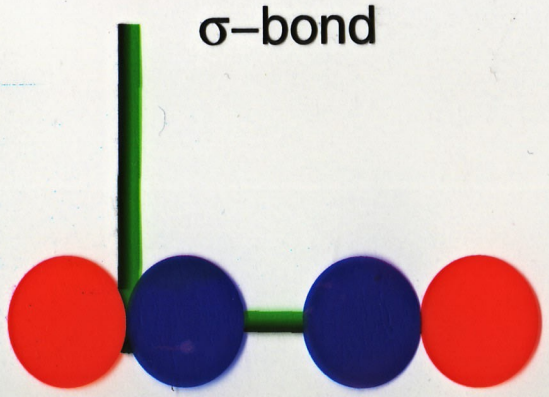
3 localized orbitals/Te or Se:

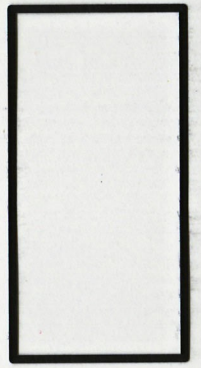
σ*–antibonding
π–nonbonding
σ–bonding

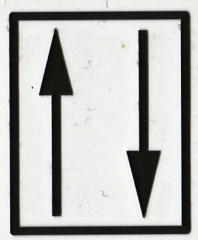
4 valence e⁻/Te or Se

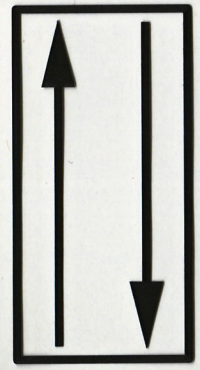




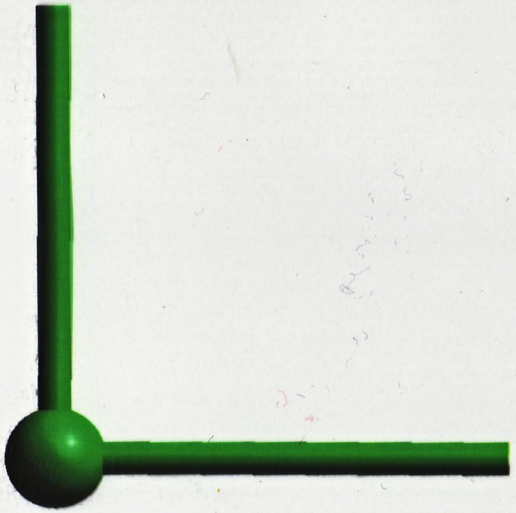


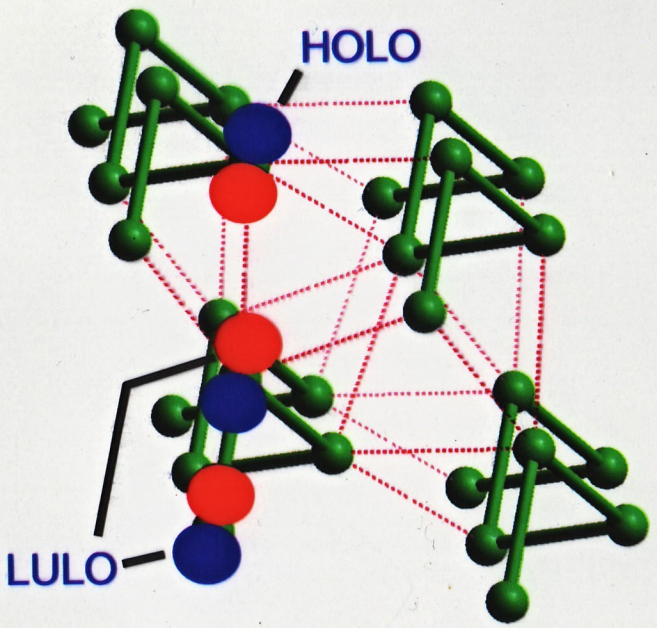




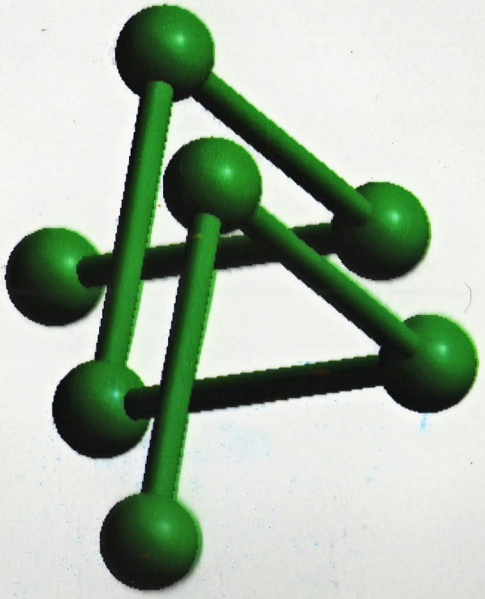


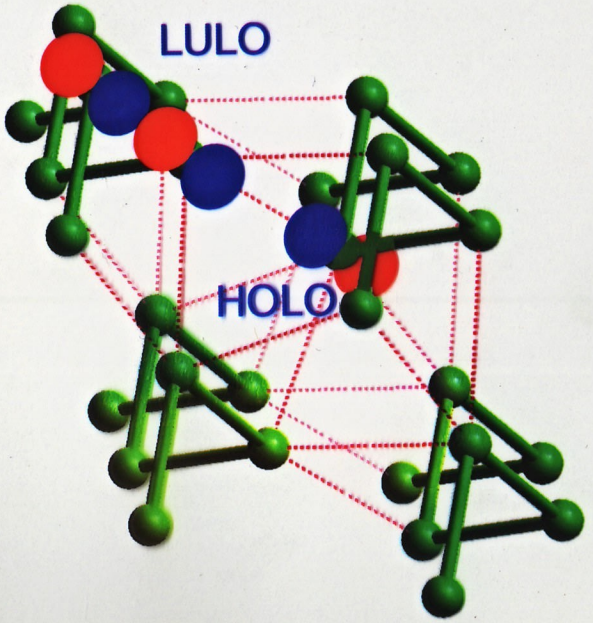
Te or Se have 2 bonds each.



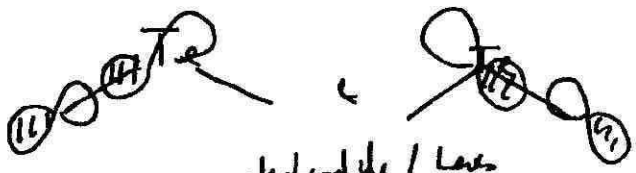


Te or Se form chains.





as nucleophile/
Lewis base

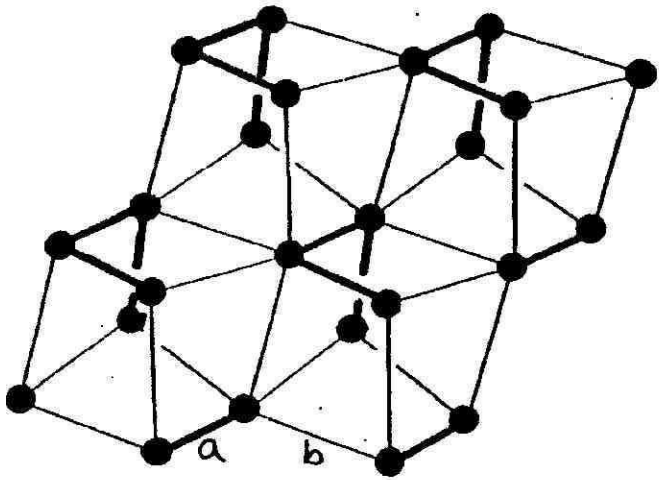


as electrophile / Lewis acid

nucleophilic sites

electrophilic sites

Te

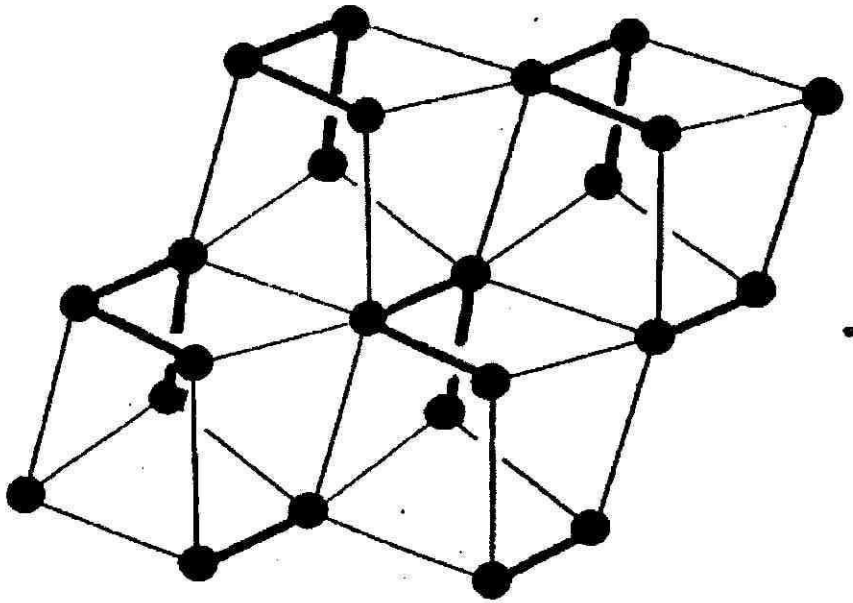


	a	b	$\frac{b}{a}$
Se	2.374 Å	3.436 Å	1.45
Te	2.834 Å	3.494 Å	1.23
Po	3.352 Å	3.352 Å	1.00

Se and Te are insulators (semicond.)

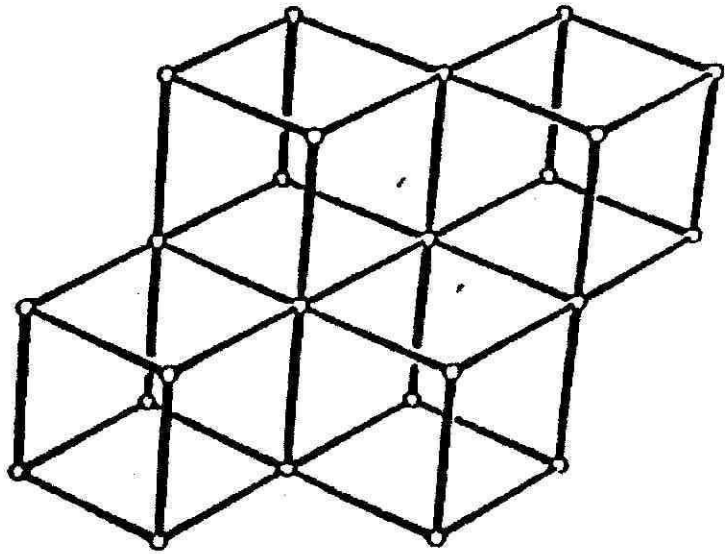
Po is a metal.

Se + Te

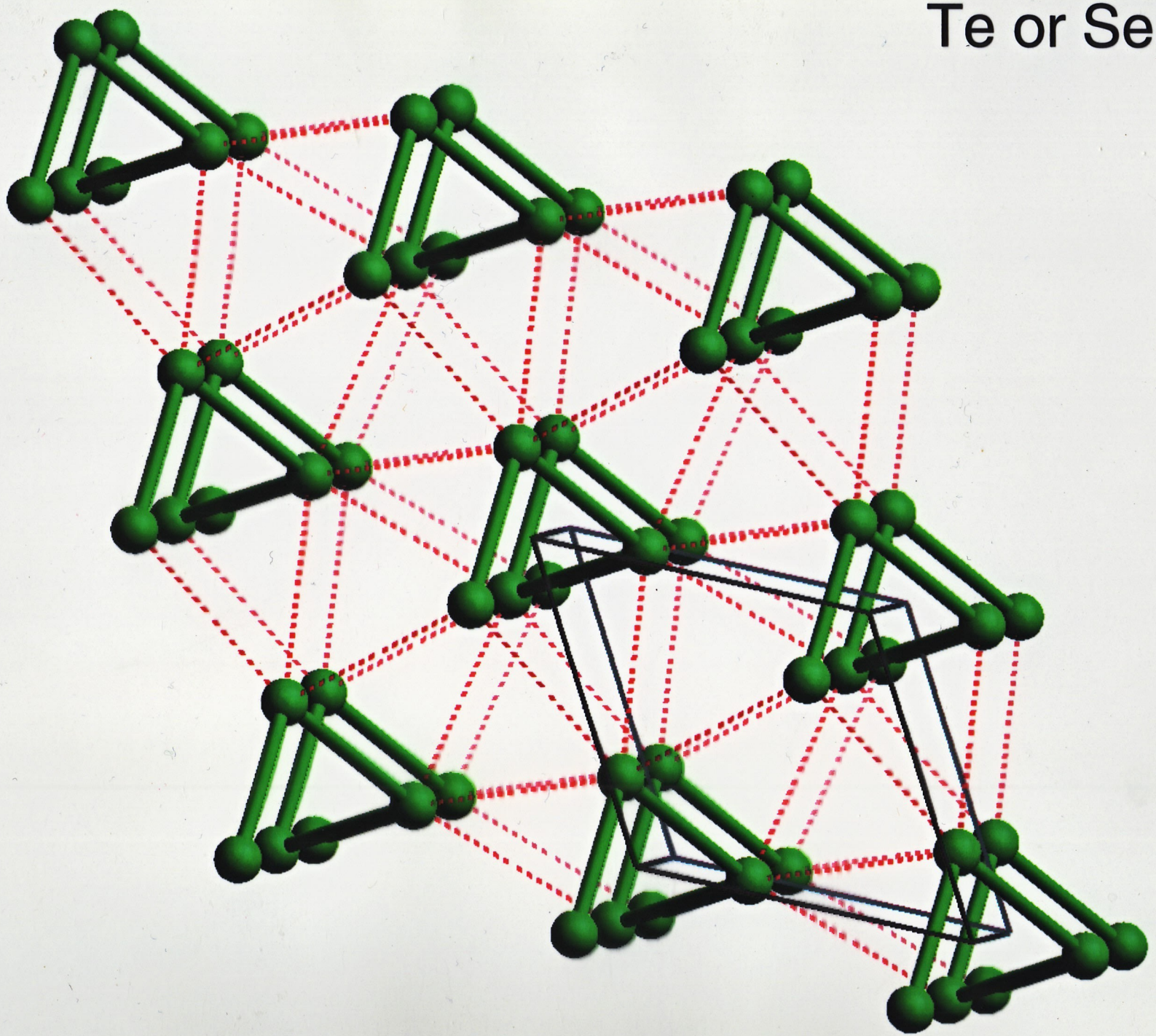


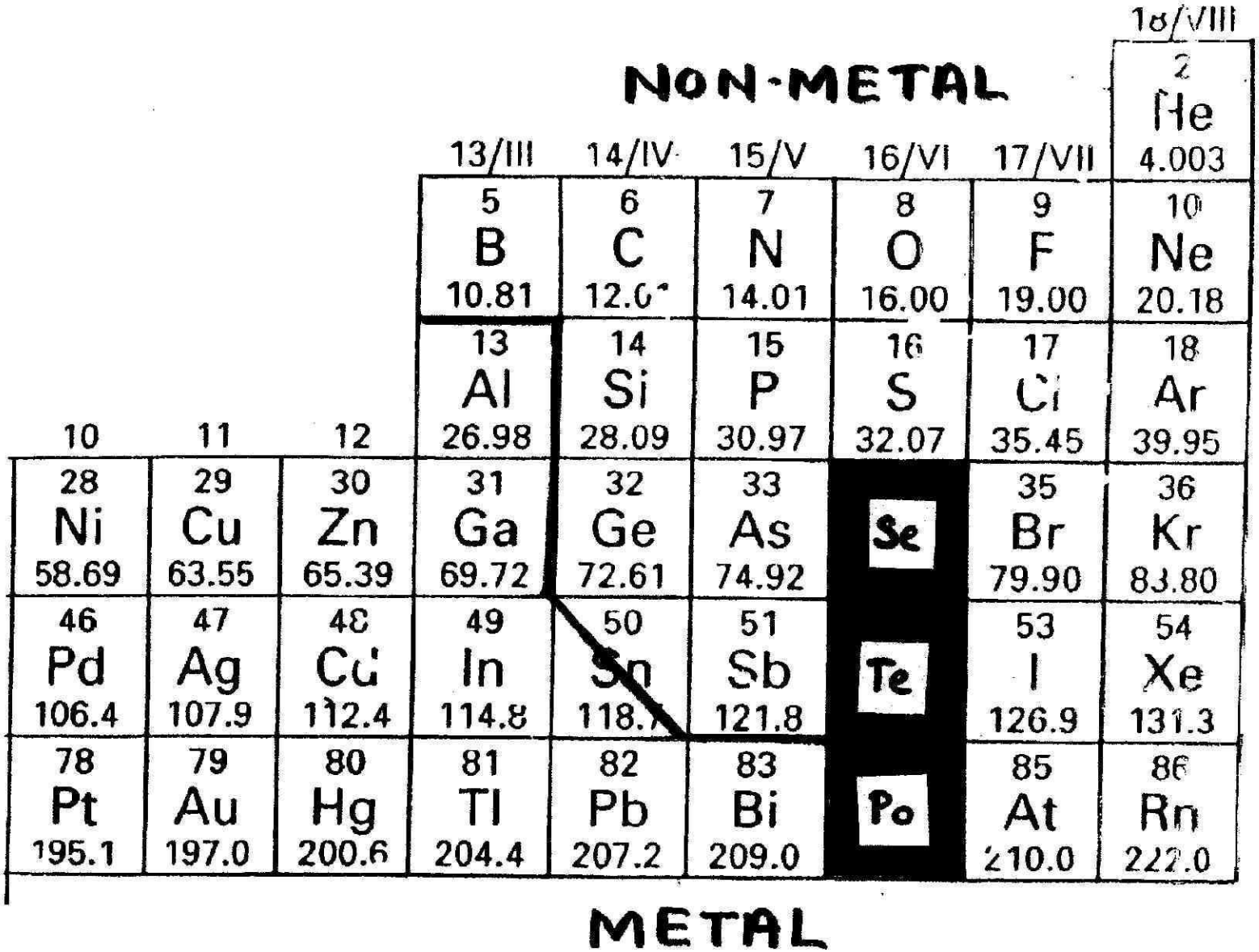
Non-Metal

Po

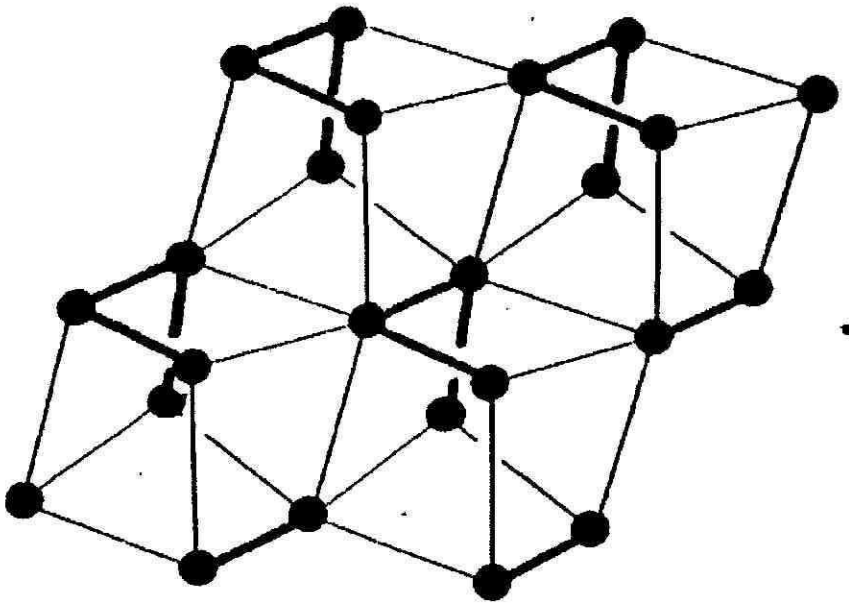


Metal


Te or Se

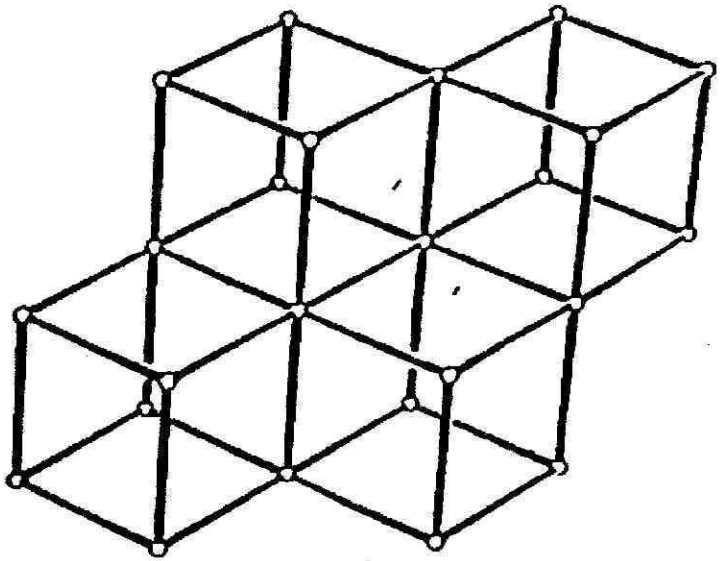

NON-METAL
METAL
13/III
14/IV
15/V
16/VI
17/VII
18/VIII
2 He 4.003
5 B 10.81
6 C 12.0
7 N 14.01
8 O 16.00
9 F 19.00
10 Ne 20.18
13 Al 26.98
14 Si 28.09
15 P 30.97
16 S 32.07
17 Cl 35.45
18 Ar 39.95
10
11
12
28 Ni 58.69
29 Cu 63.55
30 Zn 65.39
31 Ga 69.72
32 Ge 72.61
33 As 74.92
Se
35 Br 79.90
36 Kr 83.80
46 Pd 106.4
47 Ag 107.9
48 Cd 112.4
49 In 114.8
50 Sn 118.7
51 Sb 121.8
Te
53 I 126.9
54 Xe 131.3
78 Pt 195.1
79 Au 197.0
80 Hg 200.6
81 Tl 204.4
82 Pb 207.2
83 Bi 209.0
Po
85 At 210.0
86 Rn 222.0

Se + Te

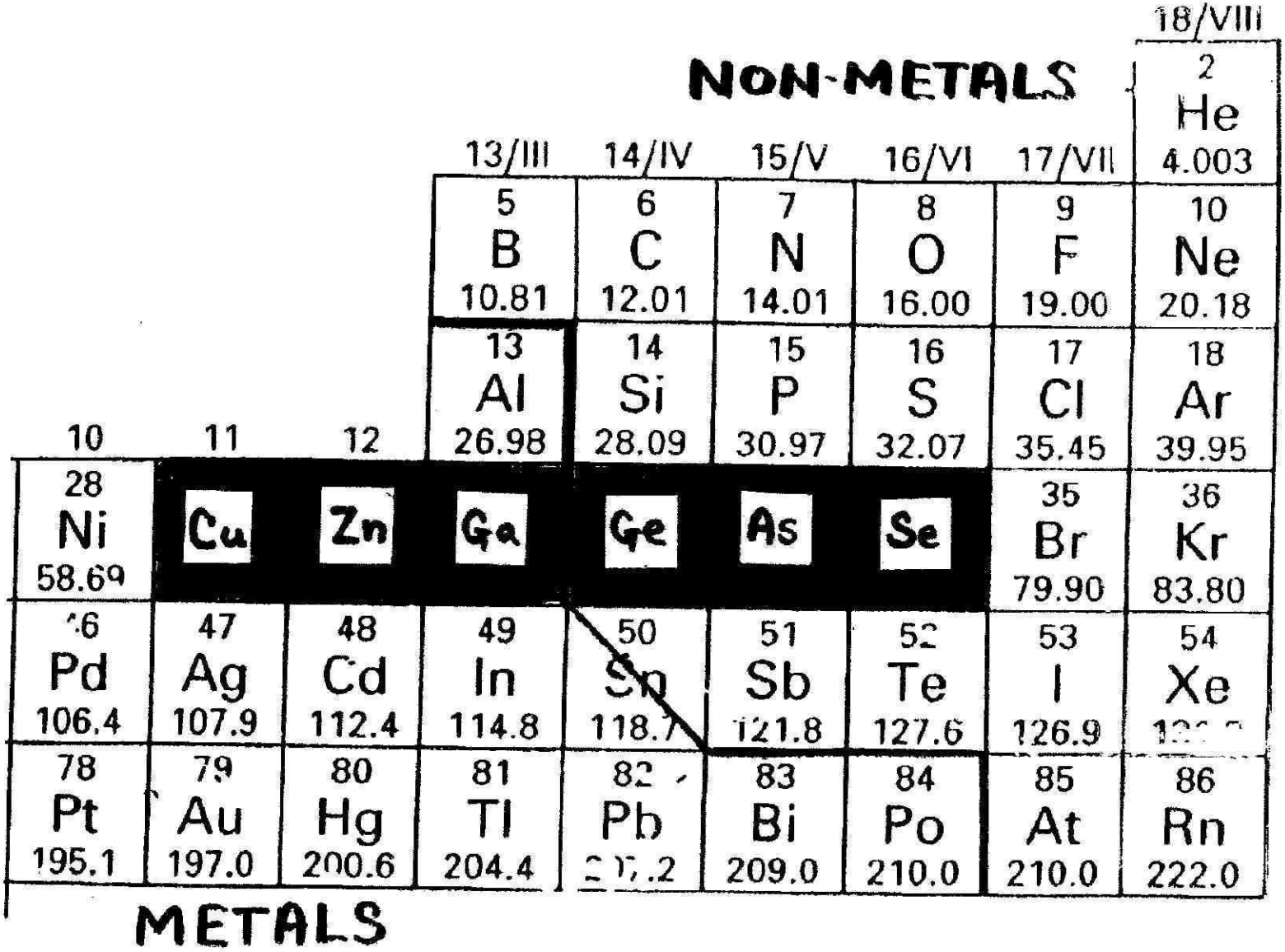


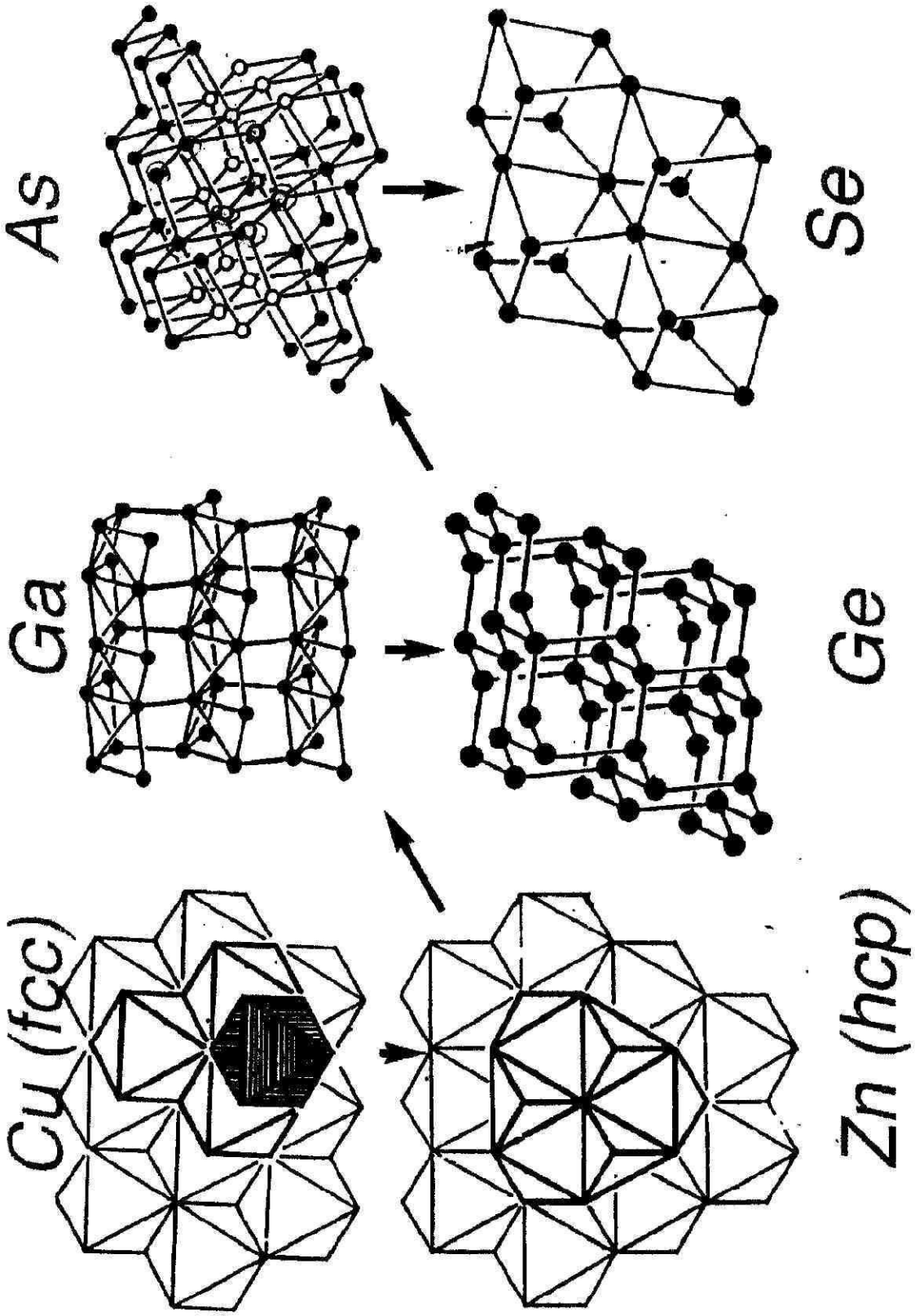
Non-Metal

Po

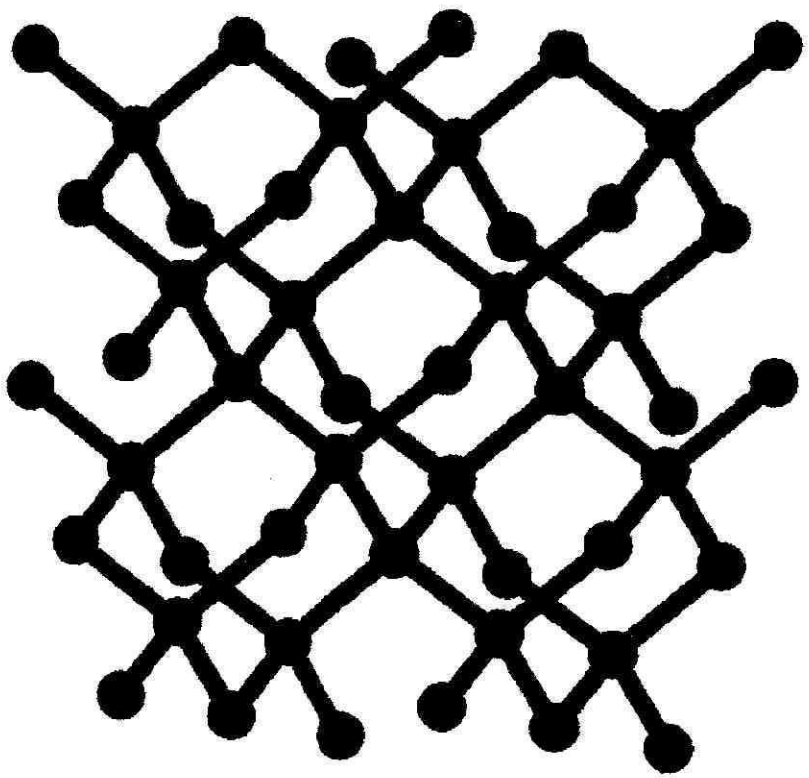


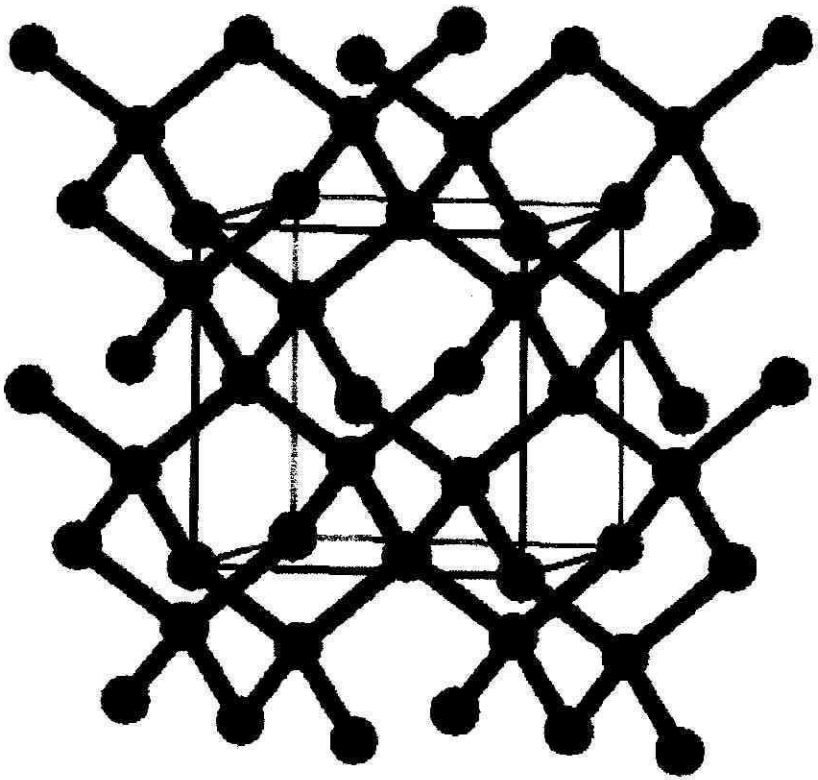
Metal


NON-METALS
METALS
18/VIII
13/III
14/IV
15/V
16/VI
17/VII
10
11
12
2 He 4.003
5 B 10.81
6 C 12.01
7 N 14.01
8 O 16.00
9 F 19.00
10 Ne 20.18
13 Al 26.98
14 Si 28.09
15 P 30.97
16 S 32.07
17 Cl 35.45
18 Ar 39.95
28 Ni 58.69
Cu
Zn
Ga
Ge
As
Se
35 Br 79.90
36 Kr 83.80
46 Pd 106.4
47 Ag 107.9
48 Cd 112.4
49 In 114.8
50 Sn 118.7
51 Sb 121.8
52 Te 127.6
53 I 126.9
54 Xe
78 Pt 195.1
79 Au 197.0
80 Hg 200.6
81 Tl 204.4
82 Pb
83 Bi 209.0
84 Po 210.0
85 At 210.0
86 Rn 222.0

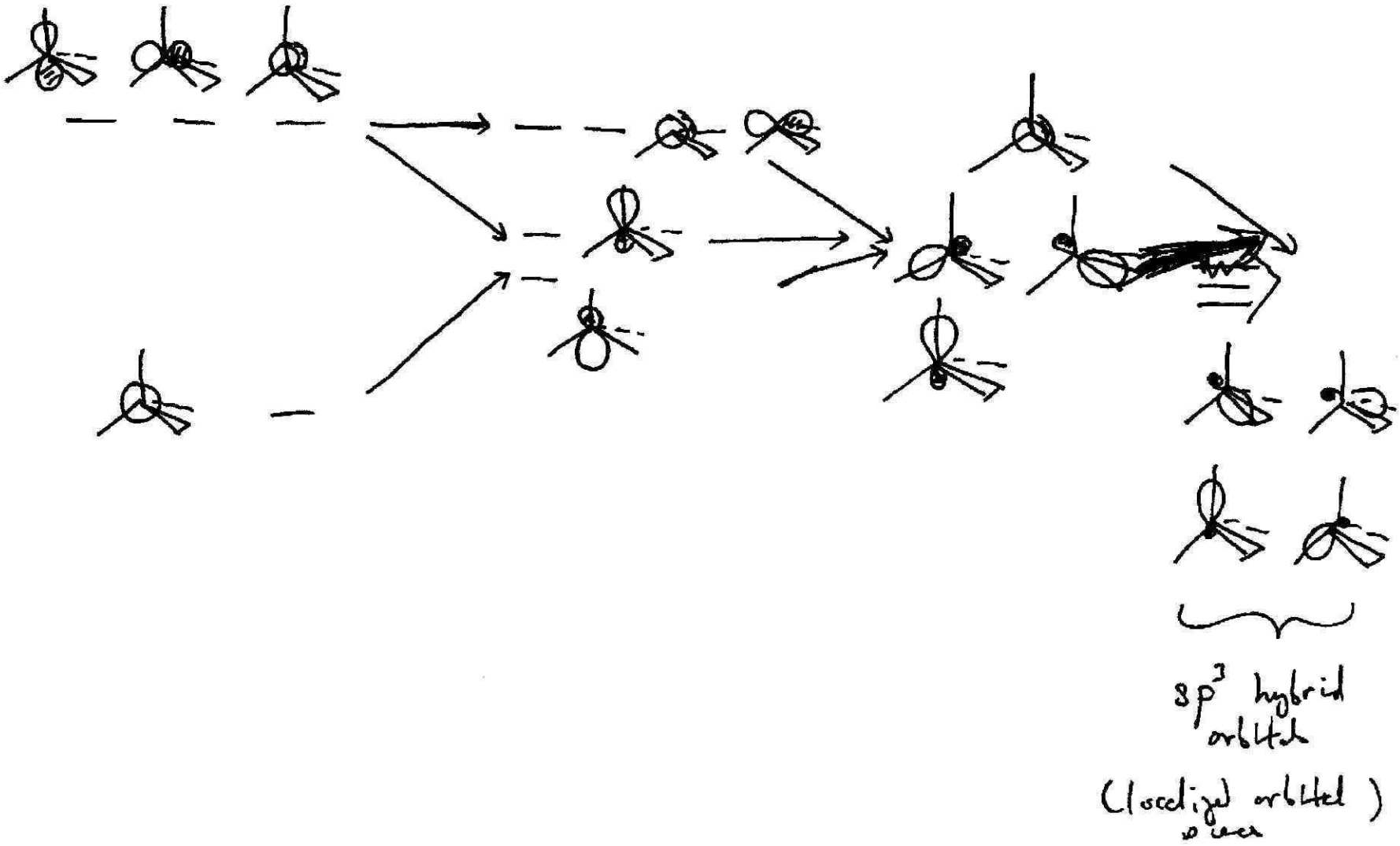

As
Se
Ga
Ge
Cu (fcc)
Zn (hcp)

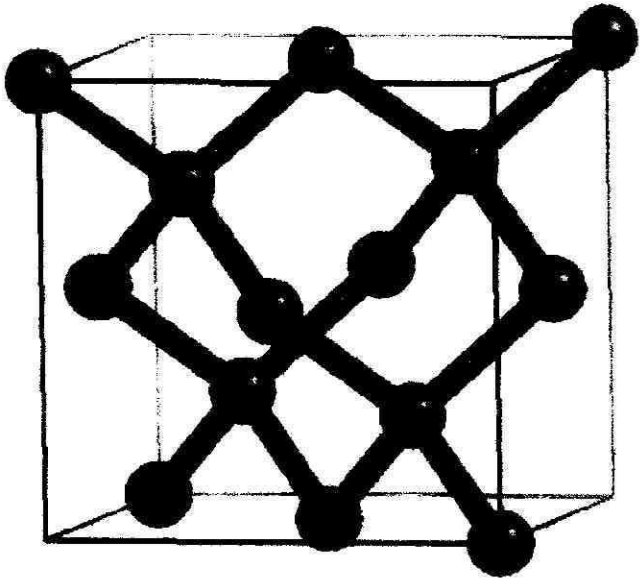
Carbon: cubic diamond



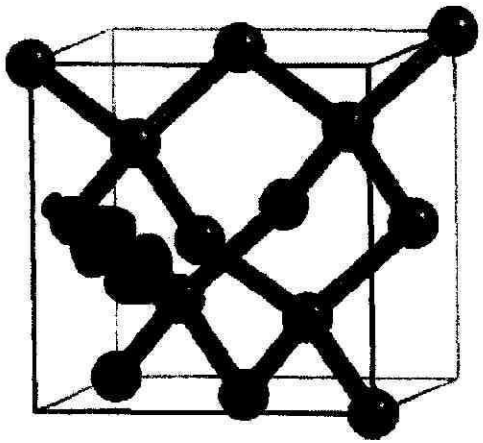


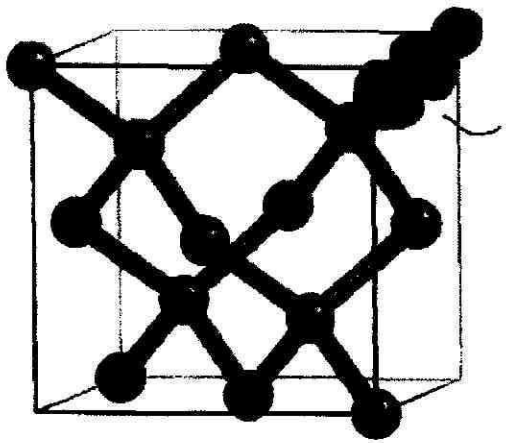
If we wish to generate localized orbitals (which are not eigenstates of anything!) we need to do the opposite of making a MO diagram, and mix orbitals so that they become of equal energy.





diamond





localized orbitals
σ-bond

diamond is not a Lewis acid or a Lewis base.

diamond: localized σ^* antibonding orbitals