BANDS AND BONDS

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CHEMICAL BONDS IN SOLIDS

The chemical bond arises from a redistribution of electronic charge when atoms are brought in close proximity. The bond in a solid results from the superposition of charge densities of all atoms in the system. In an atom all electrons reside in their ground states at equilibrium. Only a few low lying excited states are typically accessed. The chemical bond in the solid consists of excited electronic configurations which are created to satisfy the constraints of a minimum energy, semi-infinite solid. These constraints create not only a variation on atomic energy level structure, but a compromise between the limiting classifications of bonding.
These limiting classifications and their compromises are discussed in this section.

Ionic Solids

Ionic solids are *compounds* which are composed of atoms with large electronegativity differences. They typically involve the strongly electronegative group VI and VII elements together with an electropositive counterpart. In the limit of complete charge transfer (closed shells), the structure and properties are those expected from array of electrostatically interacting charges. Structure can be predicted from Pauling's radius ratio approach and electrical insulating behavior is derived from the strongly bound valence electrons ($E_g > 3$ eV).

The *internal energy* of the system can be calculated simply and accurately by superimposing the measured compressibility relation on the electrostatic interactions of a point charge array as shown in Figure 1.5.

$$U = \int_{\infty}^{r} \left[F(attractive) + F(repulsive)\right] dr$$
$$= -N\left[- Ae^2 Z^2 / R + Be^2 / R^n\right] \qquad (1.3)$$
$$= \left(NAe^2 Z^2 R\right)\left(1 - \frac{1}{n}\right)$$

$$U(attractive) = -e\sum \frac{Z_1 Z_2 N}{R_{ij}} \qquad (1.4)$$

where R is the interatomic distance, Z is the ionic charge, A is the Madelung constant, N is Avogadvo's number, B is the repulsive potential coefficient and n is the Born exponent.

Example 1.6

List the first three terms of the Madelung (attractive) potential for NaCl. $\qquad (1.5)$

$$U(attractive) = 6 \cdot \frac{e^2}{r} \cdot (+ Z_1)(- Z_2) \;\; + \;\; 12 \cdot \frac{e^2}{\sqrt{2}\,r}(+ Z_1)^2 + \;\; \frac{e^2}{\sqrt{3}\,r}(+ Z_1)(- Z_2)$$

$\quad$ (Na$^+$) $\qquad$ (nearest neighbor Cl$^-$) $\quad$ (nearest neighbor Na$^+$) $\quad$ (next nearest neighbor Cl$^-$)

The closed shell model of ionic solids begins to break down as the average principle quantum number increases. When ions possess significant polarizability, the ion size is modified by the electric field of adjacent ions. Induced dipoles lead to interpenetration of electron clouds and deviations from pure electrostatic interactions. One then classifies in terms of percent ionic (central forces) and percent covalent (noncentral forces) character.

A sub-classification of ionic bonding is the *crystal field effect*. Transition metals with incomplete d shells reconfigure their bonding interactions, by promotion of electrons among the possible *spd* configurations, to match the point charge symmetry of the nearest neighbor ligands. This deviation from spherical symmetry is the response of the *crystal field*.

Covalent Solids

Covalent solids are composed of atoms which are not electropositive enough for metallic bonding but are too polarizable for ionic bonding. Their compositions typically include groups III, IV, V and VI atoms. The distinguishing property of the covalent bond is its directionality.

Example 1.7
Define a rule of thumb which distinguishes between ionic and covalent bonding for an atomic species.

When [ionic charge ÷ ionic radius] > 7, the system is too polarizable for ionic bonding (e.g., Ge, Si).

Covalently bonded materials follow, in general, the "8-N) Rule" of structure. *If N is the number of outer shell electrons, the coordination number is CN=(8-N).*

Example 1.8
Give some examples of the "(8-N) Rule" of coordination in covalently bonded solids.

C, Si, Ge, α-Sn	CN=4 (tetrahedral)
P, As	CN=3 (hexagonal-layered)
S, Se, Te	CN=2 (rings, chains)

The tetrahedrally coordinated structures (diamond cubic, zinc blende, and wurtzite) arise from a reorganization of the spherical "s" and perpendicular "p" atomic orbitals into a four-fold degenerate set of directional bonds with intrabond angles of 109.5°. This *hybridization process* promotes electrons from a low energy s^2p^2 configuration to a higher energy s^1p^3 configuration. However, the system free energy is lowered by the improved overlap of electron clouds with those of their neighbors.

The covalent bonds created by this overlap "share" charge as the electron density fluctuates temporarily between atoms. Note the chief criterion for minimizing free energy is *maximization of overlap not packing density*. In effect,

repulsive forces are determined by the complete inner shell electrons rather than the positively charged nuclear radii.

Example 1.9
Contrast covalently bonded structures with metallic and ionically bonded structures.

The covalent structure is more open than the close packed metallic structures and the average electron density varies more slowly between atoms than in the ionic case.

The properties of the covalent solid cannot be treated in the straightforward, analytic fashion of ionic materials. The bond is not truly a local bond. The sharing of the electron density creates extended states of the crystal which cannot be described as two center excitations. As the assembly of atoms condenses, the degenerate, sharp atomic states interact and are broadened in energy to a band. (The Pauli exclusion principle prohibits two particles in the same system from occupying the same energy state.) The band of filled or bonding states is called the *valence band*. The band of empty or antibonding states is called the *conduction band*. The highest energy occupied states are separated from the lowest energy unoccupied states by an energy region containing no states known as the bandgap. The energy difference between the top of the valence band and the bottom of the conduction band is E_g, the gap energy.

At low temperatures all pure semiconductors behave as insulators, because nearly all electrons are participating in bonding. As the temperatures is increased, the electrical conductivity increases with a characteristic activation energy of $E_g/2$, reflecting the thermal excitation of carriers from bound to free conduction states.

Metallic Solids

Metallic solids are composed of the electropositive elements of Groups I, II and III. The chemical tendency to donate electrons results in a high CN (8, 12) reflecting predominantly hard sphere repulsive interactions. The valence electrons form a continuum which produces cohesion through interaction with the positive ion cores. This free electron gas readily moves through the crystal under the bias of an electric field and produces high electrical conductivity.

In contrast to semiconductors which exhibit an activated conductivity which increases with temperature, metals exhibit a high conductivity which slowly decreases with temperatures due to carrier scattering by vibrating atomic cores. The density of free carriers is not an activated quantity because the valence band is not filled and empty conduction states are available with negligible excitation. This same condition is responsible for the characteristic metallic lustre (high absorption and reflectivity of visible light). The nondirectional nature of the metallic bond leads to the ductility or ease of plastic deformation of metals.

Mixtures of Group I, II and III elements form alloys, ordered solid solutions and intermetallic compounds. Trends in the formation of these phases have been delineated by Hume-Rothery and Darken and Gurry. *Alloys* are completely miscible mixtures formed by metal atoms with similar values of atomic radii which crystallize into the same structure. *Ordering* occurs in some alloy structures at specific compositions, e.g., Cu_3Au. The structure is characterized by interpenetrating superlattices as expected for a compound, but the distribution changes to that of a random alloy at high temperatures. *Intermetallic compounds* form at fixed ratios of constituents and represent a true metallic phase, e.g., $CuZn$, Cu_5Zn_8. A special class of intermetallics is the interstitial phase which consists of a smaller nonmetallic element (B) in the interstices of a metallic (A) structure. These compounds are typically carbides, hydrides and nitrides and form when $r_B / r_A < 0.6$.

Van der Waals Solids

Van der Waals solids consist of inert gas or molecular components. The structure is, typically, close packed reflecting the repulsive potential exhibited by the complete outer electron shells of the constituents. The bonding forces are derived from the Van der Waals interaction which is dipolar in nature. The time variation in electron density about an atom produces an oscillation in the center of gravity of the charge which can order cooperatively with the same process of neighboring atoms to yield a net attractive force. Induced dipole effects of this type are weak but non-negligible. Molecules which possess a permanent dipole exhibit a higher cohesive energy.

Hydrogen Bonded Solids

Hydrogen bonded solids consist primarily of the hydrides of fluorine, oxygen, and nitrogen. The cohesive forces are derived from the unique nature of the hydrogen bridge bond between two neighboring atoms, which enhances the normal intermolecular attraction.

Chemical Trends in Covalent Solids

Primary insights into nature covalent solids are most easily recognized through the Molecular Orbital Approach. In this description, the atomic energy levels lose their identity to molecular orbitals of the system. These new orbitals are composed of hybrids or combinations of the atomic orbitals. As always, the choice of orbital combinations reflects a minimization of free energy. This minimization is driven, for covalent bonding, by maximization of the overlap (sharing) of electron density.

The prototypical structure is four fold coordinated with tetrahedral symmetry reflecting sp^3 hybridization. Under hydrostatic pressure the atomic constituents are brought closer together and the orbital overlap is no longer optimal for an sp^3 electronic configuration. The s electrons delocalize to a metallic bond and a six fold coordinated, β-Sn (tetragonally distorted, simple cubic) structure is most stable. Table 1.3 lists some properties of the elemental solids of Group IV. It is evident from the melting points that the covalent bond strength decreases as atomic number (or the principal quantum number, n increases. For this isomorphic series, the lattice constant increases and the energy gap decreases with increasing n. In general, bond strength is inversely proportional to bond length and directly proportional to the energy gap.

No trend is evident for the electron mobility. Mobility represents the ability of the electron to accelerate under an applied electric field $\left(units = \dfrac{cm/\sec}{V/cm} \right)$. This property is, therefore, solely dependent on the mass of the electron which obviously varies among the materials. This variation is derived from the influence of the periodic lattice potential on the response of the electron. The mass of a free electron in a solid is discussed in terms of an effective mass m* which is not equal to the universal electron rest mass. Trends and manifestations of m* cannot be understood without knowledge of the full electronic band structure of the solid.

TABLE 1.3

Diamond Cubic Structure

	MP(°C)	a_0 (Å)	E_g (eV)	$\mu_e \left(\dfrac{cm^2}{V - \sec} \right)$
C(diamond)	---	3.56	~6	1800
Si	1410	5.42	1.1	1600
Ge	936	5.66	0.72	4400
Sn(gray)	232	6.45	0.08	2000
Pb	<------------------metallic------------------ >			

Compound semiconductors show the same trends as the Group IV elemental materials. Of equal interest are the trends among the compounds in comparison to the elementals. The structure is tetrahedral, CN=4 zinc blende (cubic) or wurtzite (hexagonal). In the wurtzite structure the next nearest neighbor position is slightly closer than for the zinc blende structure. A greater screening of opposite charges takes place, favoring wurtzite where a more electronegative constituent (charge transfer) is involved. Table 1.4 lists the structures of the III-V compound semiconductors.

TABLE 1.4

STRUCTURES OF III-V COMPOUNDS

W = wurtzite (hexagonal)
ZB = zinc blende (cubic)

	N	P	As	Sb
B	-	ZB	ZB	-
Al	W	ZB	ZB	ZB
Ga	W	ZB	ZB	ZB
In	W	ZB	ZB	ZB
Tl	-	-	metallic	metallic

Structurally, the compound semiconductors are distinguished by crystallographic polarity. Figure 1.5 illustrates how the termination of the (111) surfaces depends on orientation. The driving force for this configurational property is the high energy contribution of an unsatisfied bond. By terminating the bottom plane with group V(B) rather than group III(A) atoms, one rather than three unsatisfied bonds are exposed. The manifestations of this polarity are key to the control of epitaxial growth and chemical etching procedures.

Table 1.5 lists a comparison of elemental and compound semiconductors having the same principal quantum number. The compounds exhibit a higher melting point, a larger bandgap and similar lattice constants. The lateral (row in Periodic Table) trend toward larger bandgaps continues into the II-VI compounds. This phenomenon is evidence of the mixed (ionic/covalent) nature of the polar covalent bond. The bandgap, E_g, increases with change transfer (ionicity), even though the average principal quantum number, $\bar{n}$, remains constant.

TABLE 1.5

COMPOSITION/STRUCTURE/PROPERTIES
Group IV/III-V Compounds

III	IV	V
B	C	N
Al	Si	P
Ga	Ge	As
In	Sn	Sb

Properties M.P.($^\circ$K)	(IV/III-V) E_g (eV)	a_o(Å)
-------------	6/10	3.56/3.16
1685/1770	1.1/3	5.42/5.46
1231/1510	0.72/135	5.66/5.65
508/798	0.08/0.18	6.45/6.09

Figure 1.5

$[\bar{1}\,\bar{1}\,2]$

$[\,111\,]$
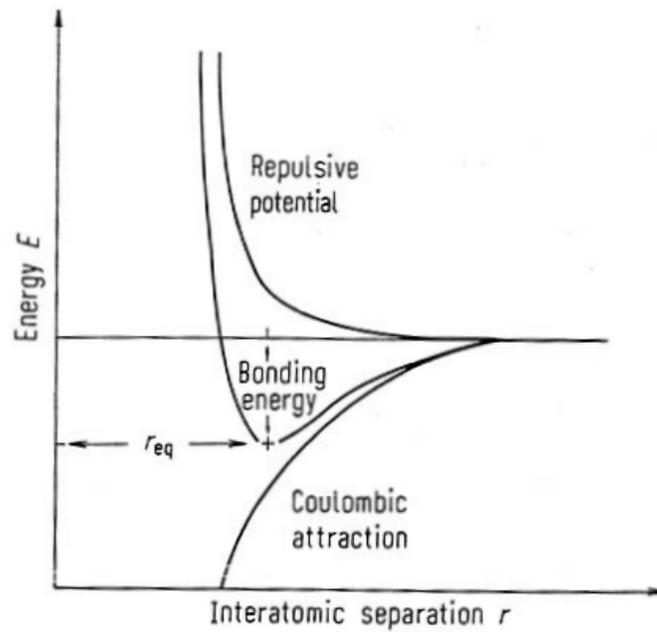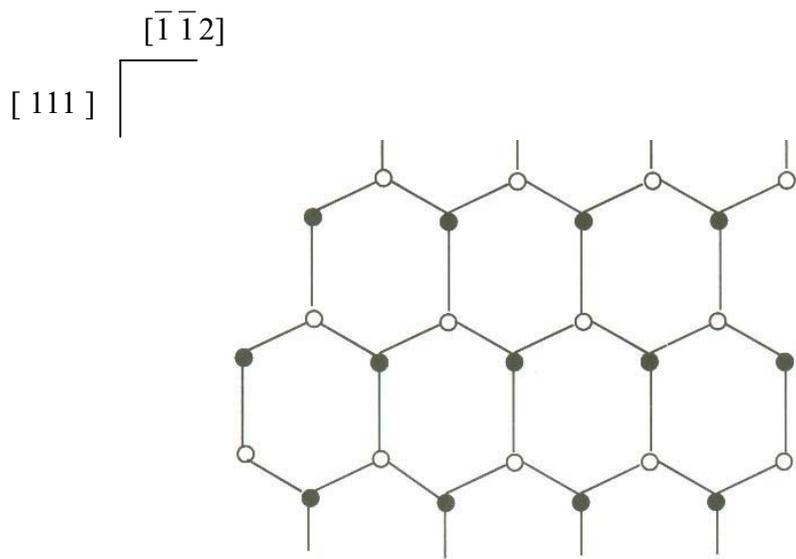
Figure 1.6
ZINC BLENDE STRUCTURE

ENERGY BANDS IN SOLIDS

When separate atoms bind together in a single system to form a solid, their electronic structure is perturbed by the bonding interaction. For a given structure this change in configuration must satisfy two primary constraints: 1) the Pauli exclusion principle and 2) the periodic lattice potential of the atomic cores.

As shown in Figure 1.7 the identical one electron states of the hydrogen atom form two distinct states upon formation of the H_2 molecule. Likewise an array of six atoms must possess six new states for each original atomic state. This behavior follows because two electrons cannot occupy the same state in the same system (Pauli exclusion principle). Therefore, discrete atomic levels broaden into a band of levels. Since the typical solid contains ~10^{22} atoms/cm^3 (Si has 5×10^{22} atoms/cm^3), a nearly continuous distribution of energies results. The "shape" of the bands of electron states are determined by the finite size of the solid and the periodic array of potentials contained therein.

Sommerfeld proposed in 1928 that free electrons in a solid should behave as a 'particle in a box'. Solution of the wave equation determines the allowed energies as

$$E = \frac{\bar{h}^2 \vec{k}^2}{2m} \qquad\qquad (1.6)$$

$$\vec{k} = \frac{\vec{p}}{\bar{h}} = \frac{2\pi}{\lambda} \qquad\qquad (1.7)$$

where m is the *mass* of the electron, $\vec{p}$ is the electron *momentum*, and $\vec{k}$ is the electron *wave vector*. The theory predicts one continuous band of energies whose allowed values vary quadratically with $\vec{k}$.

The Sommerfeld model is instructive, but fails to consider that the potential energy of an electron in a solid is *not* zero. The charge located at each lattice site presents a periodically varying potential which excludes certain states from the crystal in the same manner that an x-ray wave is diffracted at the Bragg condition. The electron wave scatters off the lattice points as it moves.

When the electron wavelength matches the condition that its maxima or minima occur at lattice points separated by a distance a, $n\lambda = 2a$, constructive interference occurs and standing waves are created. An electron in this sate must have zero velocity and, hence, cannot exist in the crystal. Two standing waves mark the boundary of this forbidden energy region: one associated with the lattice potential minima and one associated with the lattice potential maxima. As the lattice potential becomes deeper, the "energy gap" widens.

The electron wavelength is formally discussed in terms of its *wave vector*, $k = \frac{2\pi}{\lambda}$. The motion of the electron wavepacket is described by the term $e^{i\vec{k}\cdot\vec{r}}$. The electron *momentum* $\vec{p}$ is related to $\vec{k}$ through the de Broglie relation, $\lambda = h/p$. Thus,

$$\vec{p} = \bar{h}\vec{k} \qquad\qquad (1.8)$$

The mass of the electron, as for any particle, can be calculated as the second derivative of its energy with respect to its momentum.

$$m^* = \frac{\bar{h}^2}{d^2 E / d\vec{k}^2} \qquad\qquad (1.9)$$

The term m* is used to denote that the electron mass in a solid is not the same as the mass of a free electron. This difference in character is a consequence of the band distortion which is introduced by the periodic potential (energy gaps).

Figure 1.11 shows the discontinuities introduced into the free electron band scheme at the standing wave condition. Several important observations can be made regarding the electron mass and, hence, its ease of motion.

The band curvature (second derivative) is both positive and negative. Therefore, *the electron mass can be both positive and negative.* This result, practically, describes a particle which may respond both positively and negatively to the acceleration of an applied electric field. In real terms the positive mass is that of the negatively charged electron and the negative mass corresponds to a positively charged hole. In semiconductors *mobile electrons occupy empty states at the bottom of the conduction band. Mobile holes occupy states at the top of the valence band* which, in a perfect crystal, would be filled with bonding electrons.

The motion of a positively charged hole is, therefore, the motion of a bonding electron state which is empty. The positive nature of the carrier is manifested in its acceleration vector under an electronic field, which is opposite to that of an electron.

A second observation relates the curvature at the band edge discontinuity to the size of the energy gap. As the gap increases, the curvature will decrease, i.e., the effective mass, m*, will increase. Thus, for a series of semiconductor compounds with similar lattice constants and band structures, *the mobility is expected increase with decreasing energy gap.*

Table 1.6 lists the maximum mobilities, measured at low temperatures, and the energy gaps of some common III-V compound semiconductors. This result follows because a smaller energy gap implies lattice scattering potential which allows more free electron flow. This trend is most easily observed for direct gap semiconductors. *A direct gap material is one in which the minimum energy gap between the valence band and conduction band occurs at single value of $\vec{k}$.*

An indirect gap material is one in which the maximum for the uppermost filled valence band occurs at a different $\vec{k}$ than the minimum of the lowest empty conduction band. In an indirect material the energy gap need bear no relation to the curvature of the band extrema.

Figure 1.12 shows the band structures for silicon, an indirect gap semiconductor, and gallium arsenide, a direct gap semiconductor. The presentation of the band structure in this way exhibits two new features which are added for visual efficiency.

The periodic nature of $\vec{k}$ allows folding of values greater than π/a back into the same zone. This presentation is called the *reduced zone scheme.*

Since the crystal lattice is not a homogeneous, isotropic medium, the E vs $\vec{k}$ dispersion relations are dependent on direction within the crystal. An increase in the vector product $\vec{k}$ corresponds to a change in direction and, thus, the zone edge (integral, $\frac{2n\pi}{a}$) values of $\vec{k}$ correspond to high symmetry directions of the crystal lattice.

The vector nature of $\vec{k}$ is essential in describing the three dimensional crystal lattice potential.

The intrinsic electrical and optical properties of semiconductor materials are determined by the highest filled band, the valence band, and the lowest empty band, the conduction band. In the valence band all electrons are involved in localized bonding states and are not free to move. Electrons in the lower energy, filled bands are the atomic *core electrons* which are even more localized and tightly bound than those in the valence band.

The conduction band in any material is the lowest energy empty or partially filled band (see Fig. 1.13). Carriers which occupy states in the conduction band require no activation energy to move and, hence, acquire a kinetic

energy (E) in response to an electric field $(\vec{E})$ of $E = \int\limits_{o}^{x} \vec{E} dx$. This result follows because an empty state is

always available to the carrier at a negligible increase in energy. Thus, conduction through the crystal can occur with the full contribution of the externally applied potential.

TABLE 1.6

ENERGY GAPS AND ELECTRON MOBILITIES OF III-V COMPOUNDS

	$E_g(eV)\,0°K$	$\mu_n(cm^2/V\,\sec)$
GaN	3.39	150
AlAs*	2.30	180
GaP*	2.40	2100
GaAs	1.53	16,000
InP	1.41	44,000
InAs	0.43	120,000
InSb	0.23	1,000,000

*indirect gap
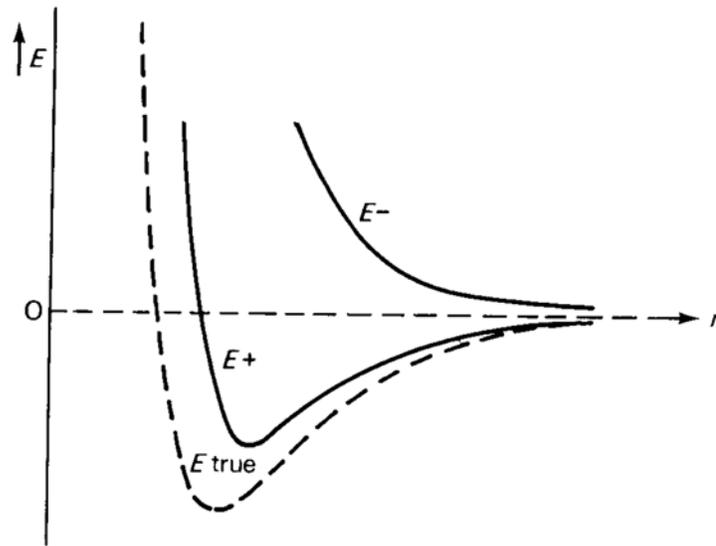
Figure 1.7(a)
VALENCE BOND ENERGIES FOR H₂
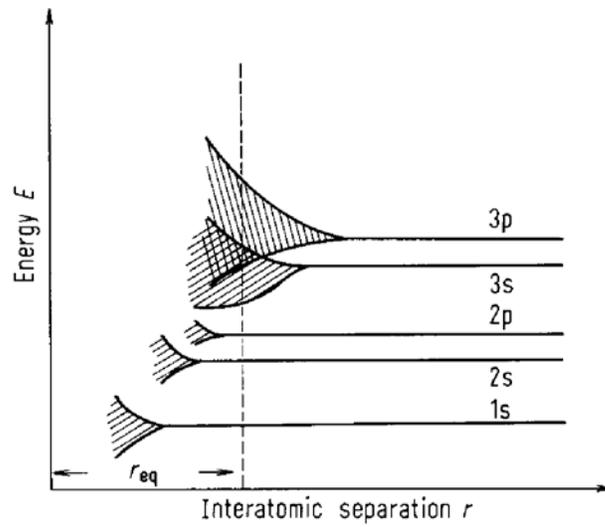
Figure 1.7(b)
ELECTRONIC ENERGY STATES FOR Mg

E

$$e^{i\vec{k}\cdot\vec{r}}$$

∞

O

L
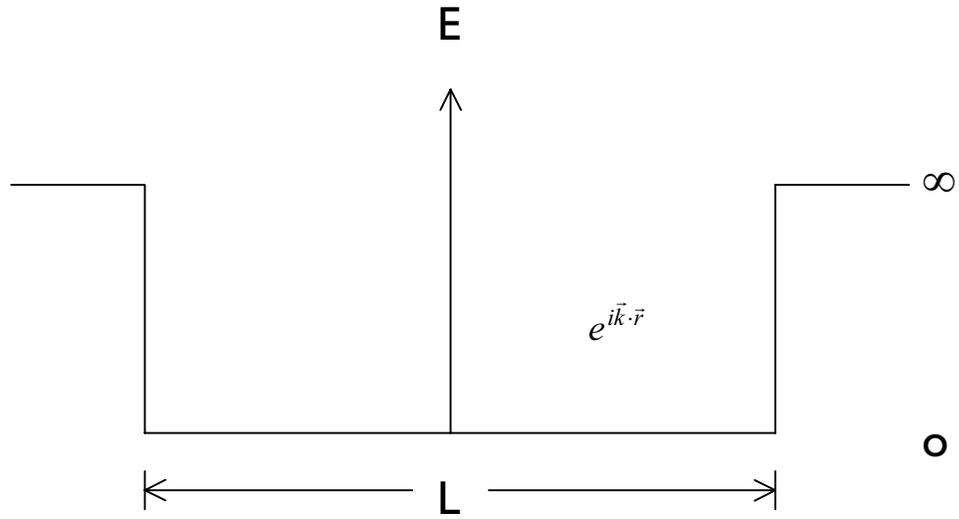
Figure 1.8
SOMMERFELD MODEL

E

$\bar{k}$

Figure 1.9

$A_o e^{i\vec{k}\cdot\vec{r}}$

o   o   o
o   o   o
o   o   o
o   o   o

$\vec{r}$
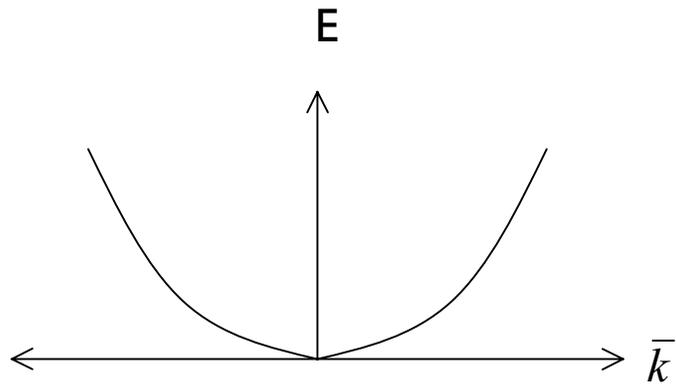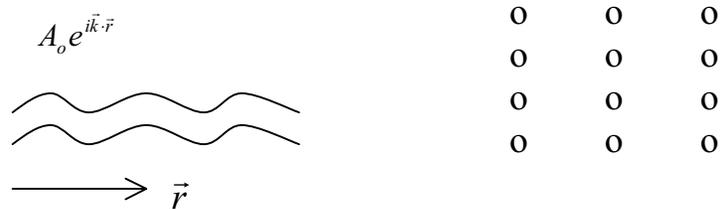
Figure 1.10
BLOCKWAVES IN A SOLID

12
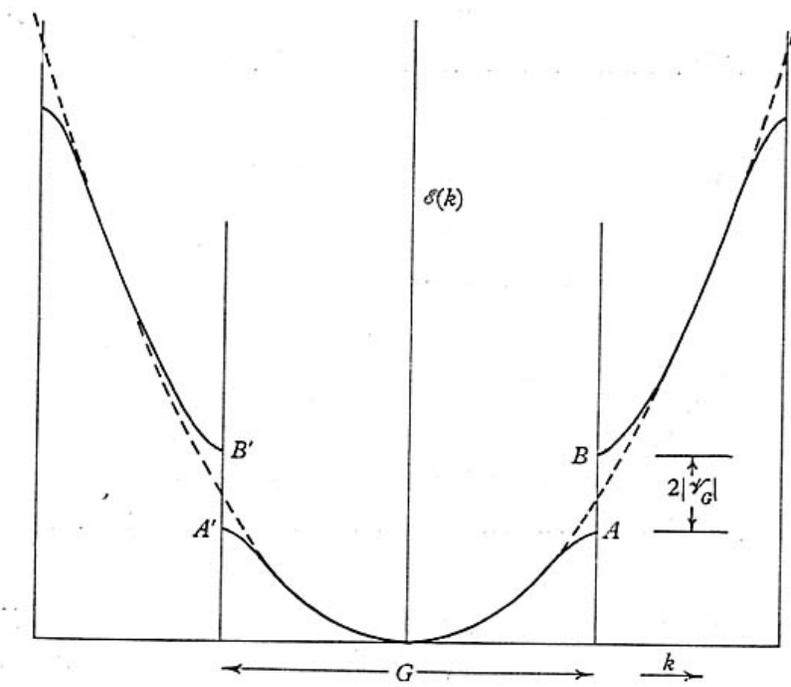
Figure 1.11
BANDGAPS USING LATTICE POTENTIAL
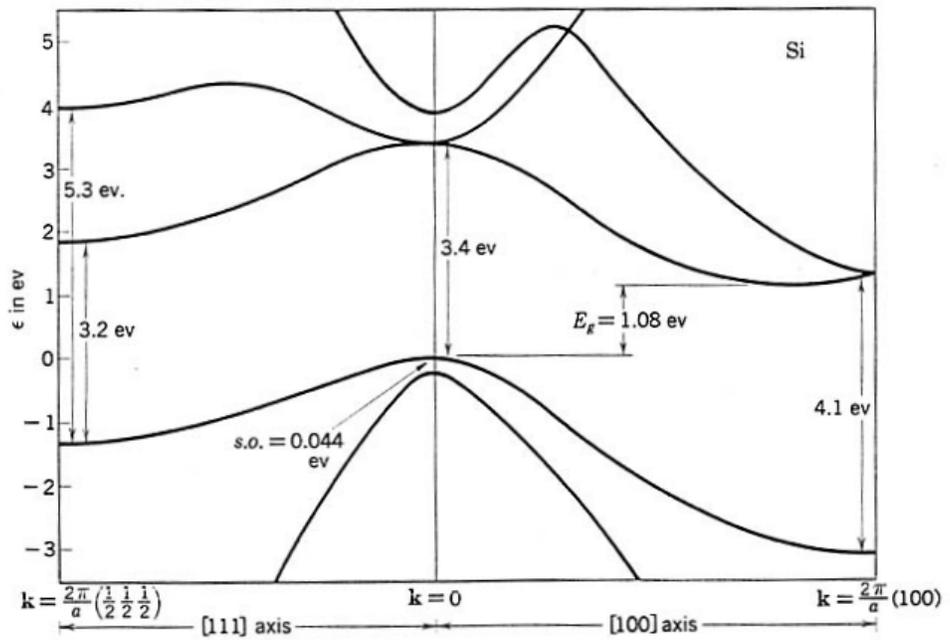
BAND STRUCTURE OF SILICON
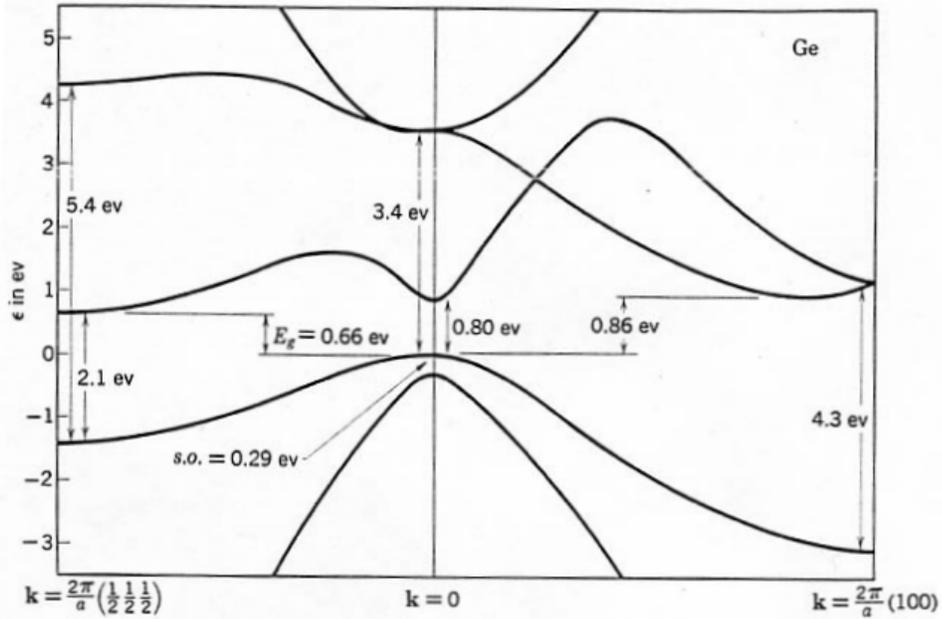
BAND STRUCTURE OF GERMANIUM
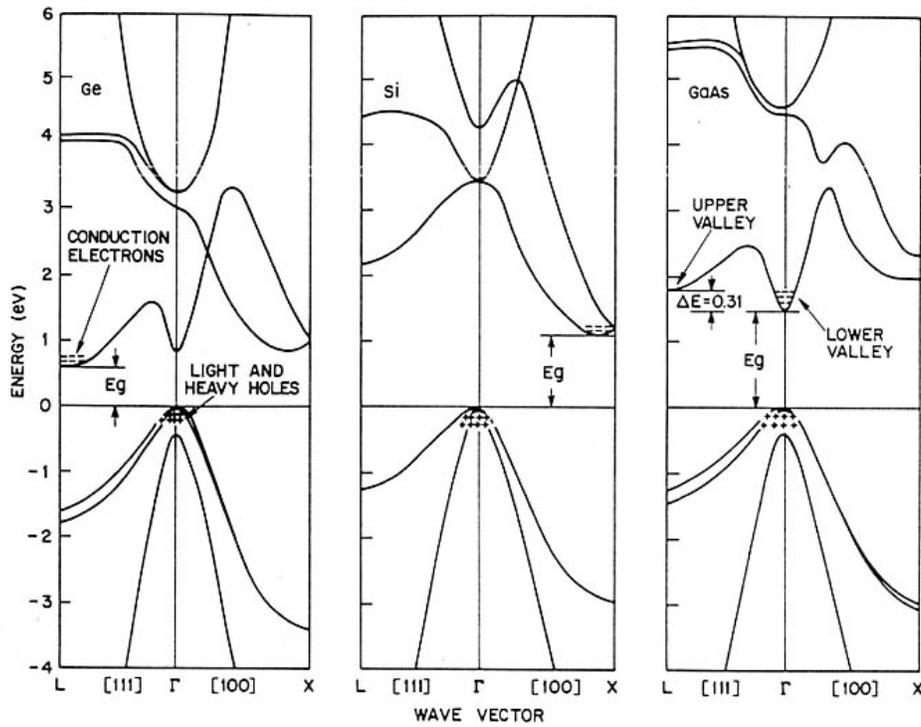
Figure 1.12
ENERGY-BAND STRUCTURES OF Ge, Si, and GaAs