

Lecture 7

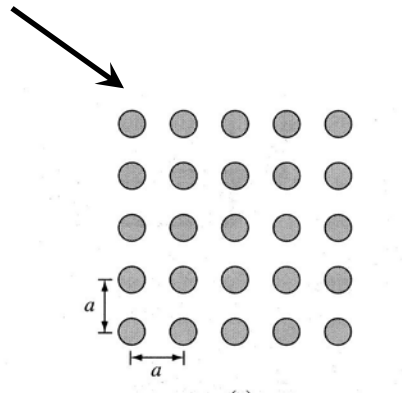
3D Crystals and Band Structure

Reading:

Notes and Brennan Chapter 7.4, 8.0-8.2

Importance of k -Space Boundaries at $k=(\pm)\pi/a$ Crystal Structures, Brillouin Zones and Bragg Reflection

The crystal lattice consists of a periodic array of atoms.

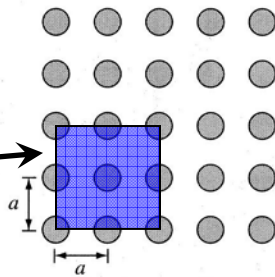


Unit Cell Concept

While crystals have rotational symmetry, we restrict ourselves to methods of reconstructing the entire crystal (every lattice point) using translation of a unit cell (a special type known as a Bravais cell) only – no rotation.

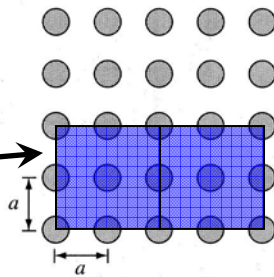
Unit Cell Concept

A “building block” that can be periodically duplicated to result in the crystal lattice is known as the “unit cell”.



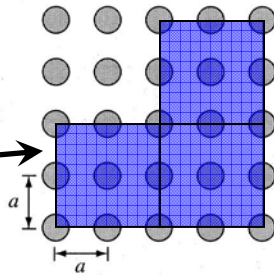
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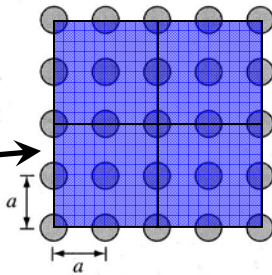
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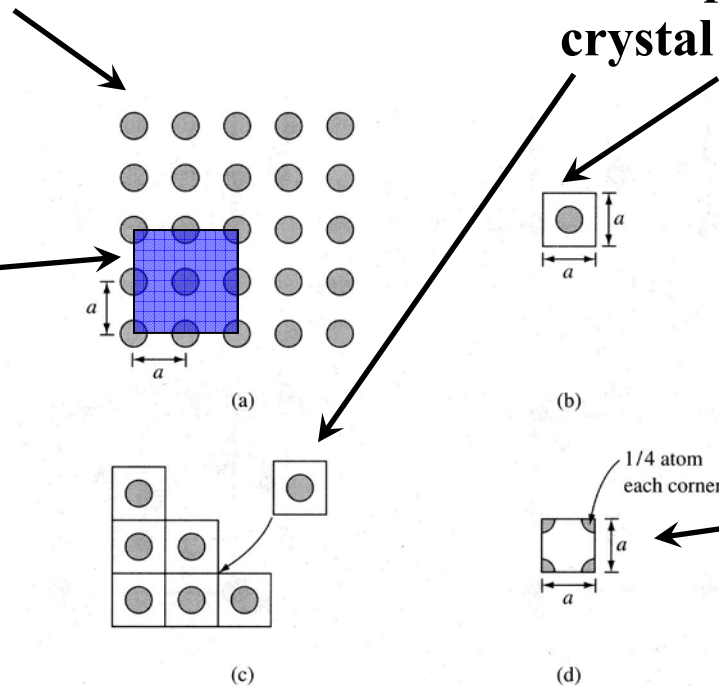


Unit Cell Concept

The crystal lattice consists of a periodic array of atoms.

A “building block” that can be periodically duplicated to result in the crystal lattice is known as the “unit cell”.

The smallest “building block” that can be periodically duplicated to result in the crystal lattice is known as the “primitive unit cell”.

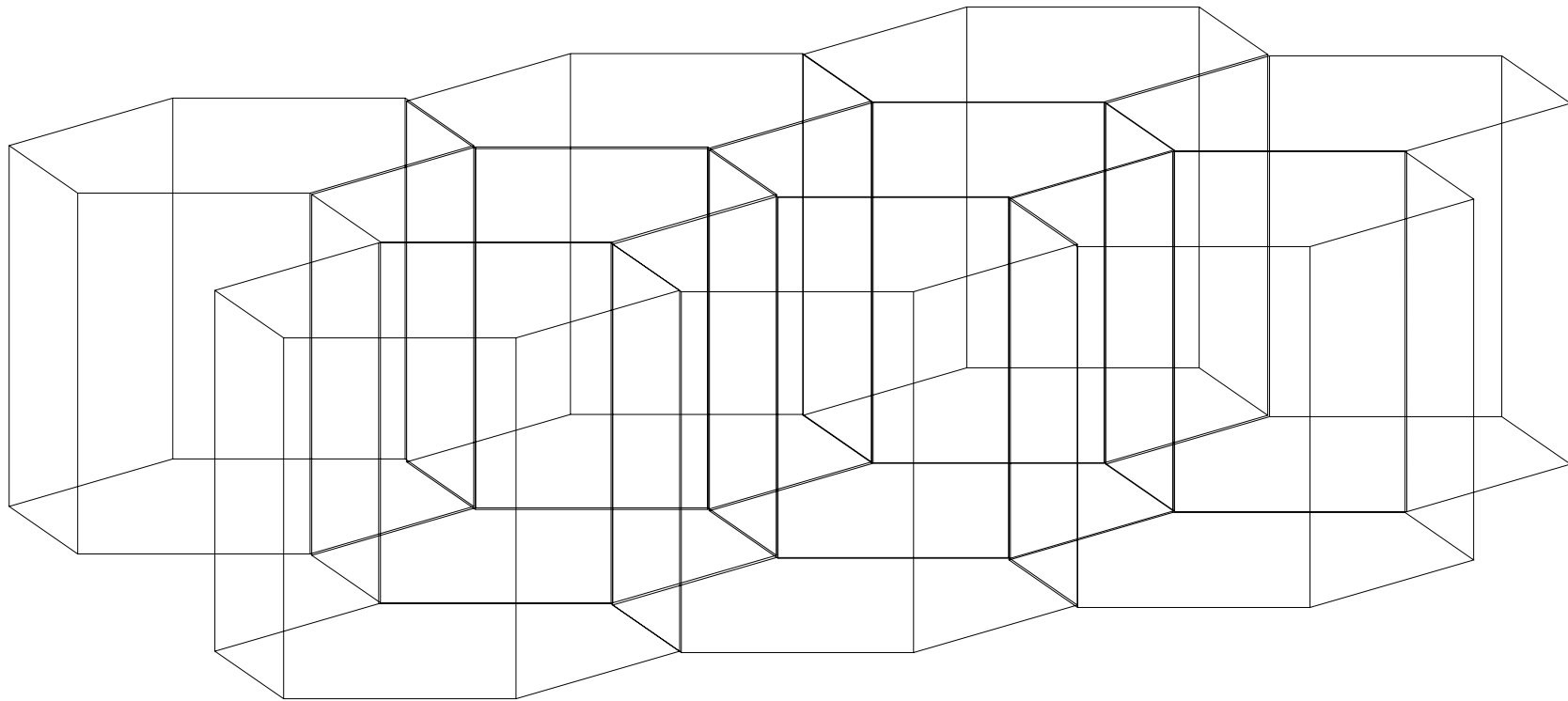


The unit cell may not be unique.

Figure 1.2 Introduction to the unit cell method of describing atomic arrangements within crystals. (a) Sample two-dimensional lattice. (b) Unit cell corresponding to the part (a) lattice. (c) Reproduction of the original lattice. (d) An alternative unit cell.

Unit Cell Concept: Translation of a 3D Bravais Lattice

Deconstructing a Hexagonal Crystal From a Trigonal P Bravais Lattice



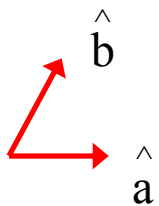
Side View

Unit Cell Concept: Translation of a 3D Bravais Lattice

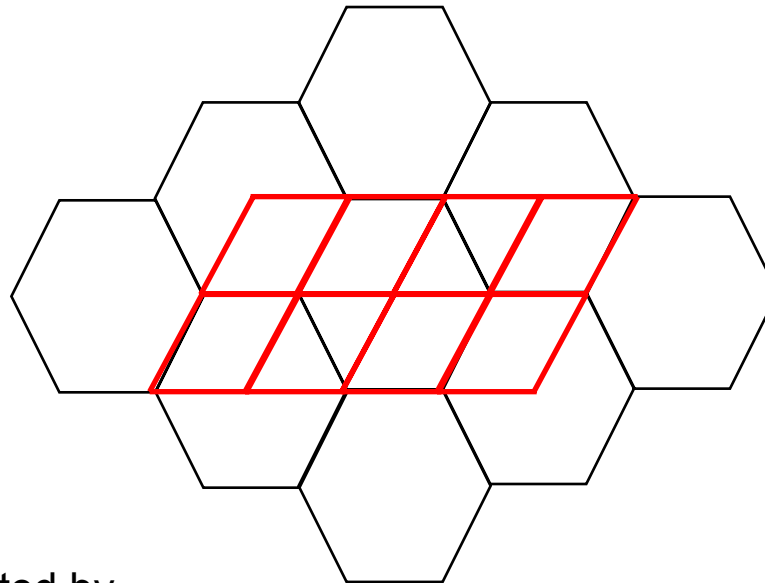
Deconstructing a Hexagonal Crystal From a Trigonal P Bravais Lattice

Real space lattice vector $\vec{R} = l_1 \hat{a} + l_2 \hat{b} + l_3 \hat{c}$

Note : \hat{a} , \hat{b} and \hat{c} do not have to be orthogonal!



\hat{c} is pointed out of the plane.



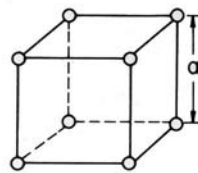
The crystal is reconstructed by translating the Bravais Lattice along vectors with 60 degree symmetry.

Top View with
Trigonal Lattice
Apparent

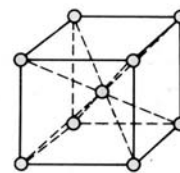
Unit Cell Concept

Lattice Constant: A length that describes the unit cell. It is normally given in Å, angstroms = $1e-10$ meters.

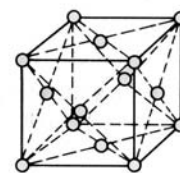
Diamond Structure:
Constructed by 2
“inter-penetrating”
FCC Lattices



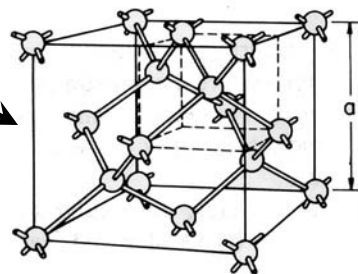
SIMPLE CUBIC
(P, etc)



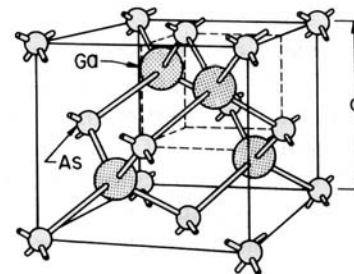
BODY-CENTERED CUBIC
(Na, W, etc)



FACE-CENTERED CUBIC
(Al, Au, etc)



DIAMOND
(C, Ge, Si, etc)



ZINCBLENDE
(GaAs, GaP, etc)

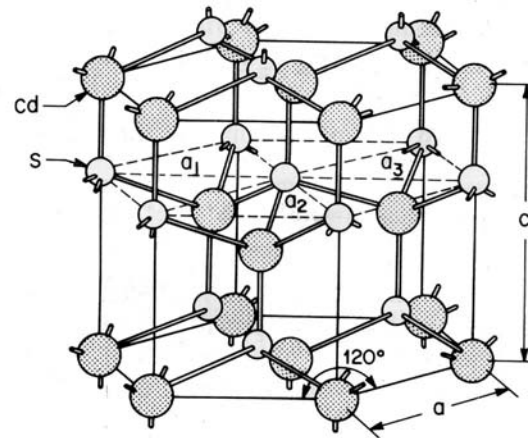
Zincblende is a diamond structure with every other atom a different element. Example: Ga only bonds to As and As only bonds to Ga.

Note: In class
show Diamond™
examples.

Fig. 1 Some important unit cells (direct lattices) and their representative elements or compounds; a is the lattice constant.

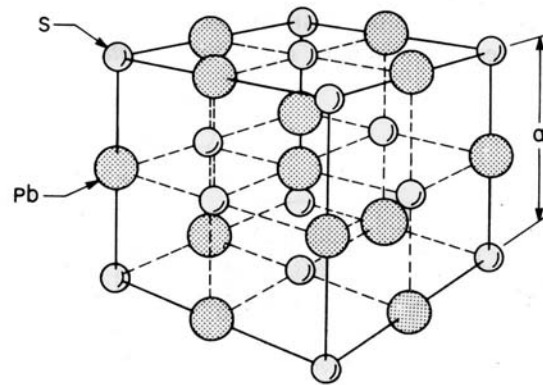
Unit Cell Concept

Some unit cells have hexagonal symmetry.



(a)

Rocksalt unit cells are one of the simplest practical unit cells.



(b)

Fig. 2 Two unit cells of compound semiconductors. (a) Wurtzite lattice (CdS, ZnS, etc.). (b) Rock-salt lattice (PbS, PbTe, etc.).

k-space or Reciprocal Space Description of a Crystal

Since the Bloch wavefunction is distributed throughout the crystal, the position of the electron is highly delocalized. Thus, from the uncertainty principle, the momentum of the electron in the crystal should be well defined*.

Therefore, it is convenient for us to consider the k-space equivalent of the crystal and in particular the Reciprocal Lattice.

Given a real space lattice vector $\vec{R} = l_1 \hat{a} + l_2 \hat{b} + l_3 \hat{c}$

then we can define a reciprocal lattice vector $\vec{G} = h \hat{a}^* + k \hat{b}^* + l \hat{c}^*$ by,

$\vec{G} \cdot \vec{R} = 2\pi n$ where n is an integer.

$$\hat{a}^* = 2\pi \frac{\begin{pmatrix} \hat{b} \times \hat{c} \end{pmatrix}}{\text{Volume of Real Space Unit Cell}} \quad \hat{b}^* = 2\pi \frac{\begin{pmatrix} \hat{c} \times \hat{a} \end{pmatrix}}{\text{Volume of Real Space Unit Cell}} \quad \hat{c}^* = 2\pi \frac{\begin{pmatrix} \hat{a} \times \hat{b} \end{pmatrix}}{\text{Volume of Real Space Unit Cell}}$$

The RS unit cell fully reconstructs the entire reciprocal space via only translations just like the real space unit cell reconstructs the entire crystal via only translations.

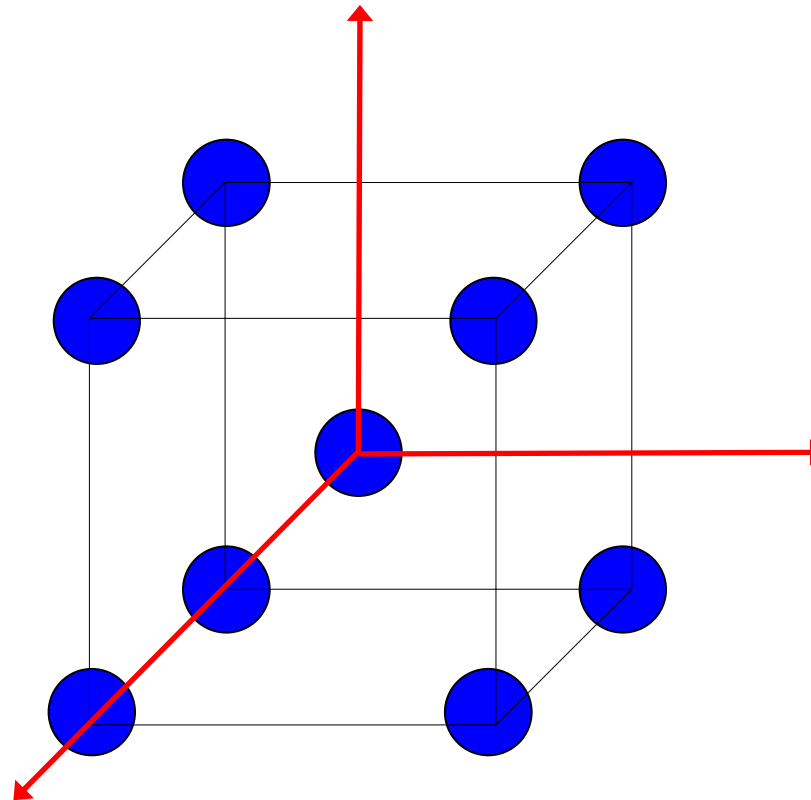
Note that the Reciprocal space unit cell maintains the same symmetry as the real space unit cell because it was derived from the real space unit cell.

* Strictly speaking the Bloch wavefunction is not an eigenfunction of the momentum operator and thus, the momentum is not exactly known. However, due to the uncertainty principle, the vast delocalization of the electron in the crystal (in Bloch states) will result in well defined but not singular value of momentum. Thus, to a good approximation, the electrons in the crystal will be treated as nearly free electrons with well defined momentum.

$$\hat{a}^* = 2\pi \frac{\begin{pmatrix} \hat{b} \times \hat{c} \end{pmatrix}}{\hat{a} \cdot \hat{b} \times \hat{c}} \quad \hat{b}^* = 2\pi \frac{\begin{pmatrix} \hat{c} \times \hat{a} \end{pmatrix}}{\hat{a} \cdot \hat{b} \times \hat{c}} \quad \hat{c}^* = 2\pi \frac{\begin{pmatrix} \hat{a} \times \hat{b} \end{pmatrix}}{\hat{a} \cdot \hat{b} \times \hat{c}}$$

k-space or Reciprocal Space Description of a Crystal

An example for a Body Centered Cubic (BCC) RECIPROCAL LATTICE material*.

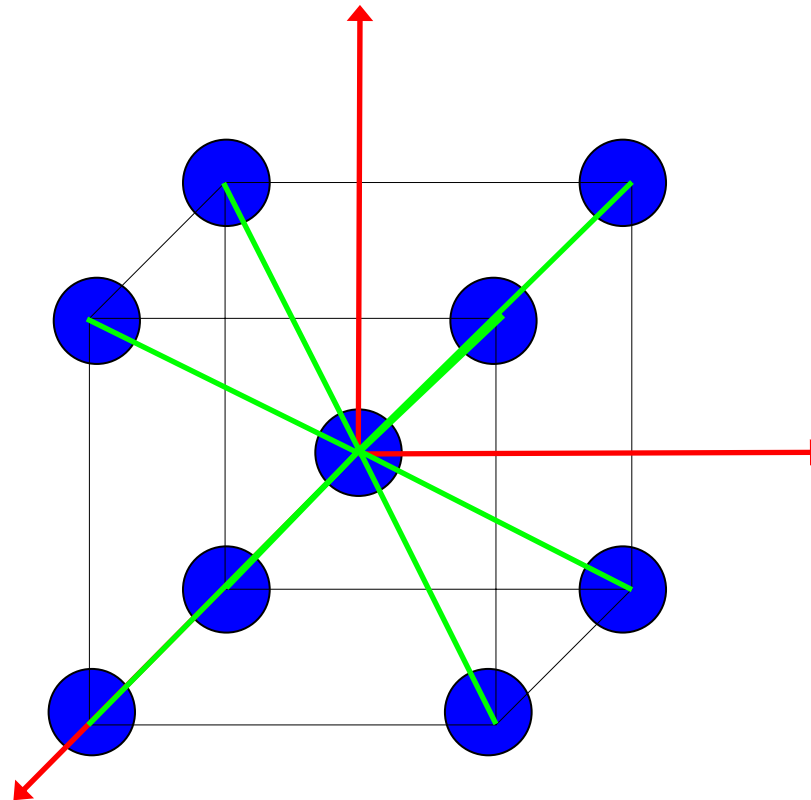


*It can be shown that the Face centered cubic and Body centered cubic structures are Fourier analogs so the above example is the reciprocal lattice equivalent of an FCC crystal.



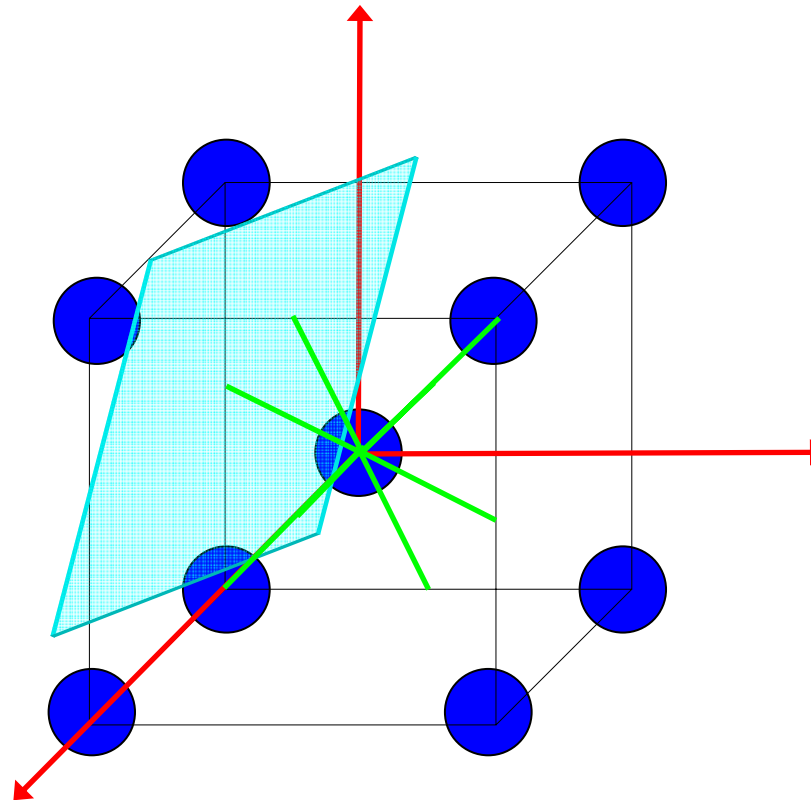
k-space or Reciprocal Space Description of a Crystal

Connect an arbitrary lattice point to all of its nearest neighbors (green lines)...



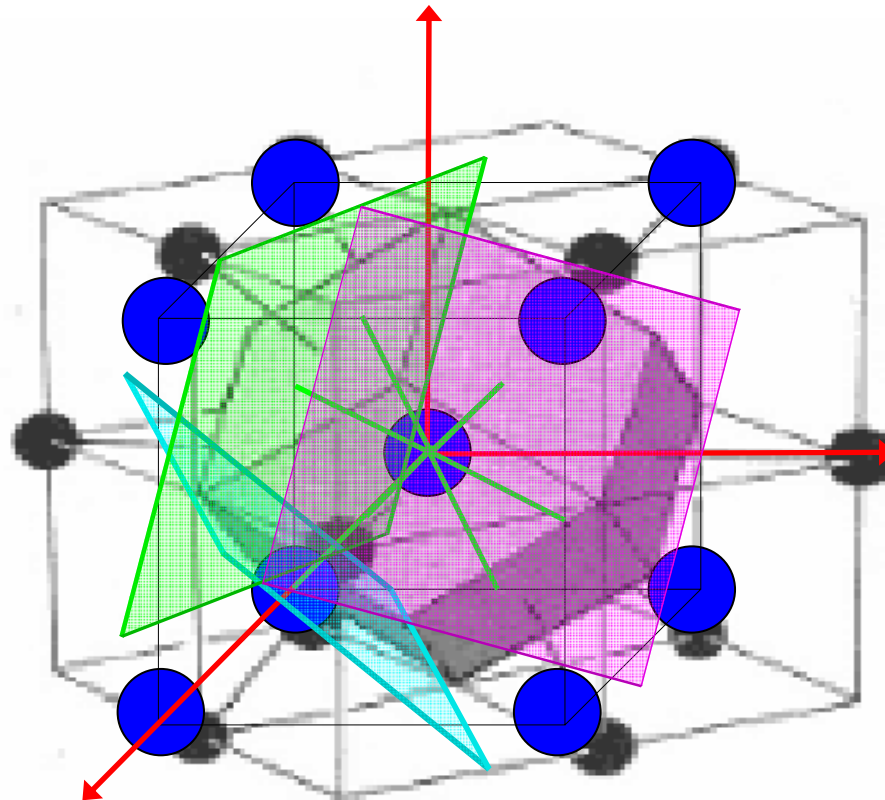
k-space or Reciprocal Space Description of a Crystal

...construct the perpendicular bisectors to all of these lines. The 1st Brillouin Zone is the volume enclosed within this region.



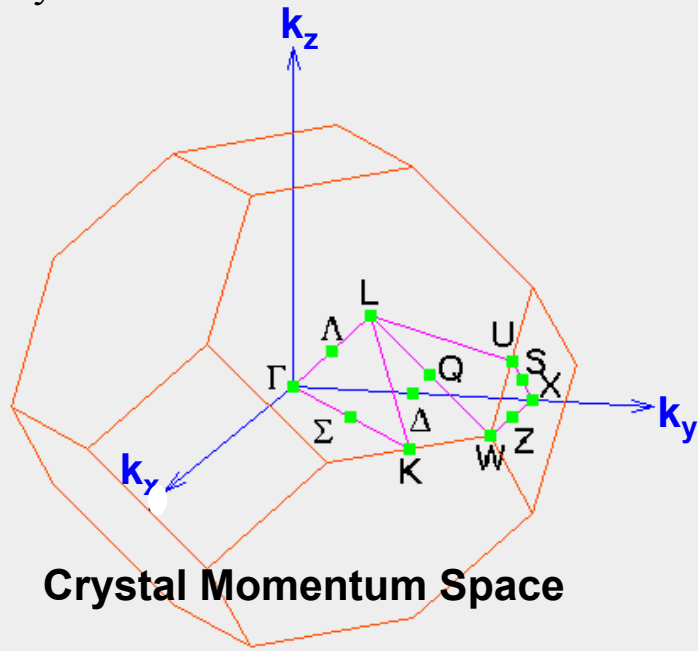
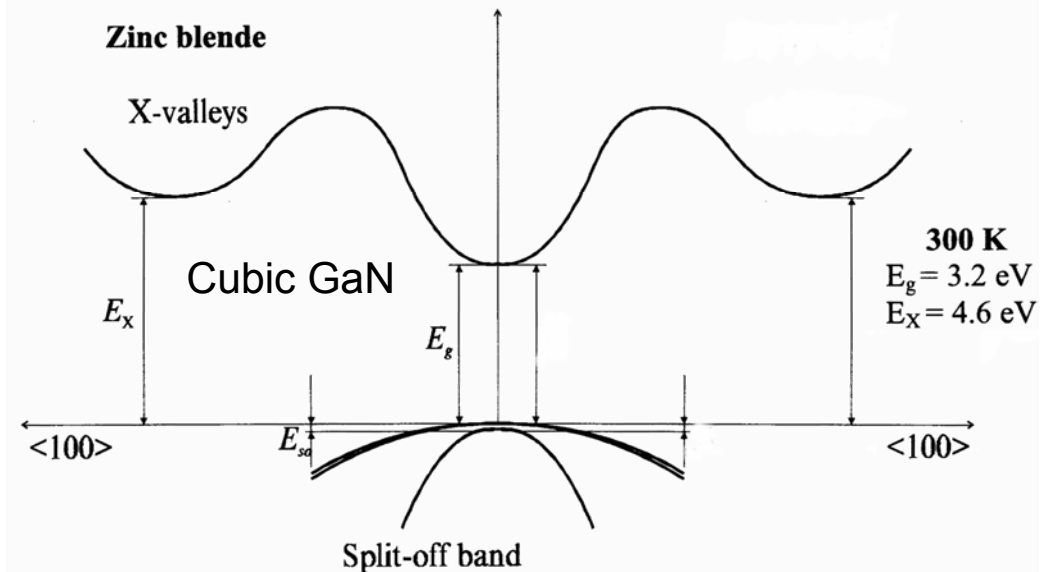
k-space or Reciprocal Space Description of a Crystal

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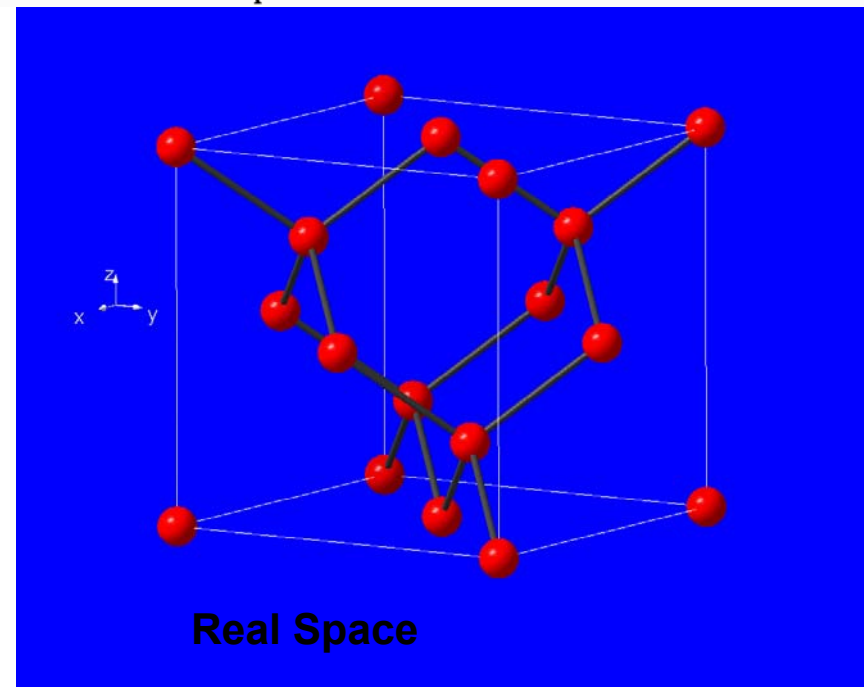


Now consider the 3D periodic potential in a cubic crystal

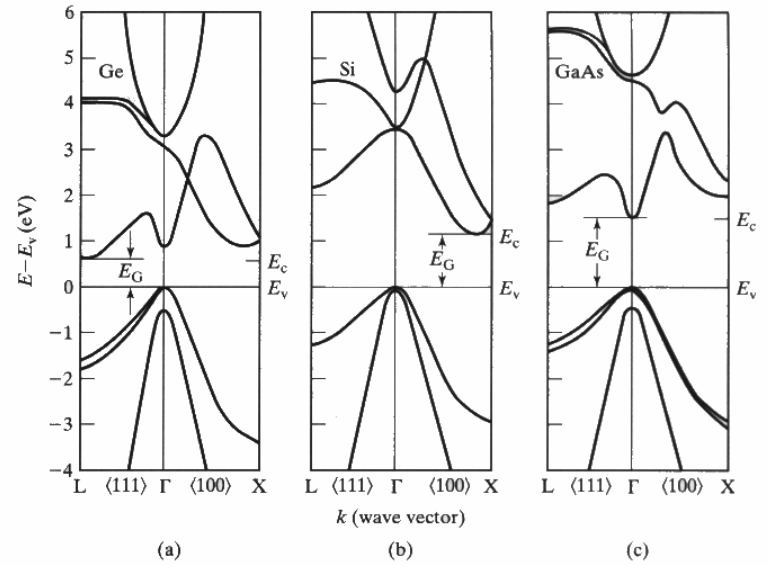
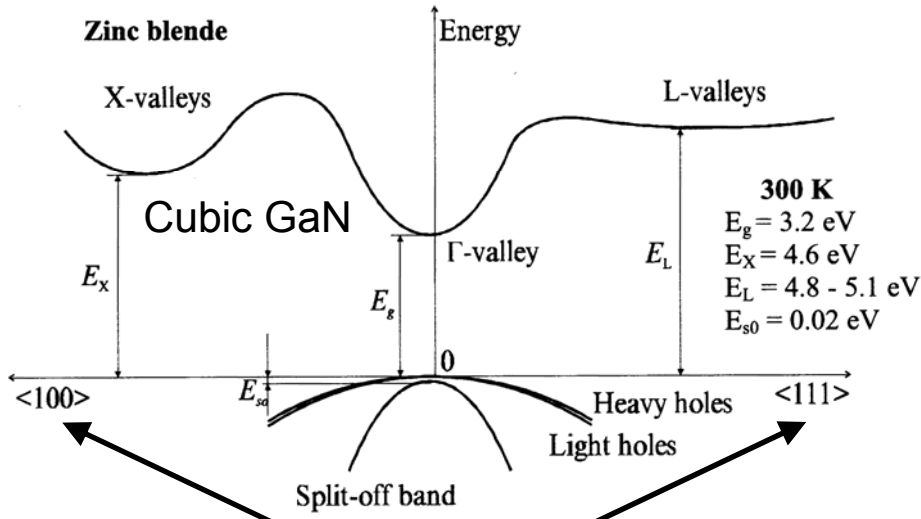
- Different potentials exist in different directions
- Electron wavelength and crystal momentum, $k=2\pi/\lambda$, differs with direction
- Plots of E-k are 4D plots, thus have to be represented in other ways (as slices along certain directions).
- Many different parabolic E-k relationships exist depending on our crystalline momentum



<http://britneyspears.ac/physics/dos/dos.htm>



Now consider the 3D periodic potential in a cubic crystal



• All equivalent directions give redundant information and thus are not repeated

• Most important k-space points

- Γ -point is the center of crystal momentum space (k-space) at $k=0$

- X-point is the edge of the first Brillouin zone (π/L edge) of crystal momentum space (k-space) in the $\langle 100 \rangle$ direction

- L-point is the edge of the first Brillouin zone (π/L edge) of crystal momentum space (k-space) in the $\langle 111 \rangle$ direction

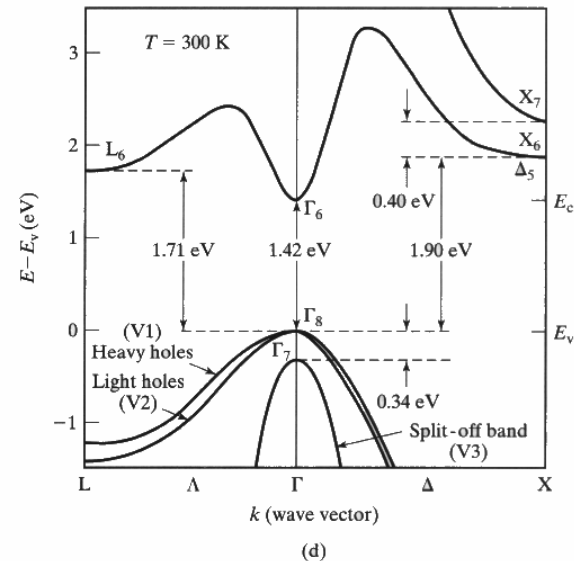
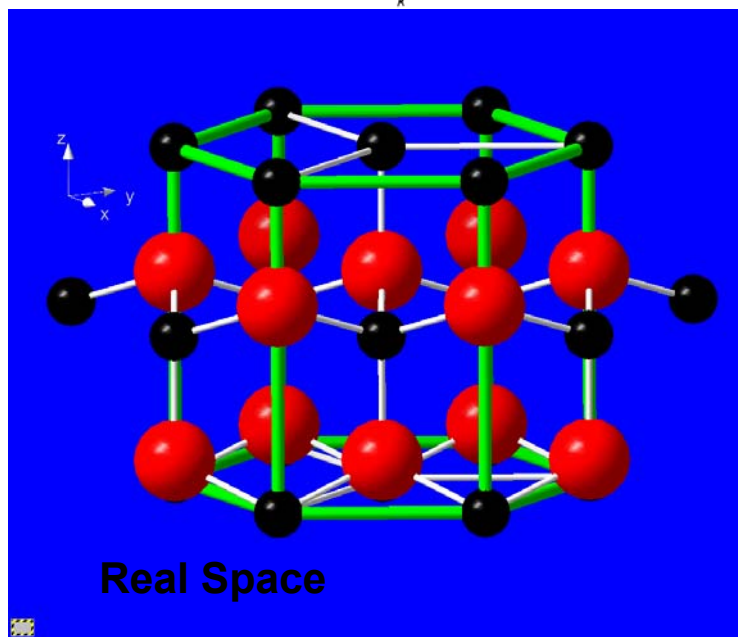
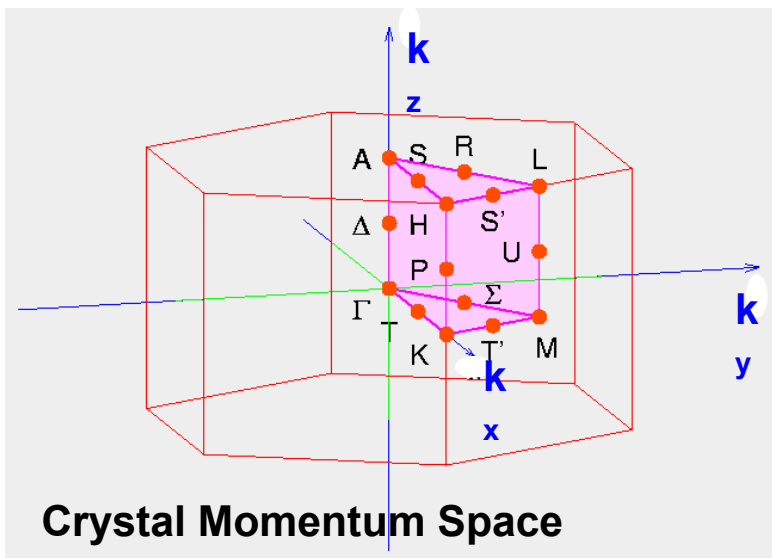
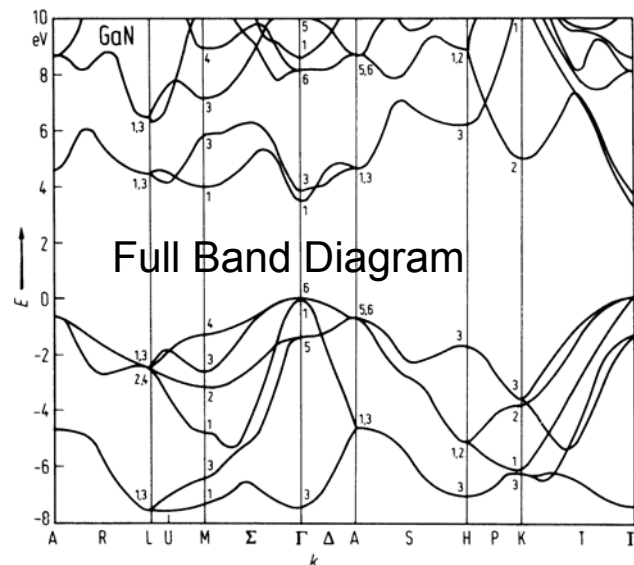
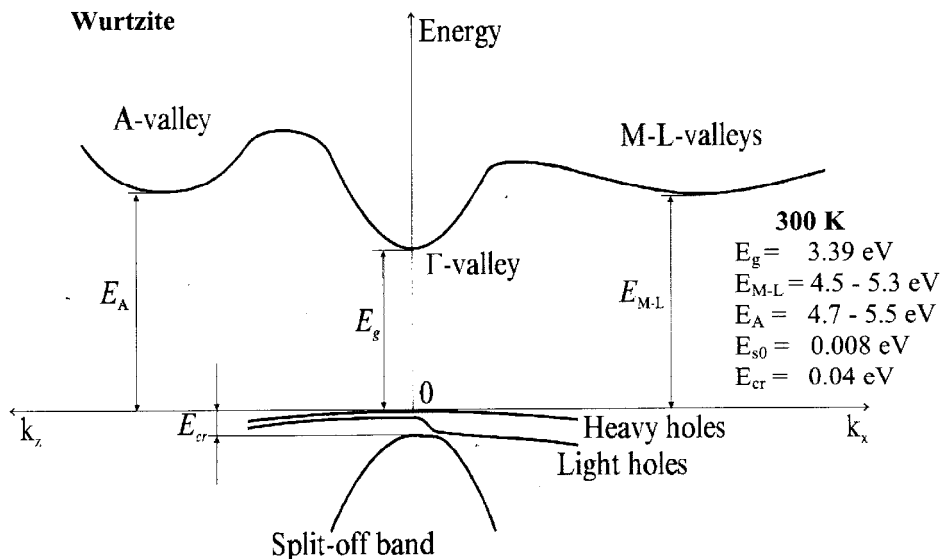
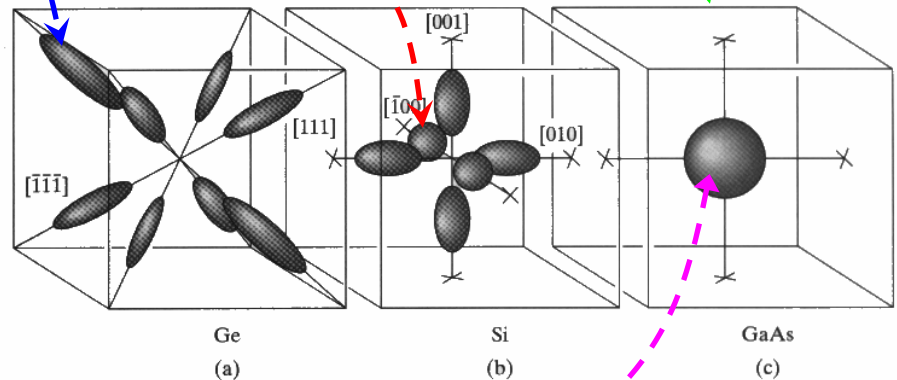
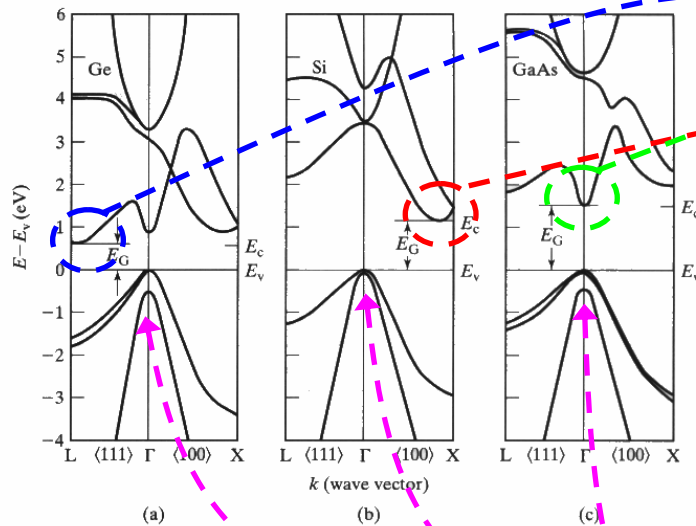


Figure 3.13 $\langle 100 \rangle / \langle 111 \rangle$ E-k diagrams characterizing the conduction and valence bands of (a) Ge, (b) Si, and (c, d) GaAs. [(a-c) after Sze^[2]; (d) from Blakemore.^[1] Reprinted with permission.] Neudeck and Peirret Fig 3.13

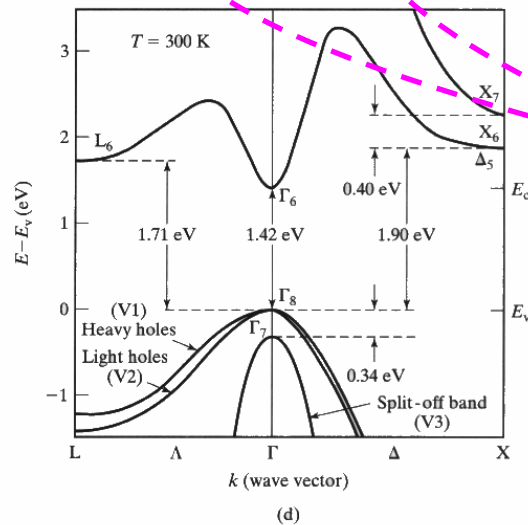
Now consider the 3D periodic potential in a hexagonal crystal



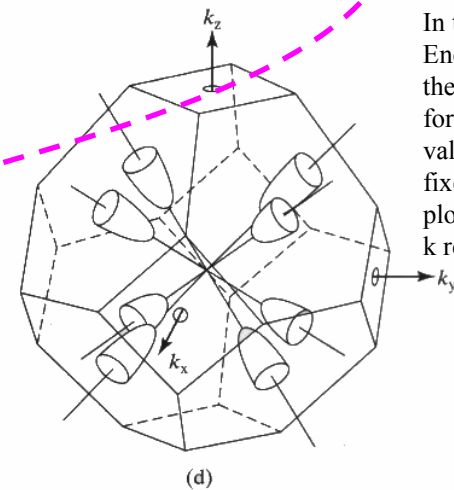
Where are the electron trajectories/momentum vectors in the crystal?



Si E_C minima occurs at $\sim 0.8(\pi/a)$



Valence Band E-k and constant energy surfaces all look similar



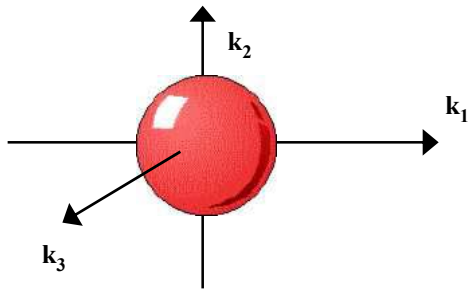
In these figures, the Energy is fixed near the band edges ($E > E_C$ for example) and all values of k having this fixed energy are plotted to give a 3D E-k representation.

Figure 3.13 $\langle 100 \rangle / \langle 111 \rangle$ E-k diagrams characterizing the conduction and valence bands of (a) Ge, (b) Si, and (c, d) GaAs. [(a-c) after Sze^[2]; (d) from Blakemore.^[1] Reprinted with permission.]
Neudeck and Peirret Fig 3.13

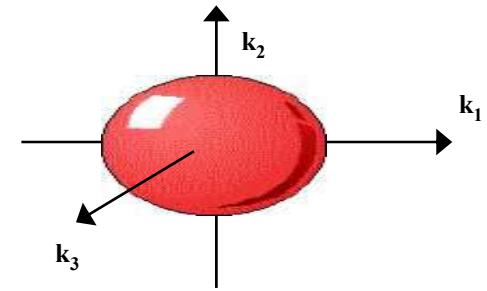
Constant-energy surfaces characterizing the conduction-band structure in (a, d) Ge, (b) Si, and (c) GaAs. (d) Shows the truncation of the Ge surfaces at the Brillouin-zone boundaries. [(a-c) after Sze^[2] and Ziman^[3]; (d) from McKelvey.^[4] Reprinted with permission; the latter from Robert E. Krieger Publishing Co., Malabar, FL.]
Neudeck and Peirret Fig 3.14

3D Crystalline Effects on Effective Mass

For Valence Bands and E_C of Direct gap materials,



For E_C of Indirect gap materials,



$$m^* a = F$$

So for 3D crystals

$$\frac{d\vec{v}}{dt} = \frac{1}{m^*} \vec{F} \quad \text{where} \quad \frac{1}{m^*} = \begin{pmatrix} m_{xx}^{-1} & m_{xy}^{-1} & m_{xz}^{-1} \\ m_{yx}^{-1} & m_{yy}^{-1} & m_{yz}^{-1} \\ m_{zx}^{-1} & m_{zy}^{-1} & m_{zz}^{-1} \end{pmatrix} \quad \text{and} \quad m_{ij}^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j} \quad \text{for } i, j = x, y \text{ and } z$$

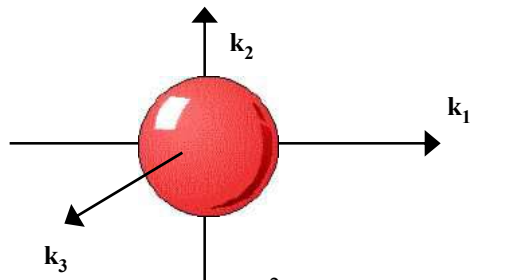
$$E - E_C = \frac{\hbar^2}{2m_e^*} (k_1^2 + k_2^2 + k_3^2)$$

$$E - E_C = \frac{\hbar^2}{2m_l^*} k_1^2 + \frac{\hbar^2}{2m_t^*} (k_2^2 + k_3^2)$$

where m_l^* and m_t^* are the longitudinal and transverse effective masses

3D Crystalline Effects on Effective Mass

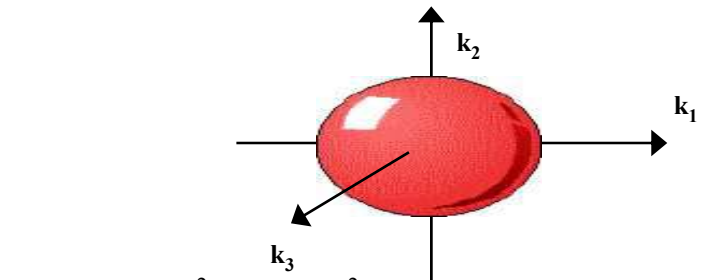
For Valence Bands and E_C of Direct gap materials,



$$E - E_C = \frac{\hbar^2}{2m_e^*} (k_1^2 + k_2^2 + k_3^2)$$

where m_l^* and m_t^* are the longitudinal and transverse effective masses

For E_C of Indirect gap materials,



$$E - E_C = \frac{\hbar^2}{2m_l^*} k_1^2 + \frac{\hbar^2}{2m_t^*} (k_2^2 + k_3^2)$$

For the ellipsoid case, we can define an average effective mass for electrons m_n^* that

averages the anisotropic properties. This is valid being that many scattering events occur and

thus, the anisotropic properties of the crystal are effectively averaged. To do so, we define a spherical

volume of radius $k_{\text{eff}} = \sqrt{\frac{2m_n^*(E_C - E)}{\hbar^2}}$ such that the volume of the new sphere is equal to the volume of ellipsoid. Thus,

$$\left(N_{\text{ellipsoids in 1st Brillouin Zone}} \left(\frac{4}{3} \pi k_1 k_2 k_3 \right) \right) = \frac{4}{3} \pi k_{\text{eff}}^3 \quad \text{this leads to,}$$

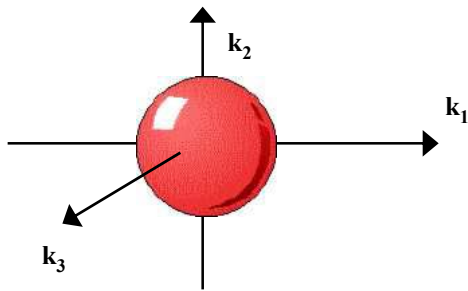
$$\left(N_{\text{ellipsoids in 1st Brillouin Zone}} \right) \left(\sqrt{m_l^* (m_t^*)^2} \right) = (m_n^*)^{3/2} \quad \text{so}$$

$$m_n^* = \left(N_{\text{ellipsoids in 1st Brillouin Zone}} \right)^{2/3} \left(m_l^* (m_t^*)^2 \right)^{1/3}$$

$$N_{\text{ellipsoids in 1st Brillouin Zone}} = 6 \text{ for Si and } (4 = \frac{1}{2} \cdot 8) \text{ for Ge}$$

3D Crystalline Effects on Effective Mass

For Valence Bands



Similarly for the valence band,

$$m_p^* = \left((m_{hh}^*)^{3/2} + (m_{lh}^*)^{3/2} \right)^{2/3}$$

where m_{lh}^* and m_{hh}^* are the light hole and heavy hole effective masses

Table 3.1 Electron and Hole Effective Masses in Ge,^[6] Si,^[7] and GaAs^[1] at 4 K. (All values referenced to the free electron rest mass m_0 .)

Effective Mass	Ge	Si	GaAs
m_e^*/m_0	1.588	0.9163	—
m_i^*/m_0	0.08152	0.1905	—
m_c^*/m_0	—	—	0.067 [†]
m_{hh}^*/m_0	0.347	0.537	0.51
m_{lh}^*/m_0	0.0429	0.153	0.082
m_{so}^*/m_0	0.077	0.234	0.154

[†] Band edge effective mass. The E - k relationship about the GaAs conduction-band minimum becomes non-parabolic and m_c^* increases at energies only slightly removed from E_c .

Table 4.1 Density of States Effective Masses for Ge, Si, and GaAs

Effective Mass	Ge	Si	GaAs	
m_n^*/m_0	T = 4 K	0.553	1.062	0.067
	T = 300 K	1.182	0.0655 [†]
m_p^*/m_0	T = 4 K	0.357	0.590	0.532
	T = 300 K	0.81	0.524

[†] The band edge effective mass ratio is 0.0632. The value quoted here takes into account the non-parabolic nature of the GaAs conduction band and yields the correct nondegenerate carrier concentrations when employed in computational expressions developed later in this chapter.

How do electrons and holes populate the bands?

Derivation of Density of States Concept

We can use the idea quantum confinement of a set of states (1D well region) to derive the number of states in a given volume (volume of our crystal).

Consider the surfaces of a volume of semiconductor to be infinite potential barriers (i.e. the electron can not leave the crystal). Thus, the electron is contained in a 3D box.

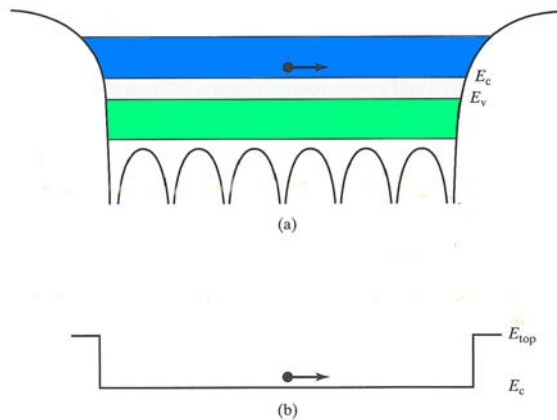


Figure 4.1 (a) Visualization of a conduction band electron moving in a crystal. (b) Idealized pseudo-potential well formed by the crystal surfaces and the band edges.

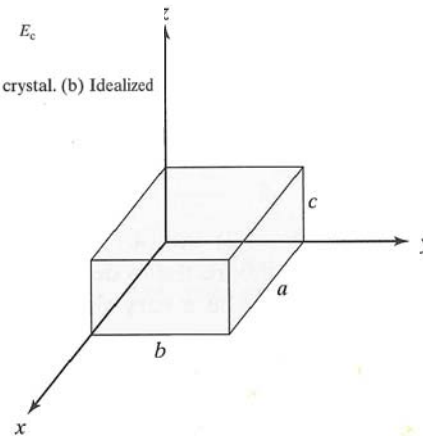


Figure 4.2 Envisioned crystal-sized box (infinitely deep three-dimensional potential well) with \$x\$, \$y\$, and \$z\$ dimensions of \$a\$, \$b\$, and \$c\$, respectively.

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \Psi = E \Psi$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} - E \Psi = 0$$

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + k^2 \Psi = 0$$

$$\dots \text{for } 0 < x < a, 0 < y < b, 0 < z < c$$

$$\text{where } k = \frac{2\pi}{\lambda} = \sqrt{\frac{2mE}{\hbar^2}} \text{ or } E = \frac{\hbar^2 k^2}{2m}$$

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Using separation of variables...

$$(1) \quad \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + k^2 \Psi = 0$$

$$(2) \quad \Psi(x, y, z) = \Psi_x(x) \Psi_y(y) \Psi_z(z)$$

Inserting (2) into (1) and dividing by (2) we get...

$$\frac{1}{\Psi_x(x)} \frac{\partial^2 \Psi_x(x)}{\partial x^2} + \frac{1}{\Psi_y(y)} \frac{\partial^2 \Psi_y(y)}{\partial y^2} + \frac{1}{\Psi_z(z)} \frac{\partial^2 \Psi_z(z)}{\partial z^2} + k^2 = 0$$

Since k is a constant for a given energy, each of the three terms on the left side must individually be equal to a constant.

$$\frac{1}{\Psi_x(x)} \frac{\partial^2 \Psi_x(x)}{\partial x^2} + k_x^2 = 0, \quad \frac{1}{\Psi_y(y)} \frac{\partial^2 \Psi_y(y)}{\partial y^2} + k_y^2 = 0, \quad \frac{1}{\Psi_z(z)} \frac{\partial^2 \Psi_z(z)}{\partial z^2} + k_z^2 = 0$$

$$\text{where } k^2 = k_x^2 + k_y^2 + k_z^2$$

So this is just 3 equivalent 1D solutions which we have already done...

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Cont'd...

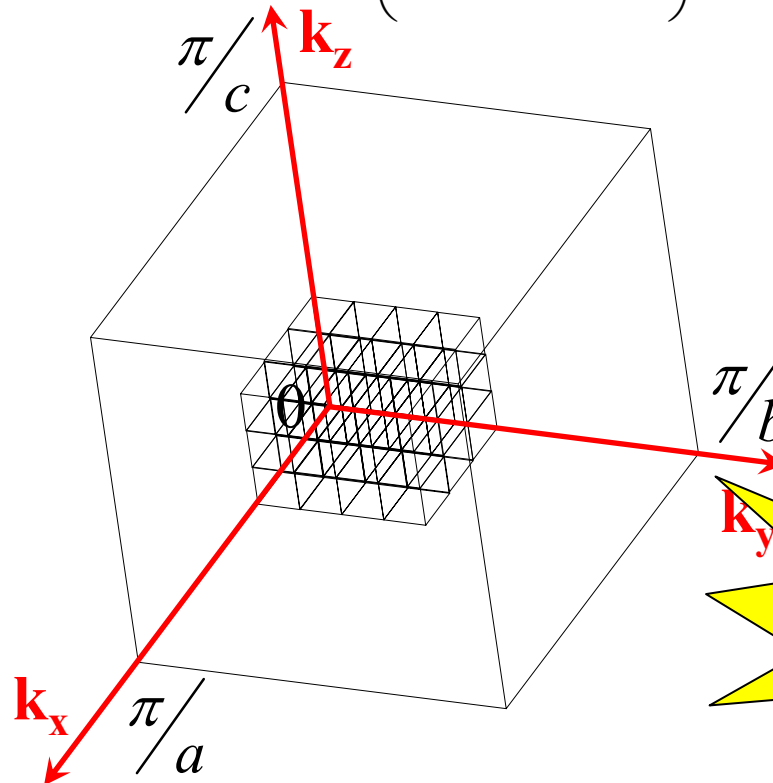
$$\Psi(x, y, z) = \Psi_x(x)\Psi_y(y)\Psi_z(z)$$

$$\Psi(x, y, z) = A \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

where $k_x = \frac{n_x \pi}{a}$, $k_y = \frac{n_y \pi}{b}$, $k_z = \frac{n_z \pi}{c}$, for $n = \pm 1, \pm 2, \pm 3 \dots$

$$\text{and } E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Each solution (i.e. each combination of n_x, n_y, n_z) results in a volume of “k-space”. If we add up all possible combinations, we would have an infinite solution. Thus, we will only consider states contained in a “fermi-sphere” (see next page).



See Pierret and Neudeck for a more general approach that does not require the fermi sphere argument. Tie this into the GaAs equi-energy surface in lecture 7.

How do electrons and holes populate the bands?

Derivation of Density of States Concept

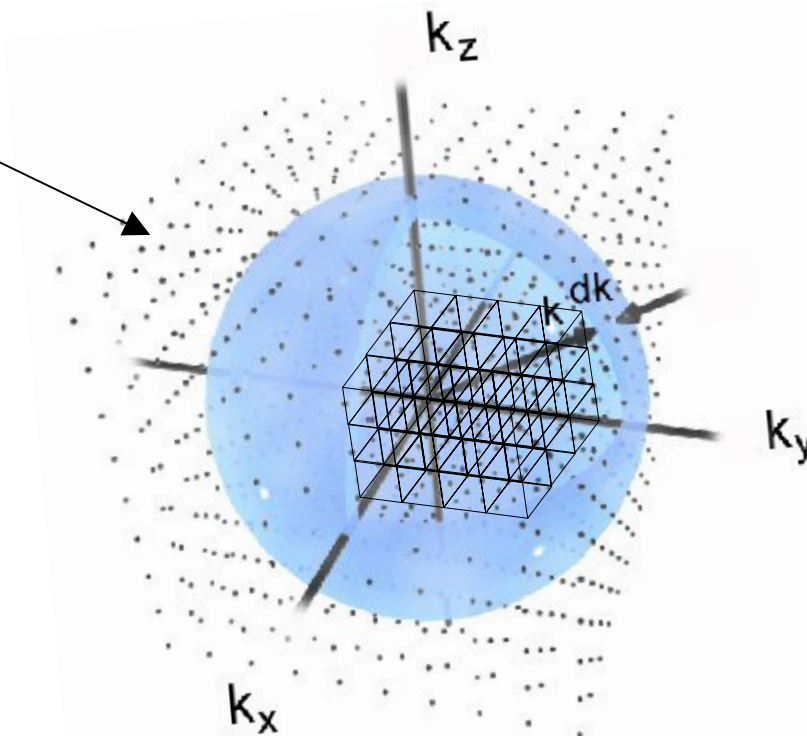
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$$E_f = \frac{\hbar^2 k_f^2}{2m} \Rightarrow \text{defines a momentum value for average electron energy } E_f$$

$$\text{Volume of a single state "cube": } V_{\text{single state}} = \left(\frac{\pi}{a}\right)\left(\frac{\pi}{b}\right)\left(\frac{\pi}{c}\right) = \left(\frac{\pi^3}{V}\right)$$

$$\text{Volume of a "fermi-sphere": } V_{\text{fermi-sphere}} = \left(\frac{4}{3}\pi k_f^3\right)$$

A "Fermi-Sphere" is defined by the number of states in k-space necessary to hold all the electrons needed to add up to the average energy of the crystal (known as the fermi energy).



"V" is the physical volume of the crystal where as all other volumes used here refer to volume in k-space. Note that: $V_{\text{single-state}}$ is the smallest unit in k-space. $V_{\text{single-state}}$ is required to "hold" a single electron.

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Cont'd...

k-space volume of a single state “cube”: $V_{\text{single state}} = \left(\frac{\pi}{a}\right)\left(\frac{\pi}{b}\right)\left(\frac{\pi}{c}\right) = \left(\frac{\pi^3}{V}\right)$

k-space volume of a “fermi-sphere”: $V_{\text{fermi-sphere}} = \left(\frac{4}{3}\pi k_f^3\right)$

Number of filled states in a fermi-sphere: $\equiv N = \frac{V_{\text{fermi-sphere}}}{V_{\text{single-state}}} 2x \left(\frac{1}{2}\right)x \left(\frac{1}{2}\right)x \left(\frac{1}{2}\right) = \frac{\left(\frac{4}{3}\pi k_f^3\right)}{\left(\frac{\pi^3}{V}\right)4} = \frac{V k_f^3}{3\pi^2}$

Correction for allowing 2 electrons per state (+/- spin)

Correction for redundancy in counting identical states resulting from +/- n_x , +/- n_y , +/- n_z . Specifically, $\sin(-\pi)=\sin(+\pi)$ so the state would be the same. Same as counting only the positive octant in fermi-sphere.

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Cont'd...

Number of filled states
in a fermi-sphere: $\equiv N = \frac{V k_f^3}{3\pi^2} \Rightarrow k_f = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$

$$E_f = \frac{\hbar^2 k_f^2}{2m} = \frac{\hbar^2 \left(\frac{3\pi^2 N}{V}\right)^{2/3}}{2m} \Rightarrow E_f = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m} \text{ where } n \text{ is the electron density}$$

E_f varies in Si from 0 to ~1.1 eV as n varies from 0 to ~ $5 \times 10^{21} \text{ cm}^{-3}$

Thus,
$$N = \frac{V k_f^3}{3\pi^2} = \left(\frac{V}{3\pi^2}\right) \left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Cont'd...

$$N = \frac{V k_f^3}{3\pi^2} = \left(\frac{V}{3\pi^2} \right) \left(\frac{2mE}{\hbar^2} \right)^{3/2}$$

Finally, we can define the density of states function:

$$G(E) \equiv \# \text{ of states per energy per volume} = \left(\frac{dN}{dE} \right) / V$$

$$G(E) = \left[\frac{3}{2} \left(\frac{V}{3\pi^2} \right) \left(\frac{2mE}{\hbar^2} \right)^{1/2} \left(\frac{2m}{\hbar^2} \right) \right] / V$$

$$G(E) = \frac{m\sqrt{2m}}{\pi^2\hbar^3} \sqrt{E}$$

Applying to the semiconductor we must recognize $m \rightarrow m^*$ and since we have only considered kinetic energy (not the potential energy) we have $E \rightarrow E - E_c$

$$G(E) = \frac{m^* \sqrt{2m^*}}{\pi^2 \hbar^3} \sqrt{E - E_c}$$