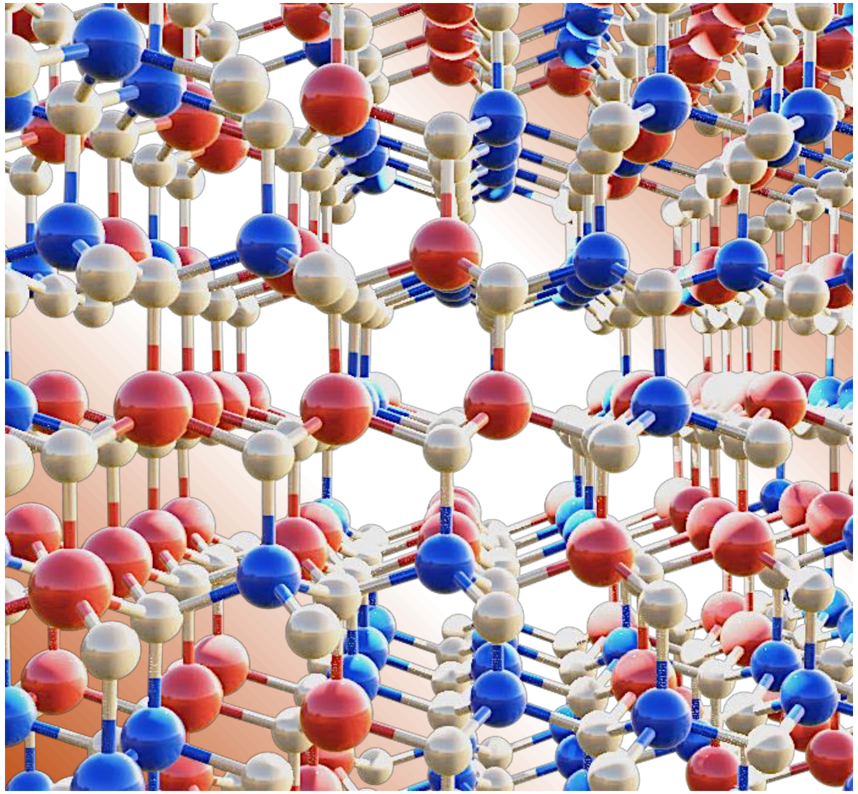
The physics of nitride semiconductors

Lecture 2: Crystals and band theory



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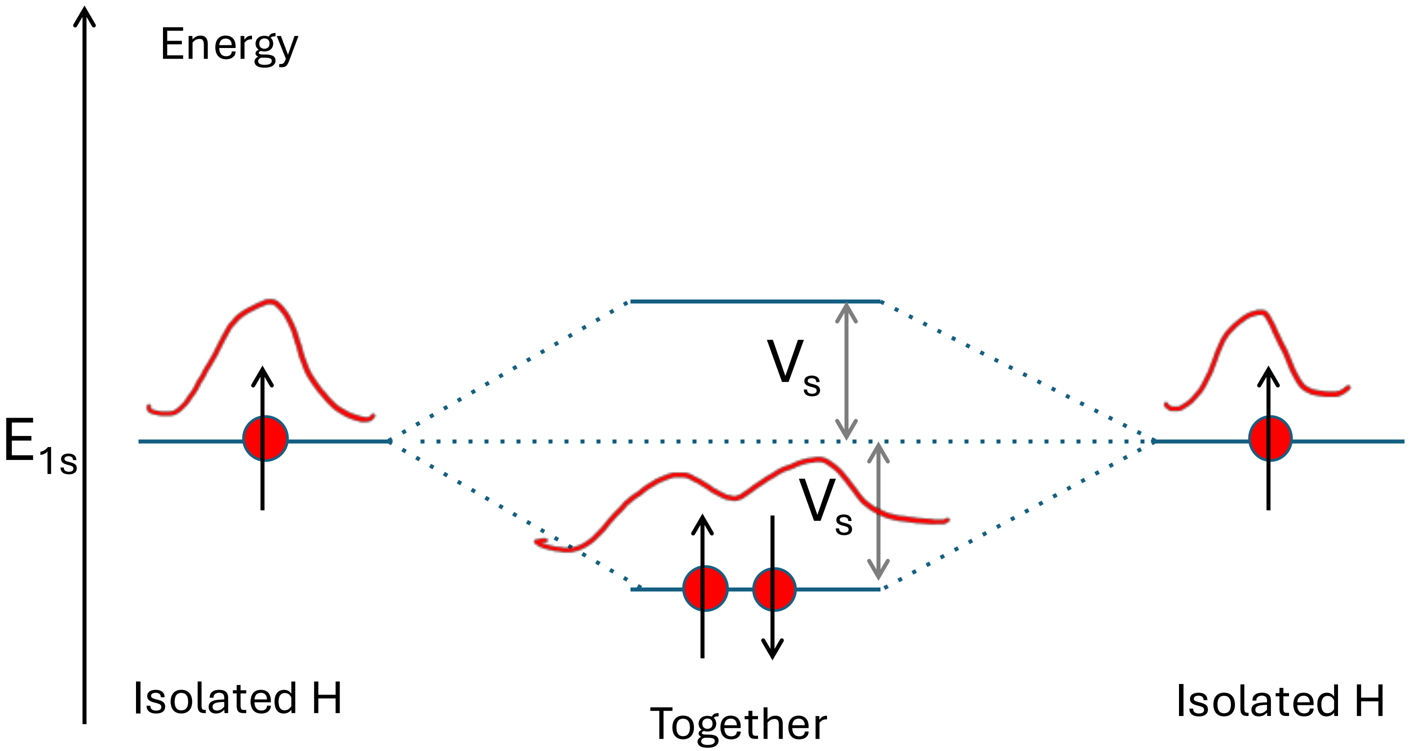
[2] Visiting Professor, IMX and IEM, STI, EPFL

Energy levels of H_2 molecular orbitals



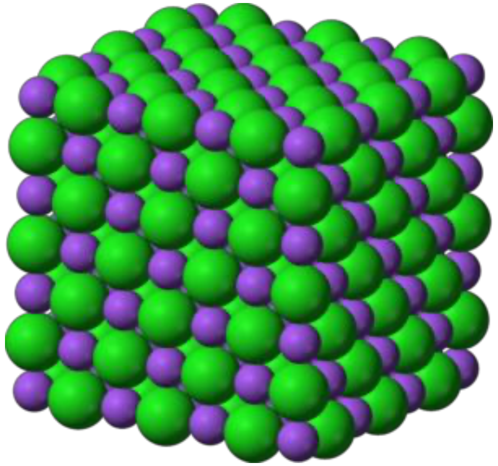
Question: Does the energy increase or decrease when the two H atoms are brought together? What can you say about bond formation?

Answer: Energy is lowered by $2V_s$, the molecule has a lower energy than individual atoms → **chemical bond** forms between H atoms.

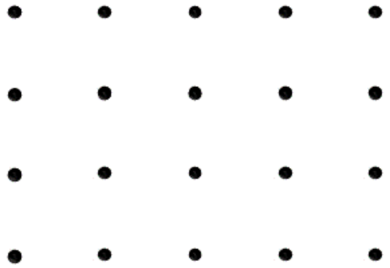
Crystals

Crystal = regular periodic arrangement of atoms in a material

As opposed to **amorphous** materials: no long-range order

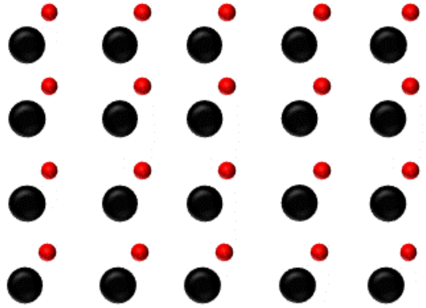


Crystal structure = space lattice + atomic basis



Space Lattice

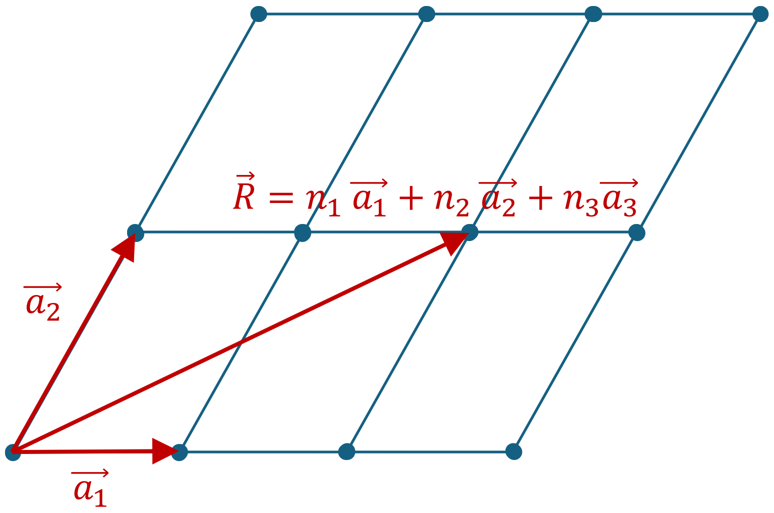
Basis (atoms)



Crystal structure

The crystal structure is formed by adding basis (atoms) to every lattice points of the lattice. The number of atoms in the basis may be one or more than one.

http://scienceline.ucsb.edu/getkey.php?key=4630



Space lattice = mathematical translation of the crystal that leaves the material unchanged.

A crystal has translational symmetry: if we perform a displacement by a vector R, the potential is identical

$$V\left(\vec{r} + \vec{R}\right) = V(\vec{r})$$

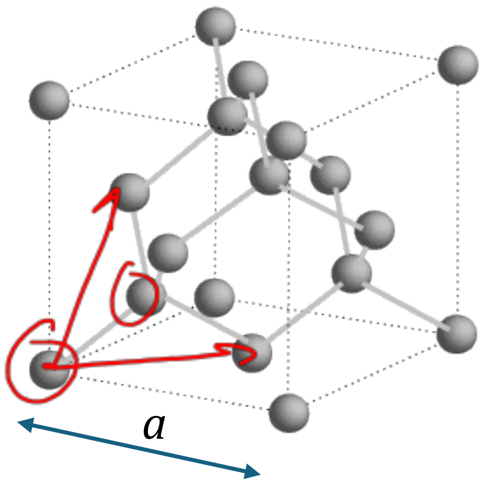
Lattice vectors $\vec{R} = n_1\overrightarrow{a_1} + n_2\overrightarrow{a_2} + n_3\overrightarrow{a_3}$

n_1, n_2, n_3 are integers

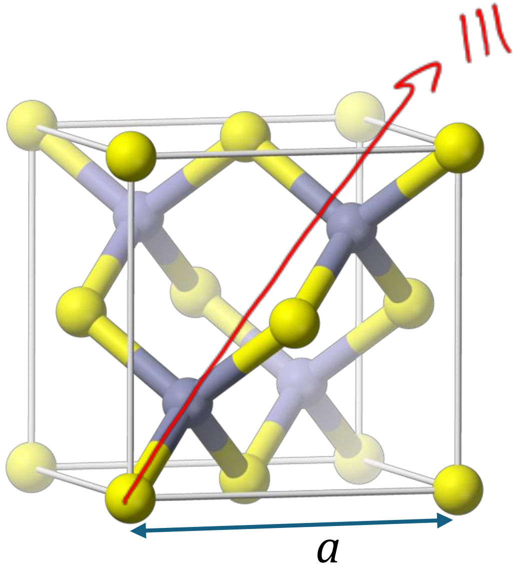
$\overrightarrow{a_1}, \overrightarrow{a_2}, \overrightarrow{a_3}$ are the basis vectors

Each point of the lattice is given by a set of integers, and each set of integers gives a point on the lattice.

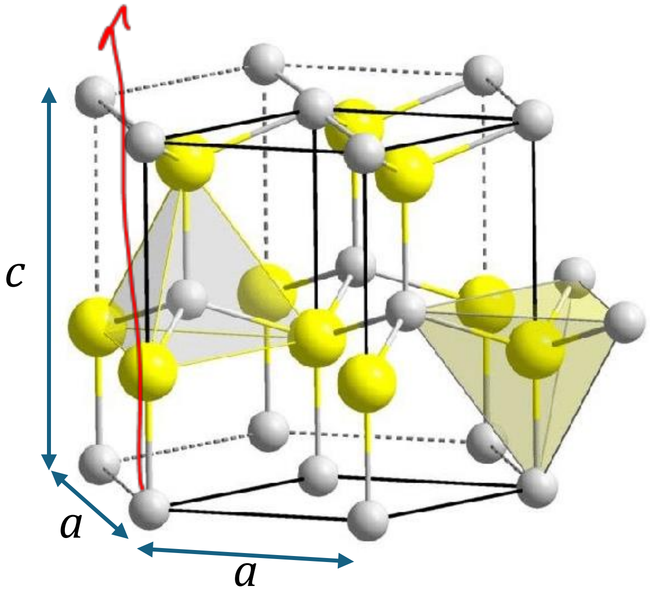
Crystal structures of semiconductors



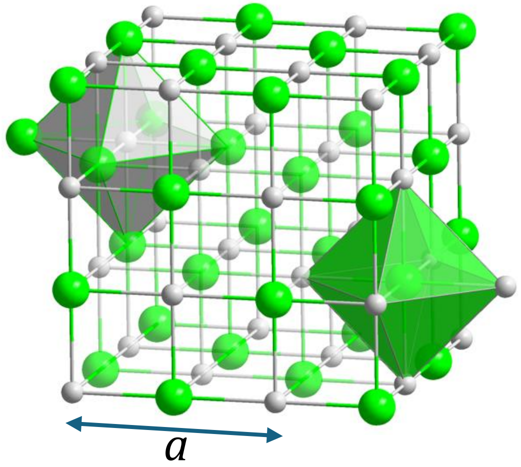
Silicon, germanium: diamond structure



GaAs: zincblende (or sphalerite) structure



GaN, AlN, InN: wurtzite structure



ScN, YN, LaN: rocksalt structure

Based on *fcc* lattice:

Lattice vectors:

$$\vec{a_1} = \frac{a}{2}(\hat{x} + \hat{y})$$
$$\vec{a_2} = \frac{a}{2}(\hat{y} + \hat{z})$$
$$\vec{a_3} = \frac{a}{2}(\hat{x} + \hat{z})$$

Basis:

$$\vec{\tau_1} = 0$$
$$\vec{\tau_2} = \frac{a}{4}(\hat{x} + \hat{y} + \hat{z})$$

Based on *hcp* lattice:

$$\vec{a_1} = a\hat{x}$$
$$\vec{a_2} = \left(\frac{a}{2}\hat{x} + \frac{\sqrt{3}a}{2}\hat{y}\right)$$
$$\vec{a_3} = c\hat{z}$$

Ga: $\vec{\tau_1} = 0$

Ga: $\vec{\tau_2} = \frac{1}{3}(\vec{a_1} + \vec{a_2}) + \frac{1}{2}\vec{a_3}$

N: $\vec{\tau_3} = u\,\hat{z}$

N: $\vec{\tau_4} = \frac{1}{3}(\vec{a_1} + \vec{a_2}) + (u + \frac{1}{2})\,\vec{a_3}$

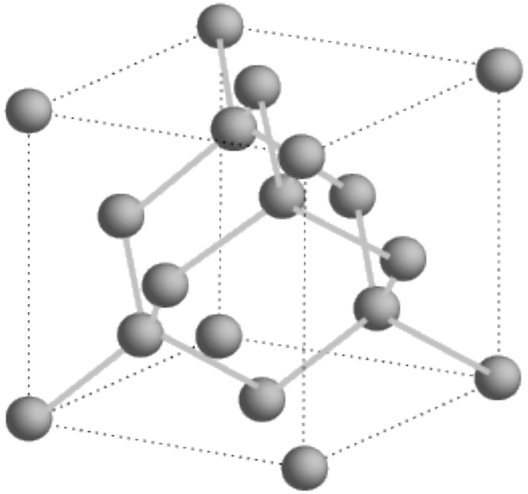
Based on *fcc* lattice:

$$\vec{a_1} = \frac{a}{2}(\hat{x} + \hat{y})$$
$$\vec{a_2} = \frac{a}{2}(\hat{y} + \hat{z})$$
$$\vec{a_3} = \frac{a}{2}(\hat{x} + \hat{z})$$

$$\vec{\tau_1} = 0$$
$$\vec{\tau_2} = \frac{a}{2}\hat{x}\ [\text{or } \vec{\tau_2} = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})]$$

Crystal structures of semiconductors: diamond

Diamond (Si, Ge)



Kittel, solid state physics

$$\overrightarrow{a_1} = \frac{a}{2}(\hat{x} + \hat{y})$$
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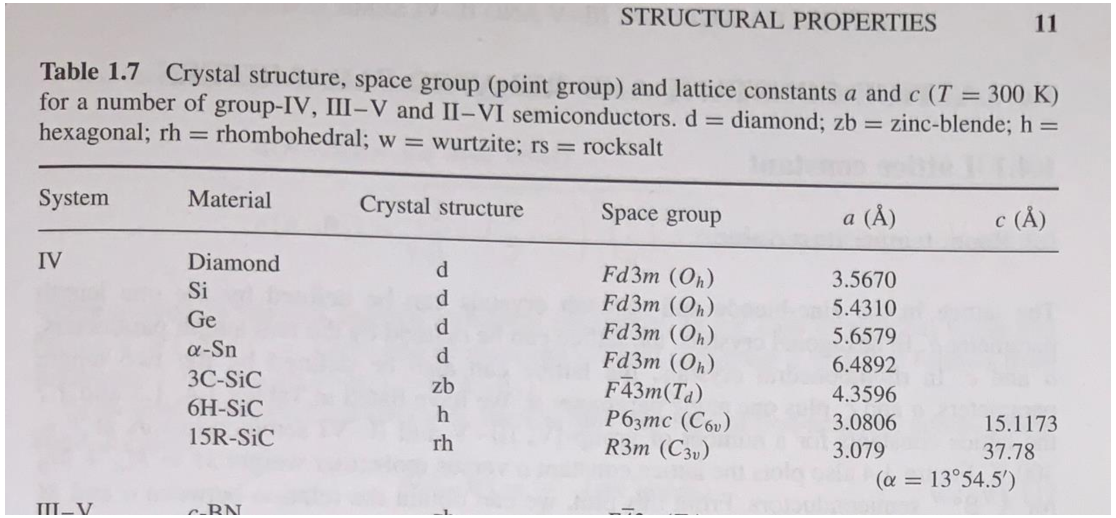


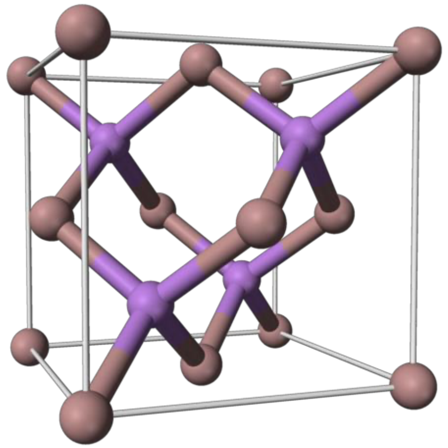
STRUCTURAL PROPERTIES 11

Table 1.7 Crystal structure, space group (point group) and lattice constants a and c ($T = 300$ K) for a number of group-IV, III–V and II–VI semiconductors. d = diamond; zb = zinc-blende; h = hexagonal; rh = rhombohedral; w = wurtzite; rs = rocksalt

System	Material	Crystal structure	Space group	a (Å)	c (Å)
IV	Diamond	d	$Fd3m$ (O_h)	3.5670	
	Si	d	$Fd3m$ (O_h)	5.4310	
	Ge	d	$Fd3m$ (O_h)	5.6579	
	α-Sn	d	$Fd3m$ (O_h)	6.4892	
	3C-SiC	zb	$F\bar{4}3m(T_d)$	4.3596	
	6H-SiC	h	$P6_3mc$ (C_{6v})	3.0806	15.1173
	15R-SiC	rh	$R3m$ (C_{3v})	3.079	37.78
				($\alpha = 13°54.5'$)	
III–V	c-BN				

Crystal structures of semiconductors: zincblende

Zincblence (GaAs)



From Wikipedia

$$\overrightarrow{a_1} = \frac{a}{2}(\hat{x} + \hat{y})$$
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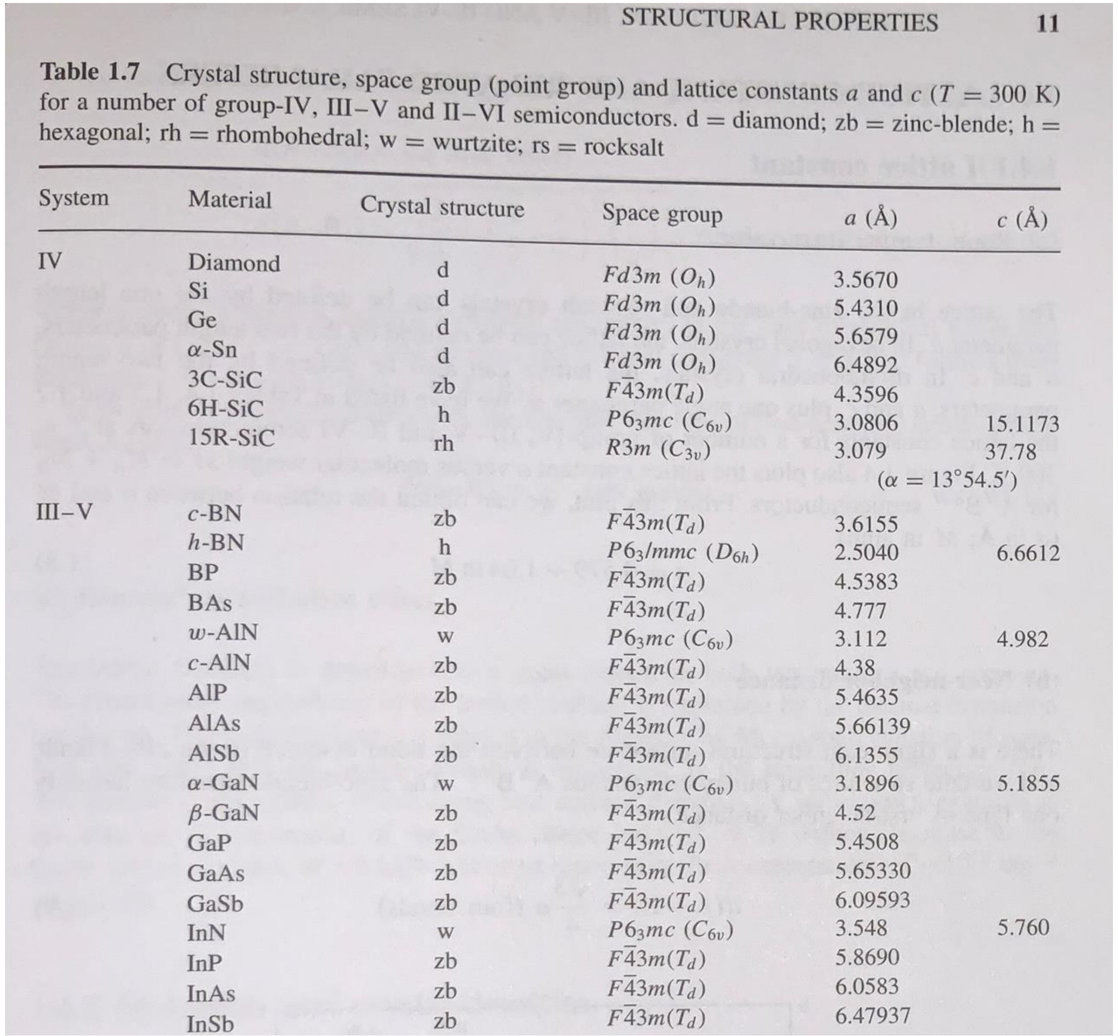

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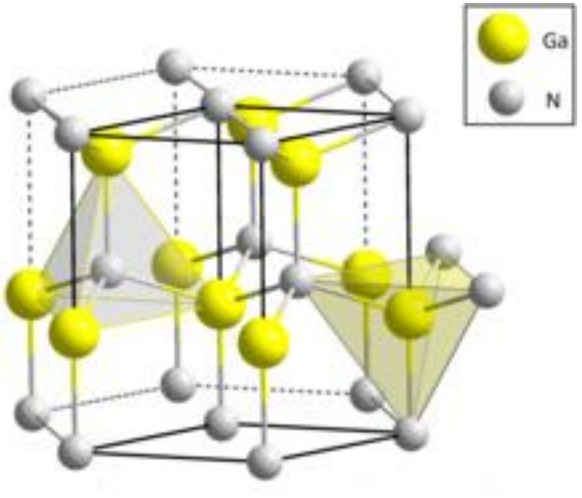
III–V	c-BN	zb	$F\bar{4}3m(T_d)$	3.6155	
	h-BN	h	$P6_3/mmc$ (D_{6h})	2.5040	6.6612
	BP	zb	$F\bar{4}3m(T_d)$	4.5383	
	BAs	zb	$F\bar{4}3m(T_d)$	4.777	
	w-AlN	w	$P6_3mc$ (C_{6v})	3.112	4.982
	c-AlN	zb	$F\bar{4}3m(T_d)$	4.38	
	AlP	zb	$F\bar{4}3m(T_d)$	5.4635	
	AlAs	zb	$F\bar{4}3m(T_d)$	5.66139	
	AlSb	zb	$F\bar{4}3m(T_d)$	6.1355	
	α-GaN	w	$P6_3mc$ (C_{6v})	3.1896	5.1855
	β-GaN	zb	$F\bar{4}3m(T_d)$	4.52	
	GaP	zb	$F\bar{4}3m(T_d)$	5.4508	
	GaAs	zb	$F\bar{4}3m(T_d)$	5.65330	
	GaSb	zb	$F\bar{4}3m(T_d)$	6.09593	
	InN	w	$P6_3mc$ (C_{6v})	3.548	5.760
	InP	zb	$F\bar{4}3m(T_d)$	5.8690	
	InAs	zb	$F\bar{4}3m(T_d)$	6.0583	
	InSb	zb	$F\bar{4}3m(T_d)$	6.47937	

Crystal structures of semiconductors: wurtzite

Wurtzite (GaN)



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Three parameters: a, c, u

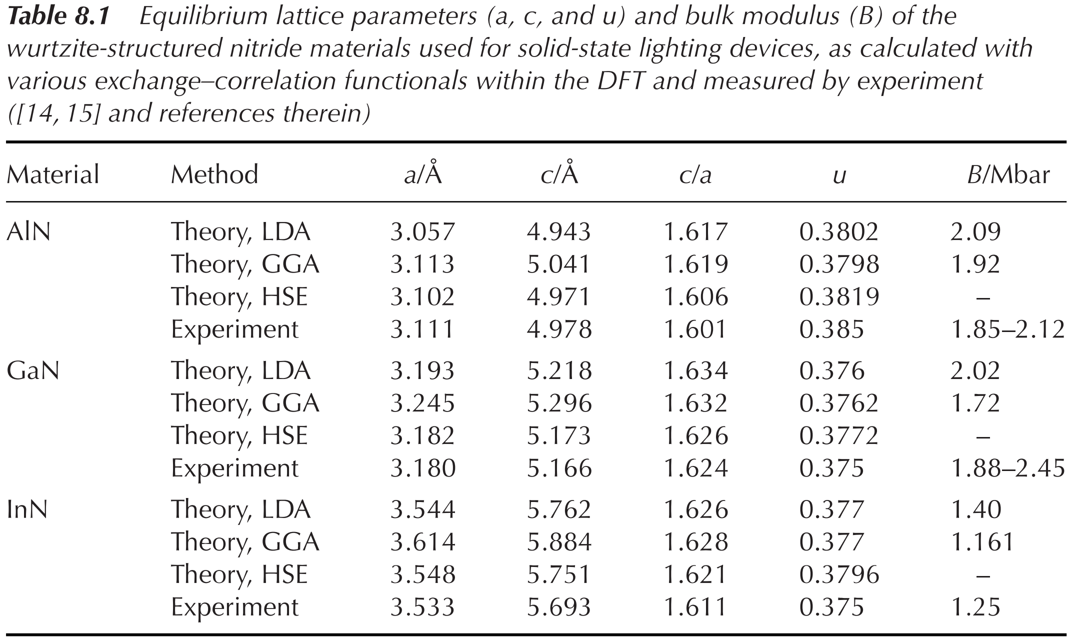


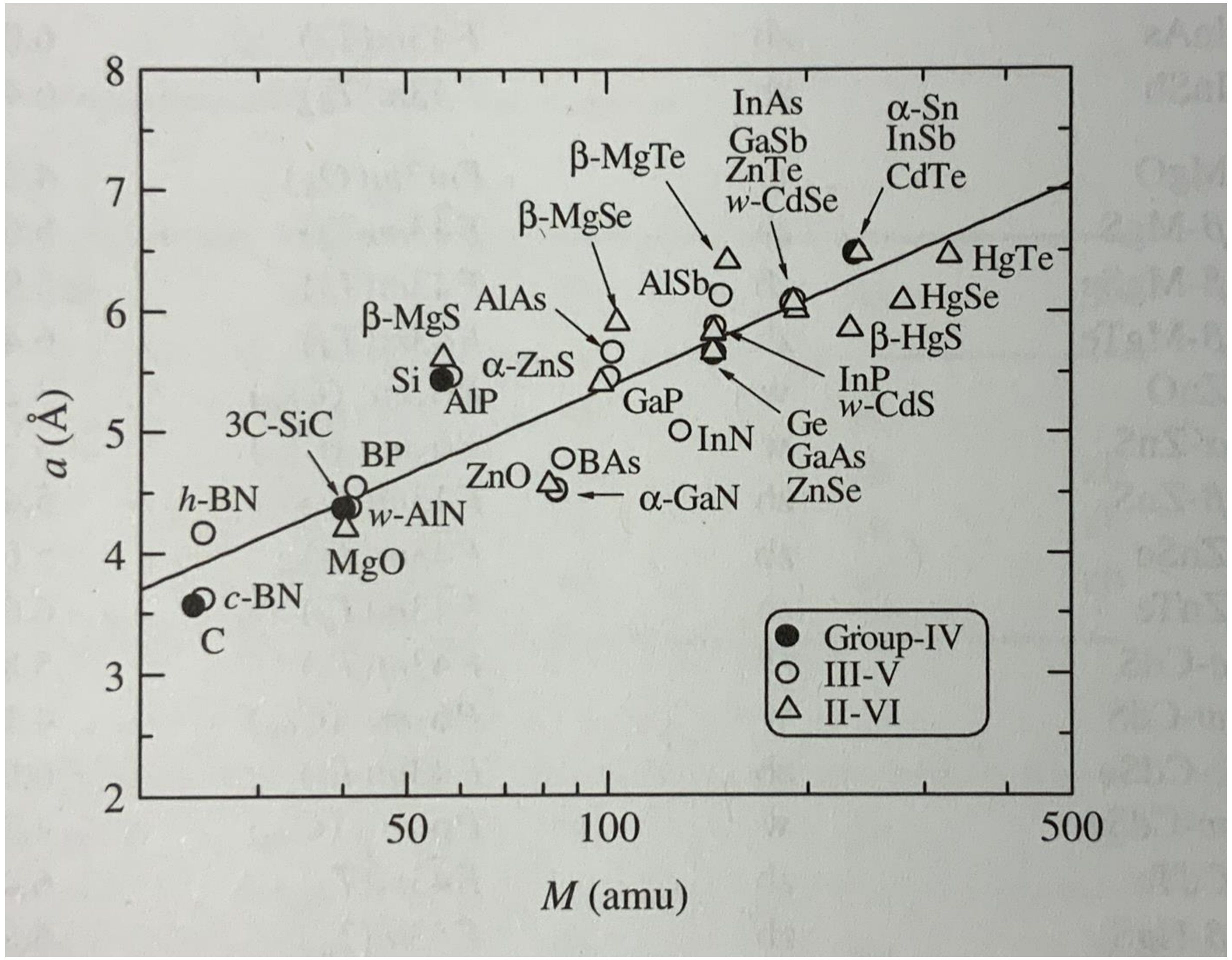
Table 8.1 *Equilibrium lattice parameters (a, c, and u) and bulk modulus (B) of the wurtzite-structured nitride materials used for solid-state lighting devices, as calculated with various exchange–correlation functionals within the DFT and measured by experiment ([14, 15] and references therein)*

Material	Method	*a*/Å	*c*/Å	*c*/*a*	*u*	*B*/Mbar
AlN	Theory, LDA	3.057	4.943	1.617	0.3802	2.09
	Theory, GGA	3.113	5.041	1.619	0.3798	1.92
	Theory, HSE	3.102	4.971	1.606	0.3819	–
	Experiment	3.111	4.978	1.601	0.385	1.85–2.12
GaN	Theory, LDA	3.193	5.218	1.634	0.376	2.02
	Theory, GGA	3.245	5.296	1.632	0.3762	1.72
	Theory, HSE	3.182	5.173	1.626	0.3772	–
	Experiment	3.180	5.166	1.624	0.375	1.88–2.45
InN	Theory, LDA	3.544	5.762	1.626	0.377	1.40
	Theory, GGA	3.614	5.884	1.628	0.377	1.161
	Theory, HSE	3.548	5.751	1.621	0.3796	–
	Experiment	3.533	5.693	1.611	0.375	1.25

http://onlinelibrary.wiley.com/doi/10.1002
/9781118551462.ch8/summary

Lattice constants of common semiconductors

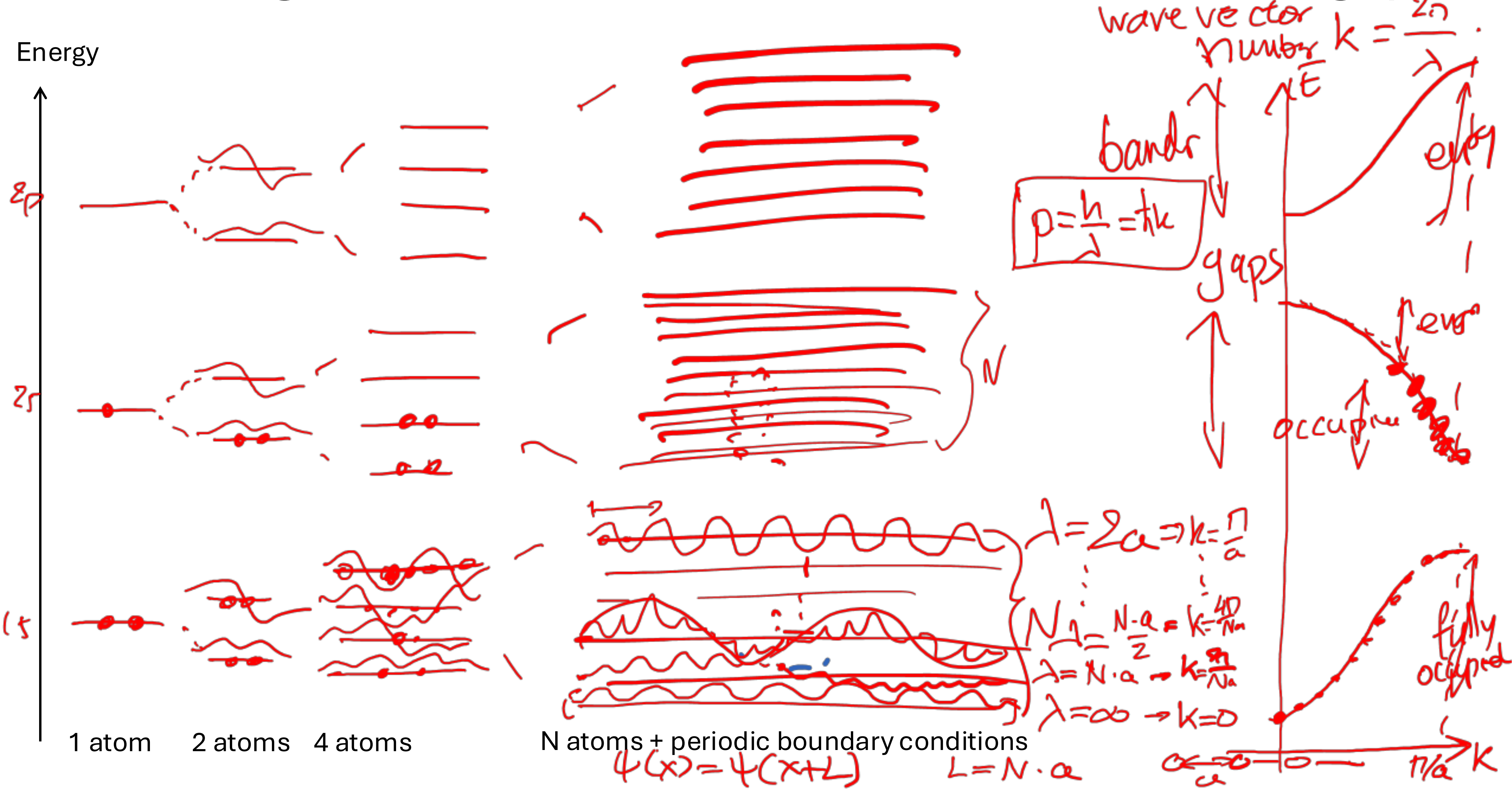
- Trends:
- What happens for heavier atoms?
- What happens as the cations size increases? (e.g., Al → Ga → In)
- What happens as the anion size increases? (e.g., N → P → As → Sb)



Molecular weight

Adachi, Properties of group-IV, III-V and II-VI semiconductors

Connecting atomic/molecular orbitals to bands and gaps



wave vector number $k = \frac{2\pi}{\lambda}$

$\boxed{p = \frac{h}{\lambda} = \hbar k}$

$\lambda = 2a \Rightarrow k = \frac{\pi}{a}$

$\lambda = \frac{N \cdot a}{2} \Rightarrow k = \frac{4\pi}{Na}$

$\lambda = N \cdot a \rightarrow k = \frac{2\pi}{Na}$

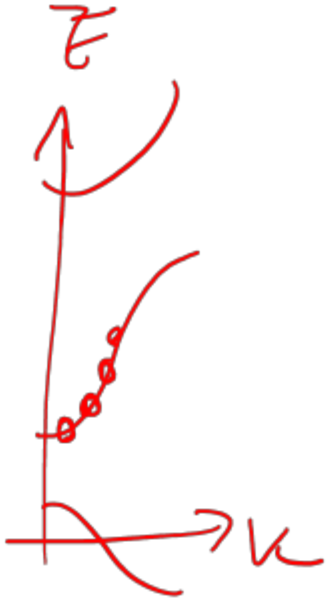
$\lambda = \infty \rightarrow k = 0$

$\psi(x) = \psi(x+L)$

$L = N \cdot a$

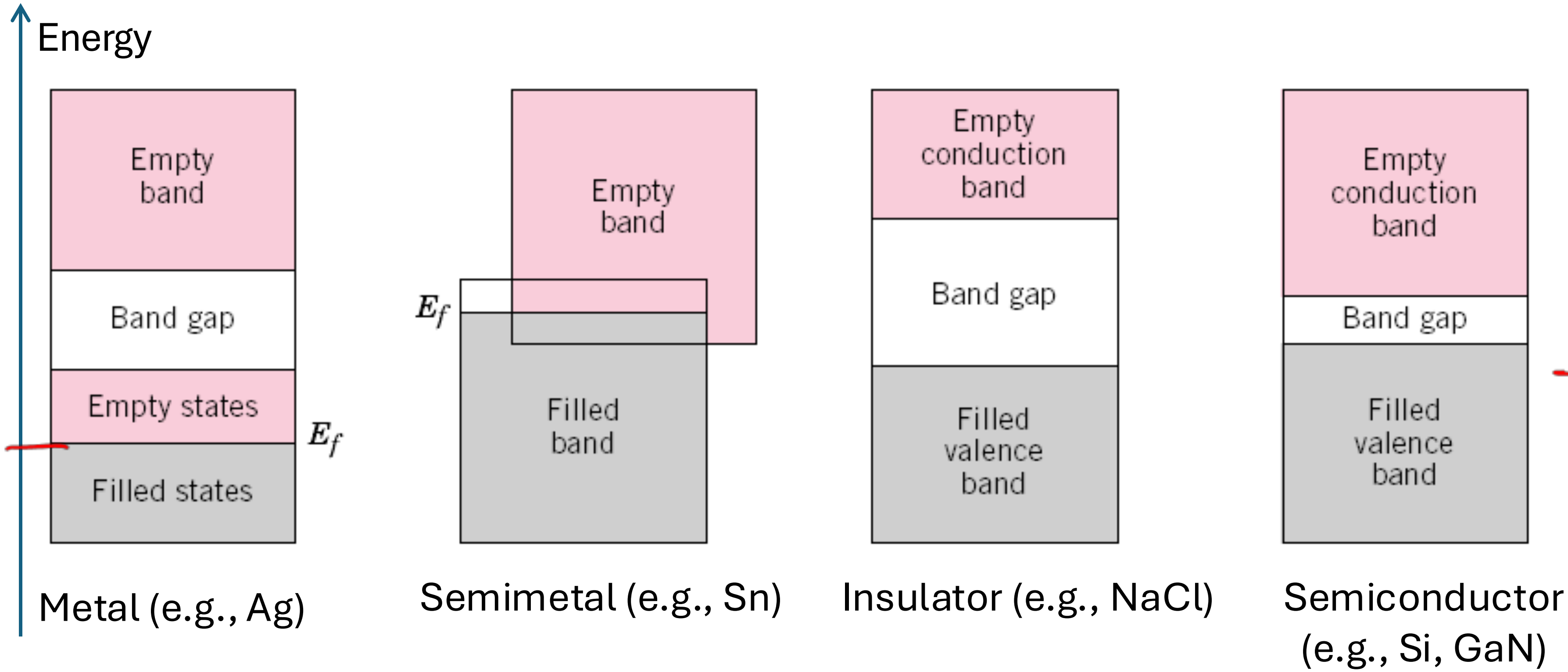
Band theory

Electron levels in materials are organized in **bands** separated by **gaps**.



Fermi energy

Sn


Energy

Empty band

Band gap

Empty states

E_f

Filled states

Metal (e.g., Ag)

E_f

Empty band

Filled band

Semimetal (e.g., Sn)

Empty conduction band

Band gap

Filled valence band

Insulator (e.g., NaCl)

Empty conduction band

Band gap

Filled valence band

Semiconductor (e.g., Si, GaN)

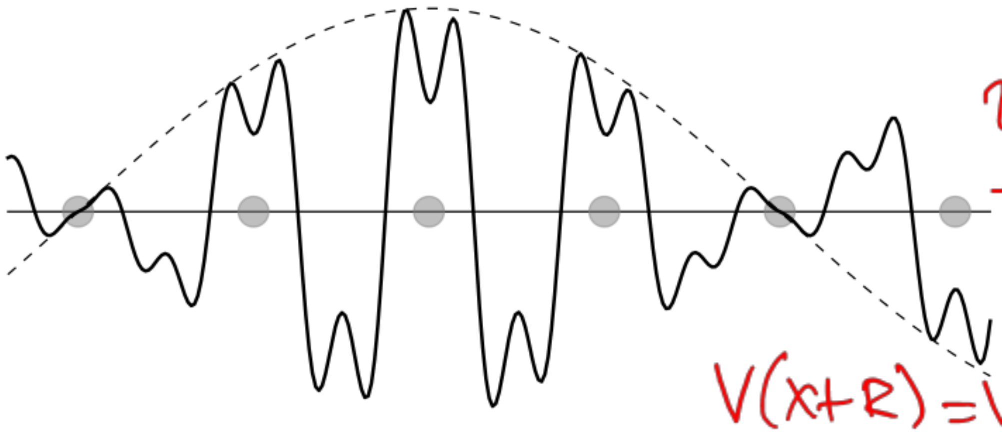
TiC

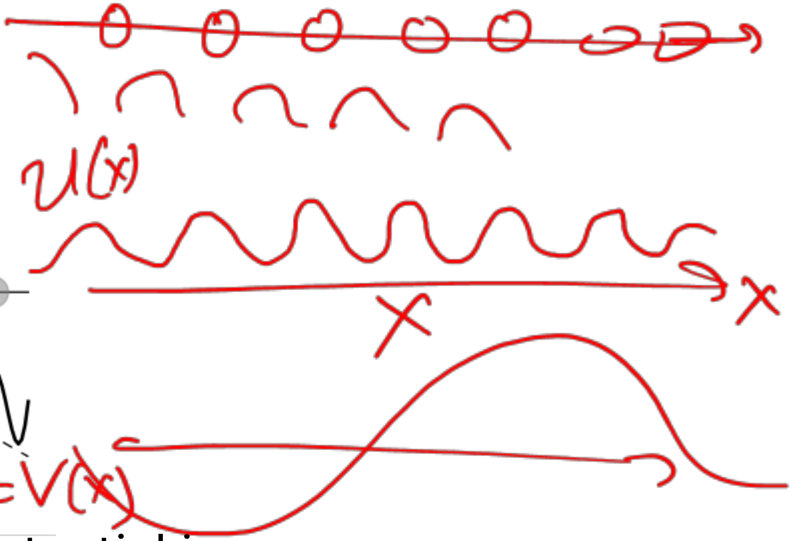
TiN

Classification of solids based on their band gap.

- Zero gap: metals
- Gap ~< 3 eV: semiconductors
- Gap ~> 3 eV: insulators
- Overlapping valence and conduction bands: semimetals

Bloch's theorem





$V(x+R)=V(x)$

The solution of Schrödinger's equation in a periodic potential is a wave (Bloch wave)

$$\psi(x) = u(x)\cdot e^{ikx}$$

$u(x+R)=u(x)$

u(x) is a periodic function with the same period as the potential (i.e., the period of the crystal).

In contrast: for empty space:

$$\psi(x) = e^{ikx}$$

→ Explains long mean-free paths of electrons in metals.

~ 100×a

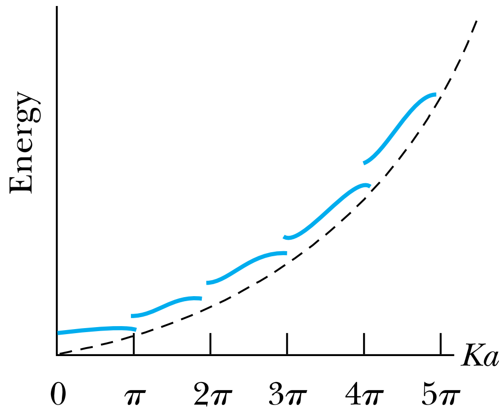
Periodicity of band structure E(k)

The bands are periodic in k with a period equal to 2π/*a*:

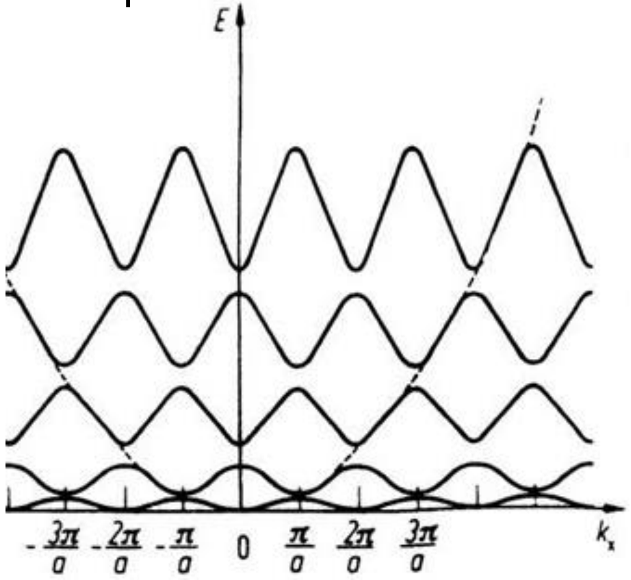
For each band: $$E(k+\frac{2\pi}{a}) = E(k)$$

Three ways to represent the periodic band structure:

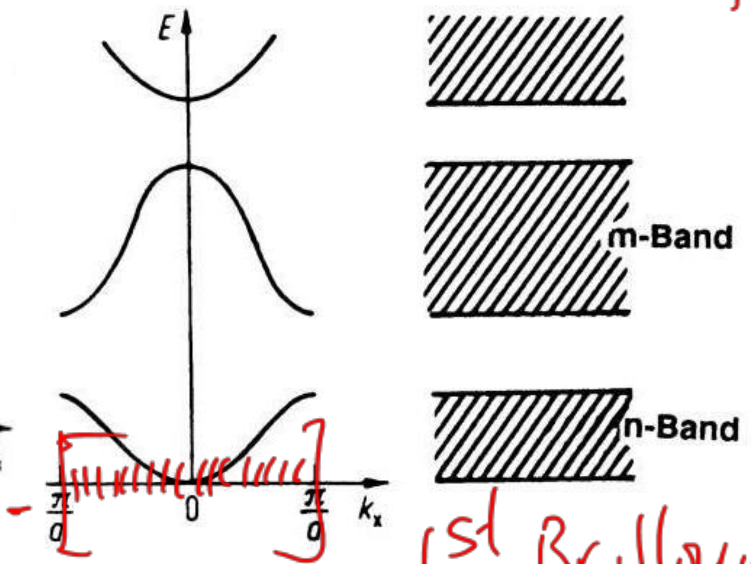
Extended zone scheme



Repeated zone scheme



Reduced zone scheme: this one used in practice



N atoms in crystal

$\vec{N}$ values for k, spaced by $\frac{2\pi}{Na}$

1st Brillouin zone

Tight binding method = LCAO for crystals

Positions of atoms: $\vec{R}_i + \vec{\tau}_j = \vec{r}_{ij}$, $i = 1,2, \ldots N$ unit cells,

$j = 1,2, \ldots$ atoms in unit cell

$\phi_{mi}\left(\vec{r} - \overrightarrow{r_{ij}}\right)$: *m*-th atomic orbital in unit cell *i* on atom *j*.

Write wave function of electrons in crystals as a periodic linear combination of atomic orbitals

$$\psi_k = \sum_{m,j} c_{mj} \sum_i e^{i\left(\overrightarrow{r_{ij}}\cdot\vec{k}\right)} \phi_{mi}(\vec{r} - \overrightarrow{r_{ij}})$$

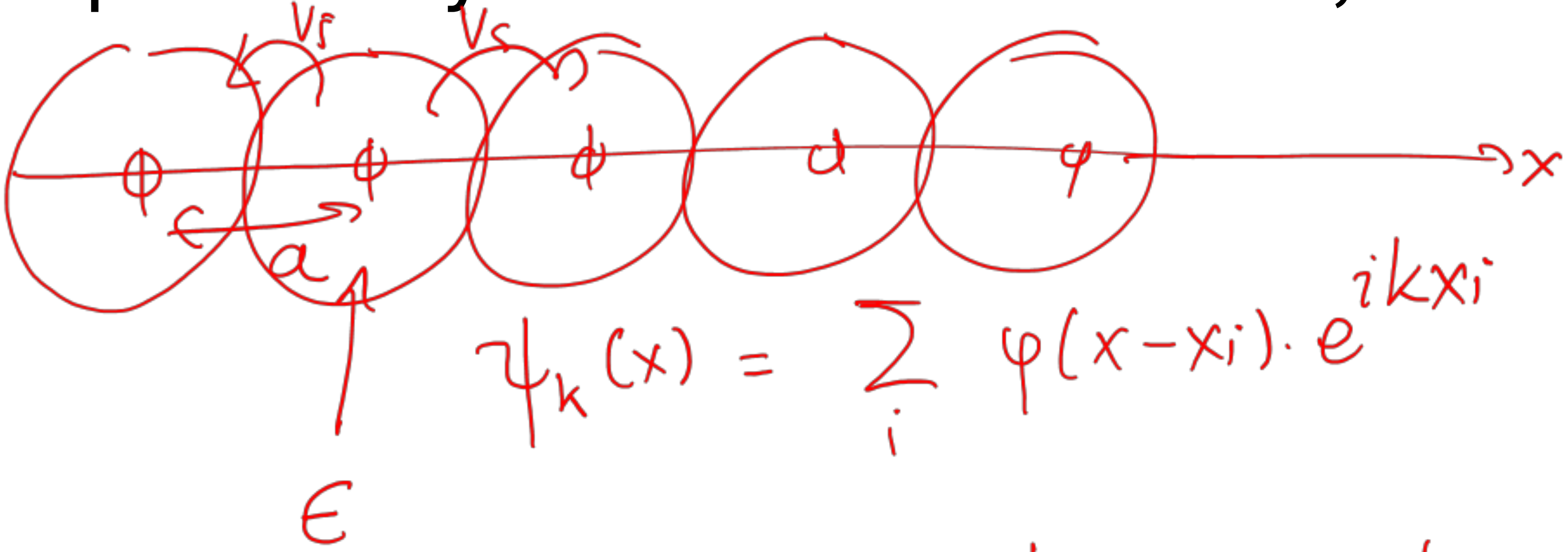
(satisfies Bloch theorem).

Number of unknown coefficients= one for each orbital in the unit cell

Tight binding recipe

- Find how many orbitals are in the unit cell (*M*). Each orbital in the unit cell will give rise to one band in the crystal.
- Create an *M*×*M* matrix. For each matrix element, write down the interaction matrix element between an orbital and itself or its neighbors.
- If it is a diagonal matrix element and the interaction is between an atom and itself in the same unit cell, use ε_i = **energy of atomic orbital** *i*.
- If it is a diagonal matrix element and the interaction is between an atom and itself in a different unit cell that differs by $\vec{R}$, use the **interatomic matrix element** (V_s, $V_{pp\sigma}$, etc.) and multiply by the factor $e^{i\vec{k}\cdot\vec{R}}$
- If it is an off-diagonal matrix element between atoms that differ by $\overrightarrow{\Delta r}$, use the **interatomic matrix element** and multiply by the factor $e^{i\vec{k}\cdot\overrightarrow{\Delta r}}$
- Diagonalize the matrix. The *M* eigenvalues as a function of $\vec{k}$ are the *M* bands of the crystal.

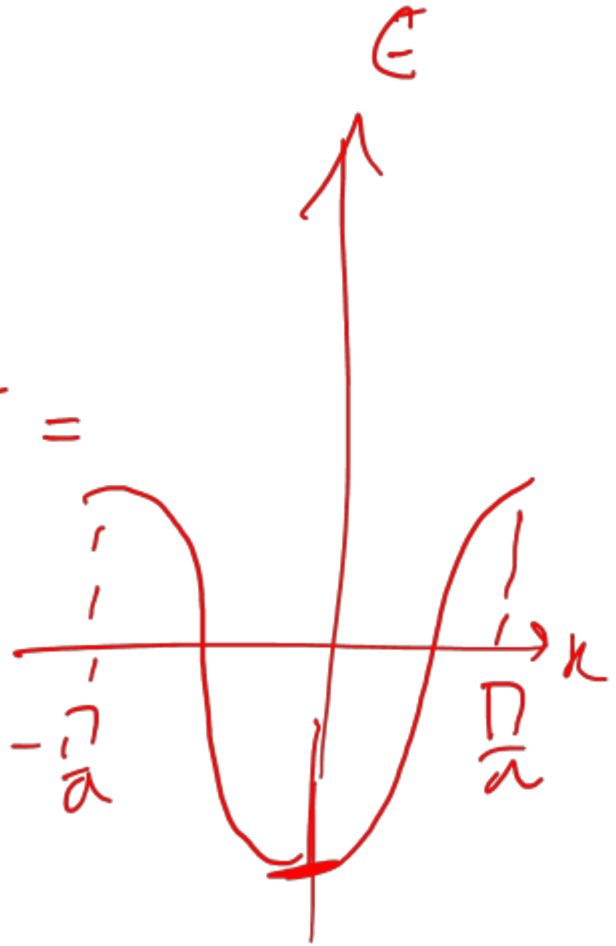
Example: 1D crystal with one atom/cell, one orbital/atom



$$\psi_k(x) = \sum_i \varphi(x-x_i)\cdot e^{ikx_i}$$

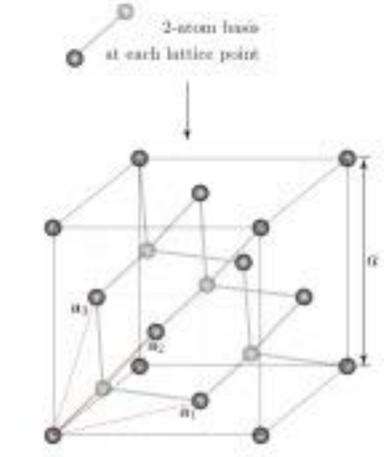
$$E = \epsilon_s + V_s\cdot e^{ika} + V_s e^{-ika} =$$

$$= \epsilon_s + 2V_s\cdot\cos(ka)$$



For 3D semiconductor crystals (e.g., Si):

2 atoms x (one *s* + three *p* orbitals per atom) = 8 unknown coefficients, 8 bands.



Crystal structure of silicon, diamond, GaAs, etc...

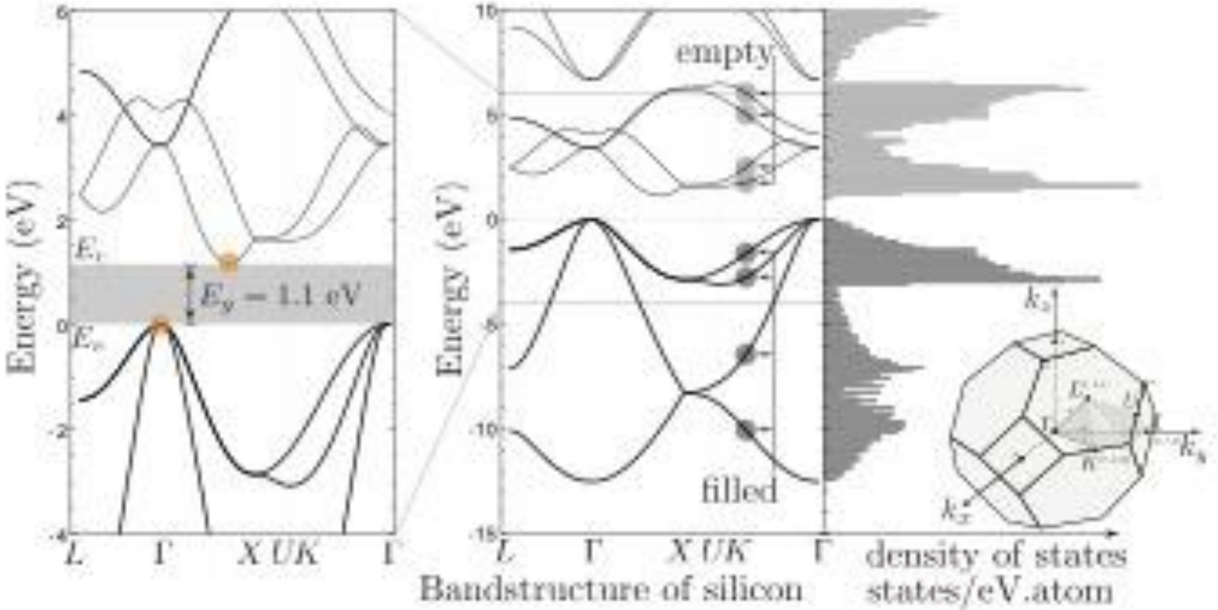
$$\begin{array}{c|cccccccccc}
 & |s^A\rangle & |p_x^A\rangle & |p_y^A\rangle & |p_z^A\rangle & |s^{A\star}\rangle & |s^B\rangle & |p_x^B\rangle & |p_y^B\rangle & |p_z^B\rangle & |s^{B\star}\rangle \\
\hline
\langle s^A| & E_s^A & 0 & 0 & 0 & 0 & V_0 g_0(\mathbf{k}) & V_1 g_1(\mathbf{k}) & V_1 g_2(\mathbf{k}) & V_1 g_3(\mathbf{k}) & 0 \\
\langle p_x^A| & 0 & E_p^A & 0 & 0 & 0 & -V_1 g_1(\mathbf{k}) & V_2 g_0(\mathbf{k}) & V_3 g_3(\mathbf{k}) & V_3 g_2(\mathbf{k}) & -V_5 g_1(\mathbf{k}) \\
\langle p_y^A| & 0 & 0 & E_p^A & 0 & 0 & -V_1 g_2(\mathbf{k}) & V_3 g_3(\mathbf{k}) & V_2 g_0(\mathbf{k}) & V_3 g_1(\mathbf{k}) & -V_5 g_2(\mathbf{k}) \\
\langle p_z^A| & 0 & 0 & 0 & E_p^A & 0 & -V_1 g_3(\mathbf{k}) & V_3 g_2(\mathbf{k}) & V_3 g_1(\mathbf{k}) & V_2 g_0(\mathbf{k}) & -V_5 g_3(\mathbf{k}) \\
\langle s^{A\star}| & 0 & 0 & 0 & 0 & E_s^{A\star} & 0 & V_4 g_1(\mathbf{k}) & V_4 g_2(\mathbf{k}) & V_4 g_3(\mathbf{k}) & 0 \\
\langle s^B| & \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & E_s^B & 0 & 0 & 0 & 0 \\
\langle p_x^B| & \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & 0 & E_p^B & 0 & 0 & 0 \\
\langle p_y^B| & \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & 0 & 0 & E_p^B & 0 & 0 \\
\langle p_z^B| & \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & 0 & 0 & 0 & E_p^B & 0 \\
\langle s^{B\star}| & \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & 0 & 0 & 0 & 0 & E_s^{B\star}
\end{array},$$

where c.c. stands for the complex conjugate (e.g. $H_{71} = H_{17}^\star$).

$$\begin{aligned}
V_0 &= V_{ss\sigma}, \\
V_1 &= \tfrac{1}{\sqrt{3}} V_{sp\sigma}, \\
V_2 &= \tfrac{1}{3} V_{pp\sigma} - \tfrac{2}{3} V_{pp\pi}, \\
V_3 &= \tfrac{1}{3} V_{pp\sigma} + \tfrac{1}{3} V_{pp\pi}, \\
V_4 &= V_{s^\star p}, \text{ and } V_5 = V_{pastc}.
\end{aligned}$$

$$\begin{aligned}
g_0(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{n_1}} + e^{i\mathbf{k}\cdot\mathbf{n_2}} + e^{i\mathbf{k}\cdot\mathbf{n_3}} + e^{i\mathbf{k}\cdot\mathbf{n_4}}, \\
g_1(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{n_1}} - e^{i\mathbf{k}\cdot\mathbf{n_2}} - e^{i\mathbf{k}\cdot\mathbf{n_3}} + e^{i\mathbf{k}\cdot\mathbf{n_4}}, \\
g_2(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{n_1}} - e^{i\mathbf{k}\cdot\mathbf{n_2}} + e^{i\mathbf{k}\cdot\mathbf{n_3}} - e^{i\mathbf{k}\cdot\mathbf{n_4}}, \\
g_3(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{n_1}} + e^{i\mathbf{k}\cdot\mathbf{n_2}} - e^{i\mathbf{k}\cdot\mathbf{n_3}} - e^{i\mathbf{k}\cdot\mathbf{n_4}}
\end{aligned}$$

Details and values of parameters for various semiconductors in D. Jena, *Quantum Physics of Semiconductor Materials and Devices*

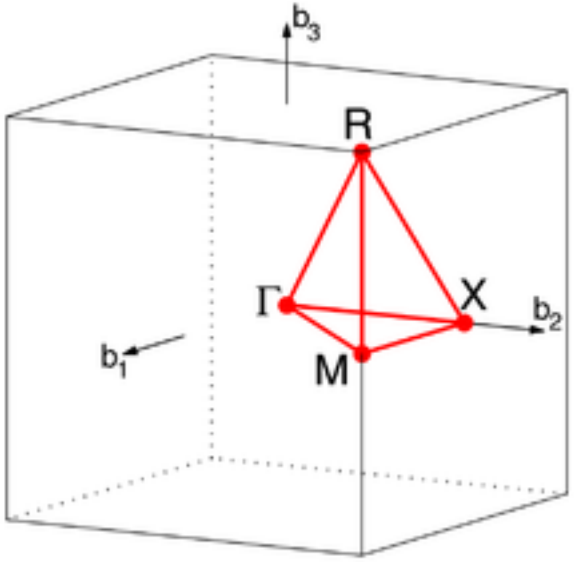


Bandstructure of silicon

1D: B-Z: $[-\frac{\pi}{a}, \frac{\pi}{a}]$

3D: Brillouin zone of fcc and bcc lattice

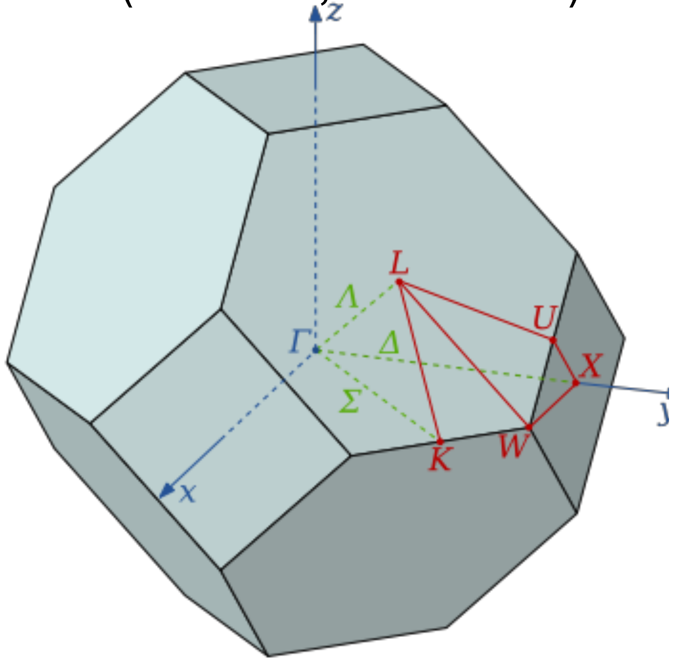
Simple cubic



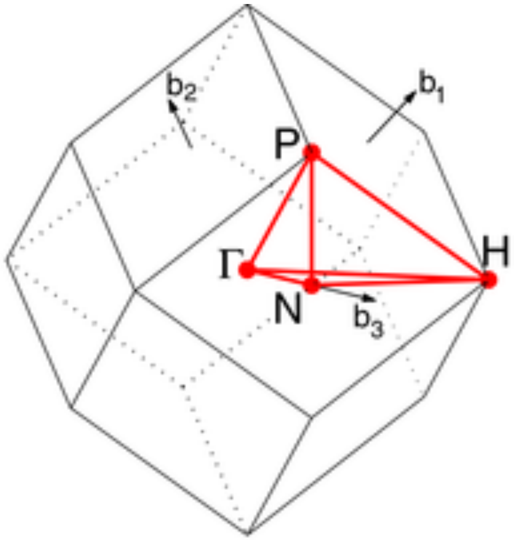
CUB path: Γ-X-M-Γ-R-X|M-R

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

FCC (diamond, zincblende)



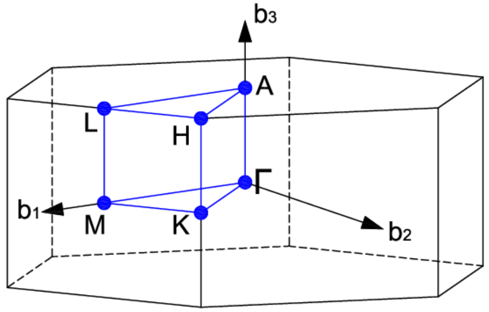
BCC



BCC path: Γ-H-N-Γ-P-H|P-N

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

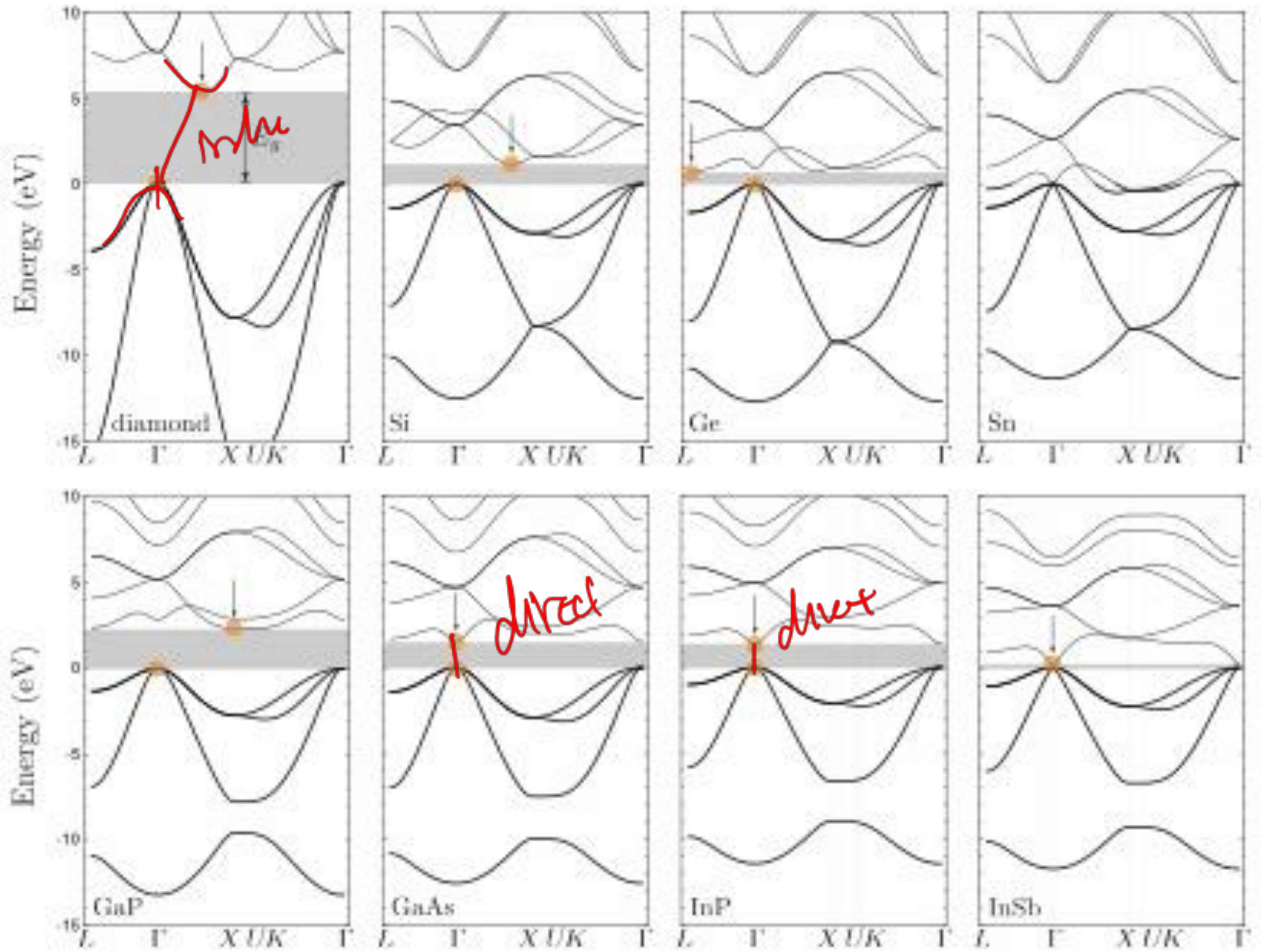
HCP (wurtzite)

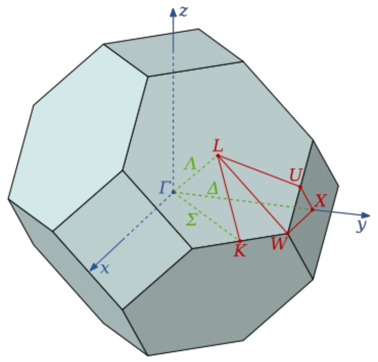


10.48550/arXiv.1807.10054

https://en.wikipedia.org/wiki/Brillouin_zone

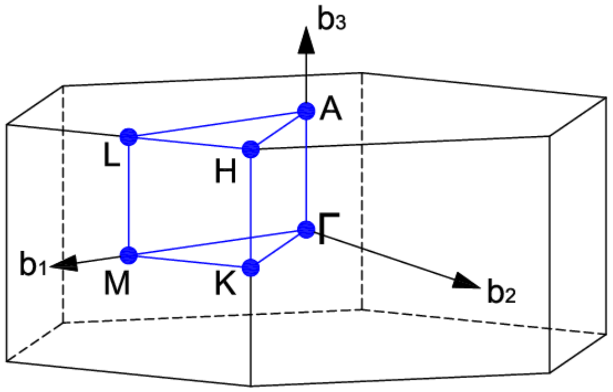
Band structures of zincblende semiconductors



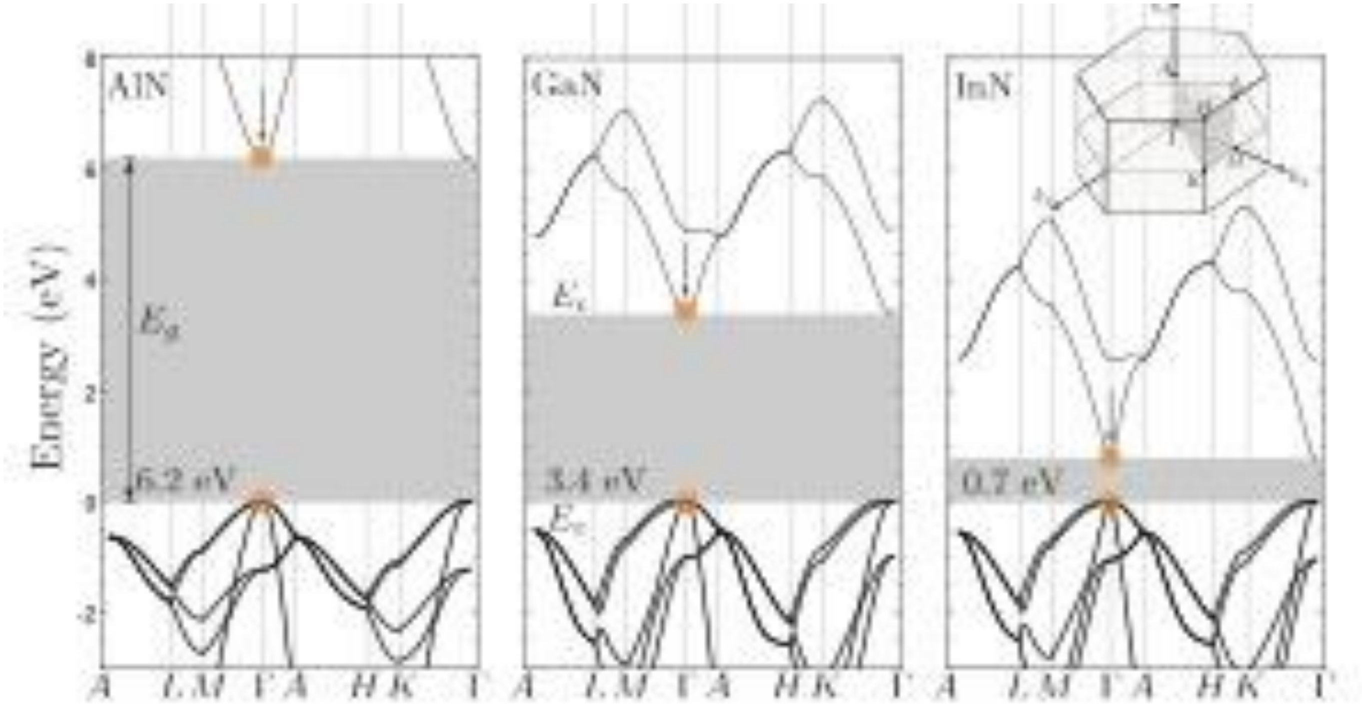


What features do you notice in the band structure of each material?

Band structures of AlN, GaN, InN

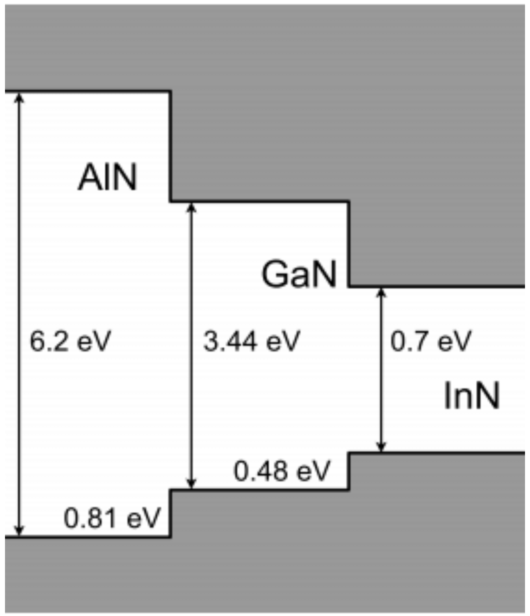


(Energies referenced to highest occupied state)



D. Jena, Quantum Physics of Semiconductor Materials and Devices

Relative band alignment



https://urn.fi/URN:NBN:fi:aalto-201412043135