ChemE 2200 – Applied Quantum Chemistry Lecture 11

Today:

The Band Theory for Solids

Insulators and Semiconductors

Photodetectors

Doping

Defining Question:

What two effects must be balanced to choose a material to detect (absorb) photons?

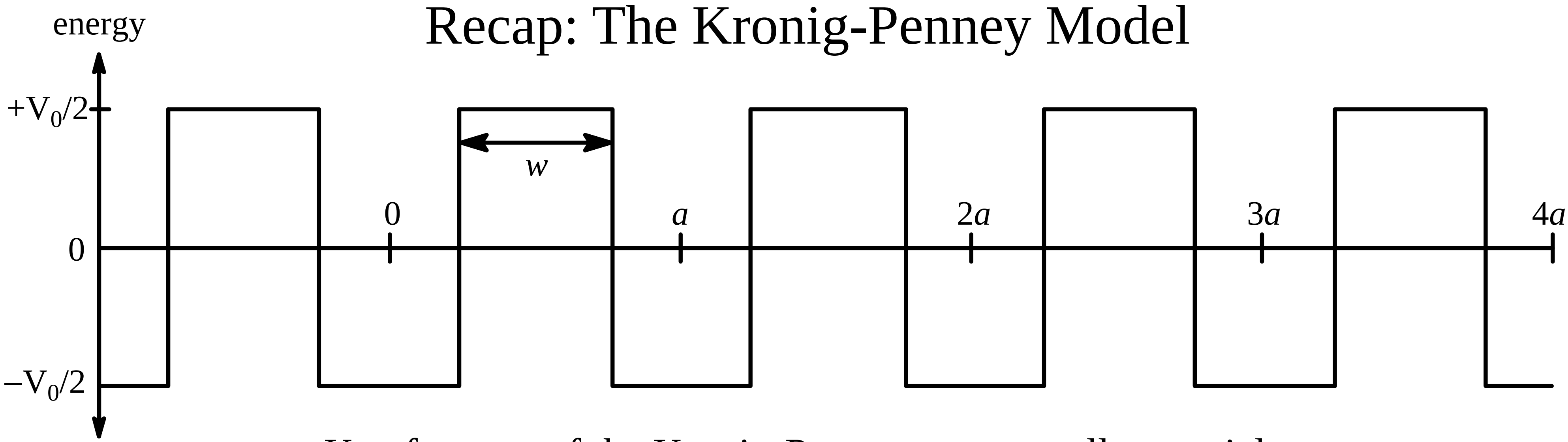
Reading for Today's Lecture:

Electrons in Solids, pp. 11-18.

Reading for Chemical Thermodynamics Lecture 1:

McQuarrie & Simon, 19.1-19.5, MathChapter H.

Recap: The Kronig-Penney Model



Key features of the Kronig-Penney square well potential:

1. The potential is periodic. Period is set by atomic lattice spacing, *a*.
2. The potential near an atomic ion (nucleus + valence electrons) is lower than the potential between atomic ions.
3. Parameters V_0 and w can be adjusted to match electronic properties.
4. The potential yields a solvable Schrödinger equation.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \quad \Rightarrow \quad \psi(x) = u_k(x)e^{ikx}$$

Boundary conditions set wavenumber *k*:

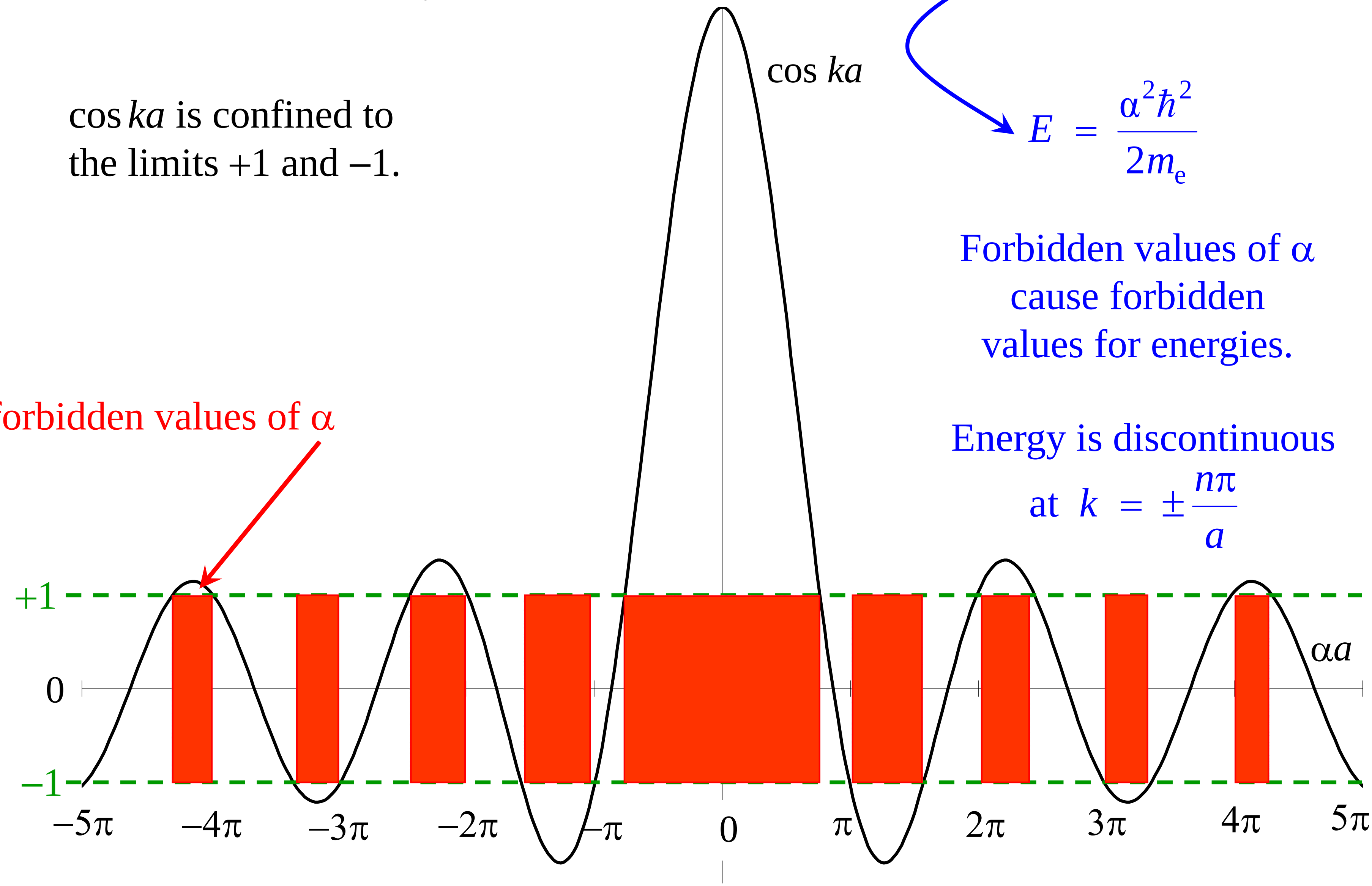
$$\cos ka = \frac{V_0 wma}{\hbar^2}\frac{\sin \alpha a}{\alpha a} + \cos \alpha a \quad \text{such that} \quad \alpha = \frac{(2m_e E)^{1/2}}{\hbar}$$

Recap: The Kronig-Penney Model - Electron Wavenumbers

$$\cos ka = \frac{V_0 w m a}{\hbar^2}\frac{\sin \alpha a}{\alpha a} + \cos \alpha a \qquad \text{such that} \quad \alpha = \frac{(2m_e E)^{1/2}}{\hbar}$$

$$E = \frac{\alpha^2 \hbar^2}{2m_e}$$

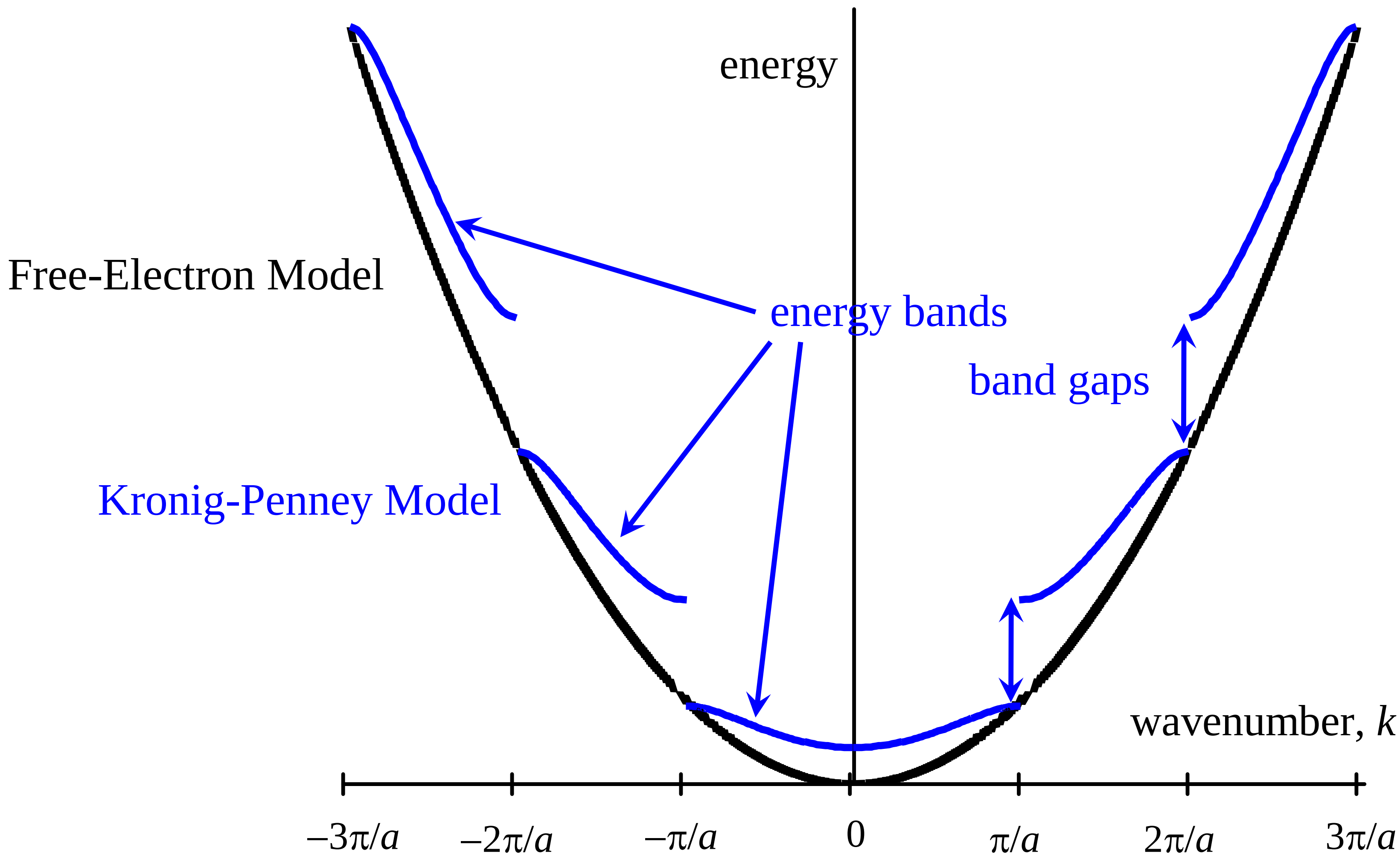
$\cos ka$ is confined to the limits +1 and –1.



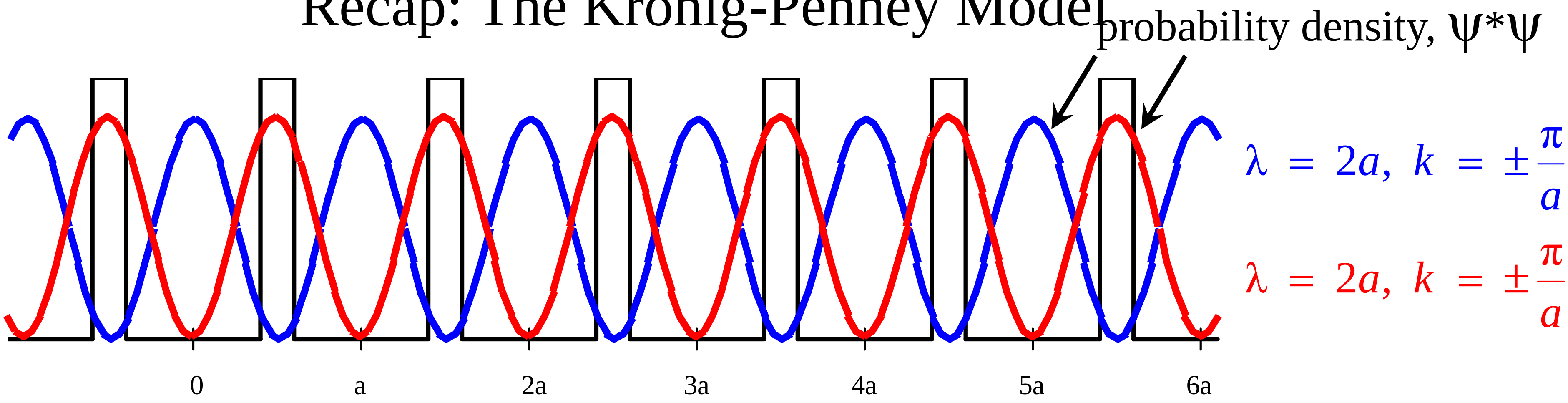
Forbidden values of α cause forbidden values for energies.

Energy is discontinuous at $k = \pm \dfrac{n\pi}{a}$

Recap: The Kronig-Penney Model - Energy Bands and Band Gaps



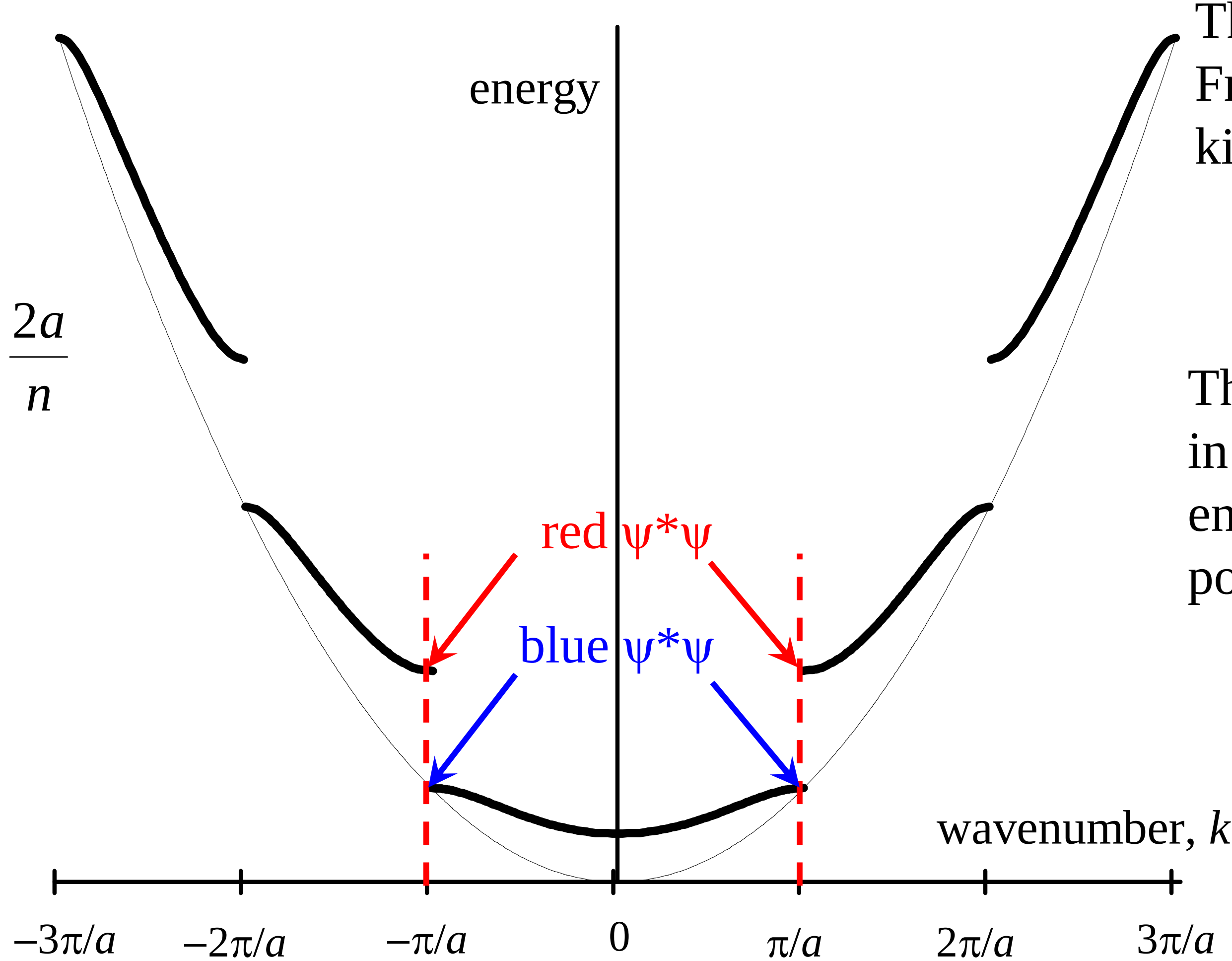
Recap: The Kronig-Penney Model



Energy gaps at $\lambda = \frac{2a}{n}$

Energy gaps at

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



The parabola is the Free-Electron Model: kinetic energy only.

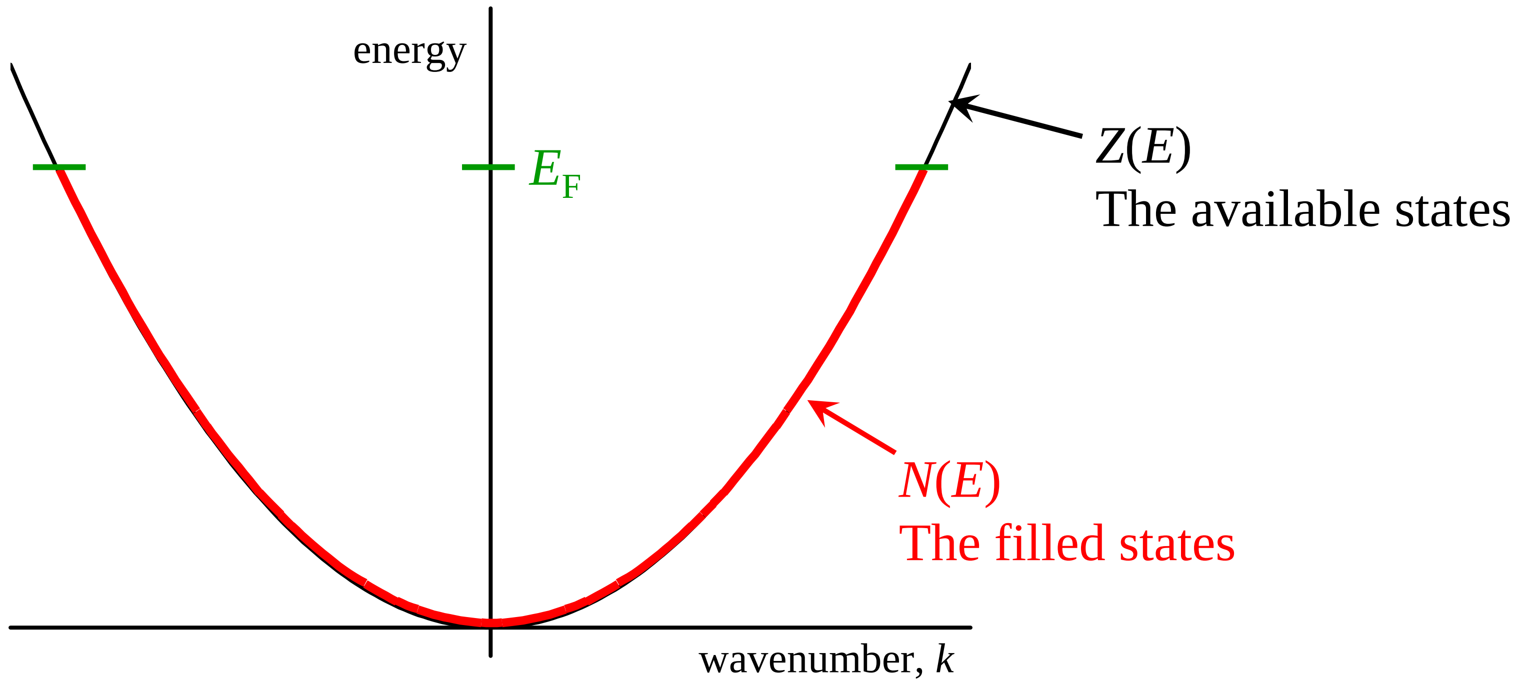
$$E = \frac{\hbar^2 k_x^2}{2m_e}$$

The additional energy in the Kronig-Penney energy bands is the potential energy.

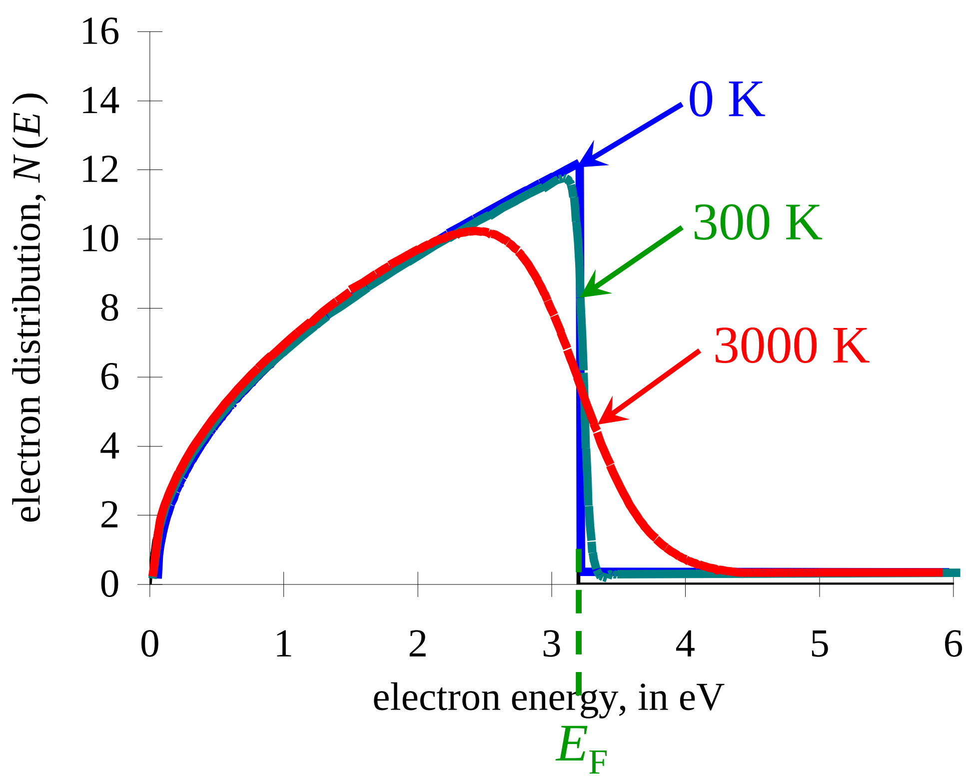
Band gaps are a quantum mechanical phenomenon.

Recap: The Free-Electron Model

$$E = \frac{\hbar^2 k_x^2}{2m_e}$$



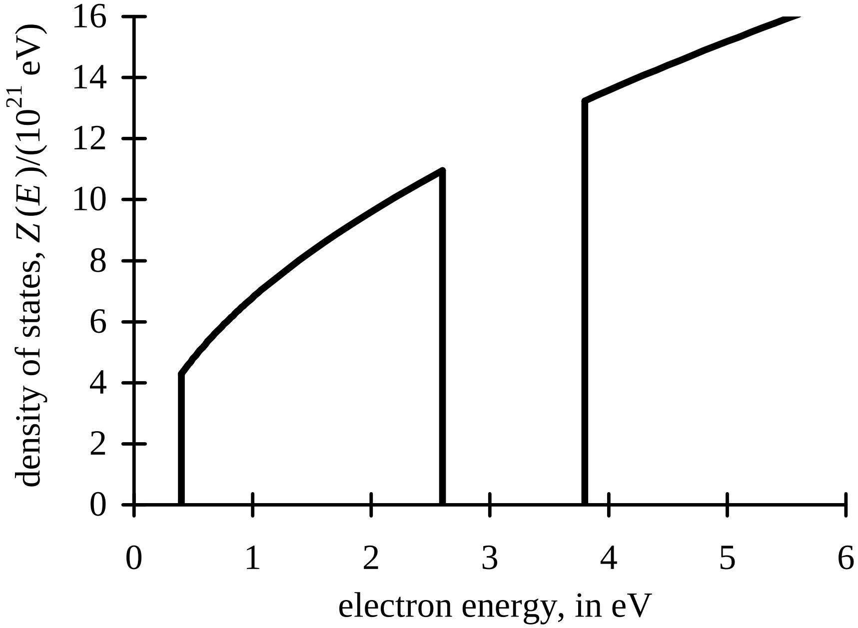
$N(E) \propto E^{1/2}$
for $E < E_F$



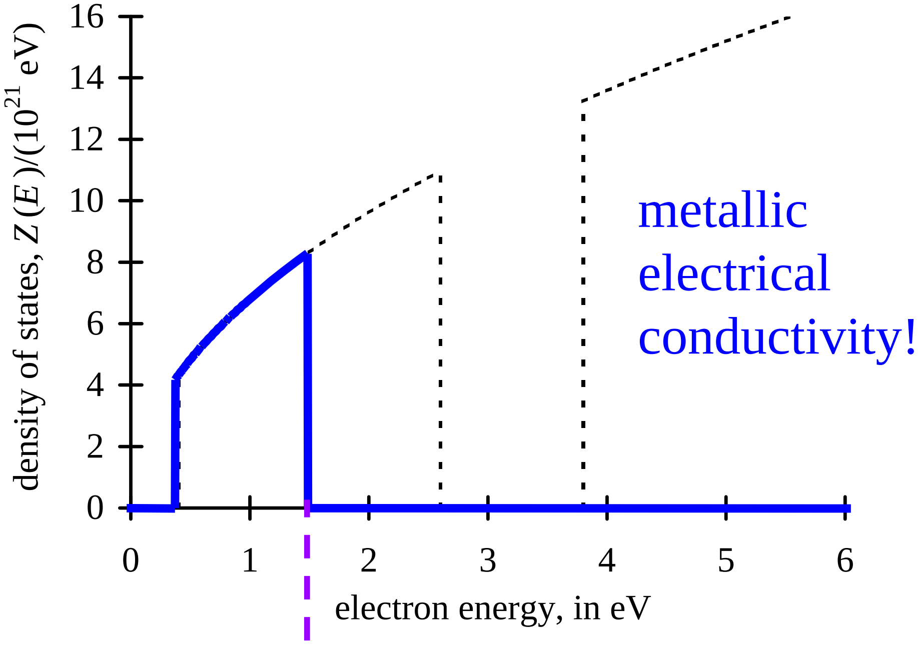
We need the analogous distribution for the Kronig-Penney Model.

The Kronig-Penney Model – Density of States

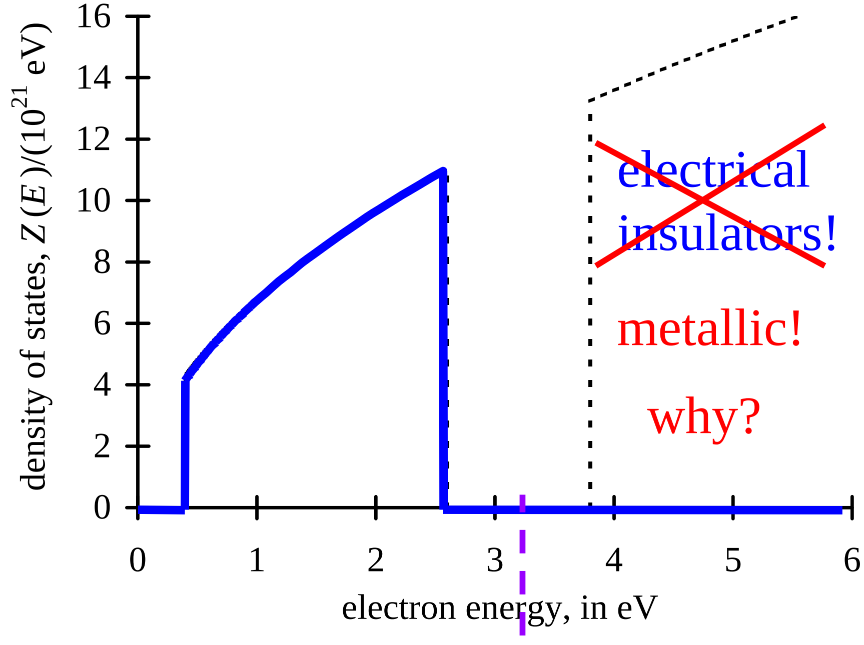
available states, $Z(E)$



Filled states for Li, Na, and K

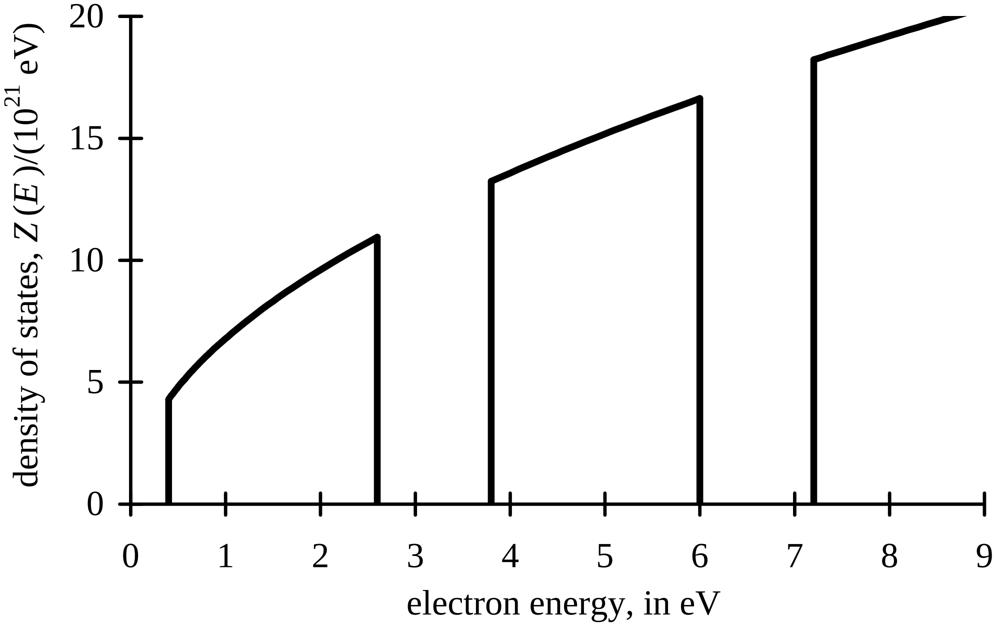


Filled states for Be, Mg, and Ca

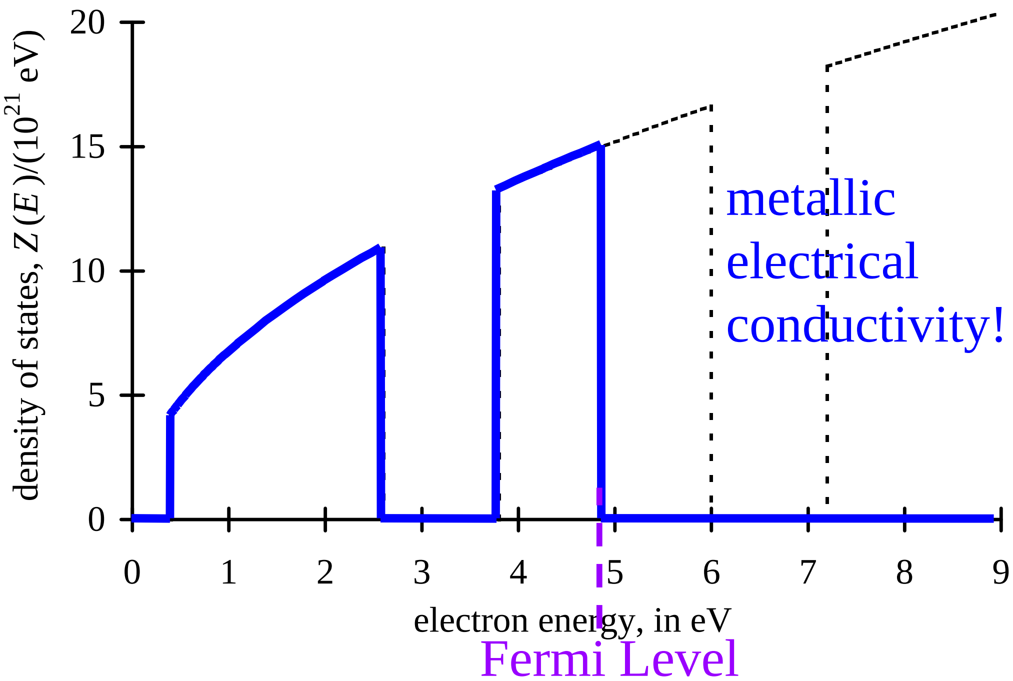


The Kronig-Penney Model – Density of States

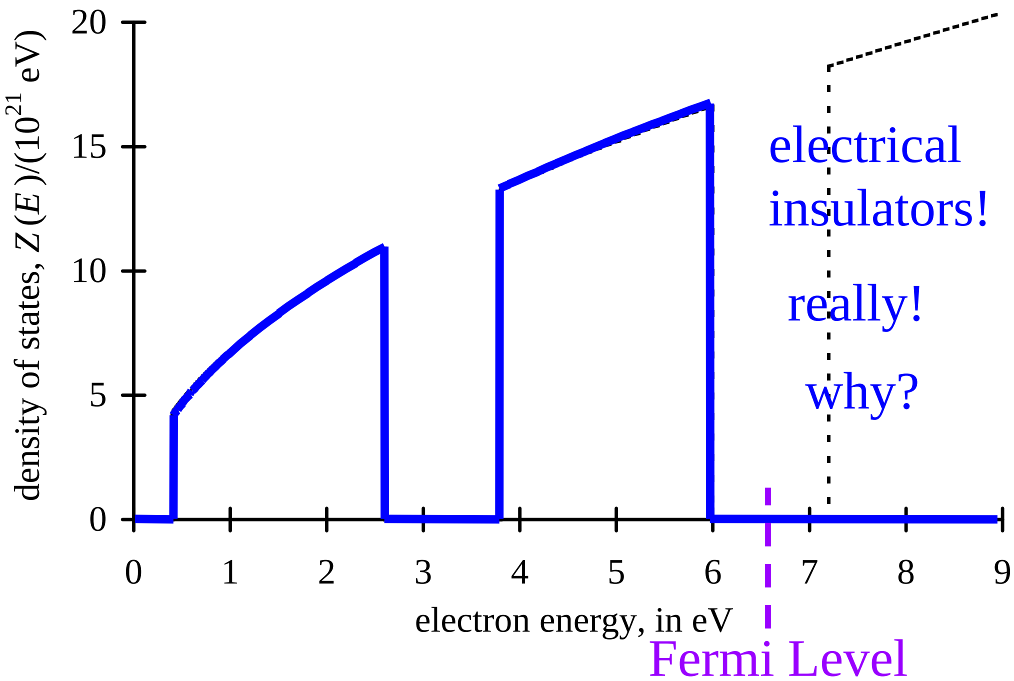
available states, $Z(E)$



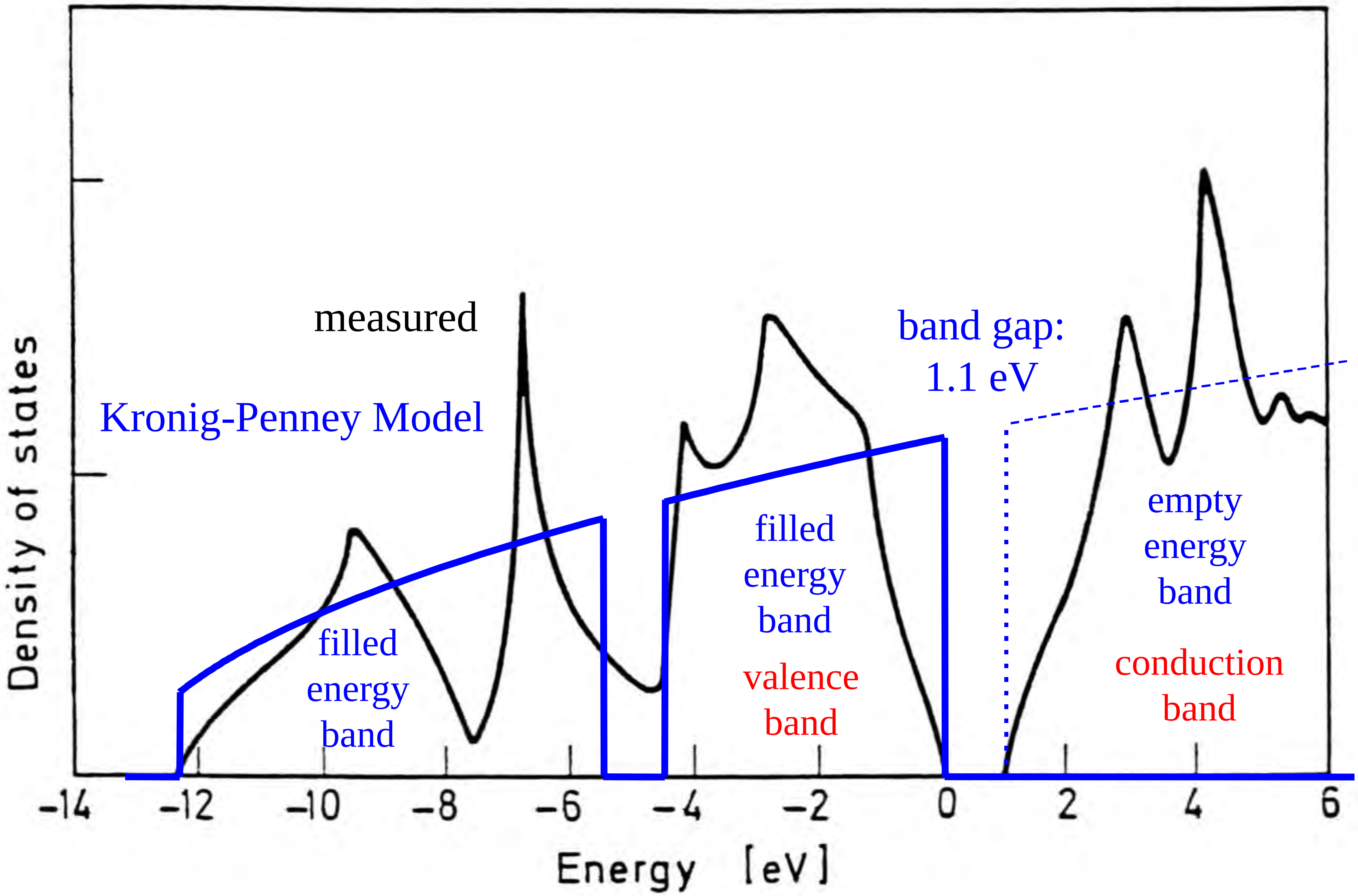
Filled states for B and Al



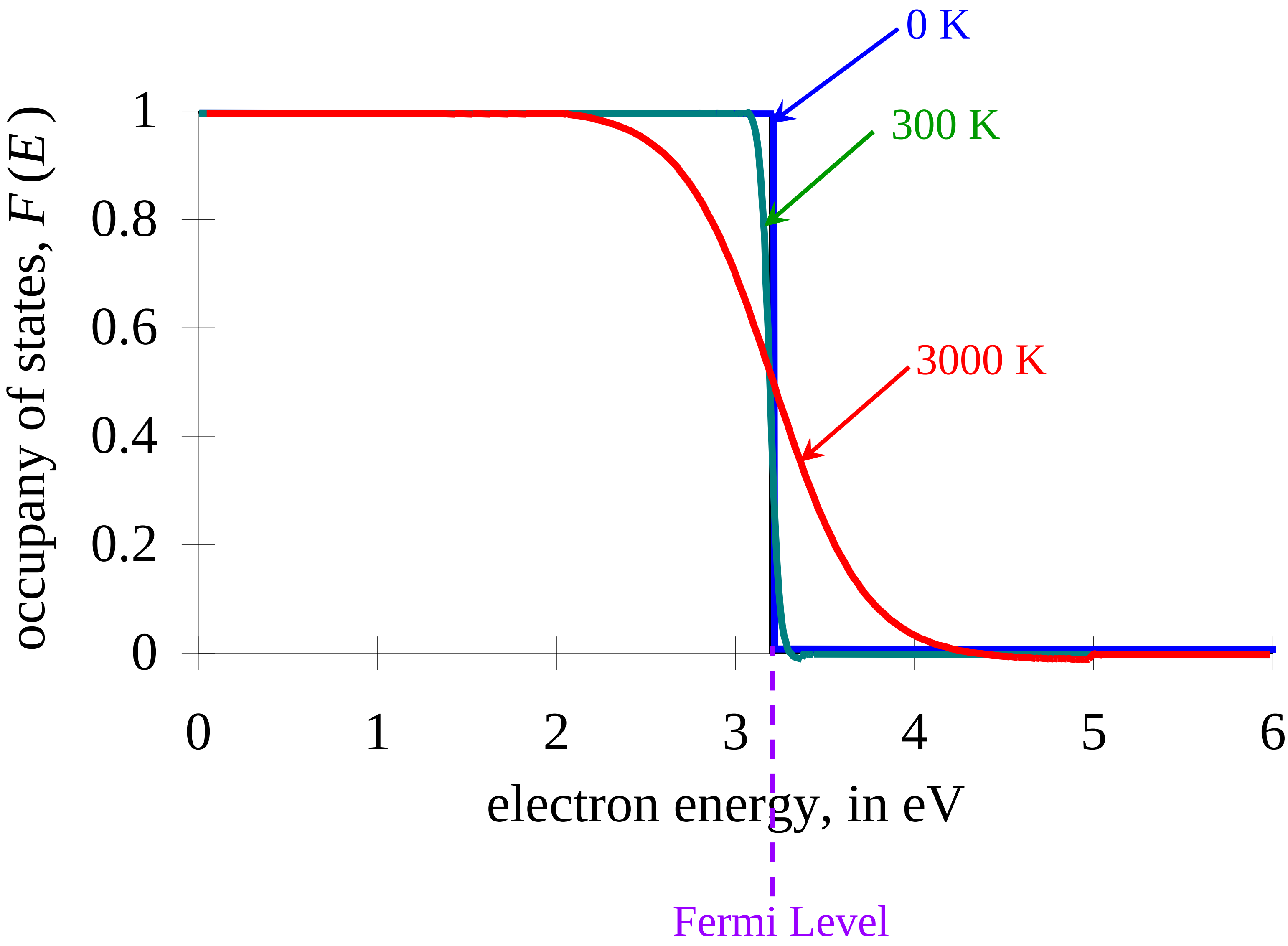
Filled states for C and Si



Density of States in Silicon

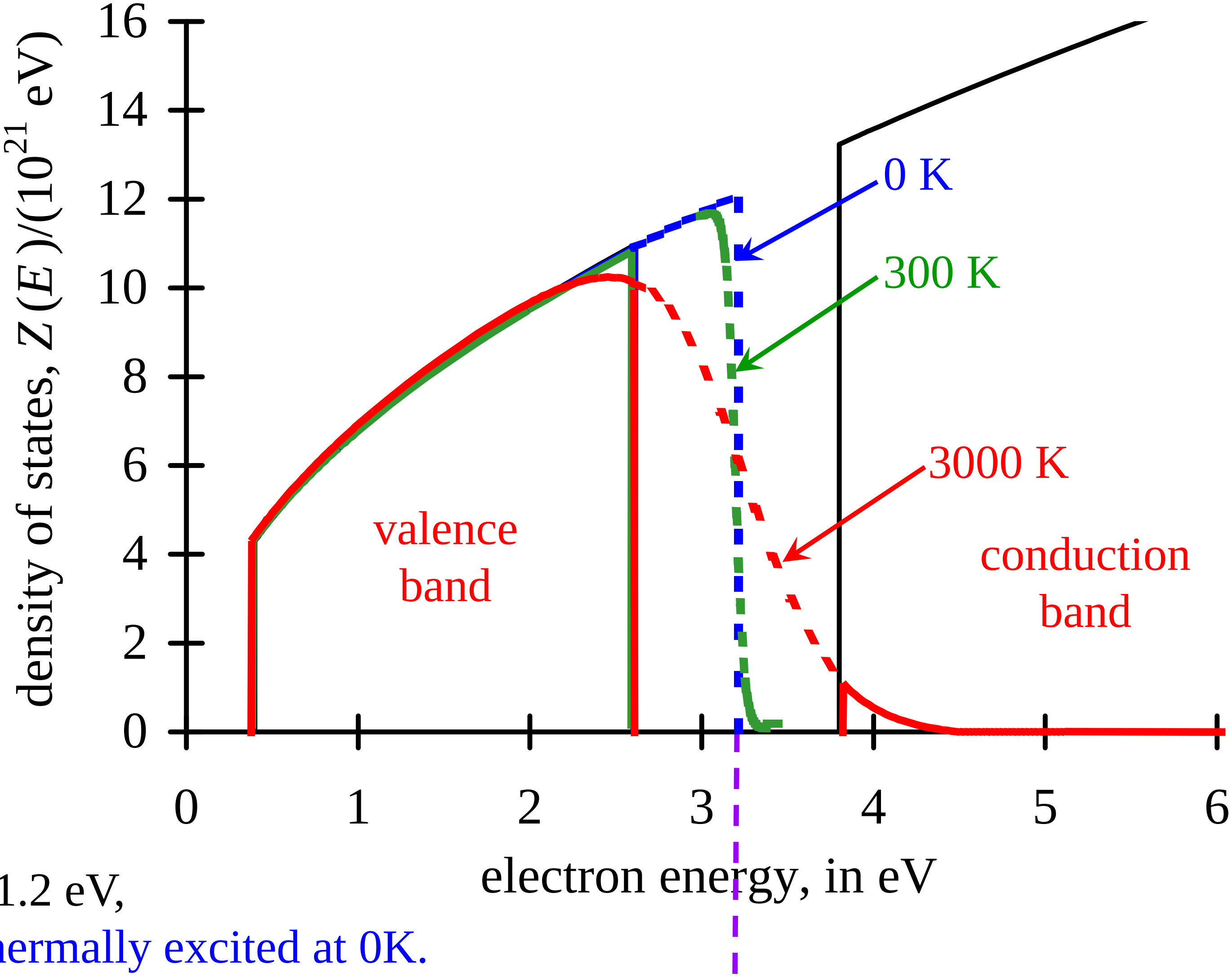


The Effect of Temperature - Fermi-Dirac Statistics



Effect of Temperature on Insulators

available states



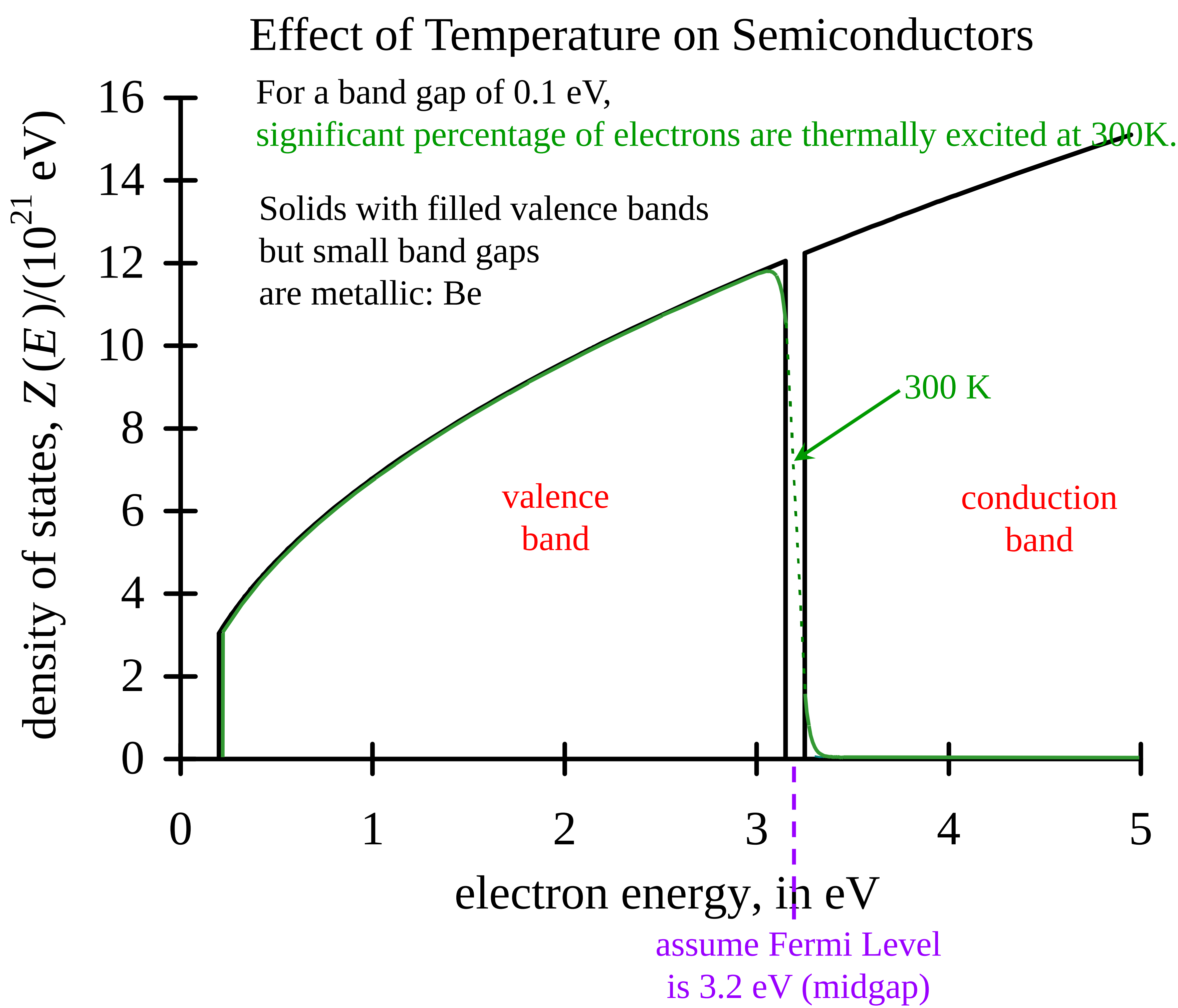
For a band gap of 1.2 eV,

No electrons are thermally excited at 0K.

~No electrons are thermally excited at 300K.

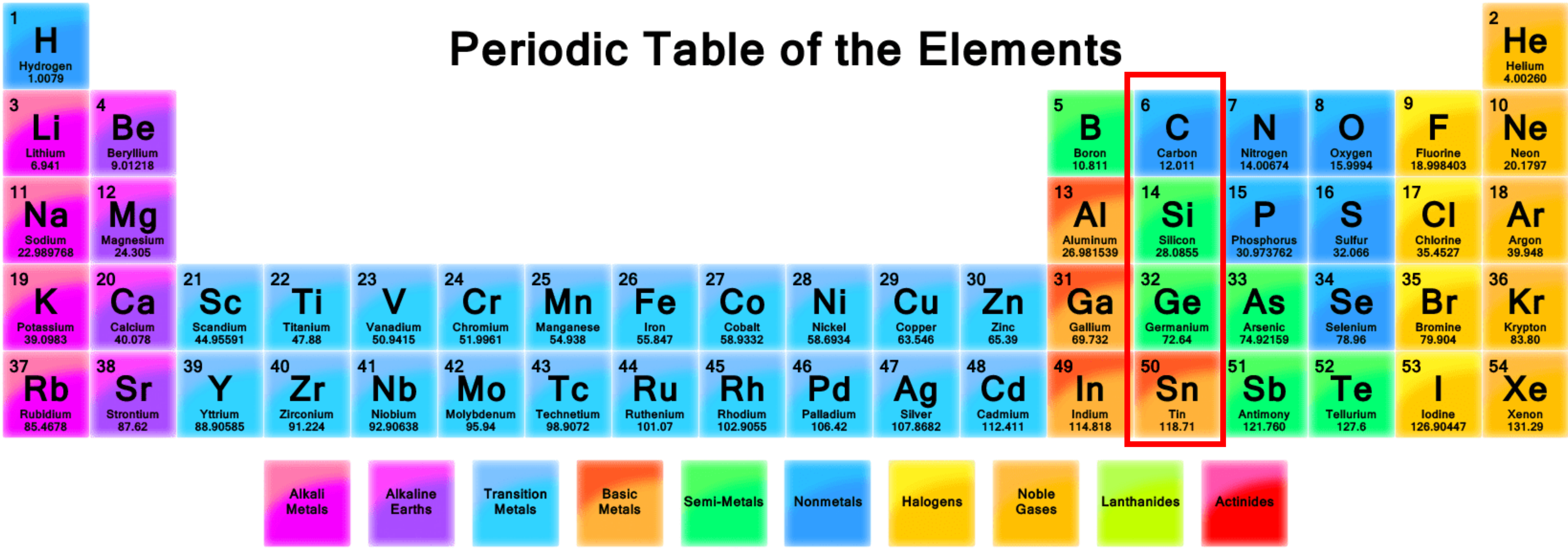
Some electrons are thermally excited at 3000K.

assume Fermi Level is 3.2 eV (midgap)



Effect of Temperature on Semiconductors
For a band gap of 0.1 eV,
significant percentage of electrons are thermally excited at 300K.
Solids with filled valence bands
but small band gaps
are metallic: Be
300 K
valence
band
conduction
band
density of states, Z(E)/(10^21 eV)
16
14
12
10
8
6
4
2
0
0
1
2
3
4
5
electron energy, in eV
assume Fermi Level
is 3.2 eV (midgap)

Some Band Gaps



C: 5.5 eV nonmetal

Si: 1.1 eV semiconductor

Ge: 0.67 eV semiconductor

Sn: 0.1 eV metal

As interatomic distance increases, band gap decreases.

Use mixed binaries to tune the band gap.

AlP: 2.5 eV

GaN: 3.4 eV Blue-light LEDs

GaAs: 1.4 eV

GaP: 2.2 eV

InSb: 0.17 eV

ZnS: 3.5 eV

ZnSe: 2.7 eV

ZnTe: 2.3 eV

CdTe: 1.5 eV

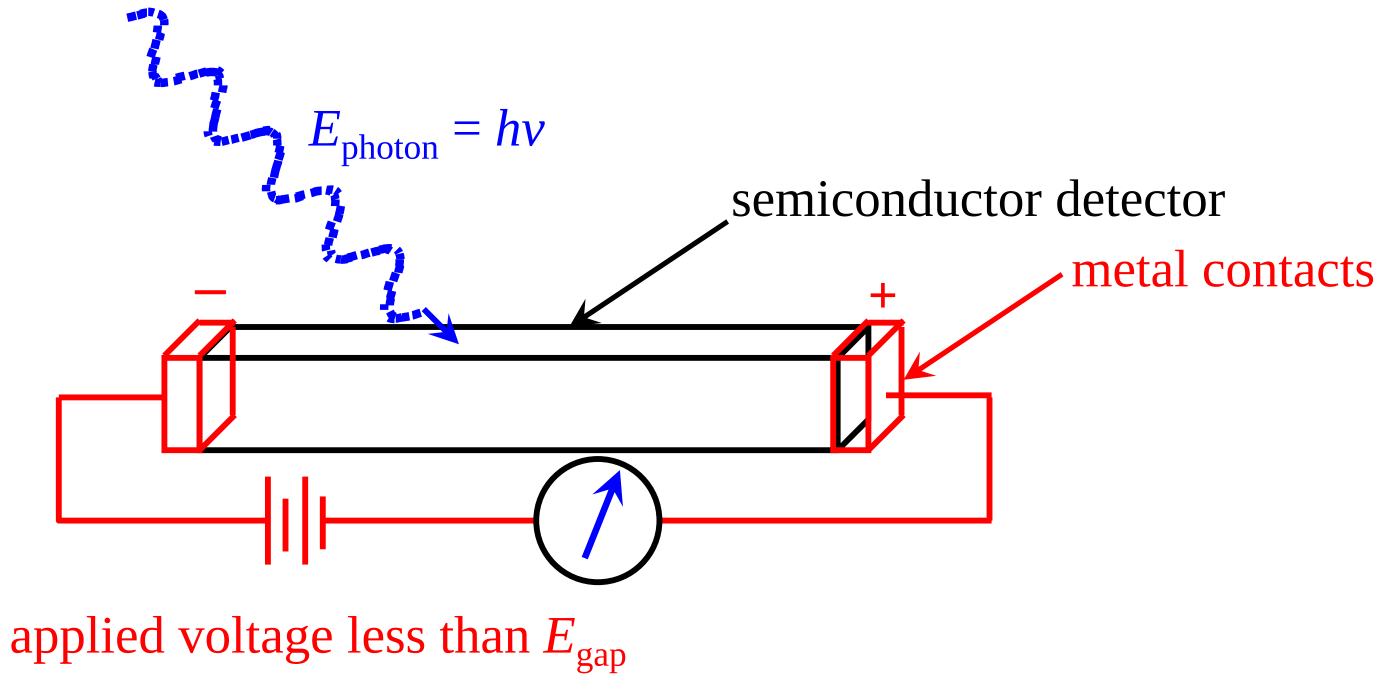
InAs: 0.35 eV

Photon Effects?

C and Si have the same crystal structure.

Why is a diamond transparent to visible light, but Si is opaque?

How to design a photon detector or a light harvester?



Photon must promote an electron from the valence band to the conduction band.

Band gap of semiconductor must be less than E_{photon}.

What is the optimum band gap?

Let's Design Thermal-Imaging (Night-Vision) Goggles

The Electromagnetic Spectrum

frequency, ν (cycles/sec)	band name	phenomenon	photon energy = $h\nu$ eV	kJ/mol	wavelength $\lambda = c/\nu$	wavenumber $\tilde{\nu} = 1/\lambda$	source temperature*
10^{23}	cosmic rays	supernovae	4×10^{8}		3 fm		10^{12} K
10^{22}	gamma	nuclear	4×10^{7}		30 fm		10^{11} K
10^{21}	rays	decay	4×10^{6}		0.3 pm		10^{10} K
10^{20}		ejection	4×10^{5}		3 pm		10^{9} K
10^{19}	x rays	of core	4×10^{4}		30 pm		10^{8} K
10^{18}		electrons	4×10^{3}		0.3 nm		10^{7} K
10^{17}	ultraviolet	excitation of	400	40,000	3 nm		10^{6} K
10^{16}		valence electrons	40	4000	30 nm		10^{5} K
10^{15}	visible light		4	400	0.3 μm		10^{4} K
10^{14}		molecular	0.4		3 μm	3000 cm^{-1}	10^{3} K
10^{13}	infrared	vibrational	0.04		30 μm	300 cm^{-1}	100 K
10^{12}		levels		0.4	0.3 mm	30 cm^{-1}	10 K
10^{11}		molecular		0.04	3 mm	3 cm^{-1}	1 K
10^{10}	microwaves	rotational			3 cm		0.1 K
10^{9}		levels			30 cm		10 mK
10^{8}		TV, FM radio,			3 m		1 mK
10^{7}	radio	computer chips,			30 m		
10^{6}	waves	shortwave radio,			300 m		
10^{5}		AM radio			3 km		
10^{4}					30 km		
10^{3}					300 km		
100	power	ac electricity			3×10^{3} km		
10					3×10^{4} km		
1					3×10^{5} km		

0.15 eV

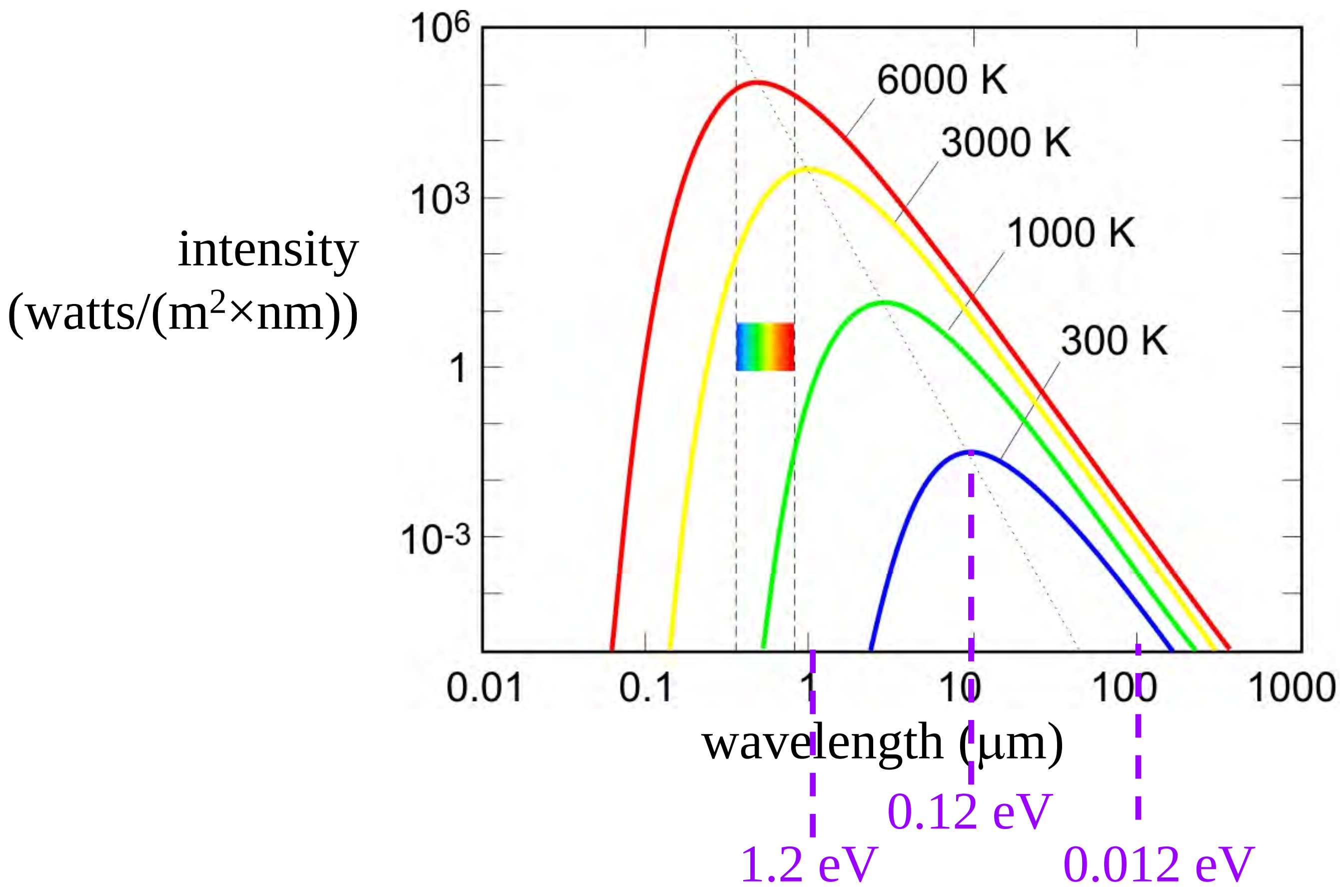
320K

design an infrared detector

1 eV = 1.60×10^{-19} J = 8066 cm^{-1}

*temperature of a body that will emit photons chiefly at this energy. The maximum of the Planck distribution, $T = h\nu/(5k)$

What Band Gap for an Infrared Detector?



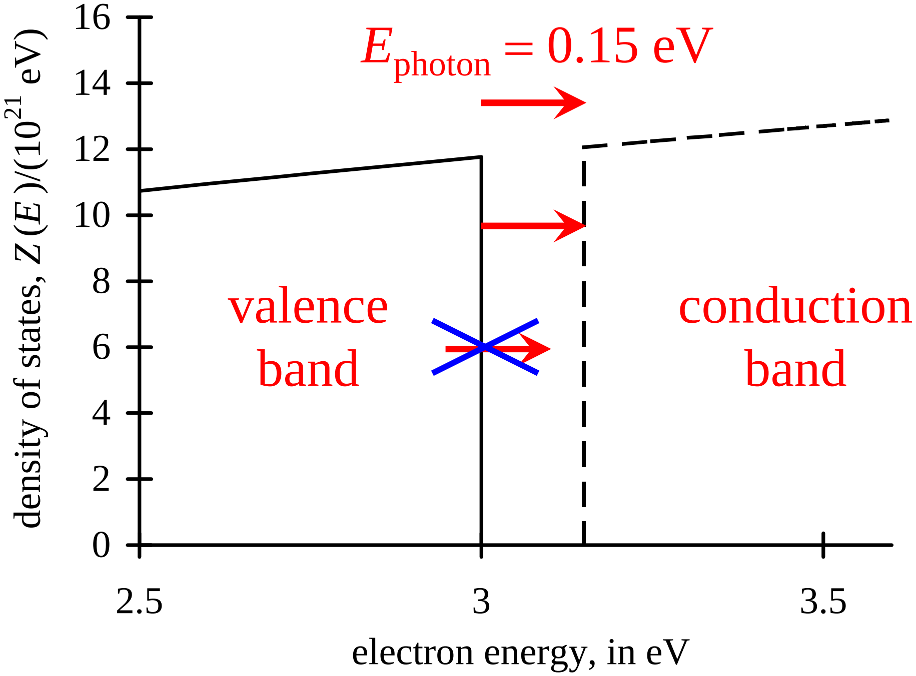
Planck distribution of electromagnetic emission from a black body.

The peak of the Planck distribution at 320K is at $E_{photon} = 0.15$ eV.

Use a material with a 0.15 eV band gap?

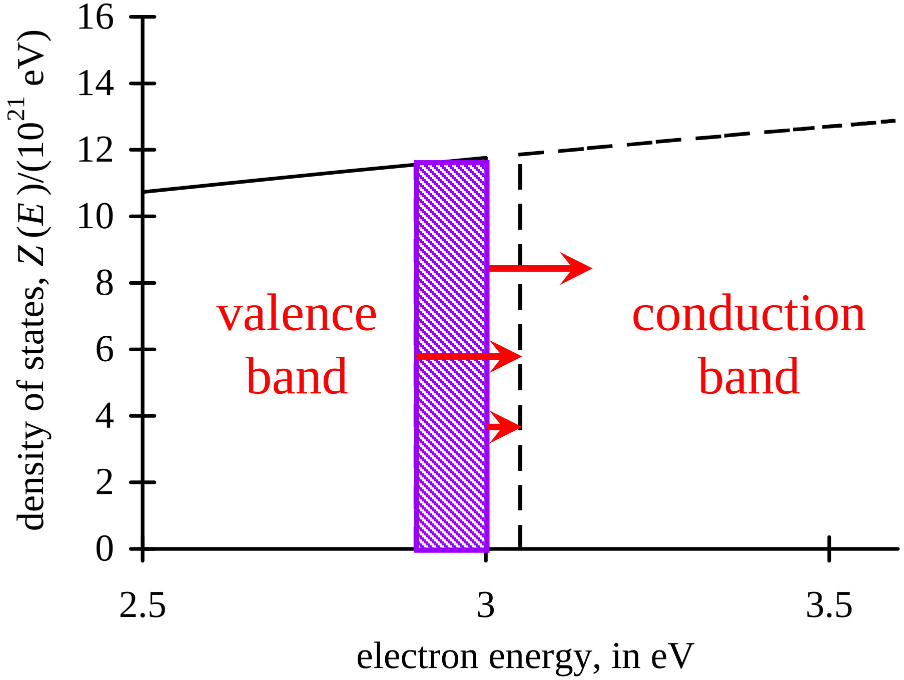
Or, use a material with a 0.05 eV band gap?

What Band Gap to Detect Photons with Energy 0.15 eV?



band gap = 0.15 eV

Only electrons at the highest filled energy level absorb 0.15 eV photons.



band gap = 0.05 eV

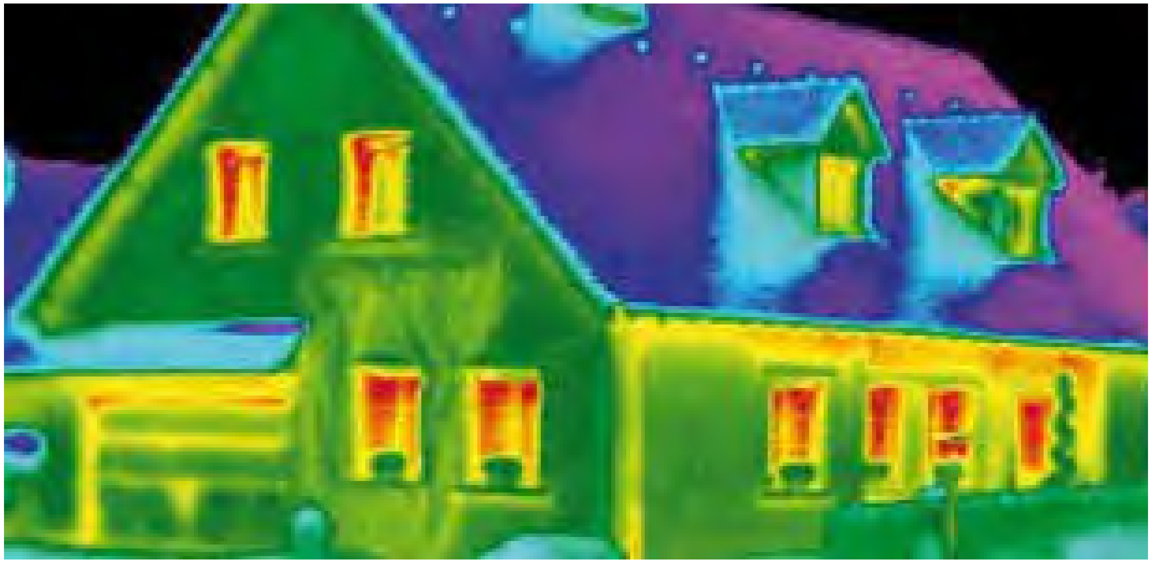
Electrons within 0.1 eV of the highest energy level can absorb IR photons. And IR photons as low as 0.05 eV can be absorbed.

~~Use a material with a 0.05 eV band gap to collect more photons.~~

A material with a 0.05 eV band gap will have more ‘noise’ owing to thermal electrons, electrons promoted to the conduction band by thermal energy.

Optimal band gap must balance electron signal and electron ‘noise’ owing to thermal electrons.

Thermal Images



Use a detector with E_{gap} as large as possible, but $E_{gap} < E_{photon}$

Keep the detector as cold as possible.

Want to know more?
ChemE 6662 (1 cr)
Solar Energy

Great interactive online resource:
www.pveducation.org/

Analysis of Sustainable Energy Systems

Parent course:

ChemE 6660: Analysis of Sustainable Energy Systems (2 credits)
Fall Semesters, ChemE 3130 required.

One-Credit Modules: (ChemE 6600 required)

- ChemE 6661: Biofuels and Bioenergy
- ChemE 6662: Solar Energy
- ChemE 6663: Geothermal Energy
- ChemE 6664: Hydrokinetic & Aerodynamic Energy
- ChemE 6667: Transportation Energy Systems
- ChemE 6670: Fossil Fuels
- ChemE 6671: Nuclear Energy
- ChemE 6672: Electric Power Systems
- ChemE 6675: Energy Life Cycle Assessment
- ChemE 6676: Energy Markets & Regulations
- ChemE 6678: Water-Energy Nexus
- ChemE 6679: Energy Storage
- ChemE 6681: Energy Analysis Project

Semiconductors – Effects of Impurities

Solids must be highly pure for semiconductor electrical conductivity.

0.01% impurity in CdS increases electrical conductivity by $\times 10^{13}$.

Impurities create electrons in the conduction band or vacancies in the valence band.

Silicon requires 99.999999% purity to use in semiconductor devices.

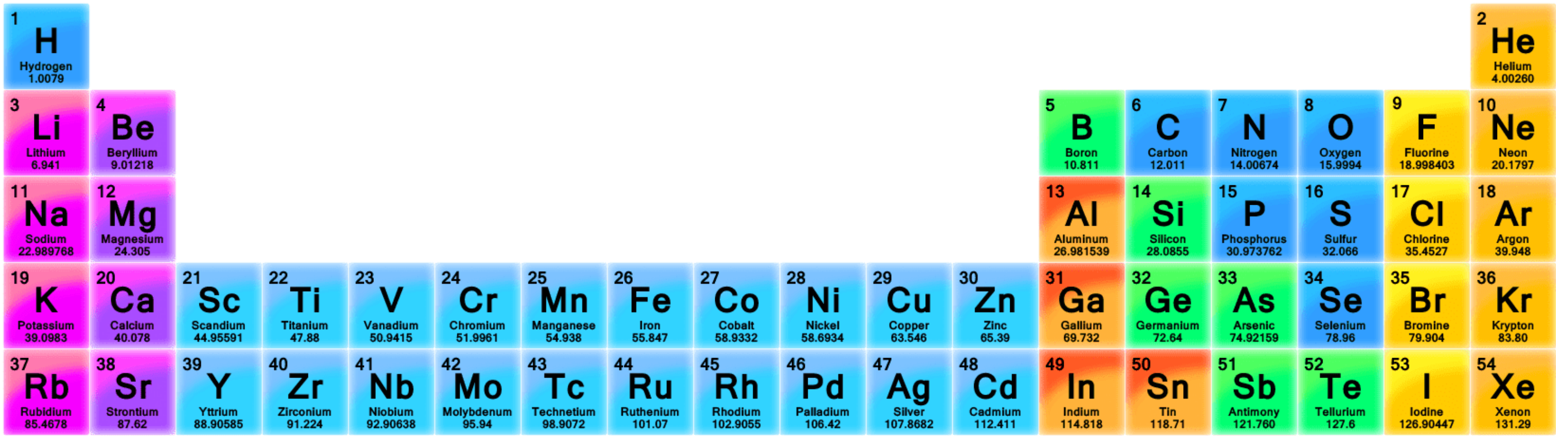
Equivalent to 1 grain of salt in a train car of sugar.

Chemical engineer William G. Pfann (Bell Labs) invented zone refining in 1951.

Created mass production of semiconductor-grade silicon.

Semiconductors and Doping

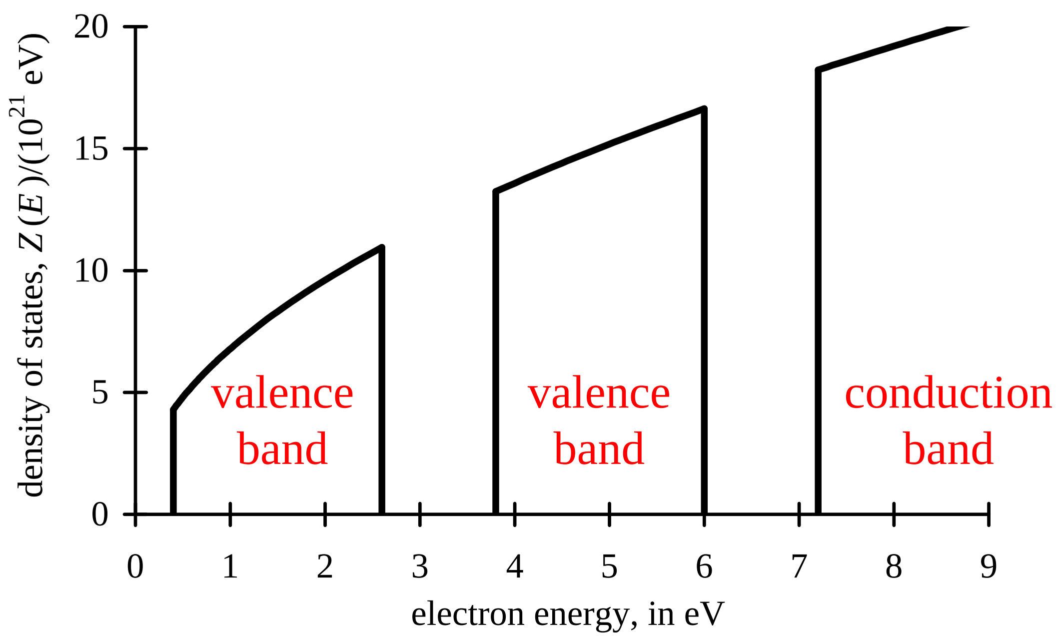
Intentionally adding impurities to change the electrical conductivity.



Replace a Si atom with a P atom.

The extra electron must occupy a state in the conduction band.

Si doped with P has metallic conductivity.



Replace a Si atom with an ~~Al~~ B atom.

The missing electron creates a vacancy in the valence band.

Si doped with ~~Al~~ B has metallic conductivity.

Si with extra negative charges is “n-doped Si.”

Si with extra positive charges is “p-doped Si.”

Photolithography

Doping Si to draw conductive paths (wires) and create devices (transistors).