BONDING IN SOLIDS AND CRYSTAL STRUCTURE

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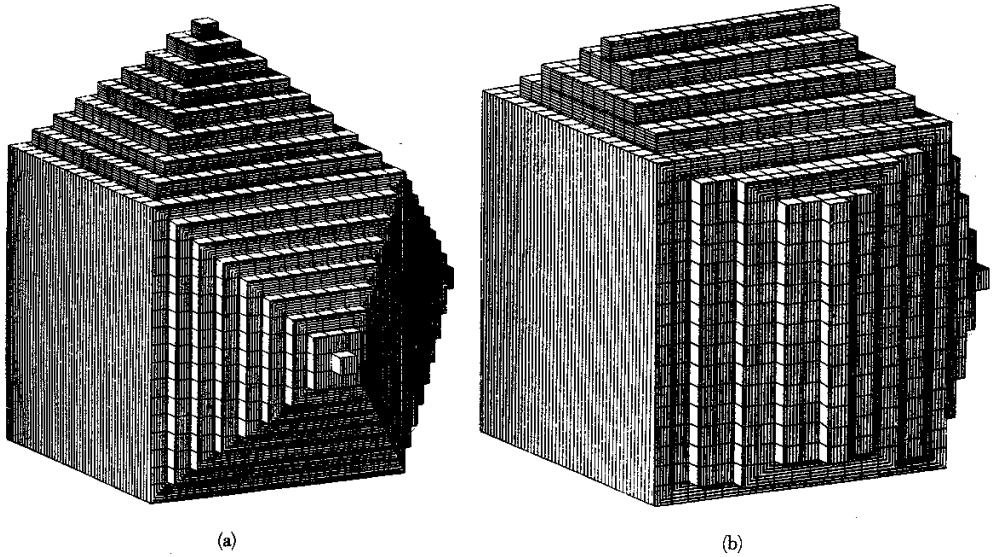
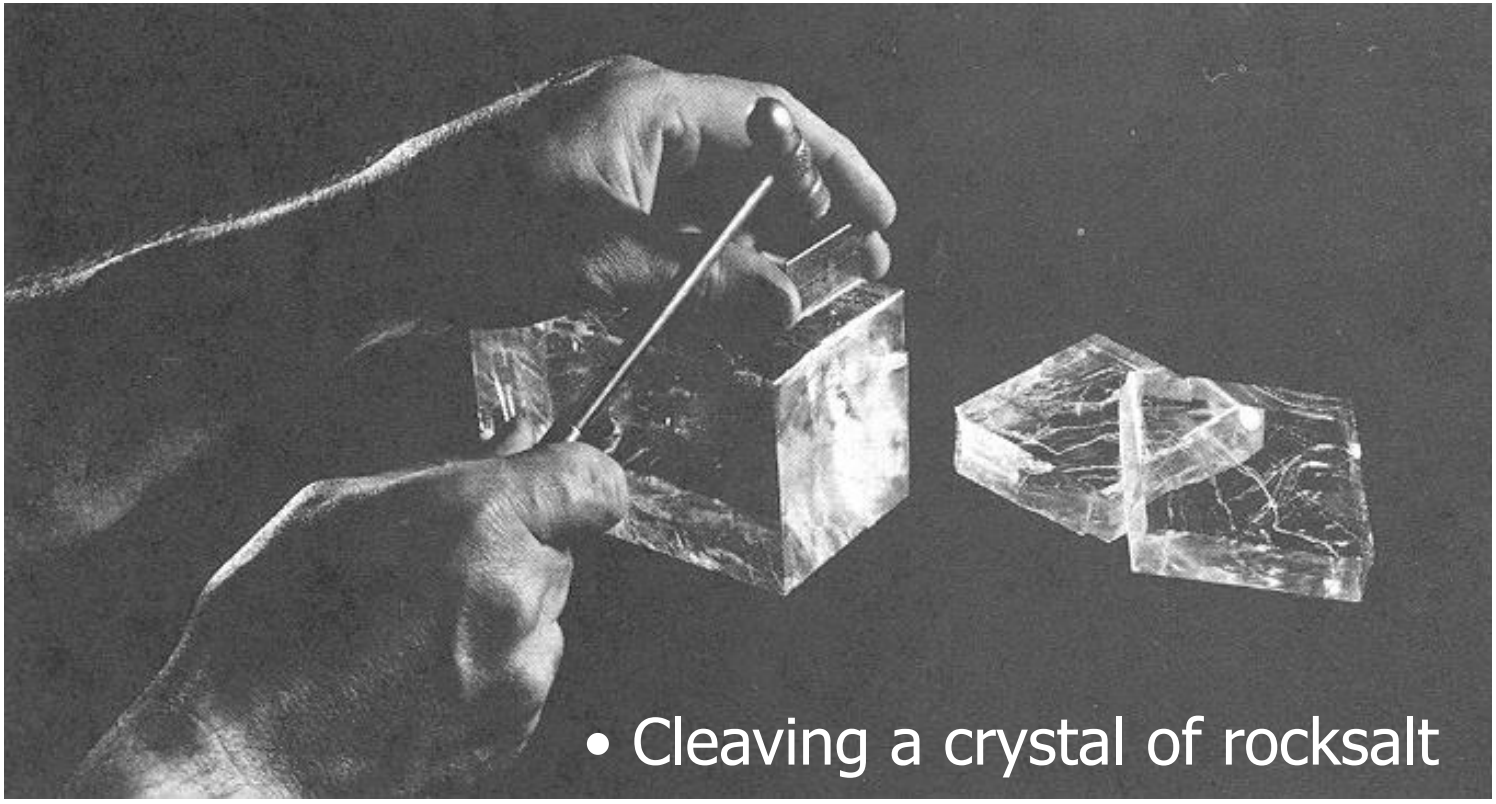
QUESTIONS

- Calculate the volume of an FCC unit cell in terms of the atomic radius R. Show that the atomic packing factor of FCC unit cell is more than that of BCC
- Define: (i) Metallic Bonding (ii) Covalent Bonding (iii) Orthorhombic and Tetragonal crystal structure
- Cu has a FCC crystal structure and a unit cell with lattice constant of 0.361 nm. What is the interplaner spacing of d111 planes? Show one prism plane (1010) and (2110) direction of HCP lattice.
- Find the atomic packing factor in case of FCC crystal
- If the lattice parameter of alpha iron is 286 pm what is its atomic radius?
- Calculate the no. of atoms per zinc crystal structure unit cell.
- Calculate and compare the atomic packing factor of the FCC and BCC cell units. What role does the atomic packing factor have on creep strengths of FCC and BCC metals at same homologous temperature?
- Al is FCC, and has an atomic radius of 0.143 nm. Calculate its lattice parameter.
- The lattice parameter of a material having FCC structure, is 0.396 nm. Determine the length of the burger's vector along[110] direction.
- Justify: FCC metals are often recommended for use at low temperature.
- Justify: Four octahedral sites are associated with one FCC unit cell.

Crystal Structure

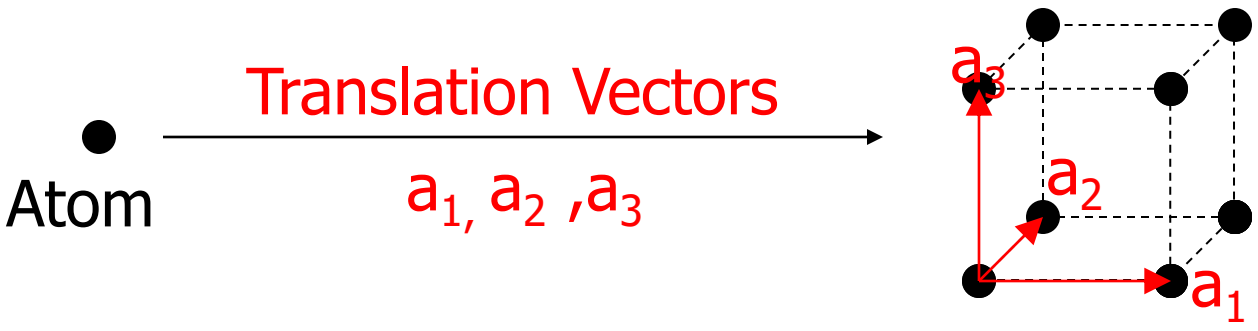
- The building blocks of these two are identical, but different crystal faces are developed

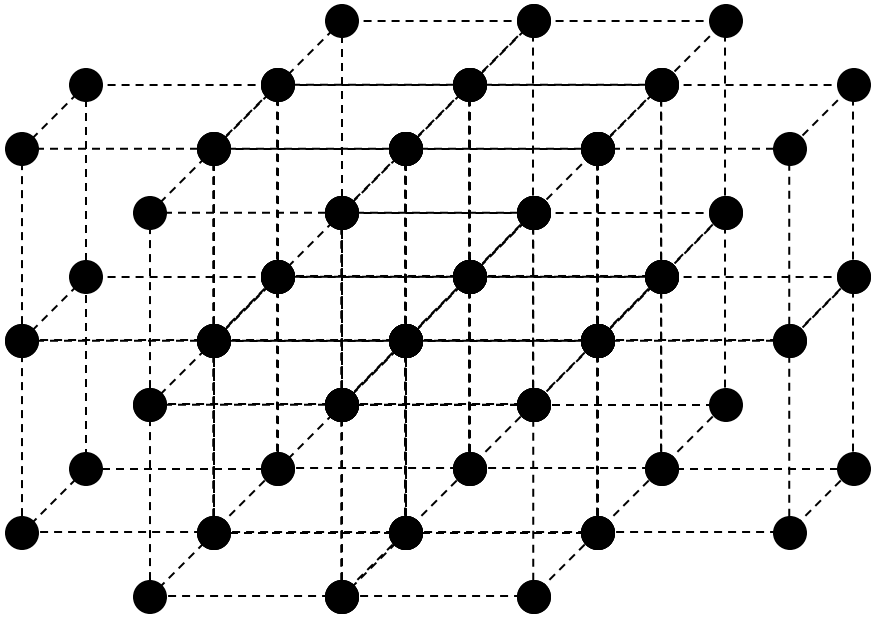




- Cleaving a crystal of rocksalt

Crystal: Periodic Arrays of Atoms





Primitive Cell:

- Smallest building block for the crystal structure.
- Repetition of the primitive cell → crystal structure

Common Lattice Types

There are 14 lattice types; Most common types are:

- Cubic: (SC, BCC, FCC)

  Li, Na, Al, K, Cr, Fe, Ir, Pt, Au etc.

- Hexagonal Closed Pack (HCP):

  Mg, Co, Zn, Y, Zr, etc.

- Diamond:

  C, Si, Ge, Sn (only four)

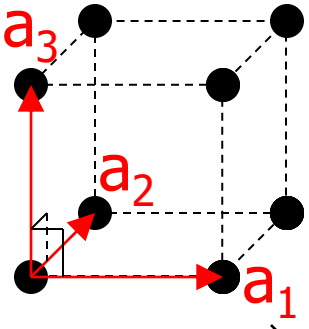
Three Cubic Lattices

1. Simple Cubic (SC)

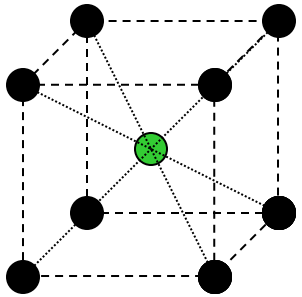
$a_1 = a_2 = a_3$

$a_1 \perp a_2 \perp a_3$

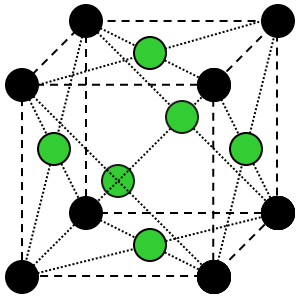
Conventional Cell= Primitive Cell



Add one atom at the center of the cubic



Add one atom at the center of each face



2. Body-Centered Cubic (BCC)

3. Face-Centered Cubic (FCC)

Conventional Cell ≠ Primitive Cell

Atomic Packing Factor

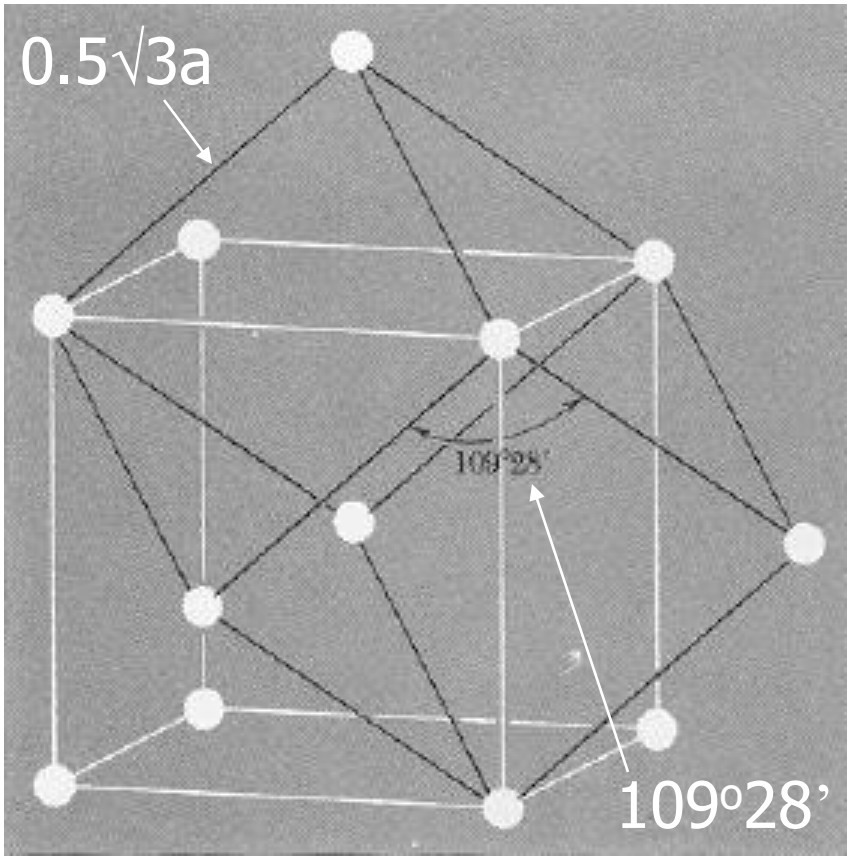
- A.P.F. is define as the ratio of total volume of atoms (in unit cell) to the total volume of unit cell.

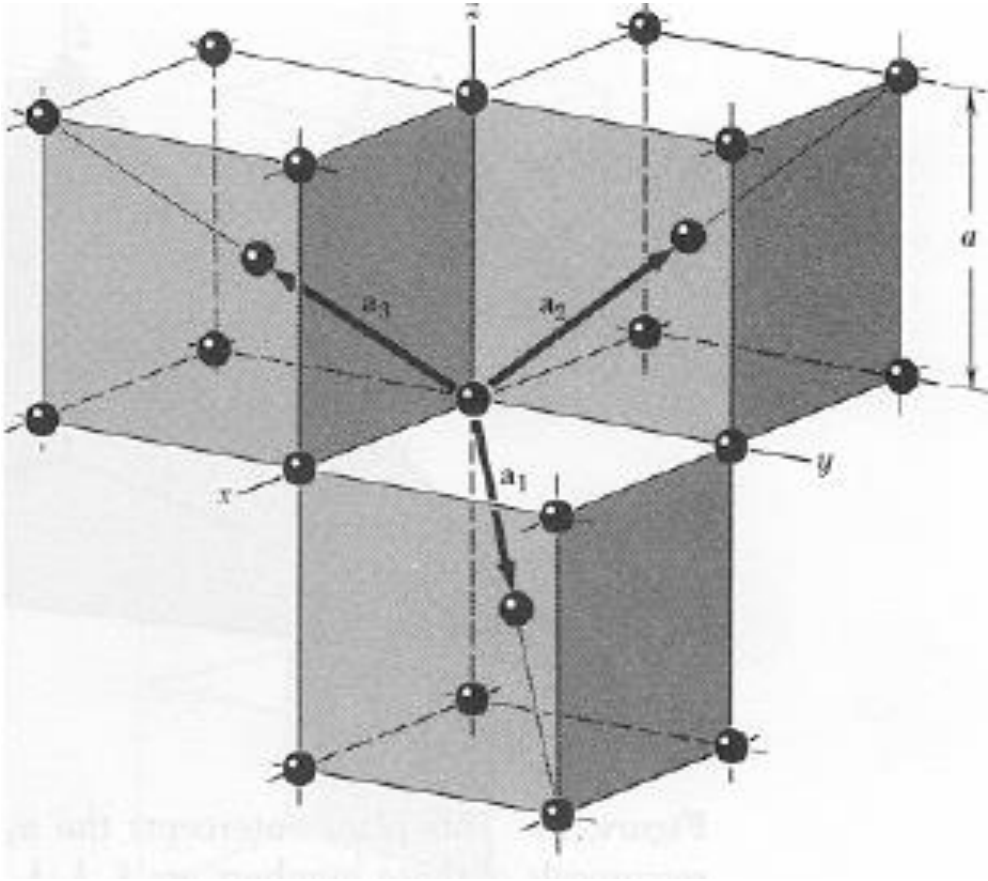
  A.P.F. = (No. of atoms) X (Volume of one atom)/Volume of unit cell

- The primitive unit cell for the body-centered cubic (BCC) crystal structure contains eight atoms on each corner of the cube and one atom in the center. Because the volume of each corner atom is shared between adjacent cells, each BCC cell contains two atoms.
- Each corner atom touches the center atom. A line that is drawn from one corner of the cube through the center and to the other corner passes through $4r$, where r is the radius of an atom. By geometry, the length of the diagonal is $a\sqrt{3}$. Therefore, the length of each side of the BCC structure can be related to the radius of the atom by
- Knowing this and the formula for the volume of a sphere, it becomes possible to calculate the APF as follows:

Primitive Cell of BCC

- Rhombohedron primitive cell



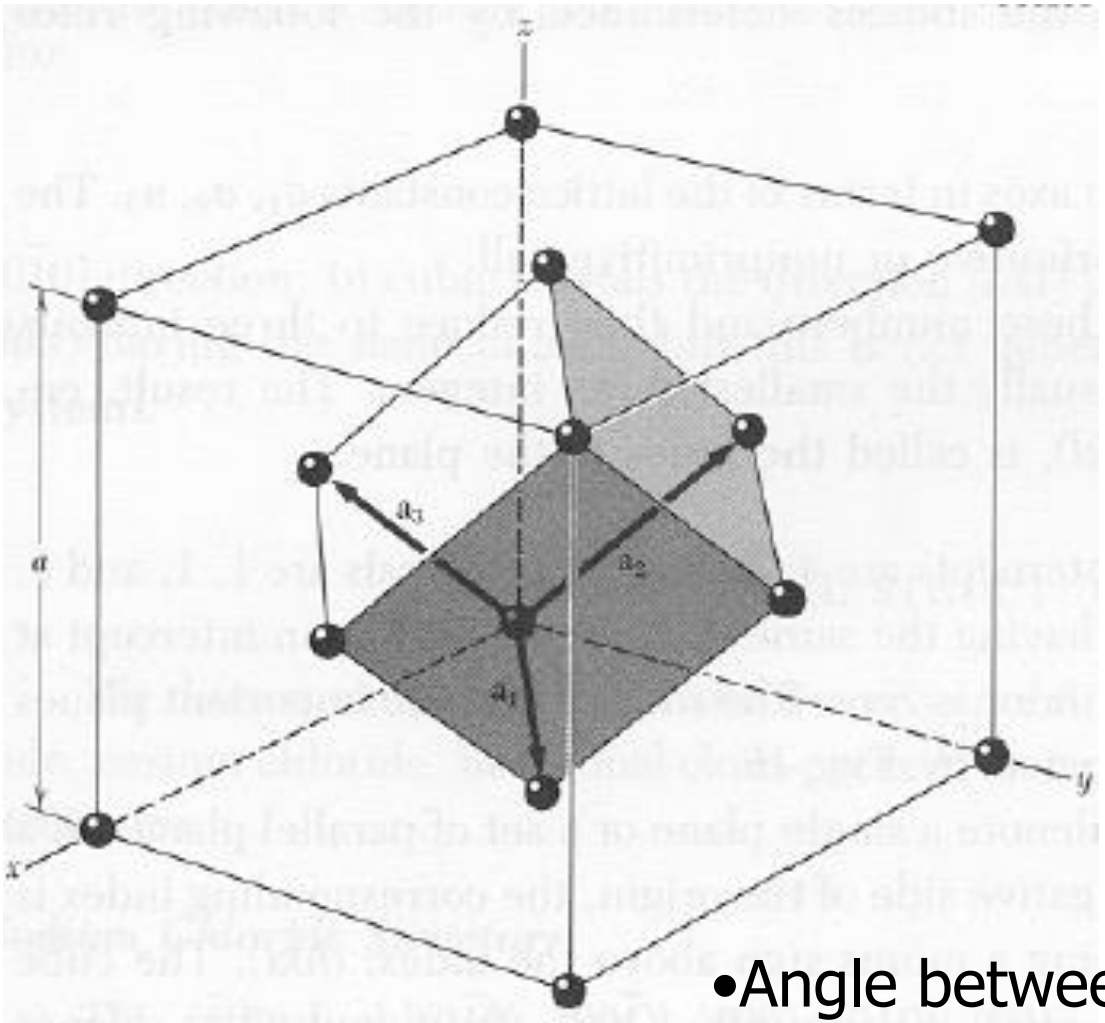


- Primitive Translation Vectors:

$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \; ; \qquad \mathbf{a}_2 = \tfrac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \; ;$$

$$\mathbf{a}_3 = \tfrac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) \; .$$

Primitive Cell of FCC



- Kittel, P. 13

- Angle between a_1, a_2, a_3: 60^o

$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \; ; \qquad \mathbf{a}_2 = \tfrac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \; ; \qquad \mathbf{a}_3 = \tfrac{1}{2}a(\hat{\mathbf{z}} + \hat{\mathbf{x}}) \; .$$

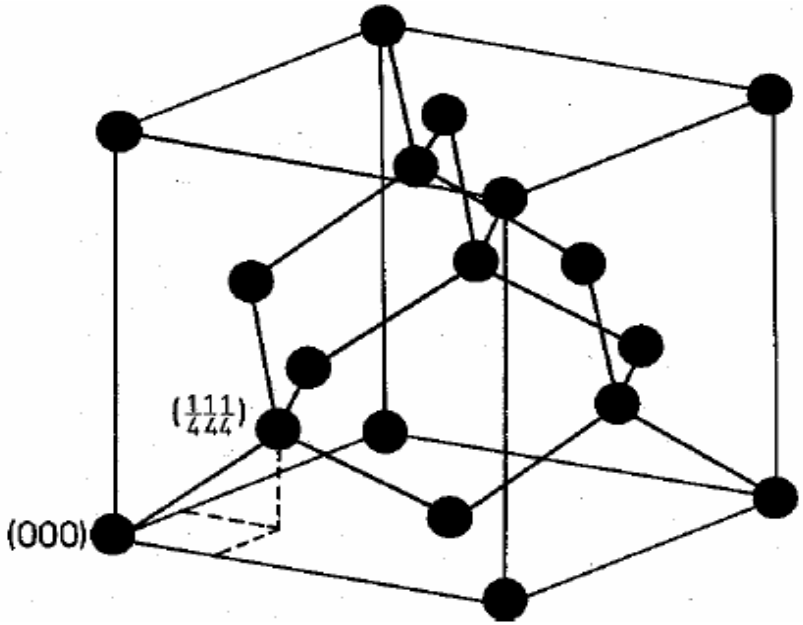
Kittel p. 12

Table 2 Characteristics of cubic lattices[a]

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors[a]	6	8	12
Nearest-neighbor distance	a	$3^{1/2}a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction[b]	$\frac{1}{6}\pi$	$\frac{1}{8}\pi\sqrt{3}$	$\frac{1}{6}\pi\sqrt{2}$
	$=0.524$	$=0.680$	$=0.740$

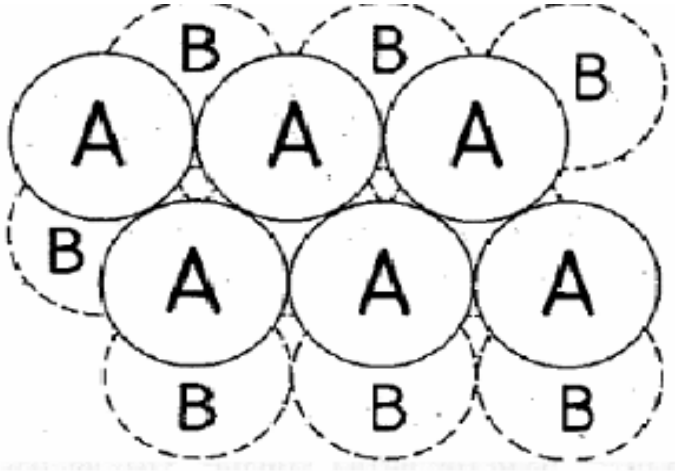
Diamond Structure

C, Si, Ge, α-Sn



- Add 4 atoms to a FCC
- Tetrahedral bond arrangement
- Each atom has 4 nearest neighbors and 12 next nearest neighbors

Hexagonal Close Packing (hcp)



A = top layer
B = middle layer
A = bottom layer

Crystal Structures of Elements

Kittel, pg. 23

there.

Notice: hcp vs. fcc in same column

Crystal structure
a lattice parameter, in Å
c lattice parameter, in Å

H[1] 4K hcp 3.75 6.12																	He[4] 2K hcp 3.57 5.83
Li 78K bcc 3.491	Be hcp 2.27 3.59											B rhomb.	C diamond 3.567	N 20K cubic 5.66 (N_2)	O complex (O_2)	F	Ne 4K fcc 4.46
Na 5K bcc 4.225	Mg hcp 3.21 5.21											Al fcc 4.05	Si diamond 5.430	P complex	S complex	Cl complex (Cl_2)	Ar 4K fcc 5.31
K 5K bcc 5.225	Ca fcc 5.58	Sc hcp 3.31 5.27	Ti hcp 2.95 4.68	V bcc 3.03	Cr bcc 2.88	Mn cubic complex	Fe bcc 2.87	Co hcp 2.51 4.07	Ni fcc 3.52	Cu fcc 3.61	Zn hcp 2.66 4.95	Ga complex	Ge diamond 5.658	As rhomb.	Se hex. chains	Br complex (Br_2)	Kr 4K fcc 5.64
Rb 5K bcc 5.585	Sr fcc 6.08	Y hcp 3.65 5.73	Zr hcp 3.23 5.15	Nb bcc 3.30	Mo bcc 3.15	Tc hcp 2.74 4.40	Ru hcp 2.71 4.28	Rh fcc 3.80	Pd fcc 3.89	Ag fcc 4.09	Cd hcp 2.98 5.62	In tetr. 3.25 4.95	Sn (α) diamond 6.49	Sb rhomb.	Te hex. chains	I complex (I_2)	Xe 4K fcc 6.13
Cs 5K bcc 6.045	Ba bcc 5.02	La hex. 3.77 *ABAC*	Hf hcp 3.19 5.05	Ta bcc 3.30	W bcc 3.16	Re hcp 2.76 4.46	Os hcp 2.74 4.32	Ir fcc 3.84	Pt fcc 3.92	Au fcc 4.08	Hg rhomb.	Tl hcp 3.46 5.52	Pb fcc 4.95	Bi rhomb.	Po sc 3.34	At —	Rn —
Fr —	Ra —	Ac fcc 5.31															

Ce fcc 5.16	Pr hex. 3.67 *ABAC*	Nd hex. 3.66	Pm —	Sm complex	Eu bcc 4.58	Gd hcp 3.63 5.78	Tb hcp 3.60 5.70	Dy hcp 3.59 5.65	Ho hcp 3.58 5.62	Er hcp 3.56 5.59	Tm hcp 3.54 5.56	Yb fcc 5.48	Lu hcp 3.50 5.55
Th fcc 5.08	Pa tetr. 3.92 3.24	U complex	Np complex	Pu complex	Am hex. 3.64 *ABAC*	Cm —	Bk —	Cf —	Es —	Fm —	Md —	No —	Lr —

Index System for Crystal Planes (Miller Indices)

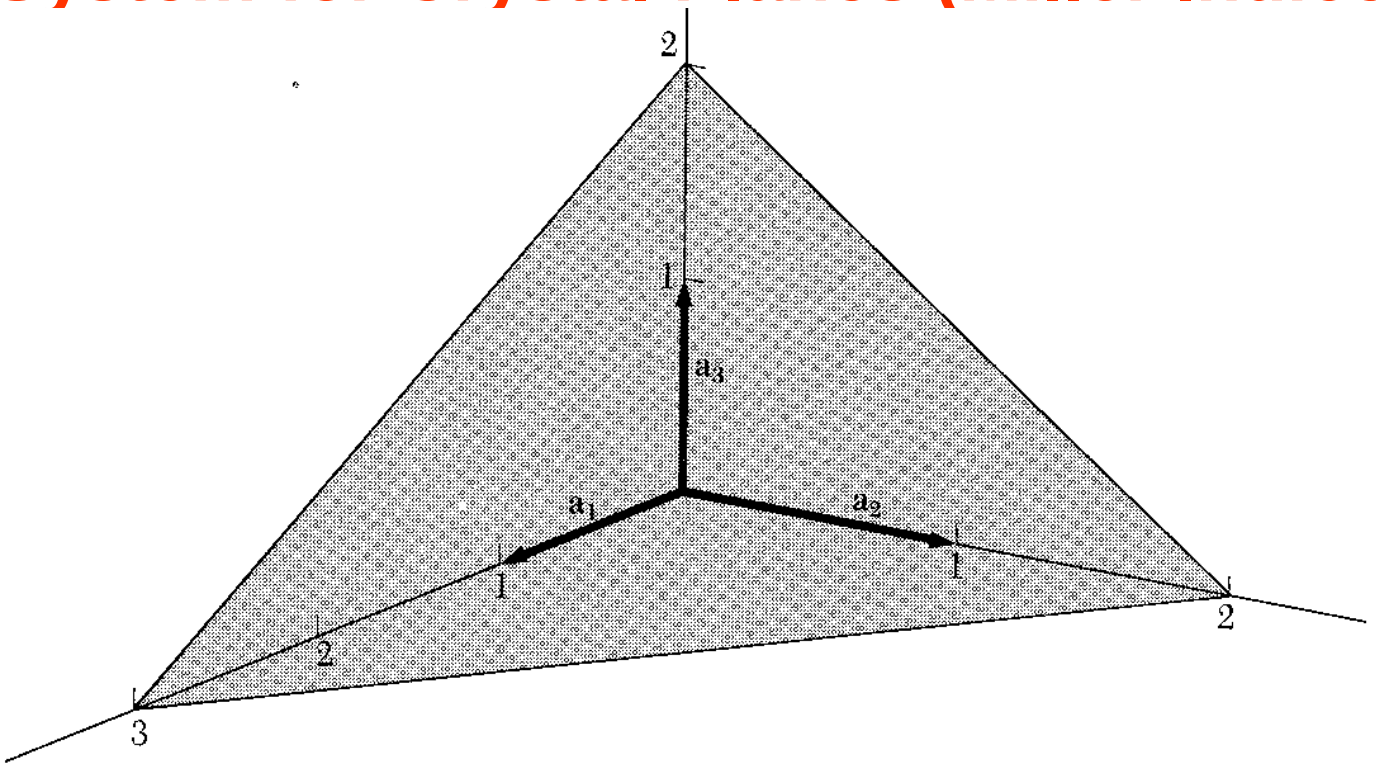
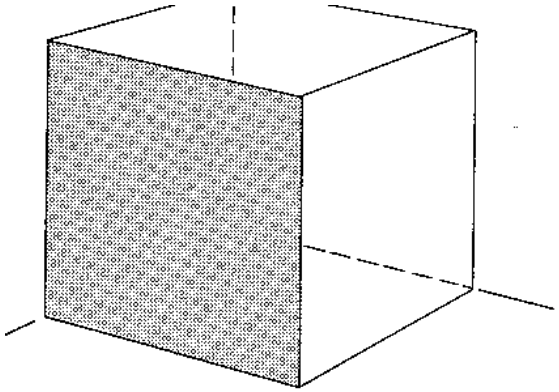


Figure 15 This plane intercepts the $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ axes at $3\mathbf{a}_1$, $2\mathbf{a}_2$, $2\mathbf{a}_3$. The reciprocals of these numbers are $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).

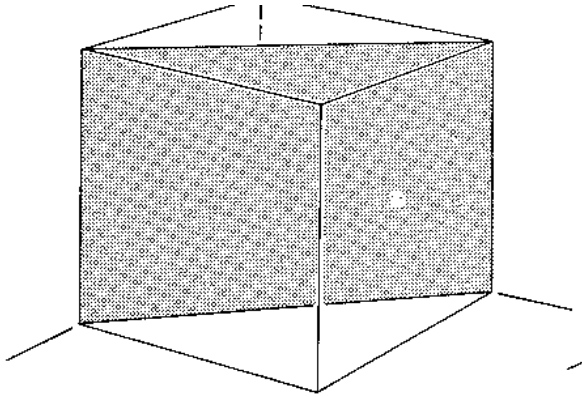
1) Find the intercepts on the axes in terms of the lattice constants $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. The axes may be those of a primitive or nonprimitive unit cell.

2) Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. The reulst enclosed in parethesis (*hkl*), is called the index of the plane.

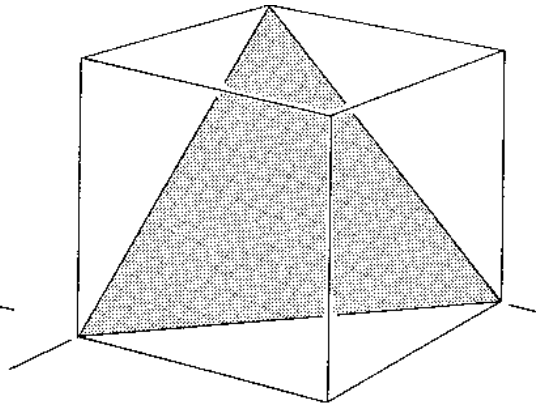
Crystal Planes



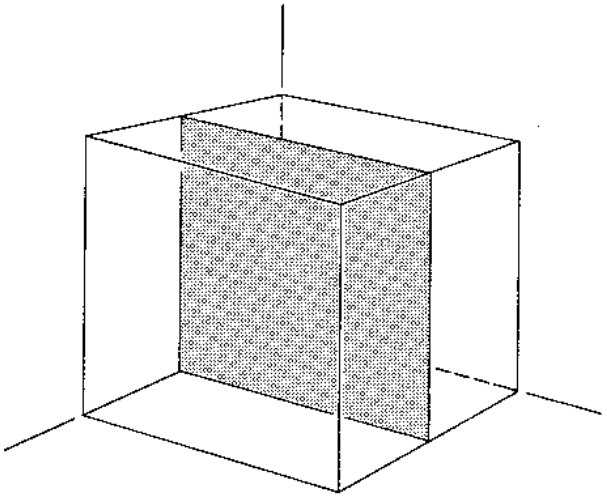
(100)



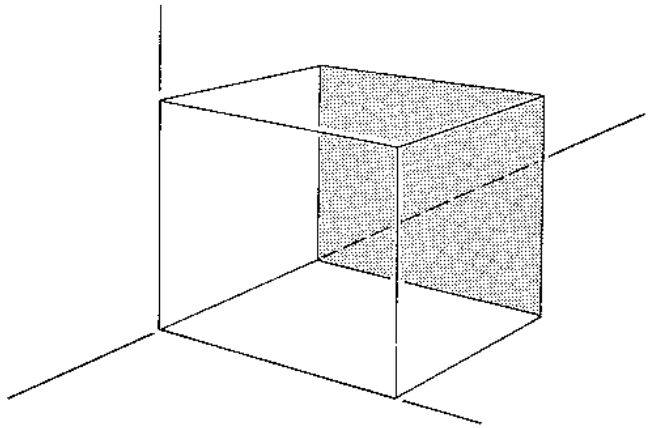
(110)



(111)



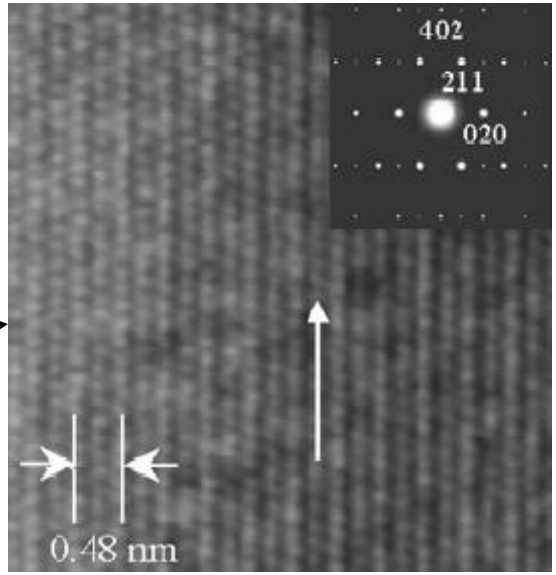
(200)

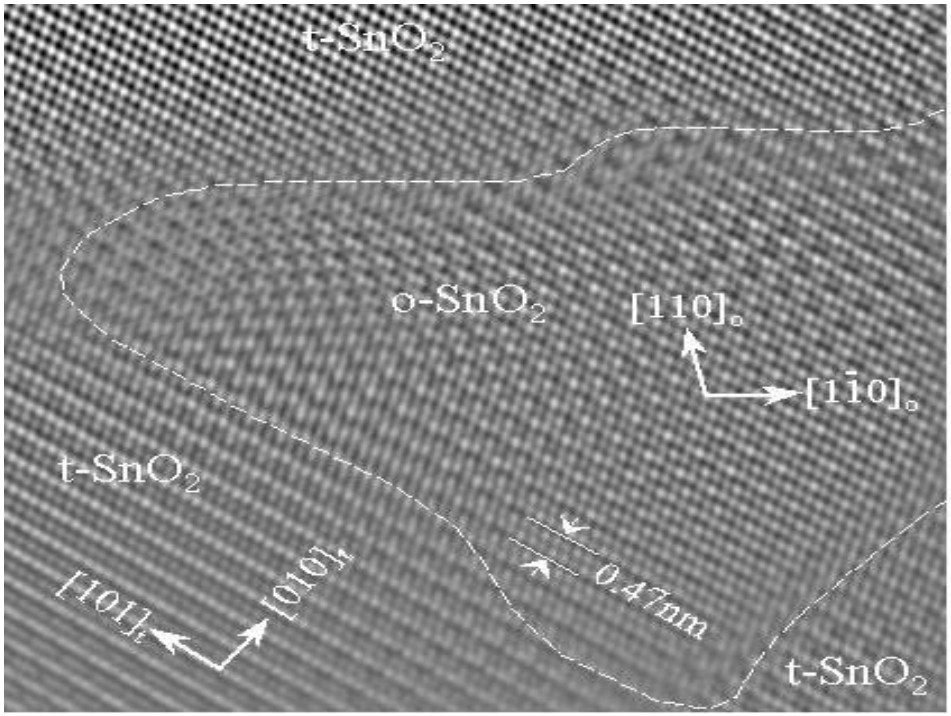


($\bar{1}00$)

Types of Microstructures

- Single Crystalline
- Polycrystalline
- Amorphous



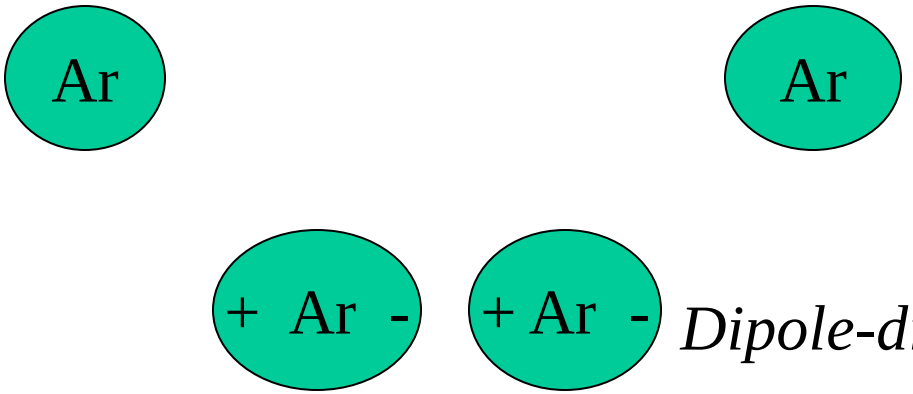


TEM images of nanobelts by Prof. Z. L. Wang

Crystal Bonding

- van der Waals bond
- Ionic bond
- Hydrogen bond
- Metallic bond
- Covalence bond

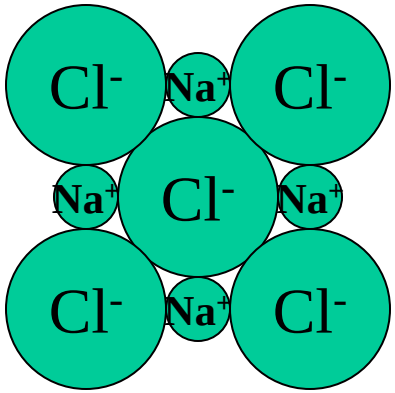
van der Waals bond



Dipole-dipole interaction

- Bonding energy: ~0.01 eV (weak)
- Compared to thermal vibration energy $k_B T \sim$ 0.026 eV at $T = 300$ K
- Examples: inert gases

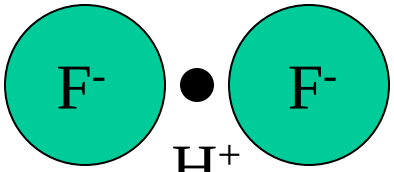
Ionic Bond



- The electron of the Na atom is removed and attached to the Cl atom
- Bonding energy: 1-10 eV (strong)

Hydrogen bond

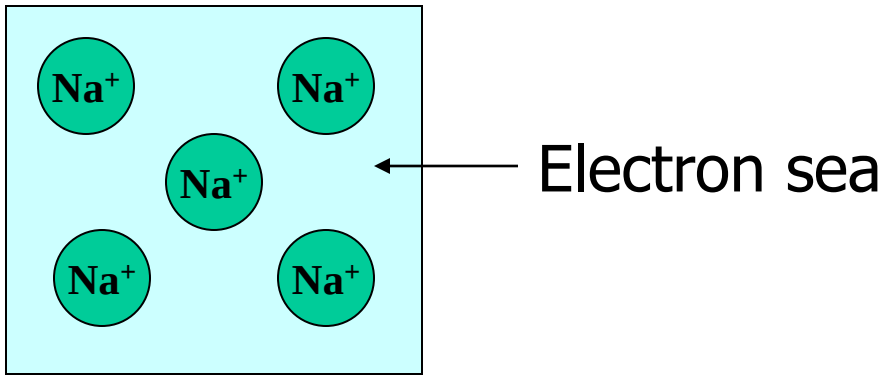
- The electron of the H atom is pulled toward the other atom
- Ionic in nature
- Bonding energy: $\sim k_B T$ (weak)
- Examples: DNA; intermolecular bond between water and ice



HF_2^- molecule

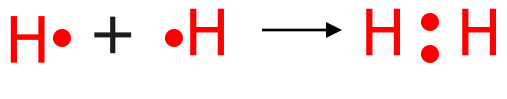
Metallic Bond

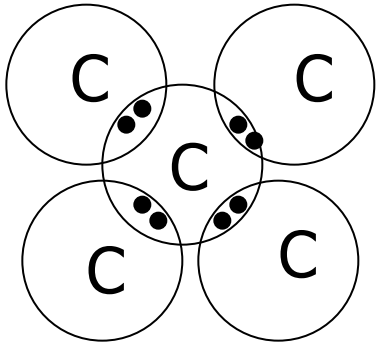
Positive ions in a sea of electrons



- Bonding energy:
  ~1-10 eV (strong)

Covalence bond





- Two atoms share a pair of electrons
- Bonding energy: ~1-10 eV (strong)
- Examples: C, Ge, Si, H_2

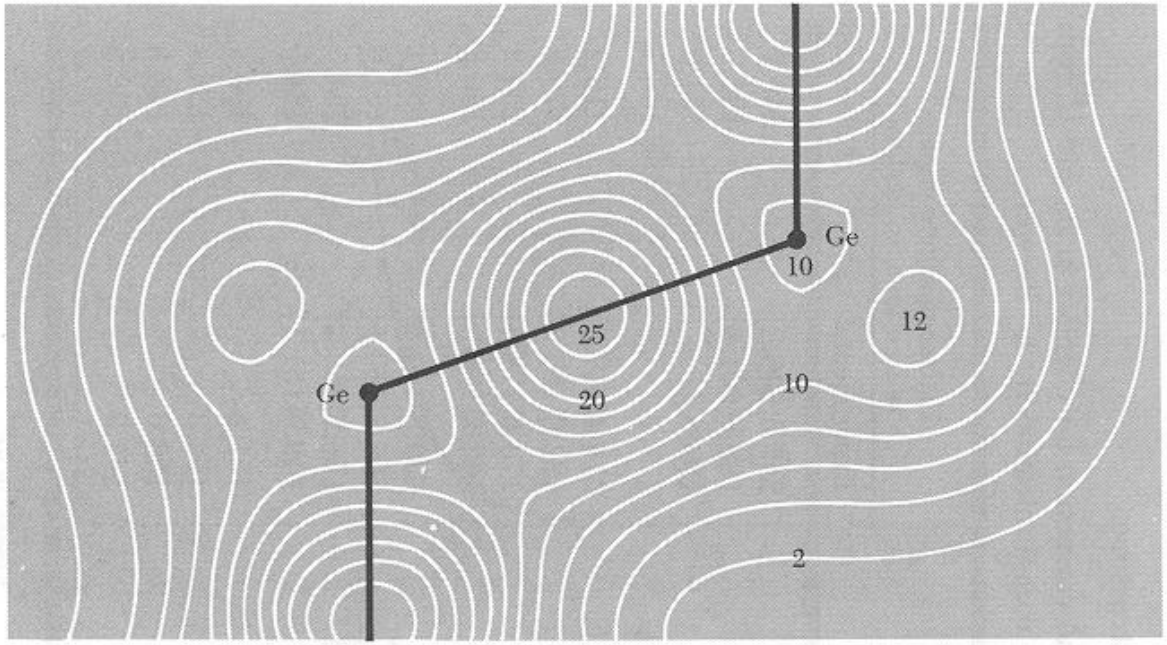
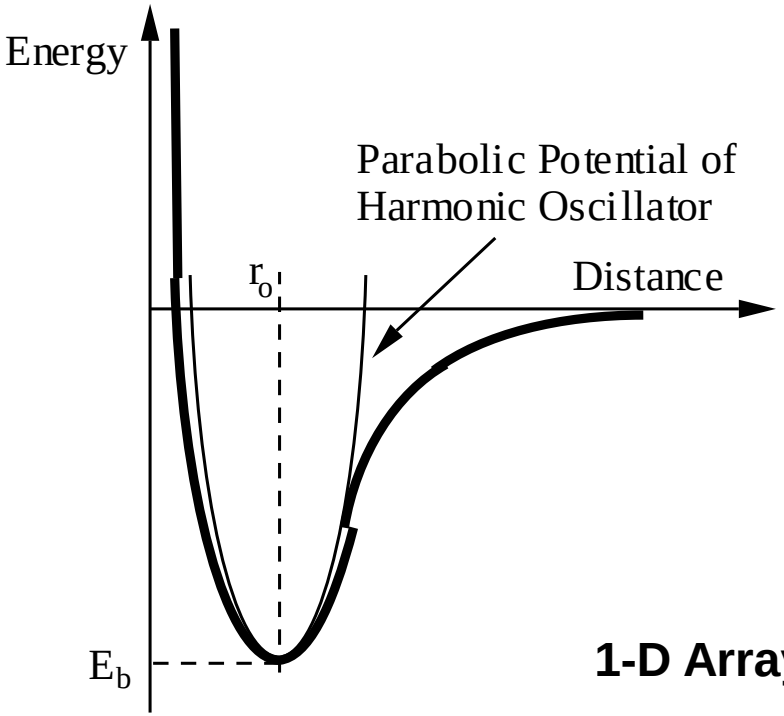


Figure 11 Calculated valence electron concentration in germanium. The numbers on the contours give the electron concentration per primitive cell, with four valence electrons per atom (eight electrons per primitive cell). Note the high concentration midway along the Ge-Ge bond, as we expect for covalent bonding. (After J. R. Chelikowsky and M. L. Cohen.)

Bonding Energy vs. Inter-atomic Distance



1-D Array of Spring Mass System