TIGHT BINDING CALCULATIONS FOR THF ENERGY BANDS OF CRYSTALS WITH DIAMOND-LIKE STRUCTURE

BY

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DECLARATION

I hereby declare that this thesis has been prepared by me and that it is a record of my review of some literature and my own research work. It has not been presented in any previous application for a higher degree.

All quotations are indicated and the sources of information are acknowledged by means of references

SADIQ UMAR

10th December, 1990
Date

CERTIFICATION

This thesis entitled "*Tight binding calculations for the energy bands of crystals with diamond-like structures*", by Sadiq Umar meets the regulation governing the award of the Degree of Master of Science in Physics of Ahmadu Bello University, Zaria, and it is approved for its contribution to knowledge.

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DEDICATION

To

"My parents, for they deserve it all"

ACKNOWLEDGEMENTS

Special thanks to Dr. I.V.S. Rathore who gave the topic and contributed immensely to my understanding of the work. My thanks also goes to my Supervisors Professor J. Adetunji and Professor M.A. Rashid for their assistance, patience and understanding.

I would also like to thank my friends, mates and critics who played different roles inthe course of this work.

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ABSTRACT

The tight binding method was used to calculate *the* valence band structures of carbon, silicon and Germanium. only the nearest neighbour interactions were considered on the assumption that the two centre integrals would get smaller as the atoms get further apart. A general discussion of *the* method is given including the detailed calculations of the matrix elements.

In obtaining the numerical values of the energies corresponding to the different symmetry points, the values of the two centre integrals i.e the interaction of two orbitals on different atomic sites were taken from the value obtained by Chadi and Cohen (1975). The top of the valence band at. *T* was considered to *have* zero energy, so all other energies were measured relative to *the* top of the valence band.

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CHAPTER ONE

INTRODUCTION

The electronic energy band structures of semiconductors, mainly silicon and germanium have been studied extensively, both experimentally and theoretically, for many years (Ham *et al*, 1955; Weaire *et al*, 1971). These studies have given a very comprehensive account of the band structure in the range covering the energy gap and the edges of the valence and conduction bands, the energy region over which the electronic transitions involved in the characteristic semiconductor phenomena occur. More recently, detailed knowledge and understanding of band structure has become increasingly important in the design and analysis of semiconductor devices.

The aim of this work is to determine using the tight binding method the electronic energy and subsequently the band structure of diamond-like crystals. In chapter one, the general properties of solids i.e. conductors, semi-conductors and insulators are discussed. The structural and bonding properties of solids are reviewed in chapter two. In chapter three the methods of calculating the electronic energy are reviewed. Chapter four deals with the calculation of the energies of the diamond-like crystals using the tight binding approach. In chapter five, the results obtained were discussed.

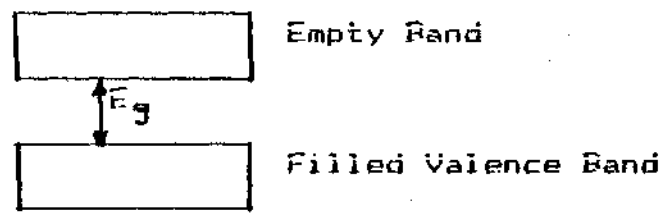
1.1 CLASSIFICATION OF SOLIDS

The electrons in a solid are distributed in a number of energy bands which are separated from each other by forbidden bands. Each energy band contains larger number of energy levels. The width of the energy bands is of the order of a few electron volts. Each enegy level in a band can accommodate two electrons having opposite spins (Pauli's exclusion principle). Normally only the lower energy bands will be filled by the electrons, and depending on the nature of band occupation by the electrons and on the width of the forbidden bands, all solids can be classified as, conductors, insulators and semiconductors.

CONDUCTORS

In some solids there is a partially-filled band above the completely filled lower bands and such band is formed from partially filled atomic levels as in the case of alkali metals. For example, a sodium atom has a single valence electron on its outer 3s energy level, thus, if there are N atoms in a solid piece of sodium, its 3s valence band will contain N energy levels and the N-valence electrons will fill in pairs only the lower half of the energy levels of the band. A partially filled band may also be the result of overlapping of completely-filled and empty-bands as in the case of Alkali -earth metals.

INSULATORS

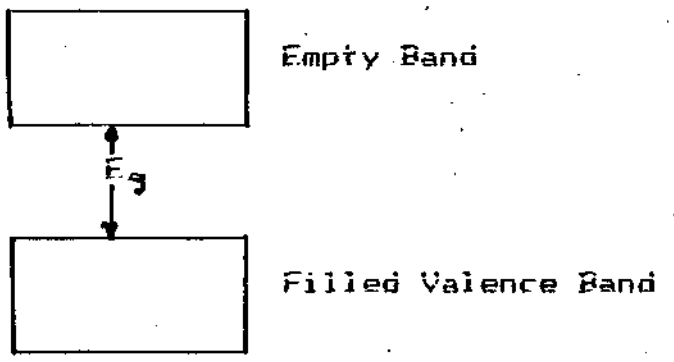


In some solids, the valence band which contains the outer electrons of the atoms is completely filled while the higher band separated by a large energy gap E_g is empty. Such a solid is an insulator i.e. a substance that does not conduct electric current. The reason being if an electric field is applied across the solid, the electrons in the valence band would not move within the band because there are no unoccupied levels in the band, they can however move to the higher empty band provided they get the required energy E_g, to cross the forbidden band. An electric field can not give the amount of energy to the electron inthe solid and so there can be no conduction of electricity and the solid will thus be an insulator.

Semiconductors

In some solids the width of the forbidden band energy gap is small (approx. 1eV). In such a case a small proportion of its electrons in the valence band at finite temperature have sufficient thermal energy to cross the forbidden band and occupy some conduction band states. Hence when an electric field is applied

some valence band electrons move in the direction of conduction band, thus permitting a limited current to flow. Such solids are known as semiconductors. Typical examples are silion (E_g = 1.1eV) and germanium (E_g = 0.7ev).



1.2 Energy Bands in Solids

A solid contains an enormous number of atoms packed closely together. Each atom when isolated, has a discrete set of electron energy levels, 1s, 2s, 2p, ... If N atoms of the solid are to be isolated from one another, they would have completely coinciding schemes of their energy levels as shown in Figure 1.1. The electrons fill the levels in each atom independently. As the atoms approach one another to form the solid, a continously increasing interaction appears between then which causes the corresponding levels of different atoms to split. Instead of a single level identical for all the N-atoms, now there are N-closely spaced levels. Thus each energy level of an isolated atom breaks up in a solid into N-densely arranged levels forming an energy band: These allowed energy bands are, in general, separated by regions which have

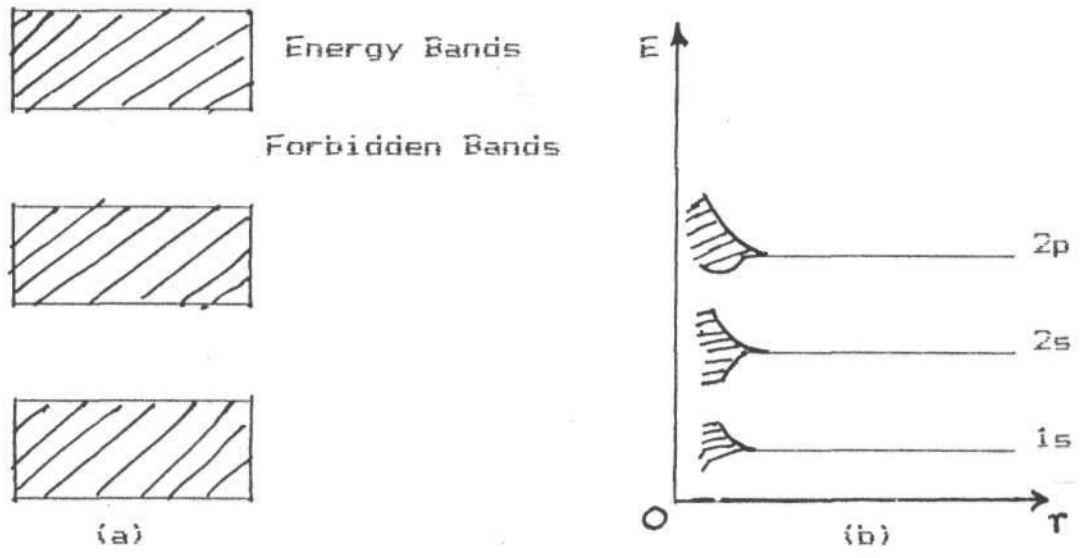


Fig. 1.1 Energy Bands in Solids

no allowed energy levels. These regions are known as 'forbidden-bands' or 'energy gaps'. In some solids, the adjacent energy bands overlap. The number of levels in such a merged band equals the sum of numbers of levels into which both levels of the atoms split up.

The amount of splitting is not the same for different levels. The levels filled by the valence band electrons in an atom are disturbed to a greater extent, while those filled by lesser electrons are disturbed only slightly. Figure 1.1 shows the splitting of the levels as a function of the distance r between the atoms.

The energy in a solid corresponds to the energy levels in an atom. An electron in a solid can have only those energies that fall within these energy bands. If the energy bands in a solid overlap, the electrons have a continous distribution of allowed energies. The energy bands structure of a solid and the occupaion of energy bands by electrons determine the electrical properties of solids.

Energy Bands

When many atoms are brought together to form a solid, the number of electron states is conserved, just as in the formation of diatomic molecules. Likewise as in diatomic molecules, the one electron states for the solid can, to a reasonable approximation, be written as linear combination of atomic orbitals. However, in solids, the number of basis

states is large. A solid of one centimeter cube may contain 10^{23} atoms, for each also, there is an atomic S-orbital and three P-orbitals. Such a problem involving some 4×10^{23} equations may seem impossible to solve, but the simplicity of the crystalline solid system allows for the effective and accurate solution. As the atoms are brought together, the atomic energy levels split into bands. The difference being, rather than splitting into a single bonding and a single antibonding state, the atomic levels split into an entire band of states distributed between extreme bonding and antibonding limits.

1.2.1 Form of the Energy Bands

At the edge of the zone, in the one dimensional case, and also at the centre of the zone, the group velocity is zero. Let us consider the points corresponding to $K=\pi/d$ and to $K=-\pi/d$. These are separated by $2\pi/d$ and so are equivalent, so that a wave function with $K = \pi/d$ must represent a standing wave. Moreover, wave functions with $K=\pi/d$ and $K=-\pi/d$ would represent waves travelling in opposite directions and the two values of K could not be equivalent. There being no transport in a standing wave, it must correspond to an electron with zero velocity i.e. the group velocity $\partial w/\partial k$ is zero, hence $\partial E/\partial K=0$. Thus the plot of E as a function of K along any of the principal directions which are perpendicular to the surface of the zone gives E versus K curves at the zone edges as shown in Figure 1.3

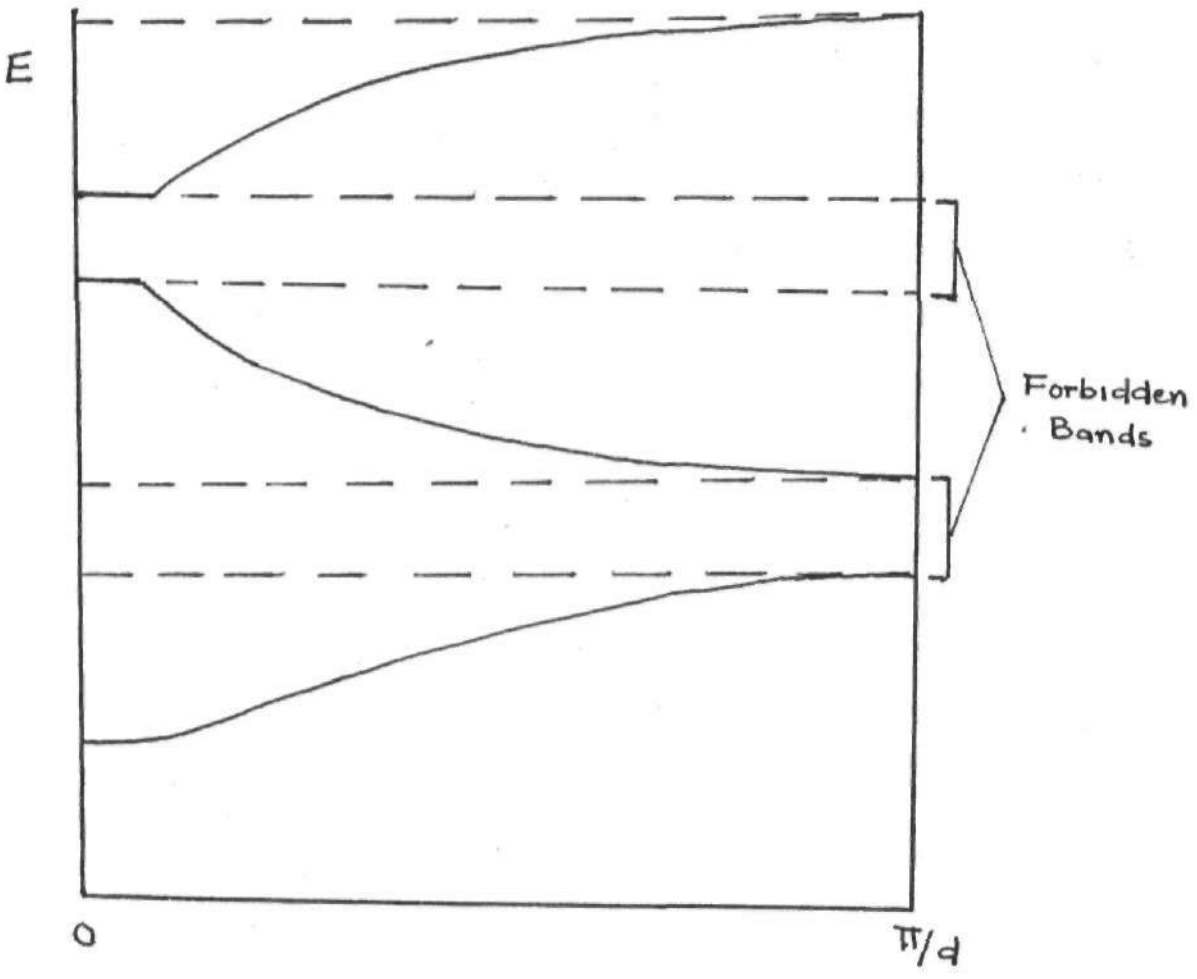


Fig 1.3 Energy Versus Wave Vector K at the Zero Edge

From the Schrondinger's equation it may also be shown that E(K) is a continous function of K with continous first and second derivatives, provided E is single valued, i.e. two branches do not meet. Since E is an even function it must therefore contain only quadratic terms near K=0. Thus, we also have $\partial E/\partial K=0$ when K=0, i.e. when we do not have degeneracy at K=0, and again the E-K curves must be similar to that shown in Figure 1.3 near K=0. At K=0 we may either have a minimum or a maximum. In practical cases either maxima or minima occur; if they lie at intermediate values of E they will be relatively unimportant; if they are the lowest minima or the highest maxima they will be of paramount importance. Various situations may arise, as discussed below.

The simplest band structure occur when the lowest unfilled band has a minimum at the centre of the zone and is single valued. We may then expand $E(K_x, K_y, K_z)$ in powers of K_x, K_y, and K_z in the form

$$E(K_x,K_y,K_z) = E_0 + AK_x^2 + BK_y^2 + CK_z^2 + \text{higher powers} \qquad 1.1$$

where A, B and C are positive constants. In particular, if we have a crystal with cubic symmetry we may reasonably suppose that A=B=C and, taking the zero energy at the bottom of the band we may express E for small values of K in the form

$$E=(\hbar^2/2M_e)(K_x^2+K_y^2+K_z^2) \qquad 1.2$$

where M_e is a constant, having dimensions of mass. Only when V(x) is constant, will M_e be equal to the free electron mass. In terms of the crystal momentum we have

$$E=(1/2M_e)(P_x^2+P_y^2+P_z^2) \qquad 1.3$$

The equations 1.2 and 1.3 differ from those for free electrons only in having the quantity M_n instead of m. Thus the electrons in this case behave like free electrons but with a different mass. The quantity M_n is generally referred to as the effective mass. In the case the energy bands are generally described as being 'Spherical', the reason being that the constant energy surfaces are spheres in K-space. Let us consider the form of the energy bands when the energy has a maximum when K=0. With the approriate choice of axes.

$$E = E'_0 - A'K_x^2 - B'K_y^2 - C'K_z^2 \qquad 1.4$$

when $A'=B'=C'$, this may be expressed in the form

$$E = E'_0 - (\hbar^2/2M_0)(K_x^2+K_y^2+K_z^2) \qquad 1.5$$

In this case, the electrons behave like free particles but with negative effective mass. The from of energy corresponding to this condition is as shown in Figure 1.4. The energy is plotted as a function of K_x but will be similar for any other direction in the crystal. The situation in which the upper band is the conduction band and the lower, the valence band represents the simplest possible band structure for a semi-conductor. The forbidden energy gap, which we represent by ΔE, is equal to $E_a - E'_a$ (in general $E_a < E'_a$) unfortunately, no semiconductor is known to correspond with this structure.

A similar situation would arise if the maxima and minima were to occur at the point on the surface of the Brillonin zone. The condition when this occurs along the x-axis is shown in Figure 1.5 for both conduction and valence bands.

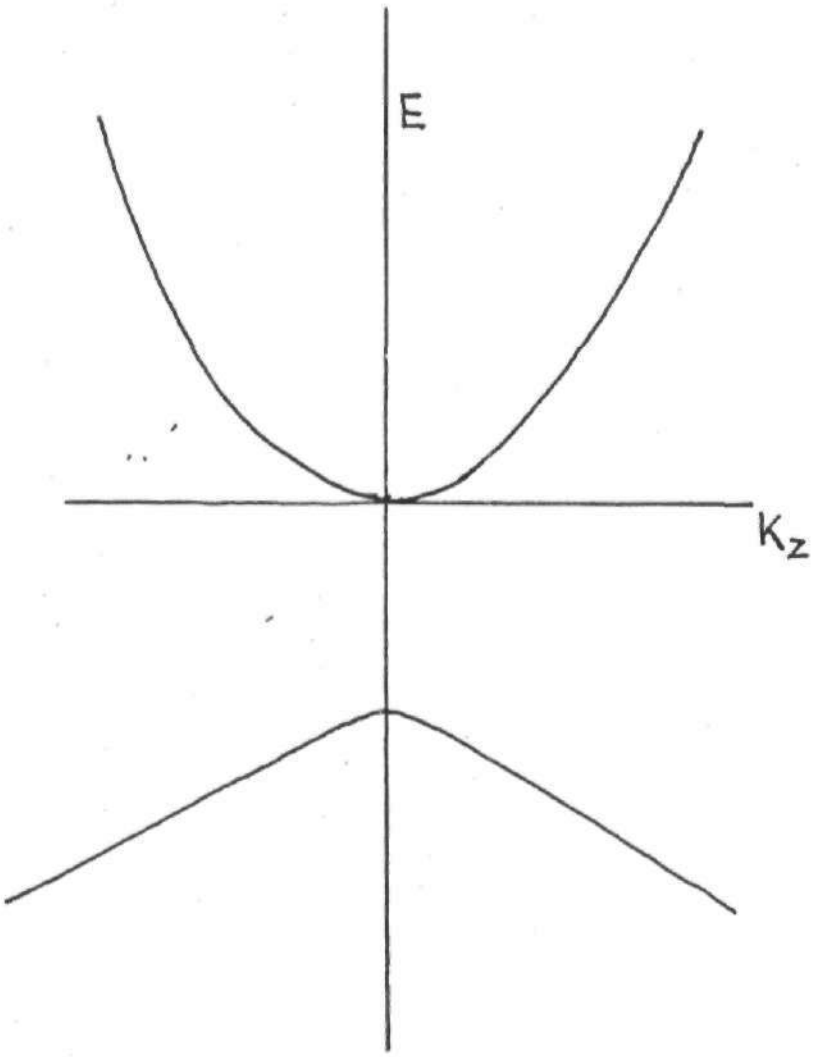


Fig 1.4 Spherical Energy Bands at the Centre of Brillouin Zone

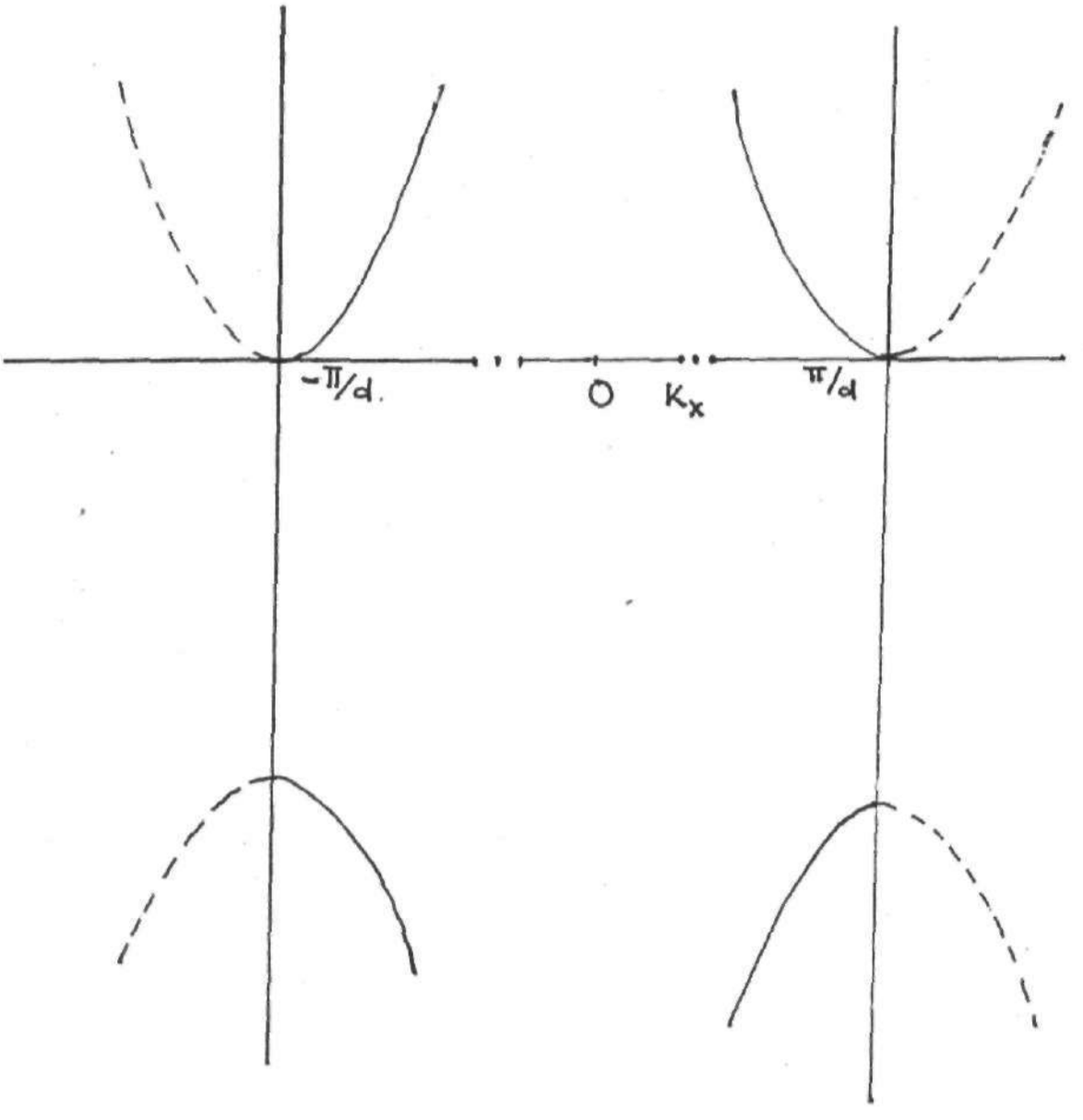


Fig 1.5 Spherical Energy Bands at the Surface of the Brillouin Zone

In this case there would not necessarily be spherical symmetry, but general cylindrical symmetry about the x-axis for a cubic crystal. For a minimum we should have, taking the zero of energy at minimum.

$$E = (\hbar^2/2)[(\pi/d - K_x)^2/M_1 + (K_y^2 + K_z^2)/M_2] \qquad 1.6$$

In this case we have two constant M_1 and M_2 and the effective mass is different in different directions. The form of the section of the constant energy surfaces by the (K_x, K_y) - plane is as shown in Figure 1.6; they are ellipsoidal in form. The dotted section represents the continuation of the ellipsoid for value of K outside of the zone. This is equivalent to the part centred on $K_x = -\pi/d$ where d is the lattice spacing. If the crystal has cubic symmetry there will be other equivalent minima, for example, along the K_y-axis and K_z-axis.

There will thus be three equivalent minima in the conduction band at the points. $(\pi/d,0,0)$, $(0,\pi/d,0)$, $(0,0,\pi/d)$ in K-space. (Note that $(-\pi/d,0,0)$ corresponds to the some minimum as $(\pi/d,0,0)$. In crystals with cubic symmetry, minima may occur along other lines of symmetry, for example along (1,1,1) directions for which $K_x = \pm K_y = \pm K_z$

If the minima are at the edges of the zone we now have four minima. This situation holds for the conduction band of Ge. In such cases the constant energy surfaces are multiple. For crystals having cubic symmetry they consist of a number of ellipsoides of revolution, when the energy is nearly equal to the minimum value for the band. The centres of these

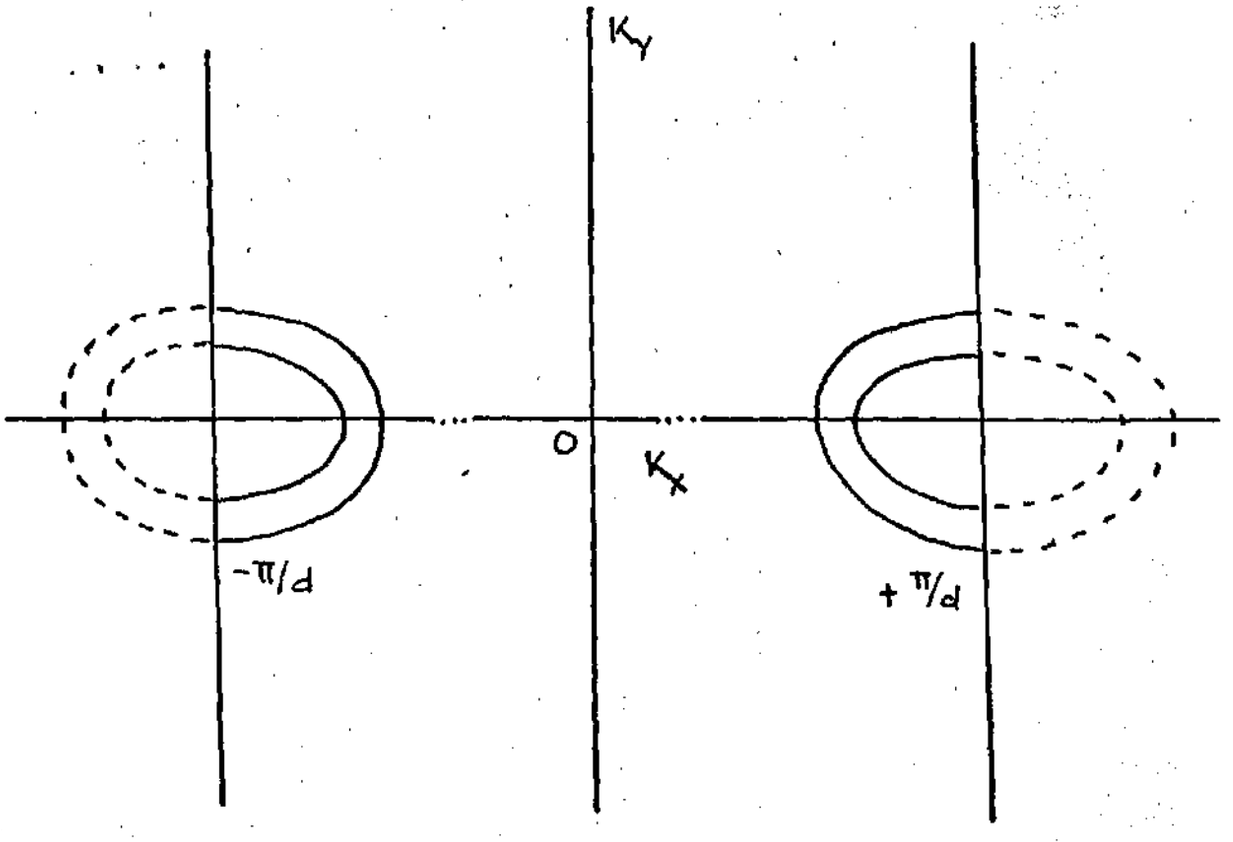


Fig 1.6 Constant Energy Surface by the (K_x, K_y) - plane

ellipsoids lie at the symmetry points corresponding to the minimum value of energy.

Suppose the minima do not occur at the edge of the zone but there is one at $(K_o,0,0)$ and others at equivalent positions, with $0<K_o<\pi/d$. There will then be minima also at $(\pm K_o,0,0)$, $(0,\pm K_o,0)$, $(0,0,\pm K_o)$ and these will all be distinct. There will thus be six minima. The energy near $(K_o,0,0)$ will then be given approximately by

$$E = \hbar^2/2\left[(K_0-K_x)^2/M_1 + (K_y^2+K_z^2)/M_2\right] \qquad 1.7$$

For the state corresponding to $(K_o,0,0)$ the crystal momentum will not be zero unless $K_o=0$ but equal to $K_o\hbar$. The velocity of an electron in this state will, however, be zero since

$$\begin{aligned} V_x &= \hbar/m_1(K_x-K_0) \\ V_y &= \hbar/m_2(K_y) \\ V_z &= \hbar/m_2(K_z) \end{aligned} \qquad 1.8$$

The deepest minima may also occur inside the zone along other symmetry axes. For the conduction band of silicon they occur along the (1,0,0) axes. There will therefore be six such minima. Constant energy surfaces corresponding to such conditions are shown in Figure 1.7 for the (K_x,K_y) plane.

From equation (1.8) the velocity V is zero at minimum of the energy (or at a maximum). It can be shown that under certain symmetry conditions, it is also zero at the edges of the Brillouin zone.

A complication arises whens there is a degeneracy i.e. when two energy bands touch at a point. For example, in the valence bands of Si and Ge we have two

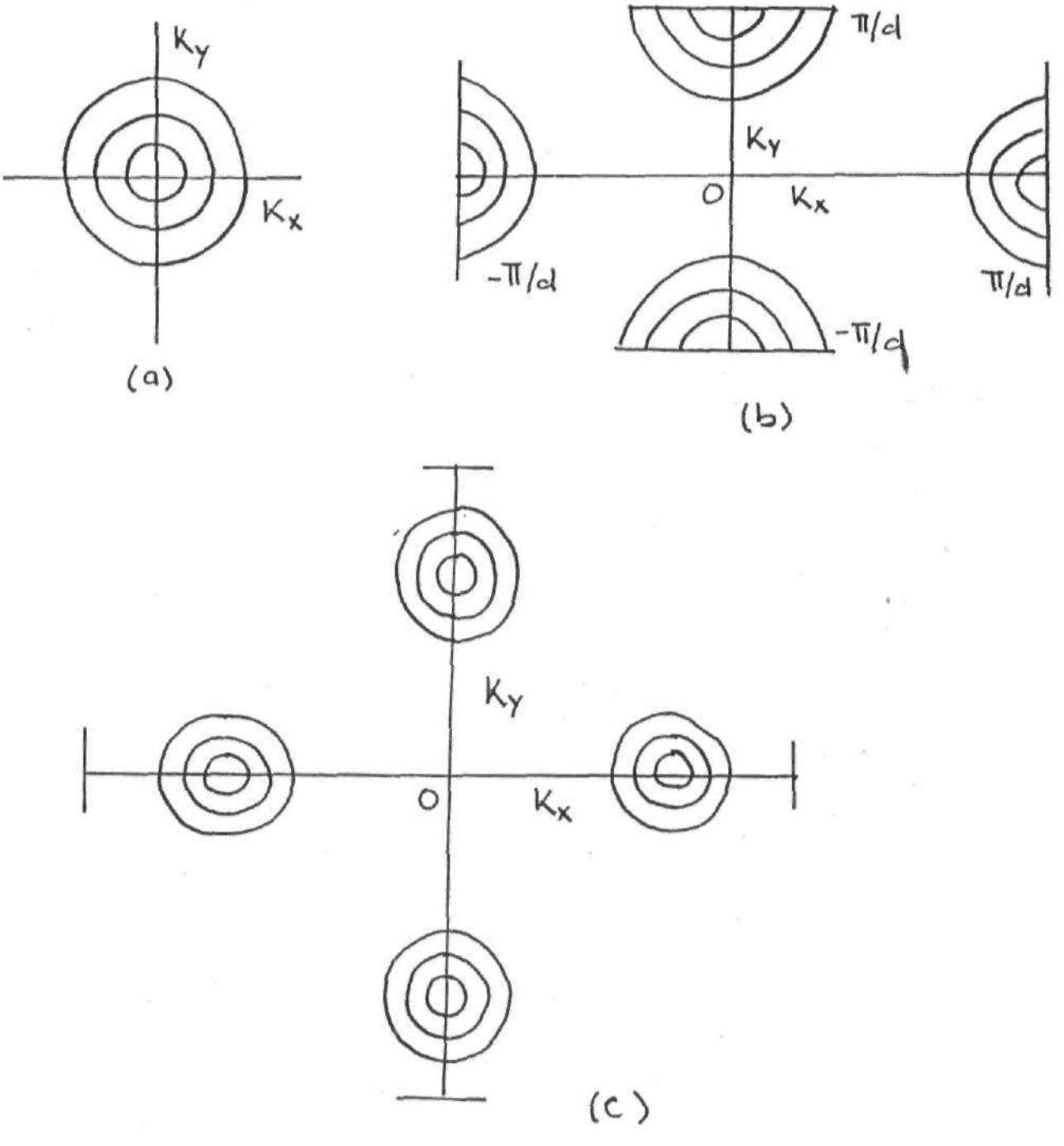


Fig 1.7 Constant Energy Surfaces Corresponding to the Deepest Minima Inside the Zone

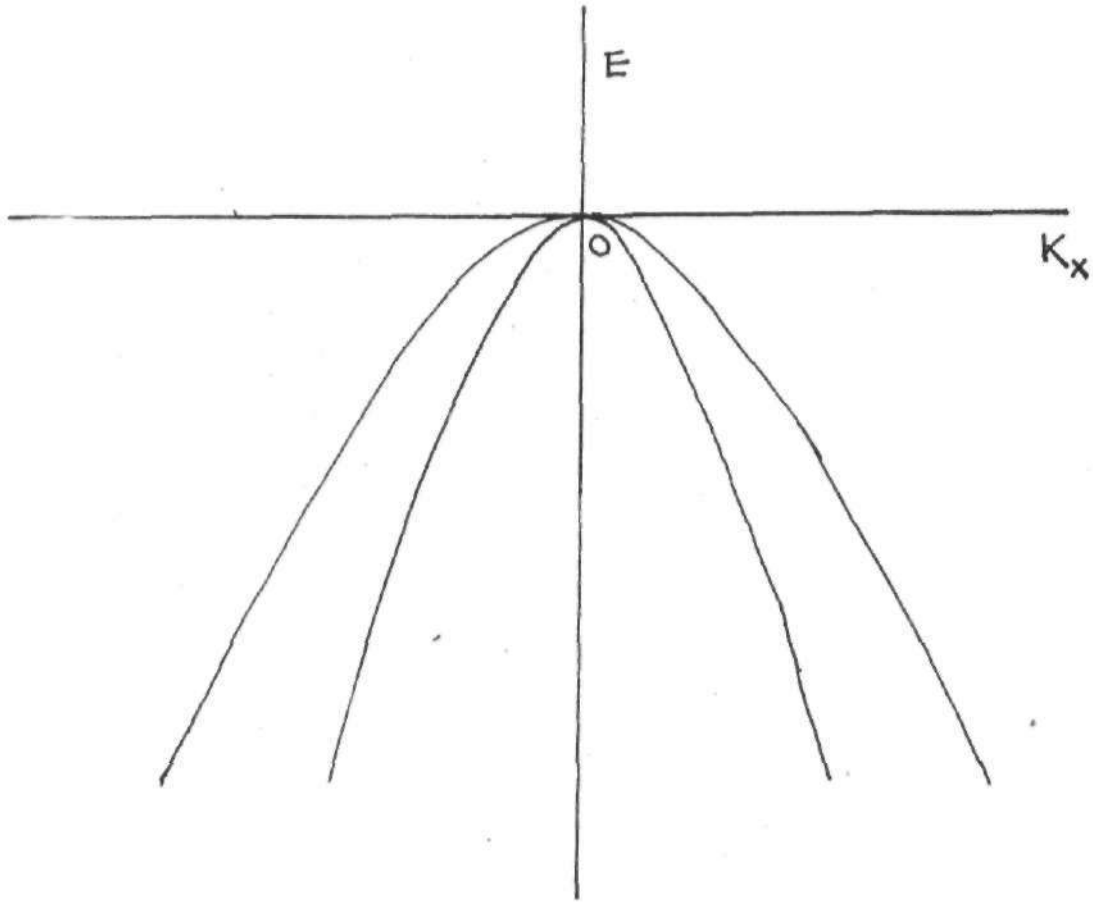


Fig 1.8 Bands Showing Degeneracy at the Centre of the Zone

nearly parabolic bands touching at the centre of the zone as shown in Fig 1.8 which shows the variation of the energy along K_x direction. Either of the values of a given value of K_x are possible and at $K_x=0$ they coincide. In this case, a simple expansion of E in even powers of K_x, K_y, K_z is not possible and a more complex form of expression must be used to express E even for small values of K. The result is that the constant energy surfaces are distorted from the spherical shape. For many purposes, however, the degenerate bands can be represented as two 'spherical bands with effective hole masses M_{h1} and M_{h2}. It usually turns out that one of the effective masses is much smaller than the other and the holes have came to be known as 'light holes' and 'heavy holes', much of the early works on their properties having been done on Si and Ge which have such a band structure.

Crystals with cubic symmetry such as Si and Ge, have diamond crystal structure and their bands are triply degenerate at K=0. If the coupling between the electron's translational motion and its spin are neglected a third band is split off from the former two and turns out to be almost 'spherical' in form with the maximum lying ΔE_s below the common maximum of the other two bands. This will have yet another effective mass M_h. The energy ΔE_s is known as the spin orbit splitting and is usually somewhat smaller than the forbidden energy gap ΔE. For some semi-conductors, however, ΔE and ΔE_s are about the same and as we

shall see, this gives them some interesting properties.

PROPERTIES OF SEMICONDUCTORS

At absolute zero (in equilibrium condition) a pure, perfect crystal of most semiconductors will be an insulator which has gained the characteristic free carriers by thermal or optical excitation becomes a conductor.

Semiconductors are electronic conductors with electrical resistivity values generally in the range 10^{-2} to 10^{9} Ohm-cm, at room temperature, intermediate between good conductors (10^{-6} Ohm-cm) and insulators (10^{14} to 10^{22} Ohm-cm). Carrier concentrations representations of metals, semimetals and semiconductors are shown in Fig. 1.9.

For most solids, one has to consider essentially two types of electrical conductivity i.e. electronic conductivity and ionic conductivity. In typical semiconductors, electronic mobility is much higher than ion mobility. It is therefore a good approximation in most cases to consider only the electronic conductivity. One may distinguish essentially two types of perfect crystals with regard to electronic conductivity, i.e. metals having approximately one electron per atom and being characterized at equilibrium conditions by a partially occupied band and insulators where at low temperature one does not have any free carriers. These materials are, therefore being characterized by completely filled bands at low temperature.

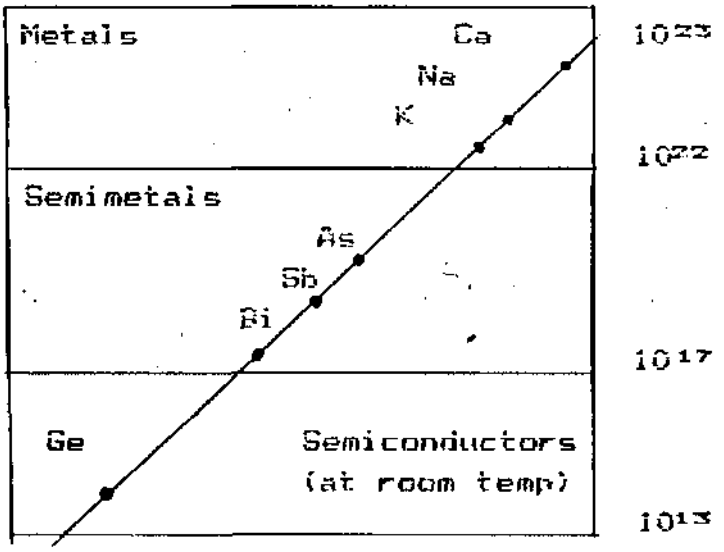


Fig 1.9 Carrier Concentration of Metals, Semimetals and Semiconductors

The electrical resistivity of a semiconductor may be strongly dependent on temperature. Devices based on the properties of semiconductors include transistors, rectifiers, modulators, detectors thermistors and photocells.

It has been observed that the thermal conductivity of semiconductor material is high and also that they show rectification i.e. they are not ohmic and also that they are sensitive to light.

The conducitivity of such a perfect crystal which also is referred to as an intrinsic semiconductor, comes from the thermal or optical excitation of an electron from the valence band into the conduction band. The minimum energy required for this process is the width of the forbidden band. Impurities in such materials give rise to localized energy states raising the fermic level (Excitation of free carriers from these states gives rise to extrinsic conductivity). Independent of the type of excitation, which can either be optical or thermal, when an electron is raised into any empty conduction band, it becomes a negatively charge free carrier. At the same time in the valence band and empty place for an electron is left which is now positively charged and is referred to as positively charged free carrier or hole. The conductivity in a semiconductor can then be either electronic and in this case is referred to as an n-type semiconductor or by a hole, in which case it is referred to as p-type semiconductor. An electronic band scheme leading to intrinsic conductivity is as

shown in Figure 1.10. The conduction band is vacant at absolute zero and is separated by an energy gap E_g from the filled valence band. The band gap is the difference in energy between the lowest point of the conduction band and the highest point of the valence band. The lowest point in the conduction band is called the conduction band edge, the highest point in the valence band is called the valence band edge. As the temperature is increased, electrons are thermally excited from the valence band to the conduction band as in Figure 1.11. Both the electrons in the conduction band and in the vacant orbitals or holes left in the valence band contribute to the electrical conductivity.

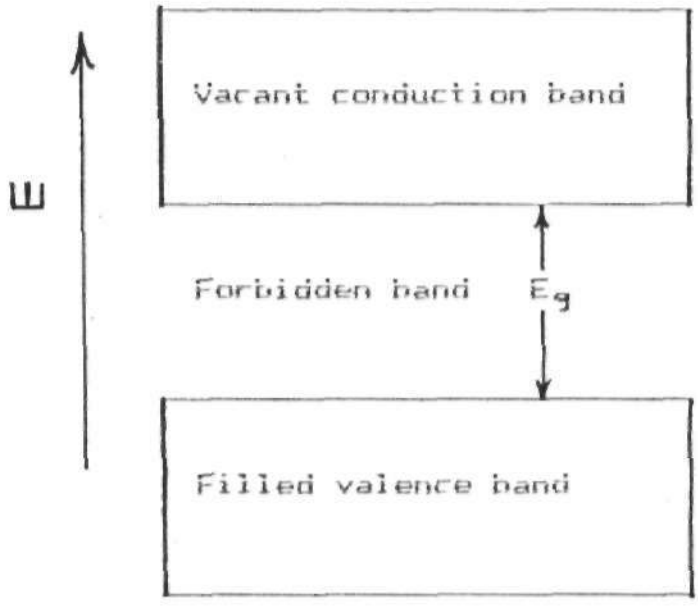


Fig. 1.10 Electronic Band Scheme Showing Intrinsic Conductivity

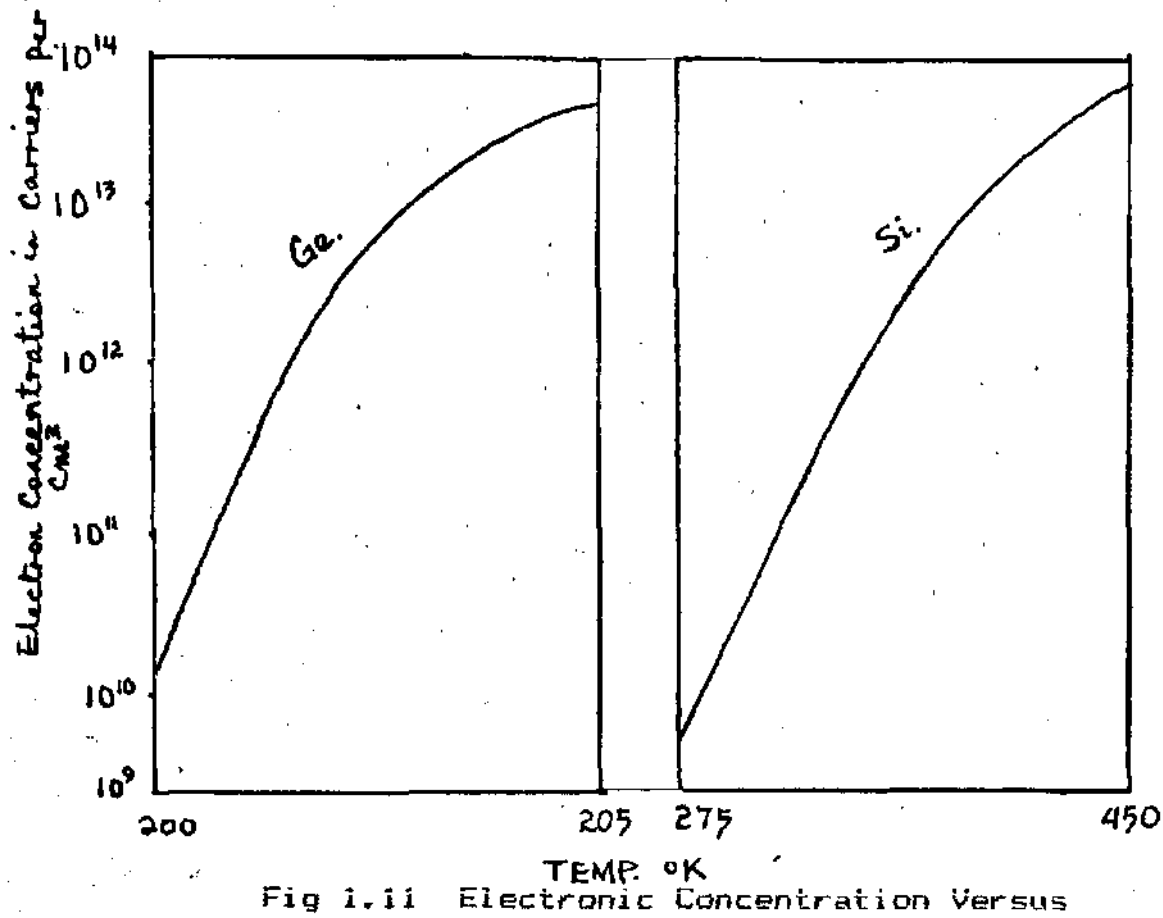


Fig 1.11 Electronic Concentration Versus Temperature for Silicon and Germaniumy

CHAPTER TWO

CRYSTAL STRUCTURE AND BONDING IN SOLIDS

2.1 ATOMIC ORBITALS

The potential energy of an electron in a free atom is spherically symmetric, and so the angular momentum of an orbiting electron is not expected to change with time. This means that the electron energy eigen states can also be chosen to be angular momentum eigen states. It is convenient to state the result in terms of the square of the magnitude of angular momentum, L^2, which takes on the discrete values.

$$L^2 = l(l+1)\hbar^2$$

where l is an integer greater than or equal to zero. For each value of l there are $2l+1$ different orthogonal eigen states; that is the component of angular momentum along any given direction can take on the values $M\hbar$ with $M = -l, -l+1, \ldots, l-1, l$.

The spatial wave functions representing these states are called orbitals since the corresponding classical electron orbits can be considered as having fixed energy and fixed angular momentum around a given axis. The term 'Orbital' will be used to refer specifically to the spatial wave function of an electron in an atom or molecule. This term 'Orbital' can also be used for electron wave functions representing chemical bonds where the corresponding electron orbits would not be simple. The $2l+1$ orthogonal eigenstates with

different M values are degenerate i.e. they have the same energy.

The first four states with angular momentum l=0 to l=3 are:

l = 0 s state

l = 1 p state

l = 2 d state

l = 3 f state

For any given value of l and m there are many different energy eigenstates. These are numbered by a third integer n, in order of increasing energy, starting with n = l+1 i.e.
E = <n, l, m /H/ n, l, m> depends only on the quantrum number n, it is hence called the principal quantum number. In each state specified by n, l and m, two electrons can be accommodated with opposite spins, according to the Pauli's principle.

The s-orbitals have vanishing angular momentum l=0 (and m=0, since /m/≤l). The wave function for an s-orbital is spherically symmetric and it is depicted by a sphere (circle on a plane) as shown in Figure 2.1.

The lowest energy state n=1 is called 1s state. Its wave function decreases gradually with distance from the nucleus. The wave function of the next state, the 2s state, drops to zero, becomes negative and then decays upward to zero. Each subsequent s orbital has an additional mode.

The p-orbitals have one unit of angular momentum l=1, there are three orbitals corresponding to m=1, m=0 m=-1 as shown in Fig 2.2.

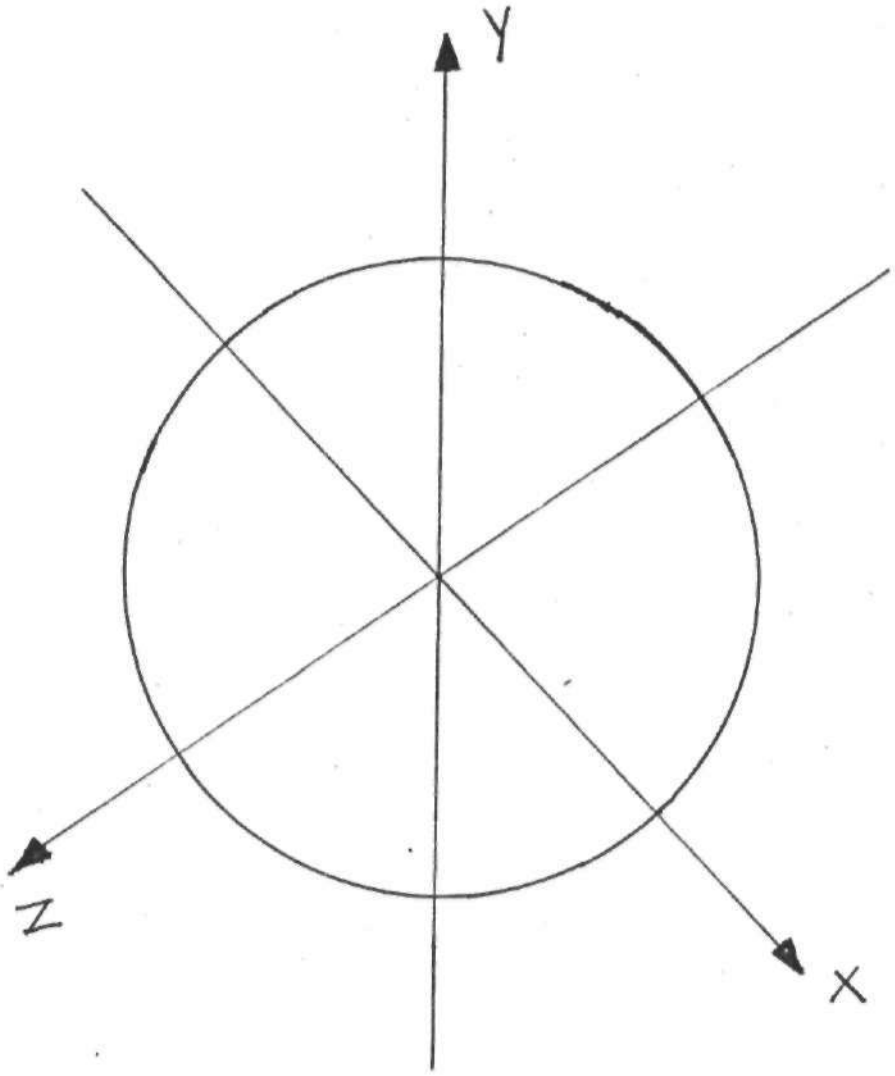


Fig 2.1 Shape of an S-Orbital

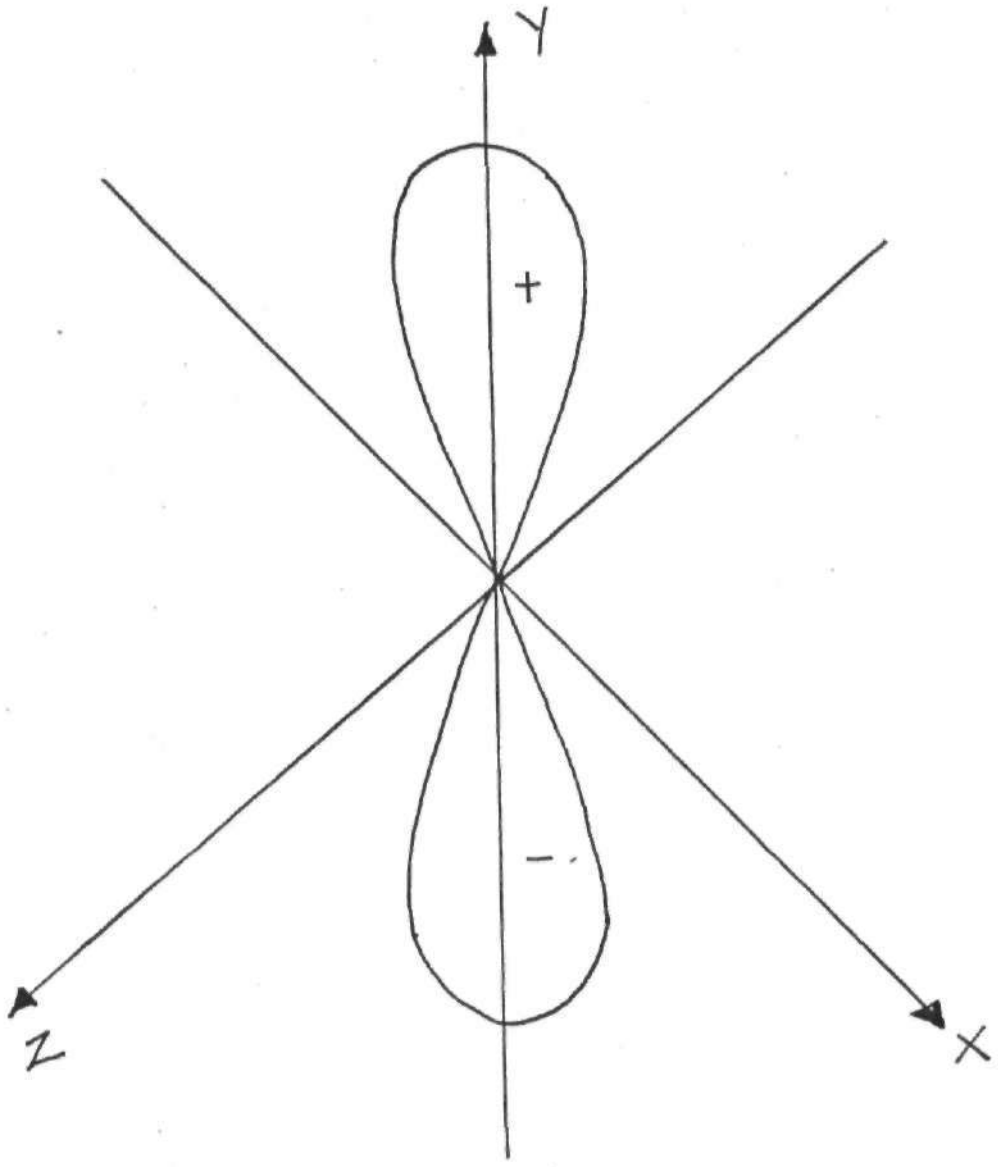


Fig 2.2 Shape of the p-Orbital

Any orbital may (or can) be written as a product of a function of Radial distance from the nucleus and one of the spherical harmonics Y_l^m which are functions of angle only.

$$\psi_{n,l,m}(r) = R_{n,l}(r) Y_l^m(\theta,\phi)$$

The three independent p-orbitals may be written

$$\psi_{n,1,m}(r) = (3/4\pi)^{1/2} R_{n,1}(r) \begin{pmatrix} X/r \\ Y/r \\ Z/r \end{pmatrix}$$

for each n when l=1 there are three p-orbitals oriented along the three cartesian axes. These are illustrated in Figure 2.3.

The d-orbitals have two units of angular momentum, l=2 and therefore five m-value m=-2, m=-1, m=0, m=1 and m=2. They can be conveniently represented in terms of cartesian coordinates in the form

$$\psi_{n,2m}(r) = (15/4\pi)^{1/2} R_{n2}(r) \begin{pmatrix} YZ/r^2 \\ ZX/r^2 \\ XY/r^2 \\ (x^2-y^2)/2r^2 \\ (3Z^2-r^2)/2r^2 3^{1/2}) \end{pmatrix}$$

An important feature of the d-orbitals is that they are concentrated much more closely at the nucleus than are s and p orbitals. The d-orbitals corresponding to the XY/r^2 form is as shown in Figure 2.4. The d-states tend to be influenced much less by neighbouring atoms than are s and p states of similar energy.

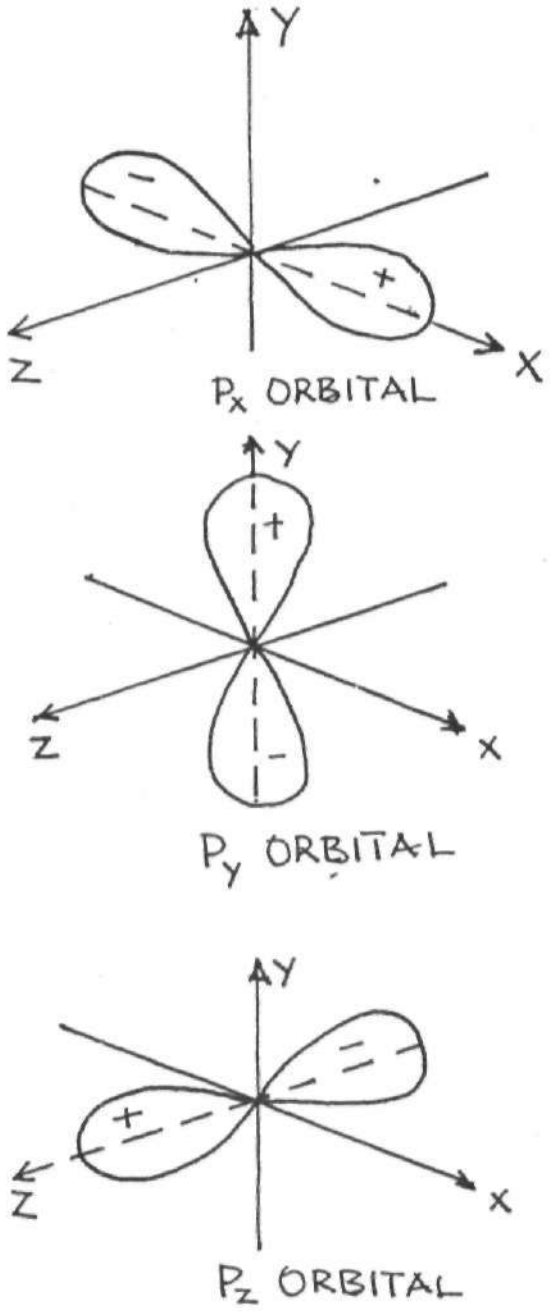


Fig 2.3 p-orbitals oriented along the 3-Cartesian Axes

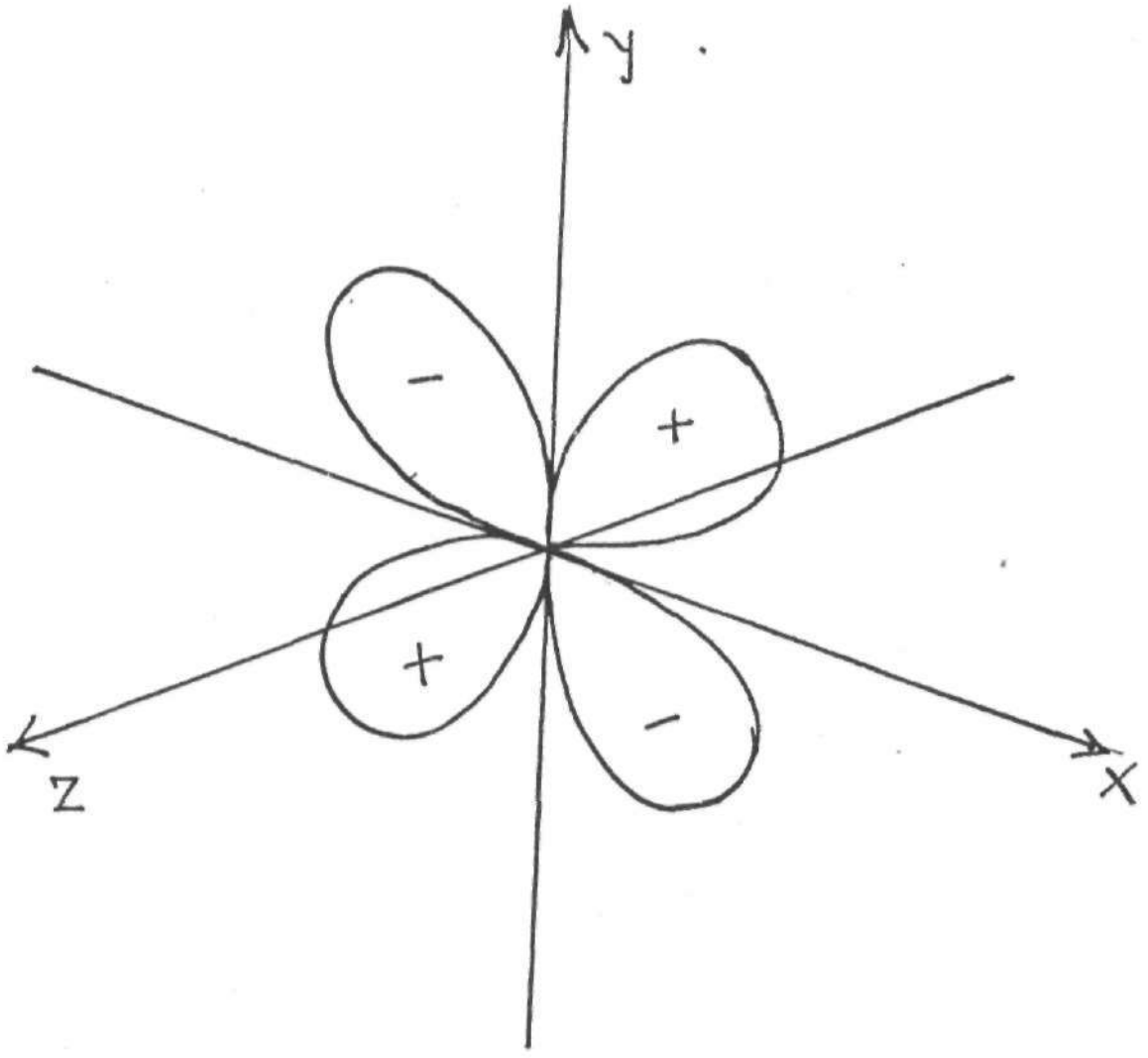


Fig 2.4 d-orbital corresponding to xy/r^2

The f-orbitals are important in studying properties of the rare earth metals. They are even more concentrated near the nucleus and isolated from neighbouring atom than the d orbitals.

2.2 COVALENT BONDING

Semiconductor compounds of chemical formula AB, where A is a trivalent element and B is a pentavalent element are called III-V (three-five) compounds. Examples are indium antimonide and gallium arsenide. Silicon and germanium are called diamond type semiconductors, because they have the crystal structure of diamond.

The covalent bond is the classical electron pair. It is a strong bond, the bond between two carbon atoms in diamond has a cohesive energy of 7.3eV with respect to separated neutral atoms. This is comparable with the bond strength in ionic crystals, although the covalent bond acts between neutral atoms. The covalent bond has strong directional properties. Thus carbon, silicon and germanium have the diamond structure, with the atoms joined to four nearest neighbours at tetrahedral angles, even though this arrangement gives a low filling of space 0.34 of the available space, compared with 0.74 for close packed structure.

The covalent bond is usually formed from two electrons, one from each atom participating in the bond. The electrons forming the bond tend to be partly localized in the region between the two atoms joined in the bond. The spins of the two electrons in the bond are antiparallel.

In typical semiconductors such as those from group IV elements like silicon and germanium, the bonding is covalent and the material is, therefore homopolar. In diamond, for example the lattice is built up from two face centred cubic lattices displaced with regard to one another by one quarter of the basic lattice vector along the main diagonal. In this structure one has 4 nearest neighbours and 12 next nearest neighbours. One then has 8 atoms forming a unit cell. With a lattice parameter 'a' one has $8/a^3$ atoms per unit volume .

Elements	C	Si	Ge	Sn
Lattice parameter '(a) [in A]	3.56	5.42	5.62	6.46
Number of atoms per unit Vol ($\times 10^{22}$ cm^{-3})	17.7	5.00	4.52	2.82

A free carrier is created when a covalent bond is broken giving a free electron capable of moving in an electric field and letting a free hole which will move in the opposite direction of an electron. The group IV elements are essentially covalent bonding but when one goes away from the centre of the periodic table, the bonding becomes less covalent and the character of covalent bonding is small. A semiconductor built from an element from group III and an element from group V e.g. gallium arsenide will have some ionic character and a semiconductor built from elements from group II and group VI such as ZnS, has a predominantly ionic

character. The ionic character increases when going farther from the central line of the periodic table.

2.3 CRYSTAL STRUCTURE

2.3.1 The Diamond Structure

The space lattice of diamond is face centred cubic. A primitive basis of two identical atoms at (0,0,0), (1/4,1/4,1/4) is associated with each lattice point, as shown in Figure 2.5. The tetrahedral bonding of the diamond structure is represented in Figure 2.6.

The diamond lattice is relatively empty, the maximum proportion of the available volume which may be filled by hard spheres is only 0.34 or about 46% of the filling factor for a close packed structure, carbon, silicon, germanium and gray tin crystallize in the diamond structure. The diamond structure is the result of directional covalent bonding.

2.3.2 Zinc Blend Structure

The diamond structure is a special case of ZnS structure. The Zinc-blend structure is based upon a face centred cubic arrangement of zinc atoms as shown in Figure 2.7. This may be thought of as a simple repeating cubic lattice of zinc atoms with a zinc atom also at the centre of every resulting cube face. This makes cartesian system of coordinates a natural choice with axes along the cube edges. It is customary to indicate the direction of a vector in the crystal by writing its components along those axes written a bracket. Thus a vector (100) lies along a cube edge,

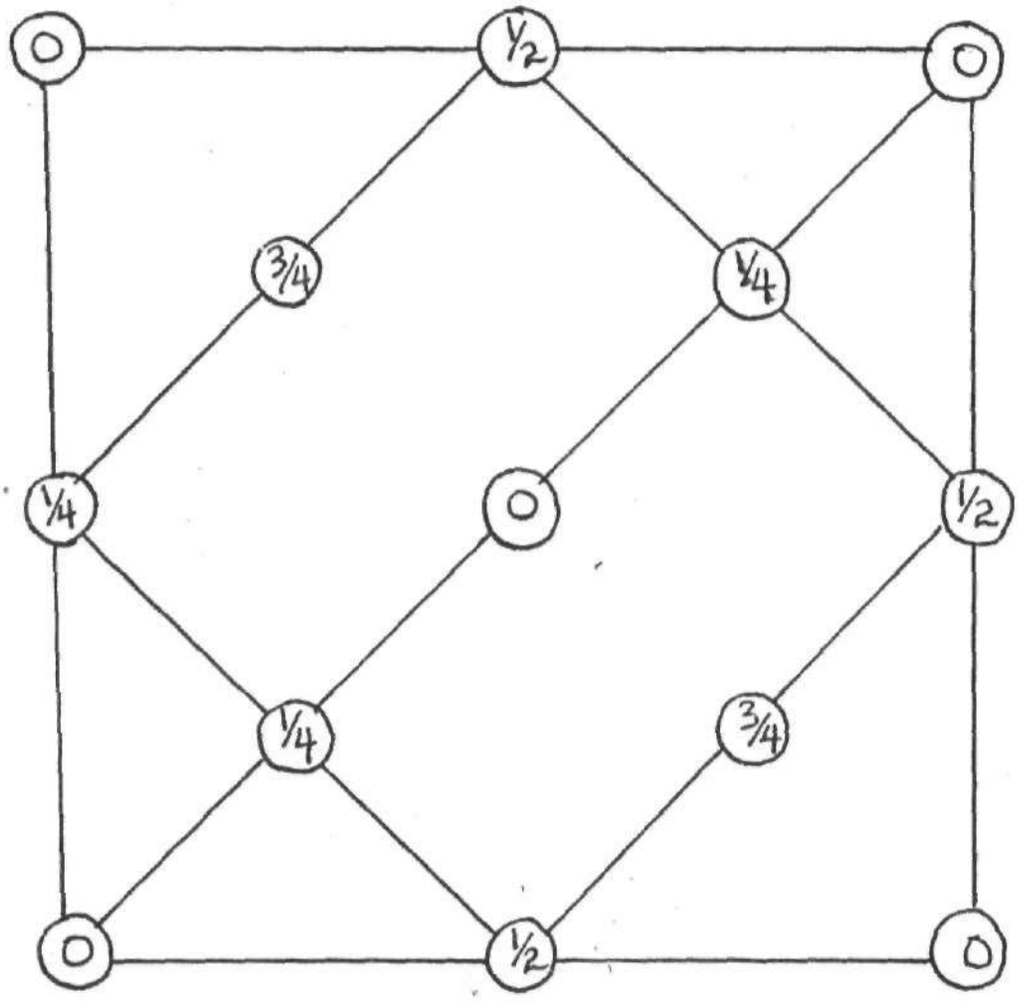


Figure 2.5 Atom positions in the cubic cell of the Diamond structure

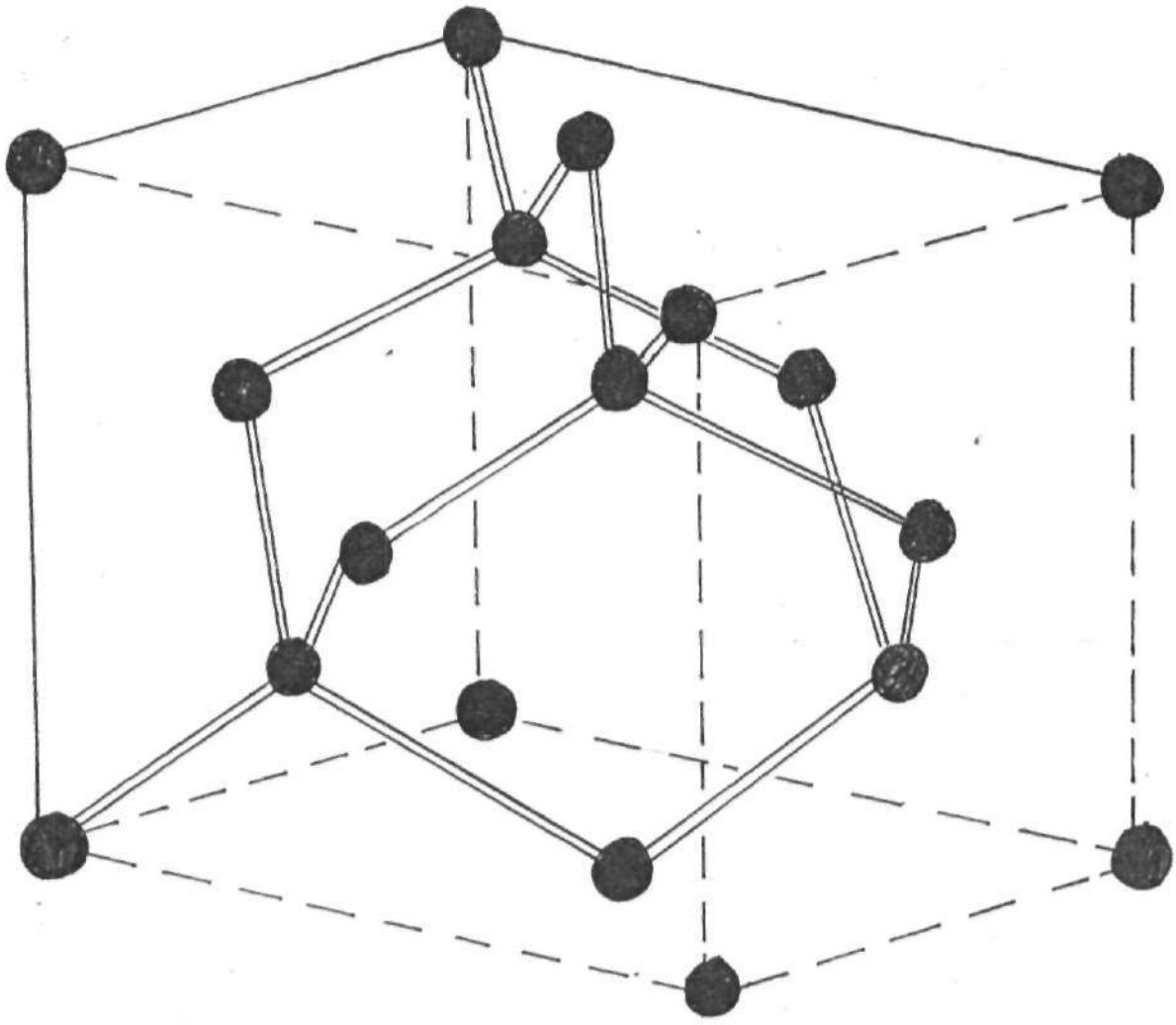


Figure 2.6 Crystal Structure of Diamond Showing the Tetrahedral Bond Arrangement

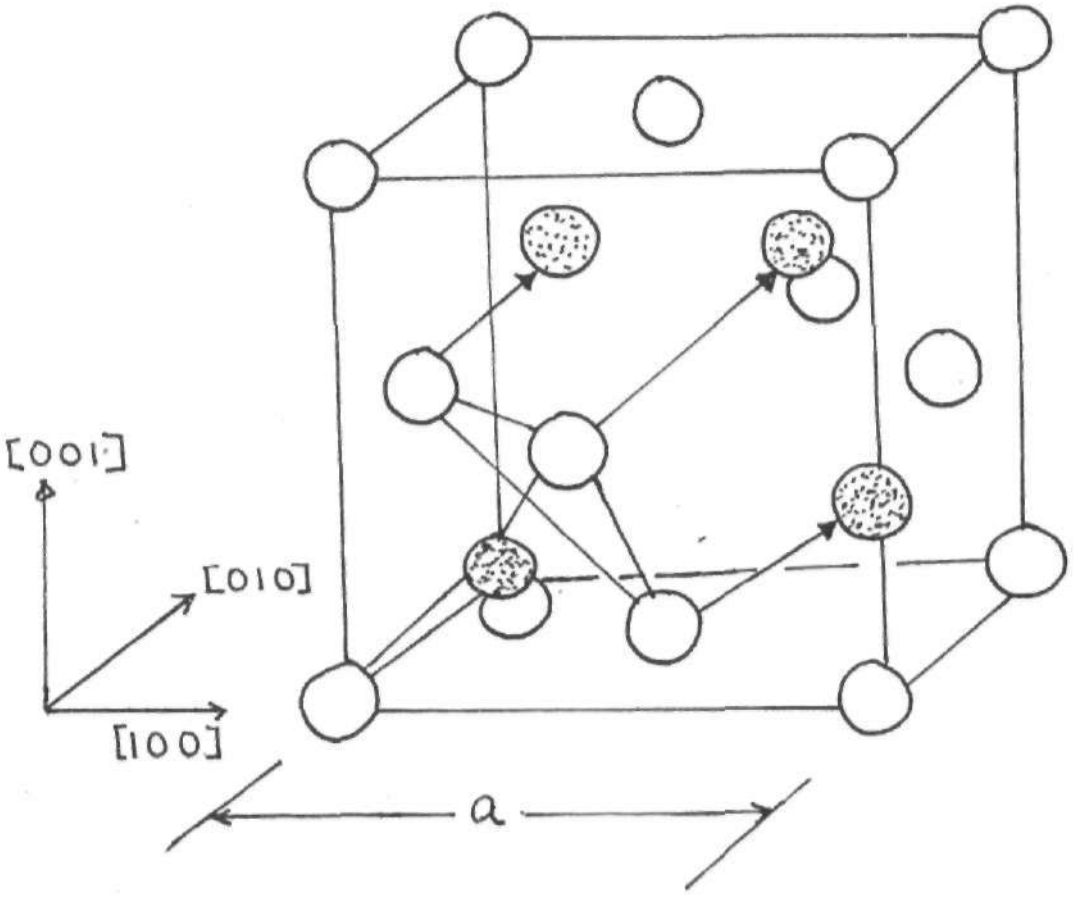


Fig 2.7 A Unit Cube of Zinc Blend Structure (Rotated)

(110) lies along a diagonal across a face of the cube, (111) lies along the main diagonal through the cube. It is important to note that the environment of every zinc atom within the arrangement is identical. Thus the crystal may also be thought of as made up of smaller unit cells (the primitive cells, each containing a zinc atom). The primitive cell of zinc-blend are of the type (110)a/2 rather than the type (100) a of the cube. Vectors of the type (011)a/2 are considered to be of the type (110)a/2.

In zinc-blend structure there are equal number of sulphur atoms, each in a position (111)a/4 relative to that of the zinc atoms (the displacements are represented by arrows in Figure 2.7 and the four shaded atoms represent sulphur atoms), other sulphur atoms are likewise displaced (111)a/4 from other zinc atoms in Figure 2.7 and lie outside the cube and those at the centre of the botiom face, left face, and front face from the corners of a regular tetrahendron that has sulphur atom as its centre. Every other sulphur atom in zinc blend is also tetrahedrally correlated to zinc atoms in exactly the same way.

Another point worth noting is that the zinc atoms lie in planes perpendicular to the (111) axis. Within each of these planes the atoms form a hexagonal array, a few atoms of which are shown in Figure 2.8 circled and labelled A. Another parallel layer of zinc atoms beyond this contains atoms at staggered

positions marked B. Notice that if the first layer were to be made up of hard spheres, tightly packed so that each touched six neighbours in the plane, the second plane would form a second close-packed layer of spheres, each touching three spheres in the preceding layer. A third layer contains atoms in positions marked C; each sphere C would be in contact with three spheres in the B layer. Next comes another A layer and the series repeats in ABCABCABC fashion. The staggered positions in A, B and C layers allow the densest possible lattice packing of hard spheres thus the face centred cubic structure is also called close packed structure. In Zinc Blend , a layer of sulphur atoms is located between each layer of zinc atoms with each sulphur atom being directly above a zinc atom of the layer below, three quarters of the way to the next zinc layer that is a sulphur layer A is positioned three quarters of the way from A to B zinc layers etc. It is easy to see that in this configuration each atom is tetrahedrally surrounded by the four atoms of the opposite species.

2.4. CONSTRUCTION OF SP^3 HYBRIDS.

A linear combination of two p-orbitals is simply another p-orbital with a different orientation. However, a linear combination of a p-orbital (with an s-orbital (called an sp hybrid) corresponds to an unsymmetric probability distribution, a distribution of electron charge that 'leans' in the direction of p-orbital. In tetrahedral solids four sp hybrids are

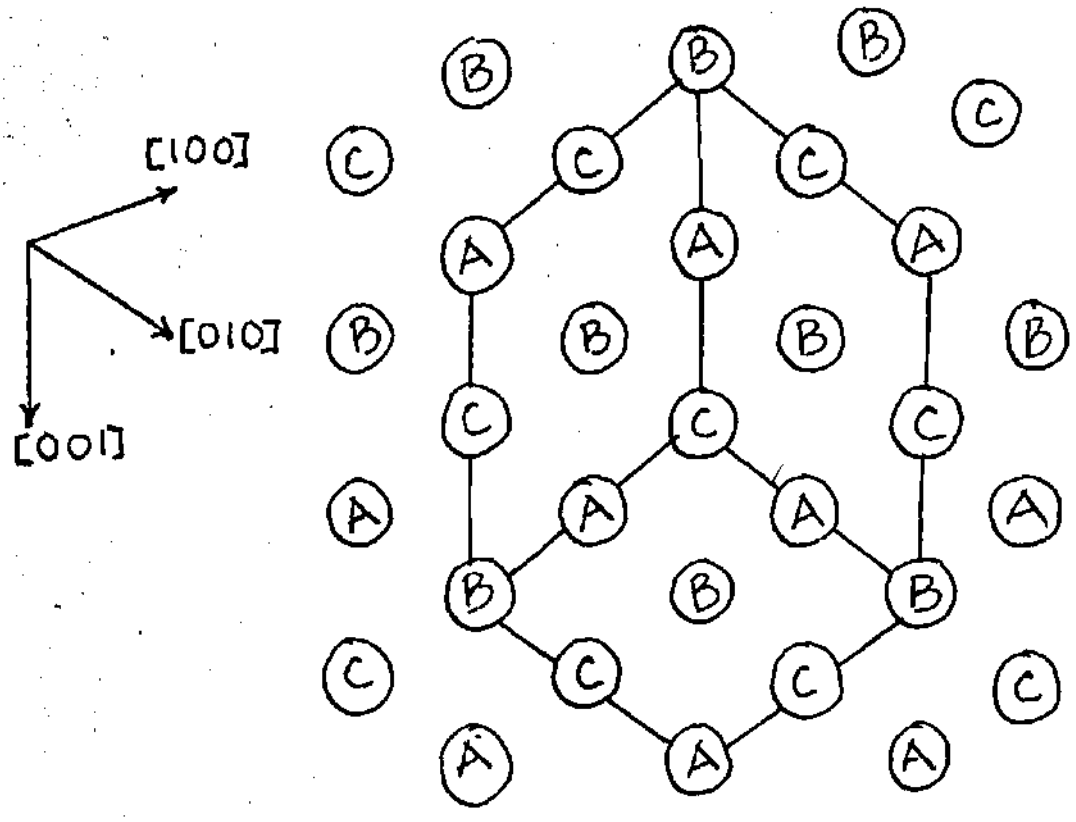


Fig 2.8 A Zinc Blend Lattice View
Along a (111) Direction

picked, the wave functions of which are orthogonal to each other, and in which the electron charge density is greatest in the direction of the nearest neighbouring atoms.

The normalization of the wave functions for p-orbitals oriented along three coordinate axes can be written as $|P_x\rangle$, $|P_y\rangle$ and $|P_z\rangle$. In terms of these and the wave function for s orbitals, $|S\rangle$, the sp^3 hybrids (3 indicating there is three times as much probability of finding an electron in a p state as of finding it in an s state) and the directions in which the charge density is greatest are:

$$|h_1\rangle = 1/2[|S\rangle + |P_x\rangle + |P_y\rangle + |P_z\rangle] \text{ with (111) orientation}$$
$$|h_2\rangle = 1/2[|S\rangle + |P_x\rangle - |P_y\rangle - |P_z\rangle] \text{ with (1,-1,-1) orientation}$$
$$|h_3\rangle = 1/2[|S\rangle - |P_x\rangle + |P_y\rangle - |P_z\rangle] \text{ with (-1,1,-1) orientation} \quad 2.1$$
$$|h_4\rangle = 1/2[|S\rangle - |P_x\rangle - |P_y\rangle + |P_z\rangle] \text{ with (-1,-1,1) orientation}$$

It is easy to show that hybrid wave functions are orthogonal, that is

$$\langle h_i | h_j \rangle = \delta_{ij}$$

by using the condition that non-hybrid atomic wave functions are orthonormal. Any hybrid rotation of this set will give another orthonormal set, oriented in the direction of a rotated tetrahendron. These hybrids are not energy eigenstates, the expectation value of the energy is an average energy called the hybrid energy E_h

$$\epsilon_h = 1/4(\epsilon_s + 3\epsilon_p) \quad 2.2$$

where

$$\epsilon_s = \langle S|H|S\rangle$$
$$\epsilon_p = \langle P_x|H|P_x\rangle$$

$$= \langle P_y | H | P_y \rangle$$
$$= \langle P_z | H | P_z \rangle$$

these values could somewhat differ in the solid from the corresponding values defined for the free atom but the free atom values will be used. The measurement of the energy of an electron described by such a hybrid wave function would give ϵ_s 25 per cent of the time and E_p 75% of the time.

For polar covalent solids, sp^3 hybrids of the form of eqn 2.1 can be constructed on each of the atom types present and oriented in the direction of its nearest neighbours. The hybrid energies will be different with the lesser energy ϵ^1_h and the greater energy ϵ^2_h. The hybrid polar energy (V_3^h) is proportional to their difference, i.e.

$$(V_3^h) = 1/2(\epsilon^2_h - \epsilon^1_h),$$

Even though hybrids are not eigenstates, non zero, matrix elements of the Hamiltonian can exist between the hybrids, they may be evaluated by setting all matrix elements of the Hamiltonian between orthogonal atomic orbitals on the same atom equal to zero. The magnitude of the resulting matrix elements is called (V_1) the metallic energy.

$$\langle h_i | H | h_j \rangle = \langle h_i | H | h_a \rangle = -V_1$$

The metallic energy depends on the sp splitting i.e. $(E_p - E_s)$ of the atom shared by the hybrids and it will have different values for the two atom types for polar crystals.

A particularly important matrix element is that between hybrids pointed at each other, or into the

bond, from two neighbouring atoms. The magnitude of this matrix element is called the hybrid covalent energy (V_2^h)

$$V_2^h = -\langle h^1|H|h^2\rangle$$

Thus

$$V_2^h = 1/4(-V_{ss}+2(3)^{1/2}V_{sp}+3V_{pp}) \qquad 2.4$$

The value of V_2^h is found theoretically to be $4.37\hbar^2/md^2$.

The values of V_2^h and V_3^h are defined for the hybrid bond and are the direct counterparts of covalent and hybrid polar energies. Hybrid covalent and hybrid polar energies also give rise to bonding-antibonding splitting and to bond polarity. Because of the interactions between neighbouring bonds the energy difference that corresponds to bonding-antibonding splitting in the analysis of dielectric properties of solids is not $2(V_2^h + V_3^h)^{1/2}$, but an expression depending principally upon the p-orbitals.

2.5 BOND ORBITALS

The electronic states can be written as linear combinations of atomic orbitals. Bond orbitals and atomic orbitals are equivalent representations but thinking in terms of bonding and antibonding orbitals, which can be made to correspond with occupied and empty states of the covalent solid is essential in making the approximations.

Using similar method of finding solutions to ordinary simultaneous equations, in which the

variables are changed by taking linear combinations. Such that the new variables form new sets that are not coupled to each other. The smaller sets of equations are solved by using the formula for the roots of a quadratic equation. In dealing with the bond orbitals the procedure leads to an additional goal, the proper linear combinations will provide a context in which approximations can be made. The procedure will be to choose linear combinations first and then to consider matrix elements of the Hamiltonian between them, since these matrix elements as in equation below.

$$\sum_{\alpha} \langle \beta/H/\alpha \rangle U_{\alpha} - EU_{\beta} = 0$$

are coefficients that are needed in the calculation of bonding states and bonding energies. The series of steps is shown in Figure 2.9. Successive transformations of linear combinations of atomic orbitals, beginning with atomic s and p-orbitals and proceeding to sp^3 hybrids to bond orbitals and finally to bond states. The bond states represent exact solutions of the linear combination of atomic orbitals (LCAO) problem.

2.5.1 CONSTRUCTION OF BOND ORBITALS

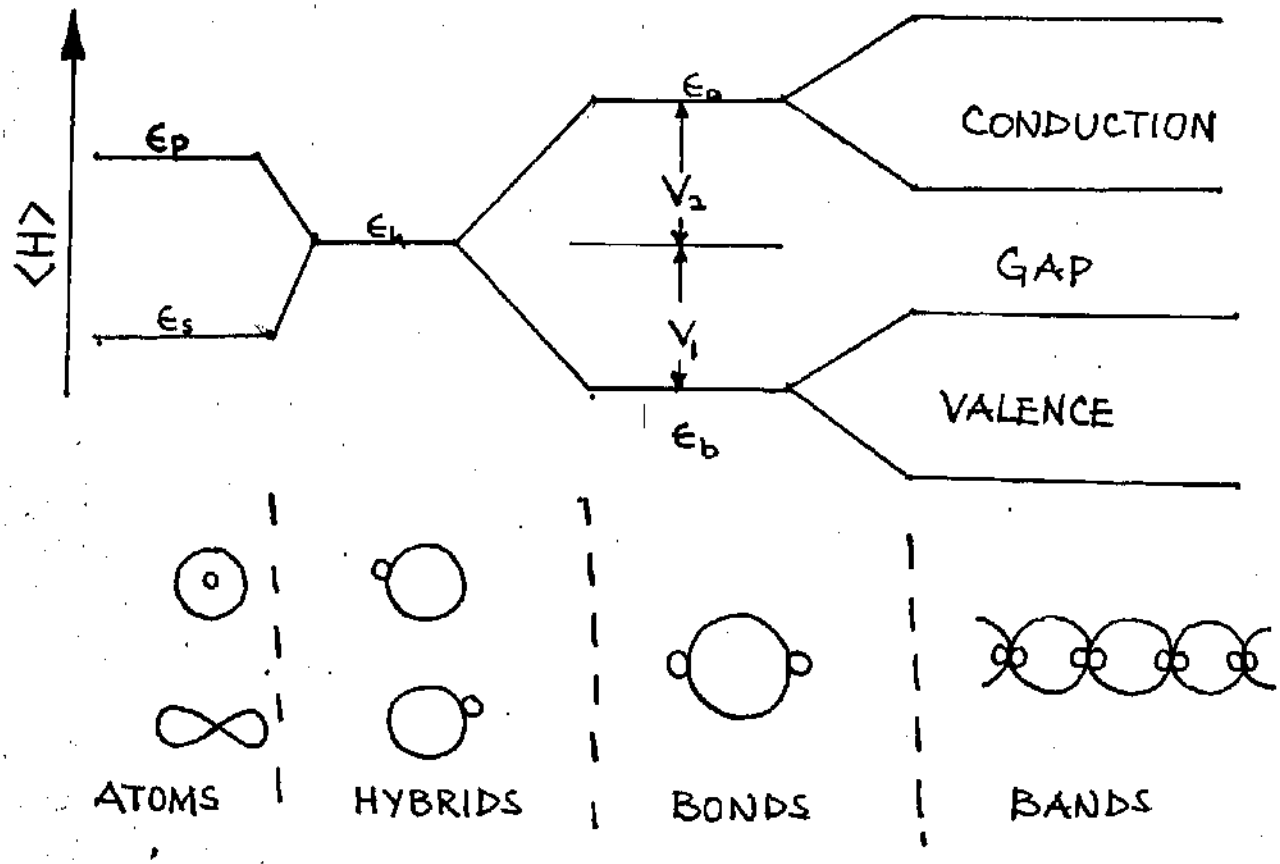
Consider the pairs of hybrid orbitals in each bond to be bonding and the antibonding combinations.

This is done by writing a general linear combination of the two hybrids.

$$|\psi\rangle = U_1|h^1\rangle + U_2|h^2\rangle$$

and minimizing the energy expectation value

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{U_1^2\epsilon_h^1 - 2U_1U_2V_2 + U_2^2\epsilon_h^2}{U_1^2 + U_2^2} \qquad 2.6$$



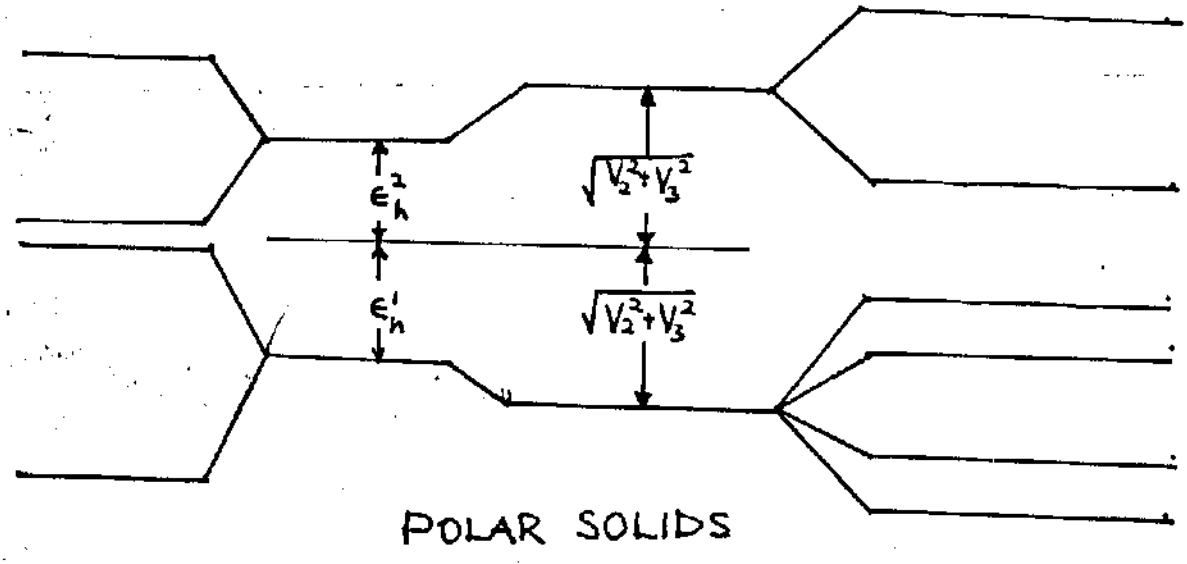


Fig 2.9 Steps Showing the Formation of Bond Status

neglecting complicated aspects of electron - electron interaction) in terms of an average potential associated with each electron. The neglect of electron interactions has been studied closely (Huang, Merarty and Sher, 1976). The effect of the electron interactions can be absorbed with the parameters of the simple theory.

Minimizing equation 2.6 gives

$$\epsilon^1_h U_1 - V_2 U_2 = E U_1$$

and $$-V_2 U_1 + \epsilon^2_h U_2 = E U_2 \qquad 2.7$$

Rewriting in terms of average energy

$$\bar{\epsilon} = (\epsilon^1_h + \epsilon^2_h)/2 \qquad 2.8$$

and the hybrid polar energy

$$V_3 = (\epsilon^2_h - \epsilon^1_h)/2 \qquad 2.9$$

Therefore $\epsilon^2_h = V_3 + \bar{\epsilon}$

and $\epsilon^1_h = \bar{\epsilon} - V_3$

equation 2.7 becomes

$$(\bar{\epsilon} - V_3) U_1 - V_2 U_2 = E U_1$$

$$-V_2 U_1 - V_2 U_2 = (E - \bar{\epsilon}) U_1$$

similarly

$$-V_2 U_1 + (\bar{\epsilon} + V_3) U_2 = E U_2 \quad (i) \qquad 2.10$$

$$-V_2 U_1 + V_3 U_2 = (E - \bar{\epsilon}) U_2 \quad (ii)$$

These equations can be written as

$$[V_3 + (E - \bar{\epsilon})] U_1 + V_2 U_2 = 0$$

$$V_2 U_1 - [V_3 - (E - \bar{\epsilon})] U_2 = 0$$

or

$$\begin{vmatrix} V_3 + (E - \epsilon) & V_2 \\ V_2 & -V_3 + (E - \epsilon) \end{vmatrix} = 0$$

or

$$[(E - \bar{\epsilon})^2 - V^2_3] - V^2_2 = 0$$

$$(E-\bar{\epsilon})^2 = V_3^2 + V_2^2$$

$$(E-\bar{\epsilon}) = (V_2^2 + V_3^2)^{1/2}$$

$$E_b = \bar{\epsilon} - (V^2_2 + V^2_3)^{1/2} \qquad 2.11$$

$$E_a = \bar{\epsilon} + (V^2_2 + V^2_3)^{1/2} \qquad 2.12$$

substituting for $E = E_b$ in equation (i) of (2.10) we have.

$$-V_3 U_1 - V_2 U_2 = (\bar{\epsilon} - (V_2^2 + V_3^2)^{1/2}) - \bar{\epsilon}) U_1$$

$$V_3 U_2 + V_2 U_2 = ((V^2_2 + V^2_3)^{1/2}) U_1$$

$$(V_3 - (V_2^2 + V_3 U_2)^{1/2}) U_1 = -V_2 U_2$$

$$U_1 = ((V_2)/(V^2_2 + V^2_3)^{1/2} - V_3)) U_2$$

Similarly putting $E=E_b$ in eqn (ii) of (2.10) we get

$$U_2 = ((V_2)/(V^2_2 + V^2_3)^{1/} - V_3)) U_1$$

If the individual atomic wave functions do not overlap, the probability of finding the electron on atom i will be

$$U^2_1/(U^2_1 + U^2_2)$$

Therefore

$$U^b_1 = (1 + \alpha_p/2)^{1/2}$$

and

$$U^b_2 = (1 - \alpha_p/2)^{1/2}$$

where

$$\alpha_p = (V_3/(V^2_2 + V^2_3)^{1/2}$$

These have been chosen to satisfy the normalization $U_1^2 + U^2_2 = 1$. The α_p is called the bond polarity.

Similarly the antibonding state wave functions, which are orthogonal to those of the bonding state have energy: $E_a = \bar{\epsilon} + (U^a_2 + V^2_3)^{1/2}$

with the parameters

$$U^a_1 = (1 - \alpha_p/2)^{1/2}$$

$$U^a_2 = (1 + \alpha_p/2)^{1/2}$$

These transformations enable the construction of bonding and antibonding orbitals starting from s-and p-orbitals without additional approximations.

The energy expectation values for these orbitals depend only upon the covalent energy V_2 and the polar energy V_3. These orbitals do not represent eigenstates of the Hamiltonian; however, there are still matrix elements between various bonding and antibonding orbitals. Thus by solving the equations for eigenstates the bonding and antibonding energy levels broaden into bands. A representation based upon bond orbitals is an invaluable guide for estimating the parameters that described the electronic structure and for extracting physical information from the representation of the electronic structure.

CHAPTER THREE

METHODS OF CALCULANG ELECTRONIC STATES

3.1 CALCULATION OF ELECTRONIC STATES IN SOLIDS

There are various methods of calculating the energy levels of electrons in actual crystals.
We start with the Schroedinger equation i.e.

$$\left(\frac{-\hbar^2}{2m}\cdot\nabla^2 + V(r)\right)\psi_K = E(K)\psi_K$$

which can be written as

$$H\psi_K = E\psi_K$$

where $H = \left(\frac{-\hbar^2}{2m}\cdot\nabla^2 + V(r)\right)$

Equation 3.1 can be solved for a periodic potential of the type.

$$V(r) = V(r + l)$$

$$V(r) = \Sigma V_g e^{ir\cdot g}$$

Where V_g is the fourier component of V for the reciprocal lattice vector g. In the free election case the wave functions are free waves like $\Sigma a_K e^{ikr}$ but the potential V(r) is very strong at the sites of the ionic cores. Therefore, one may well accept functions to be like the atomic orbitals at the ionic cores.

In the following section we review the major different methods for calculating energy levels, these are:

a) Tight binding and LCAO method

b) Othorgonalized plane wave method (OPW)

c) Cellular and augmented plane wave methods (APW)

d) Other methods

The tight binding and LCAO methods are based on the tight binding approximation and other methods are based on the free electron approximation.

3.2. a) Tight Binding and LCAO Methods

In actual solids, the ionic cores are situated at the lattice sites. Within the cores the electronic wave functions must be like the atomic orbitals. One can try to form the states running throughout the crystal by combining a number of functions localized at the lattice sites. Let $\varphi_a(r-l)$ be an atomic orbital for a free atom at l. Then the bloch function would be of the form

$$\varphi_k(r) = \Sigma \varphi_a(r-l) e^{ik.l}$$

This looks like a series of strongly localized atomic states modulated by the wave factor $e^{ik.l}$. Within each atom the local orbital predomina tes and this should be a good solution of the local Schroedinger equation.

In studying the behaviour of the system, we can calculate as a first approximation the expectation value of the energy for the wave function.

$$E(K) = \frac{\int \varphi^*_K [-\hbar^2/2m.\nabla^2 + V(r)] \varphi_K d^3r}{\int \varphi^*_K \varphi_K d^3r}$$

The atomic orbitals are strongly localized at the lattice sites and one way, as a first approximation, assume no overlap of orbitals in the neighbouring sites and take the normalizing denominator to be unity

i.e $$\int \varphi^*_\kappa \varphi_\kappa d^3r = 1$$

Then $$E(K) = \sum_{ll} e^{ik.(l-l')} \int \varphi^*_a(r-l')\left[-\frac{\hbar^2}{2m}.\nabla^2 V(r)\right]\varphi_a(r-l)\, d^3r$$

The periodicity of the lattice can be used to convert the integral into one depending on $(l-l')$ exclusively. Furthermore, one may assume that the atomic orbitals satisfy the Schroedinger equation.

$$\left[(-\hbar^2/2m).\nabla^2 + V_a(r)\right]\varphi_a = \epsilon_a \varphi_a$$

Where $V_a(r)$ is the potential of an isolated atom. With these simplifications,

$$\epsilon(K) = \sum_h e^{ik.h}\epsilon_h$$

with $\epsilon_0 = \epsilon_a$ and

$$E_h = \int \varphi^*_a(r+h)\left[V(r) - V_a(r)\right]\varphi_a(r)\, d^3r$$

Evidently there must be a small overlap between adjacent orbitals if E_h is to be non-zero.

The tight binding method is a convenient way to introduce an important general principle. Suppose there are N atoms apart, each atom will have different states $\varphi_a, \varphi_b, \ldots, \varphi_N$, and these states will be N-fold degenerate for an electron. When the atoms are brought together, the orbitals overlap and the N-fold degenerate state is split into band of states. There will be a complete band of N-staies arising from each atomic level so that one can have, for instance, the 4s or 3d bands arising from the corresponding atomic states. This classification is particularly useful in the case of transition metals, where the d-states of

the atoms are rather compact and combine to form a relaiively narrow and well defined d-band. If the overlap among the orbitals is strong the bands may broaden so much as to intersect. Then one must assume the wave function to be a linear combination of atomic orbitals (LCAO).

$$\psi_K(h) = \sum_{l,j} e^{i K.l)} \beta_j \psi^{(j)}_a (r-l)$$

where $\psi^{(j)}_a$ is one of the different atomic orbitals at site l. This trial wave function must then be used for estimating the energy to be minimized with the suitable choice of the coefficients β_j.

The LCAO method has been used for some band structure calculations, especially of ionic solids in which the overlap of atomic orbitals of neighbouring ions is relatively small. In other cases it is not a very convenient procedure. Firstly, the atomic orbitals fall off so rapidly outside the core, that it becomes difficult to get plane wave amplitude outside the cores. Secondly, the evaluation of many-centre overlap integrals prove to be a complicated task.

3.2 b). Orthogonalized Plane Wave Method (OPW)

This is a simple modification of the LCAO method introduced by Herring in 1940. In this method, we consider a set of Bloch functions constructed out of the core states of the orbitals already occupied by the ions. This will be of the form

$$\varphi_j(K) = \sum e^{i K.l)} \varphi_j(r-l)$$

The core orbital such as $\varphi_j(r-l)$ is strongly

localized so that it is really a combination of degenerate one electron states, each corresponding to the localization of the electron on a particular atom. This will be a good solution of the Schroedinger equation of the whole crystal corresponding to a core level E_j, which will form a fully occupied narrow band in the crystal.

Now the higher crystal energy states, being solutions of the some Schroedinger equation must be orthogonal to $\phi_j(K)$, i.e

$$\int \psi^*(K)\varphi_j(K)d^3r = 0$$

In addition to this it is also required that the higher energy staies must behave like a free electron wave in the region between the atoms. Therefore, suppose a trial wave function is set for the higher states.

$$\chi_K = e^{ik\cdot r} - \sum_j \beta_j \varphi_j$$

where the coefficients β_j are chosen to ensure orthogonalization, then

$$\chi_K = e^{ik\cdot r} - \sum_j \varphi_j \int \varphi^*_j e^{ik\cdot r} d^3r$$

This solution looks like the plane waves $e^{ik\cdot r}$ in the interstition regions, where each $\phi_j(K)$ is small because the latter is localized on the ion cores, and yet within the atomic core itself the solution is orthogonal to an atomic orbital $\phi_m(K)$. Therefore, the solution turns out to be a good guess and one uses the orthogonalized plane waves (OPW) as the basis states for forming the wave function

$$\psi_k(r) = \Sigma A_{k-g} \chi_{k-g}$$

The variational principle may be used to minimize the expectation value of the energy and determine coefficients A_m. It turns out that this procedure is rapidly convergent.

The OPW method has been widely used by Herring (1950), Ham (1955) for a large number of metals. It has the advantage when compared with the equally popular APW method, in that the OPW works for non-spherically symmetric atomic potentials.

3.2 Cellular and Augmented Plane Wave Methods

Wigner and Seitz in 1933 suggested a different way of calculating the electronic energy levels in solids. In the vicinity of a metallic ion the potential is spherically symmetric and one could use a spherically symmetric atomic wave function there. In the cellular method such wave functions were matched at the boundaries of the Wigner-Seitz cells.

A variant of this idea was developed by Slater in 1937 and this augmented plane waves (APW) method has become very useful procedure for calculating the energy bands in metals. APW is so much better than the cellular method. In the APW method we assume that the ionic potential is spherically symmetric within some radius R about each site and constant in the interstitial regions. It is assumed that R is less than the Wigner-Seitz cell radius so that the sphere of radius R do not intersect. Within each sphere the Schroedinger equation is solved in terms of spherical harmonics. The APW is quite rapidly convergent.

3.2 d). Other Methods

Other methods of band structure calculations include among others

i) Green's function technique

ii) The quantum defect method, and

iii) Method of pseudo-potentials.

i) The technique of using Green's functions to solve partial differential equations was applied to energy band calculations by Korringa (1947) and Kohn and Rostocher (1954). For a differental equation

$$(\nabla^2 + 2M\nabla/\hbar^2)\psi = 2ME/\hbar^2\psi$$

the Green's function or the wave emitted by a volume d^3r is $-(1/4\pi r)\int e^{-ik\cdot r}V\psi d^3r$

and so one can write self consistently

$$\psi = -1/4\pi\int\left(\frac{e^{ik\cdot r}}{r}\right)V\psi\, d^3r$$

This means that the wave function is the result of the scattering of itself by the potential. This can be converted into a form depending on $(r-1)$ and one can form a Bloch function of the type

$$\psi_k(r) = \frac{-1}{4\pi}\sum\int\frac{\exp(ik|r-r'|)}{|r-r'|}V(r-r')e^{ik\cdot l}\psi_k(r-l)\,d^3r$$

Consequently, the Green's function method has been used on a number of metals.

ii) In the quantum defect method, one uses the spectroscopic behaviour of free electrons metals. In general one needs the wave function at the site of the atomic cores and they are obtained by solving self consistently the Hartree-Fock equations. The

method has been used by Brooks and Ham (1955) on alkali metals.

iii) The pseudopotentials method developed by Phillips and Kleinman (1959) exploits a different aspect of the problem. Suppose one substitutes an OPW-like solution.

$$\Psi = U - \sum_j \varphi_j \int \varphi^*_j U d^3r$$

in the Schroedinger equation. $H\Psi=E\Psi$, Then since the core function φ_j is also an eigenfunction of H with an energy E_j, one has

$$HU + \Sigma(E-E_j)\langle\varphi_j | \varphi^*_j\rangle U d^3r = EU$$

which can be looked upon as a new Schroedinger equation $(H+V_R)U = EU$ where the operator V_R is defined by

$$V_R U = \sum_j (E-E_j)\varphi \int \varphi^*_j U d^3r$$

The "smoothed" function U therefore satisfies a Hamiltonian

$$H + V_R = -(\hbar^2/2M)\nabla^2 + V_R + V(r)$$

A plane wave solution for the effective potential Veff = V(r) + V_R had to be found. Calculations have shown that the term V_R is negative and largely cancels the positive core attraction so that Veff is usually very small. This method of treating the problem has been applied to several cases. The above simple picture, apart from outlying the central idea behind the psuedopotential method, also explains why the nearly free electron method is so successful in practice as first approximation.

CHAPTER FOUR

TIGHT BINDING CALCULATION OF THE VALENCE BANDS

4.1 INTRODUCTION

The tight binding approach to the problem of the electronic energy levels in solids provides a real space picture of the electronic interactions which give rise to the particular features of the energy band structure, density of states etc. This is extremely useful in studies of how these features change when the electronic configuration is altered. In such a case an adequate description of the system of interest can be obtained by specifying a small number of interaction parameters.

Here the tight-binding method using a few interaction parameters gives the accurate results for the valence bands of Diamond, Silicon and Germanium. The method used is equivalent to that of Slater and Koster (1954). It can also be regarded as a more complete version of the Wearie and Thorpe (1971) model in which the interactions between more distant directed orbitals are included.

4.2 PROCEDURE FOR CALCULATION

In the diamond crystal every atom is tetrahedrally coordinated and there are two atoms in the primitive cell. For each tight-binding function centred on these atoms, two Bloch functions can be constructed. For example, for a tight binding basis function $\phi(r)$ we have two Bloch functions

$$\Psi_0(k,r) = (N)^{-1/2}\sum_R e^{ik\cdot R}\phi_0(r-R) \qquad 4.1$$

$$\Psi_1(k,r) = (N)^{-1/2}\sum_R e^{ik\cdot R}\phi_1(r-R-\tau) \qquad 4.2$$

where τ is the vector joining the two atoms in the primitive cell and the subscripts on ϕ refer to the atoms in the primitive cell.

In order to have

$$\langle\psi_i(k,r)|\psi_j(k,r)\rangle = \delta_{ij} \qquad 4.3$$
$$i,j = 0,\ 1$$

we must require that the tight binding functions on different atomic sites be orthonormal; i.e.

$$\langle b_0(r-R_m)|b_1(r-R-\tau)\rangle = 0 \qquad 4.4$$

$$\langle b_i(r)|b_j(r)\rangle = 1 \qquad 4.5$$

These conditions can be effected by a method due to Lowdin (1950) without affecting the symmetry of the basis functions.

We must now find the matrix component of energy between two such Bloch sums. If H is the Hamiltonian operator, this matrix component is clearly

$$=\sum_{R_j} e^{ik(R_j-R_i)}\int\psi^*_n(r-R_i)H\psi_m(r-R_j)\,d\tau \qquad 4.6$$

$$=\sum_{R_j} e^{ik(R_j-R_i)}\int\psi^*_n(r'+R_j-R_i)H\psi_m(r')\,d\tau \qquad 4.7$$

where $r'=r-R_j$ and R_j-R_i is the vector displacement from the atom on which the orbital ψ_m is located to one of its neighbours on which ψ_n is located.

There is every reason to think the integral in 4.7 will get smaller numerically as the atoms in question get further apart, which means such an integral would be zero unless the two atoms were close enough so that their orbitals overlapped to an appreciable extent.

Now

$$\psi^*_n(r+R_j-R_i) = b_1(r+R_j-R_i) \qquad 4.8$$

also

$$\psi_m(r) = b_0(r-R_j) \qquad 4.9$$

The expression, 4.7 now becomes

$$\langle M\rangle = \sum_{R_j} e^{ik(R_j-R_i)} \int b^*_1(r+R_j-R_i) H b_0(r-R_i)\, d\tau \qquad 4.10$$

Equation 4.10 gives the matrix elements of the Hamiltonian between the various basis states (R_j-R_i) = (a/2,a/2,a/2), (a/2,-a/2,-a/2), (-a/2, a/2,-a/2), (-a/2,-a/2,a/2) for the diamond-like crystals.

4.3 The Matrix Elements

The interaction of an s-orbital with itself on the same atom is given from 4.10 by

$$\langle M\rangle_{ssss} = \int b^*_0(r) H b_0(r)\, d\tau \qquad R_j-R_i = 0$$
$$= E_{ss}$$

This implies the interaction of an orbital with itself simply yields the energy of the orbitals.

Hence

$$\langle M\rangle_{ss} = E_{s1}$$
$$\langle M\rangle_{xsxs} = E_{ps} \qquad \langle M\rangle_{xsxs} = E_{ps}$$
$$\langle M\rangle_{ysys} = E_{ps} \qquad \langle M\rangle_{y1y1} = E_{p1}$$
$$\langle M\rangle_{zszs} = E_{ps} \qquad \langle M\rangle_{z1z1} = E_{p1}$$

The interaction of an s-orbital on the first atom with an s-orbital on the second atom is

$$\langle M\rangle_{sos_1}=\Sigma e^{ik(R_j-R_i)}\int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right) b_0((x^2+y^2+z^2)^{1/2})\,dx\,dy\,dz. = V_{ss}\,g_0$$

The interaction of an s-orbital with an orbital on the same atom is

$$\langle M\rangle_{soxo}=\int b^*_0\left(((x+a/2)^2+(y+a/2)^2+(z+a/2)^2)^{1/2}\right)\chi\ b_0(x^2+y^2+z^2)^{1/2}\,dx\,dy\,dz$$

$$= 0 \qquad R_j-R_i=0$$

This shows that the interaction between an s-orbital and a p-orbital on the same atom is zero i.e

$$\langle M\rangle_{soyo} = 0$$

$$\langle M\rangle_{sozo} = 0$$

$$\langle M\rangle_{s_1x_1} = 0$$

$$\langle M\rangle_{s_1y_1} = 0$$

$$\langle M\rangle_{s_1z_1} = 0$$

$$\langle M\rangle_{xoso} = 0$$

$$\langle M\rangle_{yoso} = 0$$

$$\langle M\rangle_{zoso} = 0$$

$$\langle M\rangle_{xoyo} = 0$$

$$\langle M\rangle_{xozo} = 0$$

$$\langle M\rangle_{x_1s_1} = 0$$

$$\langle M\rangle_{y_1s_1} = 0$$

$$\langle M\rangle_{z_1s_1} = 0$$

$$\langle M\rangle_{x_1y_1} = 0$$

$$\langle M\rangle_{x_1z_1} = 0$$

$$\langle M\rangle_{yoxo} = 0$$

$$\langle M\rangle_{zozo} = 0$$

$$\langle M\rangle_{yozo} = 0$$

$$\langle M\rangle_{zoyo} = 0$$

$$\langle M\rangle_{y_1z_1} = 0$$

$$\langle M\rangle_{y_1x_1} = 0$$

$$\langle M\rangle_{z_1y_1} = 0$$

$$\langle M\rangle_{z_1x_1} = 0$$

The interactions of an s-orbital on the first atom with a p-orbital on the second atom are

$$\langle M\rangle_{s_0x_1} = \sum e^{ik(R_j-R_i)} \int b^*_1\left([(x+a/2)^2+(y+a/2)^2+(z+a/2)^2]^{1/2}\right)x \; b_0(x^2+y^2+z^2)^{1/2}\,dx\,dy\,dz.$$

$$= V_{sx}g_1$$

$$\langle M\rangle_{s_0y_1} = \sum e^{ik(R_j-R_i)} \int b^*_1\left([(x+a/2)^2+(y+a/2)^2+(z+a/2)^2]^{1/2}\right)y \; b_0(x^2+y^2+z^2)^{1/2}\,dx\,dy\,dz$$

$$= V_{s-y}g_2$$

The S-S interaction on different atoms is

$$\langle N\rangle_{s_1s_0} = \sum e^{ik(R_j-R_i)} \int b^*_1\left([(x+a/2)^2+(y+a/2)^2+(z+a/2)^2]^{1/2}\right) b_0(x^2+y^2+z^2)^{1/2}\,dx\,dy\,dz$$

$$= V_{ss}g_0^*$$

$$\langle M\rangle_{s_0z_1} = V_{s_0z_0}g^3$$

The S-P interactions on different atoms are

$$\langle M\rangle_{s_1x_0} = \sum e^{ik(R_j-R_i)} \int b^*_1\left([(x+a/2)^2+(y+a/2)^2+(z+a/2)^2]^{1/2}\right)x \; b_0(x^2+y^2+z^2)^{1/2})\,dx\,dy\,dz$$

$$= -V_{ss}g_1^*$$

$$\langle M\rangle_{s_1x_0} = -V_{s_0}g^*_1$$

$$\langle M\rangle_{s_1y_0} = -V_{s_0}g^*_2$$

$$\langle M\rangle_{s_1z_0} = -V_{s_0}g^*32$$

The interaction of a p-orbital on the first atom with an s-orbital on the second atom is

$$\langle N\rangle_{x_0s_1} = -\sum e^{ik(R_j-R_i)} \int b^*_1\left([(x+a/2)^2+(y+a/2)^2+(z+a/2)^2]^{1/2}\right)x \; b_0(x^2+y^2+z^2)^{1/2}\,dx\,dy\,dz.$$

$$= -V_{sp}g_1^*$$

The p-p interactions on different atoms are

$$\langle M\rangle_{x_0x_1} = -\Sigma e^{ik(R_j-R_i)} \int b^*_1 \left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2} \chi_0\chi_1 \, b_0\left(x^2+y^2+z^2\right)^{1/2} dx\,dy\,dz.$$

$$= V_{xx} g_0$$

$$\langle M\rangle_{x_0y_1} = V_{xy} g_z$$

$$\langle M\rangle_{x_0z_1} = V_{xz} g_y$$

$$\langle M\rangle_{y_0x_1} = -V_{yz} g_z$$

$$\langle M\rangle_{y_0x_1} = V_{xy} g_z$$

$$\langle M\rangle_{x_0y_1} = V_{yy} g_0$$

$$\langle M\rangle_{y_0y_1} = V_{yy} g_0$$

$$\langle M\rangle_{y_0z_1} = V_{yz} g_x$$

$$\langle M\rangle_{z_0x_1} = -V_{yz} g_z$$

$$\langle M\rangle_{z_0x_1} = V_{xz} g_y$$

$$\langle M\rangle_{z_0y_1} = V_{yz} g_x$$

$$\langle M\rangle_{z_0z_1} = V_{zz} g_0$$

$$\langle M\rangle_{x_1x_0} = V_{yy} g^*_x$$

$$\langle M\rangle_{x_1x_0} = V_{xx} g^*_0$$

$$\langle M\rangle_{x_1y_0} = V_{xy} g^*_z$$

$$\langle M\rangle_{x_1z_0} = V_{xy} g^*_y$$

$$\langle M\rangle_{y_1x_0} = V_{yz} g^*_y$$

$$\langle M\rangle_{y_1x_0} = V_{xy} g^*_z$$

$$\langle M\rangle_{y_1y_0} = V_{yy} g^*_0$$

$$\langle M\rangle_{y_1z_0} = V_{yz} g^*_x$$

$$\langle M\rangle_{z_1x_0} = V_{yz} g^*_z$$

$$\langle M\rangle_{z_1x_0} = V_{xy} g^*_y$$

$$\langle M\rangle_{z_1y_0} = V_{yx} g^*_z$$

$$\langle M\rangle_{z_1z_0} = V_{zz} g^*_0$$

where

$$V_{gg} = \int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right) b_0\left(x^2+y^2+z^2\right)^{1/2} dx\,dy\,dz,$$

Generally,

$$V_{cc}=\int b^{*}{}_{1}\left(\left[(x+a/2)^{2}+(y+a/2)^{2}+(z+a/2)^{2}\right]^{1/2}\right)CC$$
$$b_{0}\left((x^{2}+y^{2}+z^{2})^{1/2}\right)dxdydz$$

where C = S, X, Y or Z

$$g_{0}=\cos K_{1}\pi/2\cos K_{2}\pi/2\cos K_{3}\pi/2-i\sin K_{1}\pi/2\sin K_{2}\pi/2\sin K_{3}\pi/2$$
$$g_{1}=-\cos K_{1}\pi/2\sin K_{2}\pi/2\sin K_{3}\pi/2+i\sin K_{1}\pi/2\cos K_{2}\pi/2\cos K_{3}\pi/2$$
$$g_{2}=-\sin K_{1}\pi/2\cos K_{2}\pi/2\sin K_{3}\pi/2+i\cos K_{1}\pi/2\sin K_{2}\pi/2\cos K_{3}\pi/2$$
$$g_{3}=-\sin K_{1}\pi/2\sin K_{2}\pi/2\cos K_{3}\pi/2+i\cos K_{1}\pi/2\cos K_{2}\pi/2\sin K_{3}\pi/2$$

considering for the diamond structure crystals

$E_{s0}=E_{s1}=E_{s}$; $E_{p0}=E_{p1}=E_{p}$; $V_{sop}=V_{s1p}$ and $V_{xx}=V_{yy1}=V_{zz}$

the 8x8 matrix representing all possible nearest neighbour interactions between s-and p-orbitals on each of the crystal is

$$\begin{array}{cccccccc}
E_{s} & V_{ss}g_{0} & 0 & 0 & 0 & V_{sp}g_{1} & V_{sp}g_{2} & V_{sp}g_{3} \\
V_{ss}g^{*}_{0} & E_{s} & -V_{sp}g^{*}_{1} & -V_{sp}g^{*}_{2} & -V_{sp}g^{*}_{3} & 0 & 0 & 0 \\
0 & -V_{sp}g_{1} & E_{p} & 0 & 0 & V_{xx}g_{0} & V_{xy}g_{3} & V_{xy}g_{2} \\
0 & -V_{sp}g_{2} & 0 & E_{p} & 0 & V_{xy}g_{3} & V_{xx}g_{0} & V_{xy}g_{1} \\
0 & -V_{sp}g_{3} & 0 & 0 & E_{p} & V_{xy}g_{2} & V_{xy}g_{1} & V_{xx}g_{0} \\
V_{sp}g^{*}_{1} & 0 & V_{xx}g^{*}_{0} & V_{xy}g^{*}_{3} & V_{xy}g^{*}_{2} & E_{p} & 0 & 0 \\
V_{sp}g^{*}_{2} & 0 & V_{xy}g^{*}_{3} & V_{xx}g^{*}_{0} & V_{xy}g^{*}_{1} & 0 & E_{p} & 0 \\
V_{sp}g^{*}_{3} & 0 & V_{xy}g^{*}_{2} & V_{xy}g^{*}_{1} & V_{xx}g^{*}_{0} & 0 & 0 & E_{p}
\end{array}$$

The detailed calculations showing the procedure for calculating the matrix elements is given in the Appendix.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 INTRODUCTION

Diamond like crystals are face centred cubic (fcc), and so their first Brillouin zones are all alike as shown in Figure 5.1 where k_x, k_y, and k_z and are the wave veciors along the 3-coordinates. The coordinates of the symmetry points marked on Figure 4.1 are.

$\Gamma = 2\pi/a(0,0,0)$

$X = 2\pi/a(0,0,1)$

$W = 2\pi/a(1/2,0,1)$

$\Delta_1 = 2\pi/a(0,0,1/4)$

$\Delta_2 = 2\pi/a(0,0,1/2)$

$\Delta_3 = 2\pi/a(0,0,3/4)$

$L = 2\pi/a(1/2,1/2,1/2)$

$\Lambda_1 = 2\pi/a(1/4,1/4,1/4)$

$\Lambda_2 = 2\pi/a(3/4,3/4,3/4)$

$K = 2\pi/a(3/4,3/4,0)$

$\Sigma_1 = 2\pi/a(3/8,3/8,0)$

$\Sigma_2 = 2\pi/a(1/2,1/2,0)$

$U = 2\pi/a(0,1,1/4)$

Making a transformation $x \longrightarrow y$, $y \longrightarrow z$, and $z \longrightarrow x$, the coordinates of the points can be rewritten as

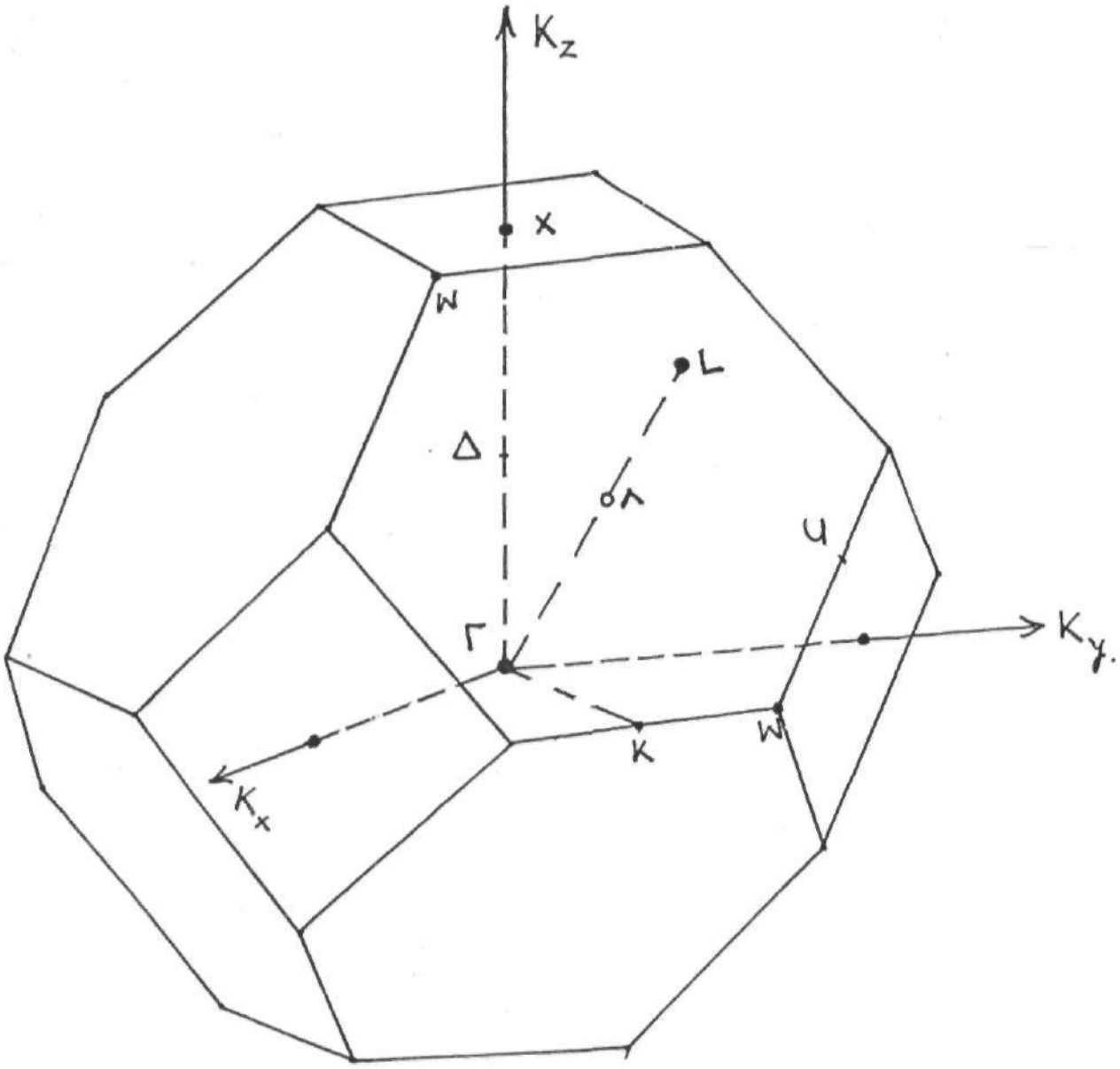


Fig 5.1 First Brillonin Zone of a Face Centred Cubic Crystal

Γ = $2\pi/a(0,0,0)$

X = $2\pi/a(1,0,0)$

W = $2\pi/a(1,1/2,0)$

Δ_1 = $2\pi/a(1/4,0,0)$

Δ_2 = $2\pi/a(1/2,0,0)$

Δ_3 = $2\pi/a(3/4,0,0)$

L = $2\pi/a(1/2,1/2,1/2)$

Λ_1 = $2\pi/a(1/4,1/4,1/4)$

Λ_2 = $2\pi/a(3/4,3/4,3/4)$

K = $2\pi/a(0,3/4,3/4)$

Σ_1 = $2\pi/a(0,3/8,3/8)$

Σ_2 = $2\pi/a(0,1/2,1/2)$

U = $2\pi/a(1/4,0,1)$

The energies of these symmetry points give the energy bonds of the crystal in the first Brillouin zone.

5.2 The S-S Interaction

Setting the S-P interaction parameters i.e V_{sap} and V_{asp} equal to zero, the 8x8 matrix decouples into a 2x2 and a 6x6 matrix. The energy eigen values of the 2x2 matrix which describes the S-states are given by

$$E(K) = E_s \pm V_{ss}|g_0(K)| \qquad 4.1$$

The values of $|g_0(K)|$ were calculated for the different symmetry points and substituted in equation 4.1 with $V_{ss}=-7.0eV$ and $E_s=0$, thus the energies of the points were determined as tabulated below.

Table 1 Energy of the symmetry points for s-s interaction

Symmetry point	$\lvert g_n(K)\rvert$	E(K)eV
$\Gamma = 2\pi/a(0,0,0)$	1	±7.0
$X = 2\pi/a(1,0,0)$	0	0
$W = 2\pi/a(1,1/2,0)$	0	0
$\Delta_1 = 2\pi/a(1/4,0,0)$	0.9739	±6.47
$\Delta_2 = 2\pi/a(1/2,0,0)$	0.7070	±4.95
$\Delta_3 = 2\pi/a(3/4,0,0)$	0.3827	±2.68
$L = 2\pi/a(1/2,1/2,1/2)$	0.5000	±3.50
$\Lambda_1 = 2\pi/a(1/4,1/4,1/4)$	0.7906	±5.55
$\Lambda_2 = 2\pi/a(3/4,3/4,3/4)$	0.7906	±5.53
$K = 2\pi/a(0,3/4,3/4)$	0.3827	±2.68
$\Sigma_1 = 2\pi/a(0,3/8,3/8)$	0.8315	±5.82
$\Sigma_2 = 2\pi/a(0,1/2,1/2)$	0.5000	±3.50
$U = 2\pi/a(1/4,0,1)$	0	0

The Energy plotted against the wave vector K gives the band structure of the S-states for the diamond structure crystals as shown in Figure 5.2.

5.2.1 Discussions

These results provide a good description of the lowest valence band in crystals with diamond structure. Specifying the width of the band determines the band structure to within a few tenth of an eV throughout the Brillouin zone. The largest errors occur along Λ and along the Z-direction which runs between the symmetry points X = 2π/a(1,0,0) and W= 2π/a(1,1/2,0) of the Brillouin zone. Along this direction the two bands are degenerate by symmetry and have no dispersion. For $V_{ss} < 0$, the lower energy band is bonding at Γ and the higher band is anti-bonding. For $V_{ss} > 0$ the order of the bonding-anti-bonding states is reversed.

5.3 The p-p Interaction

The band structure associated with the six P-states is obtained by solving the 6x6 matrix which gives the roots of the energy equation for the different symmetry points. The energy eigen values are given with the corresponding values of $|g_0(K)|$, $|g_1(K)|$, $|g_2(K)|$ and $|g_3(K)|$ in Table 2.

Table 2 Energy of the symmetry points for p-p interaction

Symmetry point	$\lvert g_a(K)\rvert$	$\lvert g_s(K)\rvert$	$\lvert g_2(K)\rvert$	$\lvert g_3(K)\rvert$	E(K) eV
$\Gamma = 2\pi/a(0,0,0)$	1	0	0	0	0; ±3.50
$X = 2\pi/a(1,0,0)$	0	1	0	0	0; ±7.00
$W = 2\pi/a(1,1/2,0)$	0	0.707	0	0.707	0; ±7.00
$\Delta_1 = 2\pi/a(1/4,0,0)$	0.9239	0.3827	0	0	0; ±6.60
$\Delta_2 = 2\pi/a(1/2,0,0)$	0.707	0.707	0	0	3.15; ±2.24
$\Delta_3 = 2\pi/a(3/4,0,0)$	0.3827	0.9239	0	0	±4.95
$L = 2\pi/a(1/2,1/2,1/2)$	0.5	0.5	0.5	0.5	±3.5; ±7.0
$\Lambda_1 = 2\pi/a(1/4,1/4,1/4)$	0.7906	0.13536	0.3536	0.3536	±7.24; ±4.95
$\Lambda_2 = 2\pi/a(3/4,3/4,3/4)$	0.7906	0.13536	0.3536	0.3536	±2.50; ±4.95
$K = 2\pi/a(0,3/4,3/4)$	0.1464	0.8536	0.3536	0.3536	±1.6±6.65; ±7
$\Sigma_1 = 2\pi/a(0,3/8,3/8)$	0.6913	0.3087	0.4619	0.4619	±2.4; ±6.65
$\Sigma_2 = 2\pi/a(0,1/2,1/2)$	0.5	0.5	0.5	0.5	±3.5; ±7.0
$U = 2\pi/a(1/4,0,1)$	0	0	0.3827	0.9239	±7.0
$W' = 2\pi/a(0,1/2,1)$	0	0.707	0	0.707	0; ±7.0

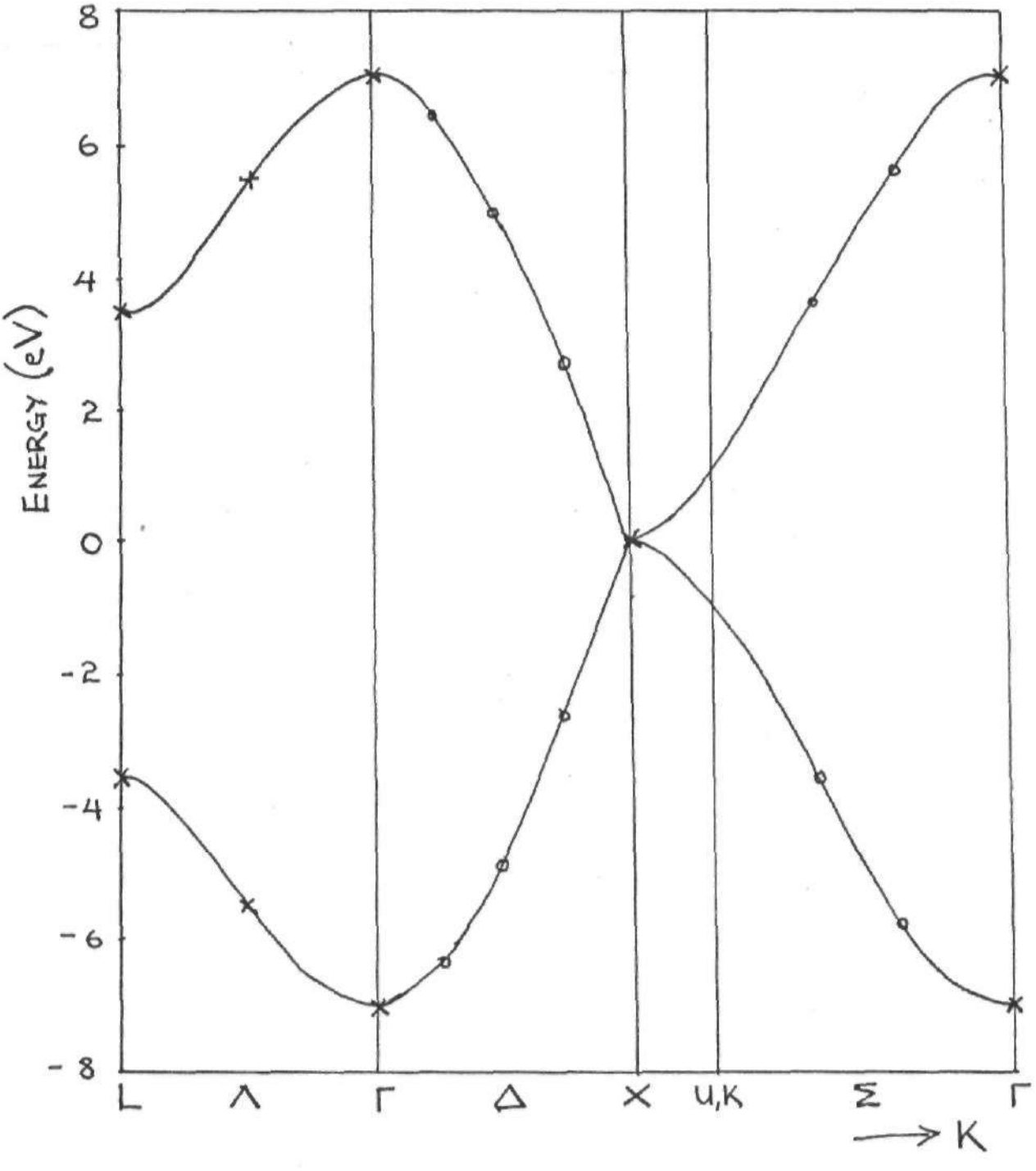


Figure 5.2 Band Structure of the S-states of Diamond Structure

The plot of the Band structure for the p-states of the diamond structure crystals is as shown in Figure 5.3 for $V_{xx}=0$; $V_{xy}=7.0$ and $E_p=0$.

5.3.1 Discussions

As in the case of the s-bands there is no dispersion along the line joining the symmetry points X and W of the Brillouin zone. The maximum of the lower 3 bands and the minimum of the upper 3-bands occur at X. The zero slope of the bands at X gives, as in the case of the s-states, rise to a sharp structure in the density of states.

5.4 The S-P Interaction

The bond structure associated with the S-P interaction is obtained by solving the 8x8 secular matrix which gives the desired energy equation that defines the S-P interaction. The values of $|g|$ for each symmetry point are then substituted and a quadratic equation in E(K) is obtained which when solved yields the roots. These energy roots define energy variation for each symmetry point. A plot of E(K) against the wave vector K shows the band structure of the particular crystal considered. The results of carbon (diamond), silicon and germanium were calculated in this work and presented below.

5.4.1 Carbon (diamond)

The energy roots E(K) for each symmetry point are as given in Table 3 below.

Table 3 Energy of the symmetry points for s-p interaction

Symmetry point	E(K)eV
Γ	0, -19.6
X	-5.3; -11.6
Δ_1	-3.52, -5.82, -7.7, -16.42
Δ_2	-2.0, -4.99, -17.99
Δ_5	-3.0, -19.23
L	-2.3, -9.138, -18.65
Λ_3	-1.95, -4.66, -18.91
K	-4.55, -7.02, -8-72, -12.73
Σ	-2.01, -4.0, -8.38, -19.00
U	-5.73, -6.35, -10.2, -13.0

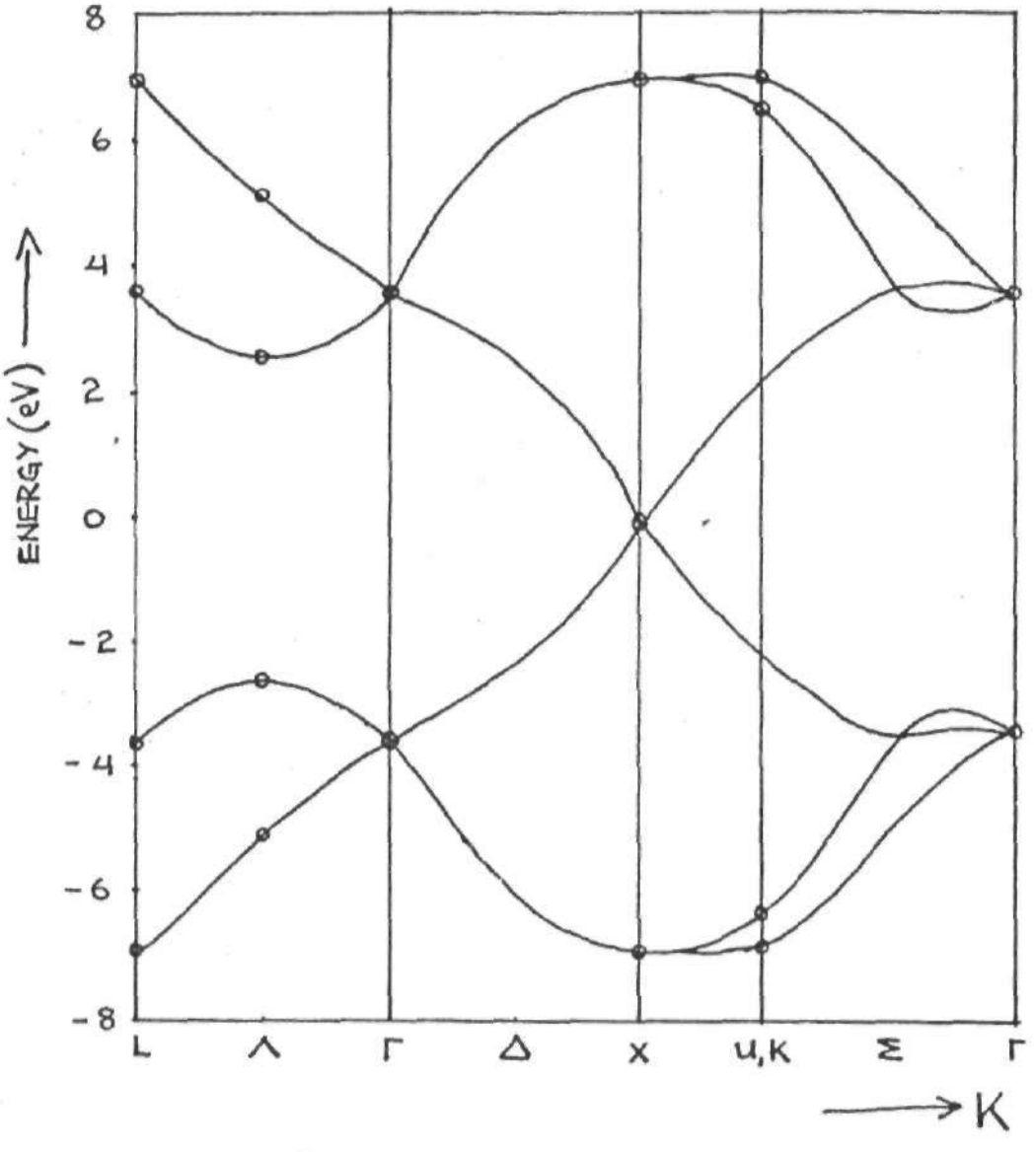


Figure 5.3 Band Structure of the P-states of Diamond Structure crystals.

The energies are measured relative to the top of the valence bands at Γ i.e the top of the valence band was made zero and V_{ss}=-15.2; V_{xx}=3.0; and V_{xy}=8.30. The plot of the band structure is as given in Figure 5.4.

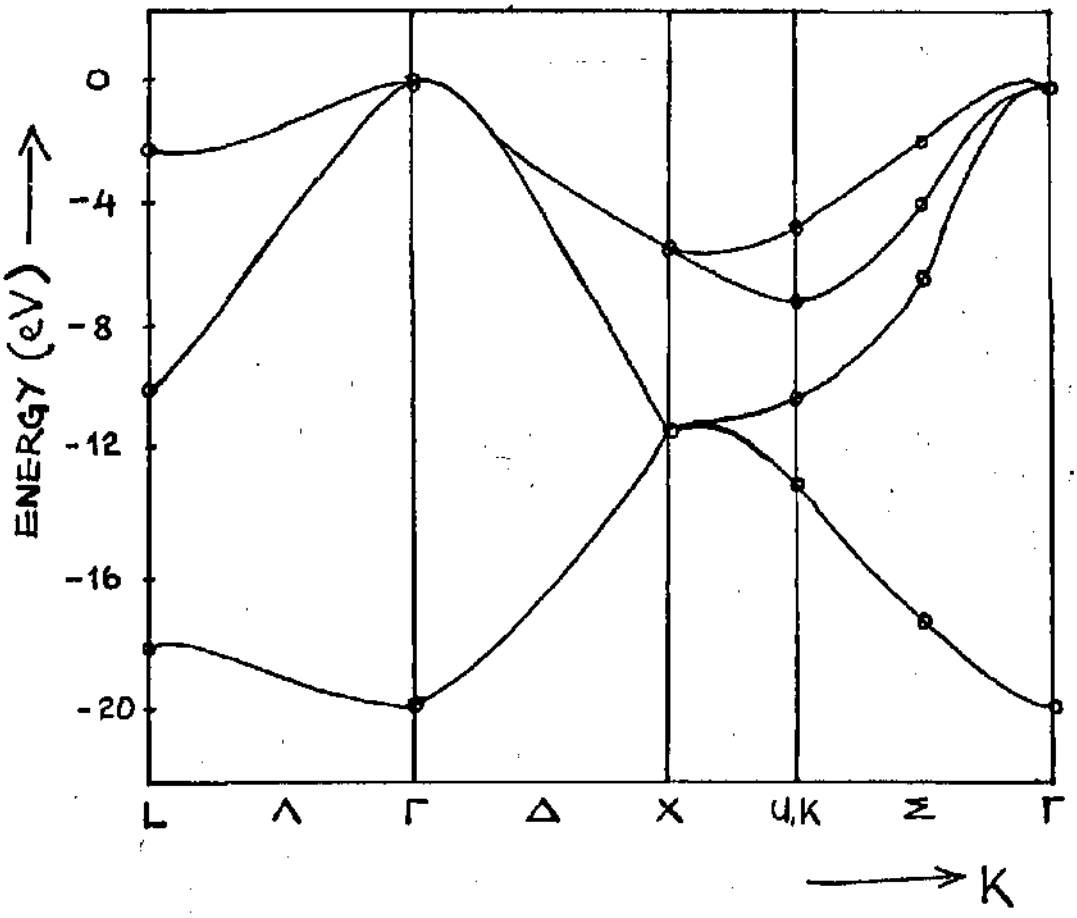


Figure 5.4 The Plot of the Band Structure of Diamond.

5.4.2 Silicon

The roots of the energy E(K) for each symmetry point are as given in Table 4.

Table 4 Energy of the symmetry points in silicon

Symmetry point	E(K)eV
Γ	0, -12.4
X	-3.0; -10.0
$-\Delta_1$	-3.0, -6.0, -9.8,
Δ_2	-2.83, -4.0, -11.2
Δ_5	-1.20, -12.0
L	-1.60, -7.0, -9.6
Λ_1	-0.52, -1.51, -12.0
Λ_3	-1.54, -6.0, -10.0
K	-2.07, -4.11, -6-70, -7.38
Σ_1	-1.07, -3.53, -4.98, -9.6
Σ_2	-0, -0.59, -1.32, -12.0
U	-2.6, -3.2, -7.6, -8.2

For V_{ss} = -8.13; V_{sp} = 5.88; V_{xx} = 1.71 and V_{xy} = 7.51.

NB: All energies are measured relative to the top of the valence bands at Γ

The band structure plot is as shown in Figure 5.5.

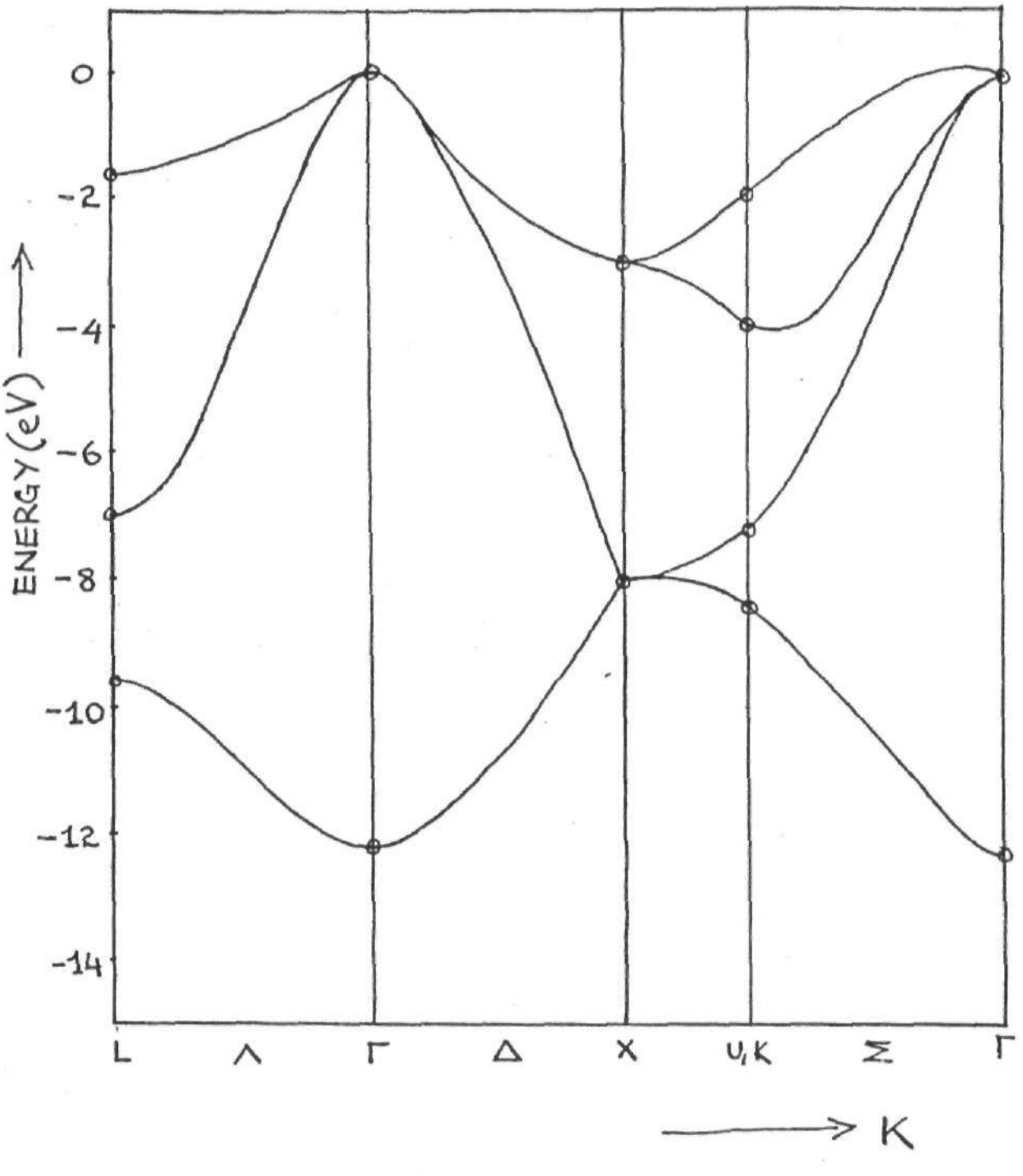


Figure 5.5 Plot of the Band Structure of silicon

5.4.3 Germanium

The energy roots E(K) for each symmetry point are given in Table 5.

Table 5 Energy of the symmetry points in germanium

Symmetry point	E(u)eV
Γ	0, -12.8
X	-3.6; -7.0, -10.0
$-\Delta_1$	-3.0, -5.65, -11.0,
Δ_2	-2.0, -3.4, -12.0
Δ_3	-1.0, -12.8
L	-2.01, -7.8, -9.83
Λ_1	-0.8, -3.0, -12.02
Λ_2	-1.41, -7.0, -10.8
K	-2.37, -3.72, -6.93, -9.76
Σ_1	-1.27, -2.73, -5.67, -10.92
Σ_2	-0, -0.39, -0.97, -12.8
U	-5.6, -7.4, -9.7

For V_{ss} = -6.78; V_{sp} = 5.31; V_{xx} = 1.62 and V_{xy} = 6.82.

The plot of the band structure is as given in Figure 5.6

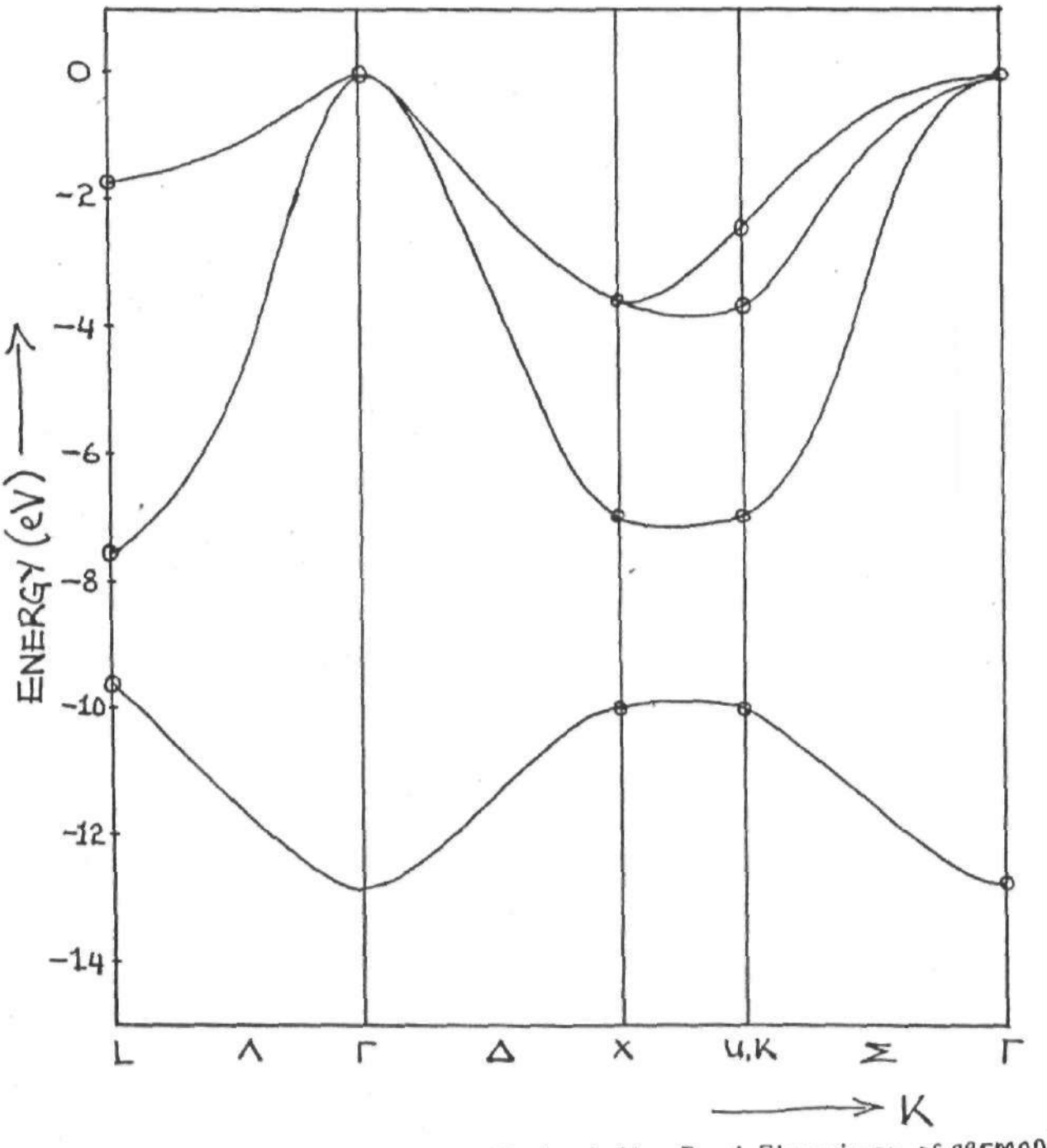


Figure 5.6 Plot of the Band Structure of germanium.

5.5 Discussions

The conduction bands in all three cases are not well reproduced by the tight binding method except at Γ where the splittings were fitted. To obtain more accurate conduction bands the second nearest neighbour interactions have to be used especially those between s- and p- states, but a few parameters are sufficient to give an accurate description of the valence bands and an approximate description of the first few conduction bands.

The tight binding method allows for a simple calculation of the S- and P- character of the valence bands and it is intersting to note how close to the ideal SP^3 they are. The top two valence bands are completely p-like in character in all three crystals. If $V_{xx} = V_{xy}$, then two sets of bands which are doubly degenerate and flat throughout the Brillouin zone would be obtained, independent of the magnitude of the other nearest neighbour interactions. This implies the broadening of the p-bands is related to $V_{xx}-V_{xy}$, but this is not a good approximation since the interaction V_{xy} is expected to be stronger than V_{xx}, because the overlap between the orbitals $X_a Y_1$, is larger than the overlap between the orbitals X_a and X_1.

REFERENCES

ASHCROFT W.N. (1976). Solid state Physics, Holt Saunders International ed. U.S.A.

BROOKS M. and HAM, F.S. (1955) Phys. Rev B6 244.

CHADI, J.D. and COHEN, M.L. (1975). Physica status solidi B68 405.

CHELIKOWSKY J.R., CHADI J.D. and COHEN M.L. (1973) Phys. Rev. B8: 2786.

CIRACI, S. and BATRA, I.P. (1977). Phys Rev B15 4923.

HAM, F.S. and MATTIS, D. (1955). Phys Rev B6 1656.

HARRISON W.A. (1980). Electronic structure and the properties of solids, 2nd ed., W.H. Freeman and Company, San Francisco.

HERRING, M. (1950). Phys Rev B4 1423.

HUANG, C., MORIARTY, J.A. and SHER, A. (1976). Phys Rev B12 5395.

JOANNOPOULOS J.D. and COHEN M.L. (1973). Phys. Rev. B7: 2644.

KHEINMANS, L. and PHILIPS, J.C. (1959). Phys Rev. B6 116.

KITTEL, C (1984). Introduction to solid state physics, Fifth ed.; Wiley Eastern Limited London

LONG D. (1968). Energy bands in semiconductors, Interscience Publishers (USA).

LOWDIN P.O. (1950). J. Chem. Phys. 18: 365.

SLATER, J.C. and KOSTER, G.F. (1954). Phys Rev. 94; 1498.

THORPE M.F. and WEAIRE D. (1971). Phys. Rev. B4: 3518.

WEAIRE, D. and THORPE, M.F. (1971). Phys Rev. B4 3518.

APPENDIX

THE MATRIX ELEMENTS

The basic problem of the tight binding method is to find the matrix elements of the Hamiltonian between the various basis states. The matirx elements can be caculated as thus:

$$\langle M\rangle = \sum_{R_j} e^{ik\cdot(R_j-R_i)} \int \Psi^*_n(r-R_i) H \Psi_m(r-R_j)\,d\tau$$

$$= \sum_{R_j} e^{ik\cdot(R_j-R_i)} \int \Psi^*_n(r-R_i-R_j) H \Psi_m(r)\,d\tau$$

where $r = r-R_j$ and R_j-R_i is the vector displacement from the atom on which the orbital Ψ_m is located to one of its neighbours on which Ψ_n is located.

$R_j-R_i=(a/2,a/2,a/2),\ (a/2,-a/2,-a/2),(-a/2,a/2,-a/2),\ (-a/2,-a/2,a/2)$

$$\Psi^*_n(r-R_i-R_j) = b^*_i(r-R_j-R_i)$$

$$\Psi(r) = b_m(r-R_j)$$

The expression becomes

$$\langle M\rangle = \sum_{R_j} e^{ik\cdot(R_j-R_i)} \int b^*_i(r+R_j-R_i) H b_m(r-R_j)\,d\tau$$

The interaction of an s orbital with itself on the same atom is given by:

$$\langle M\rangle_{sass} = \int b^*(r) H b_s(r)\,d\tau \qquad R_j-R_i = 0$$

$$= \int (H b_s(r))^* H b_s(r)\,d\tau$$

$$= E_{ss} \int b^*_s(r) b_s(r)\,d\tau$$

$$= E_{ss}$$

This implies the interaction of an orbital with itself simply yields the energy of the orbital. Hence:

$$\langle M\rangle_{sisi} = E^{ss}$$

$$\langle M\rangle_{xaxa} = E^{pp} \qquad \langle M\rangle_{xixi} = E^{p_1}$$

$$\langle M\rangle_{yayo} = E^{pp} \qquad \langle M\rangle_{yiyi} = E^{p_1}$$

$\langle M\rangle_{s=s=0} = F^{p0}$ $\qquad\qquad$ $\langle M\rangle_{s=1=1} = F^{p1}$

The interaction of an s orbital on the first atom with an s-orbital on the second atom gives:

$$\langle M\rangle_{s=s=1} = +e^{(1k)(1/2,1/2,1/2)a}\int b_1^*\left([(x+a/2)^2+(y+a/2)^2+(z+a/2)^2]^{1/2}\right) b_0\left((x^2+y^2+z^2)^{1/2}\right)dxdydz$$

$$+e^{(1k)(1/2,-1/2,-1/2)a}\int b_1^*\left([(x+a/2)^2+(y+a/2)^2+(z+a/2)^2]^{1/2}\right) b_0\left((x^2+y^2+z^2)^{1/2}\right)dxdydz$$

$$+e^{(1k)(-1/2,1/2,-1/2)a}\int b_1^*\left((x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right) b_0\left((x^2+y^2+z^2)^{1/2}\right)dxdydz$$

$$+e^{(1k)(-1/2-1/2+1/2)a}\int b_1^*\left((x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right) b_0\left((x^2+y^2+z^2)^{1/2}\right)dxdydz$$

Making the transfformation $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$ we get

$$\langle M\rangle_{s=s=1} = +\int b_1^*\left([(x+a/2)^2+(y+a/2)^2+(z+a/2)^2]^{1/2}\right) b_0\left(x^2+y^2+z^2\right)^{1/2}dxdydz\left[e^{(1k)(1/2,1/2,1/2)a}+(-1/2,1/2,-1/2)a\right.$$

$$\left.e^{(1k)(1/2,-1/2,-1/2)a}+e^{(1k)(-1/2,-1/2,\ 1/2)a}\right]$$

$$= +K\left(e^{(1k)a/2)}\ (e^{(1)(k_2+k_3)a)/2}+e^{(-1)(k_2+k_3)a)/2}+e^{-(1k)a/2}(e^{(1)(k_2+k_3)a)/2})\right)$$

$$= +K\left((\cos K_1a/2+(i)\sin K_1a/2)(\cos(K_2-K_3)/2)a+(i)\sin(K_2-K_3)/2)a+\cos(K_2-K_3)/2)a-(i)\sin(K_2-K_3)/2)a\right)$$

$$= +2K\left((\cos K_1a/2+(i)\sin K_1a/2)(\cos(K_2a/2\cos(K_3a/2-\sin K_2a/2\sin K_3a/2+(\cos K_1a/2-(i)\sin K_1a/2)(\cos K_1a/2\cos K_3)a/2)+\sin(K_2a/2\sin(K_3a/2))\right)$$

$$= +4K\left(\cos K_1a/2\cos K_2)a/2\cos K_3)a/2)-(i)\sin(K_1a/2\sin(K_2a/2\sin(K_3a/2))\right)$$

$$= +V_{ss}g_0$$

The interaction of a s-orbital with a s-orbital on the same term i.e $R_j-R_{j1}=0$ gives

$$\langle M\rangle_{s\alpha s\alpha} = \int i\cdot {}^{*}_{a}\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$x b_a\left(x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+\int b^{*}_{a}\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$x b_a\left(x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+\int b^{*}_{a}\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$x b_a\left(x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+\int b^{*}_{a}\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$x b_a\left(x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz .$$

Making the transformation $x \longrightarrow -x$, $y \longrightarrow -y$, $z \longrightarrow -z$ gives

$$\langle M\rangle_{s\alpha s\alpha} = \int b^{*}_{a}\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$+x b_a\left(x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz\ x(i\ +\ i\ -i\ -j)$$

$$\langle M\rangle_{s\alpha s\alpha} = 0$$

This shows that the matrix elements between an s- and a p-state on the same atom are zero

i.e $\langle M\rangle_{s\alpha y\alpha} = 0$

$\langle M\rangle_{s\alpha x\alpha} = 0$

$\langle M\rangle_{s\downarrow x\downarrow} = 0$

$\langle M\rangle_{s\downarrow y\downarrow} = 0$

$\langle M\rangle_{s\downarrow z\downarrow} = 0$

$$\langle M\rangle_{s\alpha x\downarrow} = +e^{ik(1/2,1/2,1/2)a}\int b^{*}_{a}\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$+x b_a\left(x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+e^{ik(1/2,-1/2,-1/2)a}\int b^{*}_{\downarrow}\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$+x b_a\left(x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+e^{ik(-1/2,1/2,-1/2)a}\int b^{*}_{\downarrow}\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$x b_a\left(x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+e^{ik(-1/2,-1/2,1/2)a}\int b^{*}_{\downarrow}\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$+x b_a\left(x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$

Making the transformation $x \longrightarrow -x$, $y \longrightarrow -y$, $z \longrightarrow -z$ we get

$$\langle M\rangle_{s\alpha x\downarrow} = \int b^{*}_{\downarrow}\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$

$$x b_a\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz \qquad \left[+e^{1k(1/2,1/2,1/2)a} + \right.$$

$$\left. + e^{1k(1/2,-1/2,-1/2)a} - e^{1k(-1/2,1/2,-1/2)a} - e^{1k(1/2,-1/2,-1/2)a}\right]$$

$$= K\left((+e^{1k_1a/2}\left(e^{1(k_2+k_3)a/2}\right) + e^{-1(k_2+k_3)a/2}\right.$$

$$\left. -e^{-1k_1a/2}\left(e^{1(k_2-k_3)a/2} + e^{-1(k_2-k_3)a/2}\right)\right)$$

$$= K\left((+\cos K_1a/2+i\sin K_1a/2)\left(\cos(k_2+k_3)a/2+i\sin(k_2+k_3)a/2\right)\right.$$

$$+\cos(k_2+k_3)a/2-i\sin(k_2+k_2)a/2+(\cos(k_1a/2-i\sin(k_1a/2)$$

$$(\cos(k_2-k_3)a/2+i\sin(k_2-k_3)a/2+(\cos(k_2-k_3)a/2-i\sin(k_2-k_3)a/2))$$

$$\langle M\rangle_{eav1} = 2K\left(+(\cos k_1a/2+i\sin k_1a/2)(\cos k_2a/2\cos k_3a/2)-\sin k_2a/2\right.$$

$$\sin k_3a/2)-(\cos k_1a/2-i\sin k_1a/2)(\cos k_2a/2\cos k_3a/2)$$

$$\left.+\sin k_2a/2\sin k_3a/2)\right)$$

$$= 2K\left(-(\cos k_1a/2\cos k_2a/2\cos k_3a/2+i\sin k_1a/2\sin k_2a/2\right.$$

$$\sin k_3a/2-\cos k_1a/2\sin k_2a/2\sin k_3a/2+\sin k_1a/2$$

$$\cos k_2a/2\cos k_3a/2+\cos k_1a/2\cos k_2a/2\cos k_3a/2-$$

$$\sin k_1a/2\sin k_2a/2\sin k_3a/2-\cos k_1a/2\sin k_2a/2+$$

$$\left.\sin k_3a/2+i\sin k_1a/2\cos k_2a/2\cos k_3a/2\right)$$

$$= 4K\left(-\cos k_1a/2\sin k_2a/2\sin k_3a/2+i\sin k_1a/2\cos k_2a/2\right.$$

$$\left.\cos k_3a/2\right)$$

$$= V_{eav}\, g_1$$

$$\langle M\rangle_{eav1} = e^{1k(1/2,1/2,1/2)a}\int j_0 \psi^*_a\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$

$$+y b_a\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

$$e^{1k(1/2,-1/2,-1/2)a}\int j_0^*{}_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$

$$+y b_a\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

$$e^{1k(-1/2,1/2,-1/2)a}\int j_0 \psi^*{}_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$

$$y b_a\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

$$e^{1k(-1/2,-1/2,1/2)a}\int j_0^*{}_1\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$

$$+y b_a\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

Making the transformation $x \longrightarrow -x$, $y \longrightarrow -y$, $z \longrightarrow -z$ we get

$$\langle M\rangle_{eav} = \int h^*_a\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$+y b_a\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz \times \left[e^{ik(1/2,1/2,1/2)a}\right.$$
$$-e^{ik(1/2,-1/2,-1/2)a}+e^{ik(-1/2,1/2,-1/2)a}+e^{ik(-1/2,1/2,-1/2)a}$$
$$= K\{(e^{ik_1a/2}(e^{i(k_2+k_3)a/2} - e^{-i(k_2+k_3)a/2})$$
$$+ e^{-ik_1a/2}(e^{i(k_2-k_3)a/2} - e^{-i(k_2-k_3)a/2})\}$$

$$\langle M\rangle_{eav1} = K\{(\cos k_1a/2+i\sin k_1a/2)(\cos k_2(k_2+k_3)a/2+\sin(k_2+k_3)a/2$$
$$-\cos(k_2+k_3)a/2+i\sin(k_2a/2+k_3)a/2+(\cos k_1a/2-i\sin k_1a/2)$$
$$(\cos(k_2-k_3a/2)+i\sin(k_2-k_3)a/2-\cos(k_2-k_3)a/2+i\sin(k_2-k_3)a/2)\}$$
$$= 2K\{(\cos k_1a/2+\sin k_1a/2)(i\sin k_2\cos k_2+i\cos k_2\sin k_3)$$
$$+(\cos k_1a/2-i\sin k_1a/2)(i\sin k_2a/2)(i\sin k_2\cos k_3$$
$$- i\cos k_3\sin k_3)\}$$
$$= 2K\{i\cos k_1a/2\sin k_2a/2\cos k_3a/2-\sin k_1a/2\cos k_2a/2$$
$$\sin k_3a/2+i\cos k_1a/2\cos k_2a/2\sin k_3a/2)-\sin k_1a/2$$
$$\sin k_2a/2+\cos k_3a/2+i\cos k_1a/2\sin k_2a/2\cos k_3a/2-\sin k_1a/2\cos k_2a/2$$
$$-i\cos k_1a/2\sin k_2a/2\sin k_3a/2+\sin k_1a/2\sin k_2a/2\cos k_2a/2)\}$$
$$= 4K\{-\sin k_1a/2\cos k_2a/2\sin k_3a/2+i\cos k_1a/2\sin k_2a/2$$
$$\cos k_3a/2)\}$$
$$= V_{eav}g_z$$

This implies $\langle M\rangle_{eax} = V_{eav}g_x$

$$\langle M\rangle_{e1ea} = e^{-ik(1/2,1/2,1/2)a}\int h^*_p\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$h_a\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$
$$+e^{-ik(1/2,-1/2,-1/2)a}\int h^*_1\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$h_a\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$
$$+e^{-ik(-1/2,1/2,-1/2)a}\int b^*_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$h_a\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$
$$+e^{-ik(-1/2,-1/2,1/2)a}\int b^*_1\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$h_a\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$

Making the transformation $x \longrightarrow -x$, $y \longrightarrow -y$, $z \longrightarrow -z$ we get

$$\langle M\rangle_{a1ma} = \int b^*_m\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right) b_m\left(x^2+y^2+z^2+\right)^{1/2} dxdydz \times \left(e^{-ik(1/2,1/2,1/2)a}\right.$$

$$\left.+e^{-ik(1/2,-1/2,-1/2)a}+e^{-ik(-1/2,1/2,-1/2)a}+e^{-ik(-1/2,1/2,-1/2}\right.$$

$$= K\left(\left(e^{-ik_1a/2}\left(e^{-i(k_2+k_3)a/2}+e^{i(k_2+k_3)a/2}\right)\right.\right.$$

$$\left.\left.+e^{ik_1a/2}\left(e^{-i(k_2-k_3)a/2}+e^{i(k_2-k_3)a/2}\right)\right)\right.$$

$$\langle M\rangle_{a1ma} = K\left(\left(\cos k_1a/2-i\sin k_1a/2\right)\left(\cos(k_2+k_3)a/2-i\sin(k_2+k_3)a/2\right.\right.$$

$$\left.+\cos(k_2+k_3)a/2+i\sin(k_2+k_3)a/2+\left(\cos k_1a/2+i\sin k_1a/2\right)\right.$$

$$\left.\left.\left(\cos(k_2-k_3a/2)-i\sin(k_2-k_3)a/2+\cos(k_2-k_3)a/2+i\sin(k_2-k_3)a/2\right)\right)\right.$$

$$= 2K\left(\left(\cos k_1a/2-i\sin k_1a/2\right)\left(\cos k_2a/2\cos k_3a/2-\sin k_2a/2\sin k_3a/2\right)\right.$$

$$+\left(\cos k_1a/2+i\sin k_1a/2\right)\left(\cos k_2a/2\cos k_3a/2+\sin k_2a/2\cos k_3+\right.$$

$$+\cos k_3a/2\sin k_2a/2\sin k_3a/2+i\sin k_1a/2\cos k_2a/2\cos k_3a/2$$

$$\left.\left.+i\sin k_1a/2\sin k_2a/2\sin k_3a/2\right)\right)$$

$$= 4K\left(\cos k_1a/2\cos k_2a/2\cos k_3a/2+i\sin k_1a/2\sin k_2a/2\sin k_3a/2\right.$$

$$= V_{ma}g^*_m$$

$$\langle M\rangle_{m1ma} = -e^{-ik(1/2,1/2,1/2)a}\int b^*_n\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right) xb_m\left(x^2+y^2+z^2+\right)^{1/2} dxdydz$$

$$-e^{-ik(1/2,-1/2,-1/2)a}\int b^*_1\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right) xb_m\left(x^2+y^2+z^2+\right)^{1/2} dxdydz$$

$$-e^{-ik(-1/2,1/2,-1/2)a}\int b^*_2\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right) xb_m\left(x^2+y^2+z^2+\right)^{1/2} dxdydz$$

$$-e^{-ik(-1/2,-1/2,1/2)a}\int b^*_3\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right) xb_m\left(x^2+y^2+z^2+\right)^{1/2} dxdydz$$

Making the transformation $x \longrightarrow -x$, $y \longrightarrow -y$, $z \longrightarrow -z$, gives

$$\langle M\rangle_{m1ma} = -\int b^*_n\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right) xb_m\left(x^2+y^2+z^2+\right)^{1/2} dxdydz \times \left[e^{-ik(1/2,1/2,1/2)a}\right.$$

$$\left.+\left(e^{-ik(1/2,-1/2,-1/2)a}-e^{-ik(-1/2,1/2,-1/2)a}-e^{-ik(-1/2,-1/2,1/\right.\right.$$

$$= -K((e^{-ik_1a/2}(e^{-i(k_2+k_3)a/2} + e^{i(k_2+k_3)a/2}) + e^{ik_1a/2}(e^{-i(k_2-k_3)a/2} + e^{i(k_2-k_3)a/2}))$$

$$\langle M\rangle_{\alpha i\nu\alpha} = -K((\cos k_1a/2 - i\sin k_1a/2)(\cos(k_2+k_3)a/2 - i\sin(k_2+k_3)a/2 + \cos(k_2+k_3)a/2 + i\sin(k_2+k_3)a/2 - (\cos k_1a/2 + i\sin k_1a/2)(\cos(k_2-k_3)a/2 - i\sin(k_2-k_3)a/2 + \cos(k_2-k_3)a/2 + i\sin(k_2-k_3)a/2))$$

$$= -2K((\cos k_1a/2 - i\sin k_1a/2)(\cos k_2a/2\cos k_3a/2 - \sin k_2a/2\sin k_3a/2) - (\cos k_1a/2 + i\sin k_1a/2)(\cos k_2a/2\cos k_3a/2 + \sin k_2a/2\sin k_3)$$

$$= -2K(\cos k_1a/2\cos k_2a/2\cos k_3a/2 + i\sin k_1a/2\sin k_3a/2 - \cos k_1a/2 \sin k_2a/2\sin k_3a/2 - i\sin k_1a/2\cos k_2a/2\cos k_3a/2 - \cos k_1a/2 \cos k_2a/2\cos k_3a/2 - i\sin k_1a/2\sin k_2a/2$$

$$= -4K(-\cos k_1a/2\sin k_2a/2\sin k_3a/2 - i\sin k_1a/2\cos k_2a/2\cos k_3a/2))$$

$$= -V_{\alpha\alpha}g^*_1$$

$$\langle M\rangle_{\alpha i\nu\alpha} = -e^{-ik(1/2,1/2,1/2)a}\int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right) b_\alpha\left(x^2+y^2+z^2+\right)^{1/2}\right) dxdydz$$

$$-e^{-ik(1/2,-1/2,-1/2)a}\int b^*_1\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right) b_\alpha\left(x^2+y^2+z^2+\right)^{1/2}\right) dxdydz$$

$$-e^{-ik(-1/2,1/2,-1/2)a}\int b^*_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right) b_\alpha\left(x^2+y^2+z^2+\right)^{1/2}\right) dxdydz$$

$$+e^{-ik(-1/2,-1/2,1/2)a}\int b^*_1\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right) b_\alpha\left(x^2+y^2+z^2+\right)^{1/2}\right) dxdydz$$

Making the usual transformation $x \longrightarrow -x$, $y \longrightarrow -y$, $z \longrightarrow -z$ we get

$$\langle M\rangle_{\alpha i\nu\alpha} = -K(e^{-ik(1/2,1/2,1/2)a} - (e^{-ik(1/2,-1/2,-1/2)a} + e^{-ik(-1/2,1/2,-1/2)a} - e^{-ik(-1/2,-1/2,1/2)a}))$$

$$= -K((e^{-ik_1a/2}(e^{-i(k_2+k_3)a/2} - e^{i(k_2+k_3)a/2}) + e^{ik_1a/2}(e^{-i(k_2-k_3)a/2} - e^{i(k_2-k_3)a/2}))$$

$$= -K((\cos k_1a/2 - i\sin k_1a/2)(\cos(k_2+k_3)a/2 - i\sin(k_2+k_3)a/2 - \cos(k_2+k_3)a/2 - i\sin(k_2+k_3)a/2) + (\cos k_1a/2 + i\sin k_1a/2)$$

$$(\cos(k_2-k_3a/2)-i\sin(k_2-k_3)a/2+\cos(k_2+k_3)a/2-i\sin(k_2-k_3)a/2))$$

$$=-2K((\cos k_1a/2-i\sin k_1a/2)(i\sin k_2a/2\cos k_3a/2+\cos k_2a/2\sin k_3a/2)$$

$$+(\cos k_1a/2+i\sin k_1a/2)(i\sin k_2a/2\cos k_3a/2-\cos k_2a/2\sin k_3a/2))$$

$$= 2K(i\cos k_1a/2\sin k_2a/2\cos k_3a/2+\sin k_1a/2\cos k_2a/2\sin k_3a/2$$

$$+i\cos k_1a/2\cos k_2a/2\sin k_3a/2+\sin k_1a/2\cos k_3a/2+i\cos k_1a/2$$

$$\sin k_2a/2\cos k_3a/2+\sin k_1a/2\cos k_2a/2\sin k_3a/2-i\cos k_1a/2$$

$$\cos k_2a/2\sin k_3a/2-\sin k_1a/2\sin k_2a/2\cos k_3a/2))$$

$$= 4K(\sin k_1a/2\cos k_2a/2\sin k_3a/2+i\cos k_1a/2\sin k_2a/2\cos k_3a/2)$$

$$=-4K(-\sin k_1a/2\cos k_2a/2\sin k_3a/2-i\cos k_1a/2\sin k_2a/2\cos k_3a/2)$$

$$= -V_{ep}q^{-2}$$

$$\langle M\rangle_{e\,1\,e} = -e^{-1k(1/2,1/2,1/2)a}\int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$

$$z b_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

$$-e^{-1k(1/2,-1/2,-1/2)a}\int b^*_1\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$

$$z b_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

$$-e^{-1k(-1/2,1/2,-1/2)a}\int b^*_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$

$$z b_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

$$+e^{-1k(-1/2,-1/2,1/2)a}\int b^*_1\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$

$$z b_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

Making the usual transformation $x \longrightarrow -x$, $y \longrightarrow -y$, $z \longrightarrow -z$ gives

$$\langle M\rangle_{e\,1\,e} = -K(e^{-1k(1/2,1/2,1/2)a} - (e^{-1k(1/2,-1/2,-1/2)a}$$

$$-e^{-1k(-1/2,1/2,-1/2)a} + e^{-1k(-1/2,-1/2,1/2)a}))$$

$$= -K((e^{-1k1a/2}(e^{-1(k_2+k_3)a/2} - e^{1(k_2-k_3)a/2})$$

$$- e^{1k1a/2}(e^{-1(k_2-k_3)a/2} - e^{1(k_2-k_3)a/2}))$$

$$=-K((\cos k_1a/2-i\sin k_1a/2)(\cos(k_2+k_3)a/2-i\sin(k_2+k_3)a/2$$

$$-\cos(k_2+k_3)a/2-i\sin(k_2+k_3)a/2)-(\cos k_1a/2+i\sin k_1a/2)$$

$$(\cos(k_2-k_3a/2)-i\sin(k_2-k_3)a/2-\cos(k_2+k_3)a/2-i\sin(k_2-k_3)a/2))$$

$$=+2K(i(\cos k_1a/2-i\sin k_1a/2)\sin(k_2+\sin k_3)a/2-i(\cos k_1a/2+i\sin k_2a/2)$$
$$\sin(k_2-k_3)a/2))$$

$$= +2K(i\cos k_1 a/2 - i\sin k_1 a/2)\sin(k_2 - k_3)a/2 - (\cos k_1 a/2 + i\sin k_1 a/2)\sin(k_2 - k_3)a/2))$$

$$\langle M\rangle_{a_1 a_2} = 2K(i(\cos k_1 a/2 - i\sin k_1 a/2)(\sin k_2 a/2\cos k_3 a/2 + \cos k_2 a/2\sin k_3 a/2) - i(\cos k_1 a/2 + i\sin k_1 a/2)(\sin k_2 a/2\cos k_3 a/2 - \cos k_2 a/2\sin k_3 a/2))$$

$$= 2K(i\cos k_1 a/2\sin k_2 a/2\cos k_3 a/2 + \sin k_1 a/2\cos k_2 a/2\sin k_3 a/2 + i\cos k_1 a/2\cos k_2 a/2\sin k_3 a/2 + \sin k_1 a/2\sin k_2 a/2\cos k_3 a/2 - i\cos k_1 a/2\cos k_3 a/2 - \sin k_1 a/2\cos k_2 a/2\sin k_3 a/2 + i\cos k_1 a/2 \cos k_2 a/2\sin k_3 a/2 + \sin k_1 a/2\sin k_2 a/2\cos k_3 a/2))$$

$$= 4K(\sin k_1 a/2\sin k_2 a/2\cos k_3 a/2 + \cos k_1 a/2\cos k_2 a/2\sin k_3 a/2))$$

$$= -4K(-\sin k_1 a/2\sin k_2 a/2\cos k_3 a/2 - i\cos k_1 a/2\cos k_2 a/2\sin k_3 a/2)$$

$$= -V_{a_1 a} g^* x$$

$$\langle M\rangle_{nn\pm 1} = -e^{-ik(1/2,1/2,1/2)a}\int b^*_n\left(\left[(x+a/2)^2 + (y+a/2)^2 + (z+a/2)^2\right]^{1/2}\right) x b_n\left((x^2+y^2+z^2+)^{1/2}\right) dx dy dz$$

$$- e^{-ik(1/2,-1/2,-1/2)a}\int b^*_1\left(\left[(x+a/2)^2 + (y-a/2)^2 + (z-a/2)^2\right]^{1/2}\right) x b_n\left((x^2+y^2+z^2+)^{1/2}\right) dx dy dz$$

$$- e^{-ik(-1/2,1/2,-1/2)a}\int b^*_1\left(\left[(x-a/2)^2 + (y+a/2)^2 + (z-a/2)^2\right]^{1/2}\right) x b_n\left((x^2+y^2+z^2+)^{1/2}\right) dx dy dz$$

$$+ e^{-ik(-1/2,-1/2,1/2)a}\int b^*_1\left(\left[(x-a/2)^2 + (y-a/2)^2 + (z+a/2)^2\right]^{1/2}\right) z b_n\left((x^2+y^2+z^2+)^{1/2}\right) dx dy dz$$

Making the usual transformation $x \longrightarrow -x$, $y \longrightarrow -y$, $z \longrightarrow -z$ gives

$$\langle M\rangle_{nn\pm 1} = -K((e^{-ik_1 a/2}(e^{i(k_2+k_3)a/2} + e^{-i(k_2-k_3)a/2}) + e^{-i(k_2-k_3)a/2}))$$

$$= -K((\cos k_1 a/2 + i\sin k_1 a/2)(\cos(k_2+k_3)a/2 + i\sin(k_2+k_3)a/2 + \cos(k_2+k_3)a/2 - i\sin(k_2+k_3)a/2) - (\cos k_1 a/2 - i\sin k_1 a/2)(\cos(k_2-k_3)a/2) + i\sin(k_2-k_3)a/2 + \cos(k_2-k_3)a/2 - i\sin(k_2-k_3)a/2))$$

$$= -2K((\cos k_1 a/2 + i\sin k_1 a/2)(\cos k_2 a/2\cos k_3 a/2 - \sin k_2 a/2\sin k_3 a/2) - (\cos k_1 a/2 - i\sin k_1 a/2)(\cos k_2 a/2\cos k_3 a/2 + \sin k_2 a/2\sin k_3 a/2))$$

$$\langle M\rangle_{nn\pm 1} = -2K(\cos k_1 a/2\cos k_2 a/2\cos k_3 a/2 - i\sin k_1 \sin k_2 a/2\sin k_3 a/2 -$$

$$\cos k_1 a/2 \sin k_2 a/2 \sin k_3 a/2 - i \sin k_1 a/2 \cos k_2 a/2 \cos k_3 a/2 -$$

$$\cos k_1 a/2 \cos k_2 a/2 \cos k_3 a/2 + i \sin k_1 a/2 \sin k_2 a/2 \sin k_3 a/2$$

$$-\cos k_1 a/2 \sin k_2 a/2 \sin k_3 a/2 + i \sin k_1 a/2 \cos k_2 a/2 \cos k_3 a/2))$$

$$= -4K(-\cos k_1 a/2 \sin k_2 a/2 \sin k_3 a/2 + i \sin k_1 a/2 \cos k_2 a/2 \cos k_3 a/2)$$

$$= -V_{mn} q_1$$

$$\langle M \rangle_{mnx1} = -e^{-1k(1/2,1/2,1/2)a} \int b^*_n \left(\left[(x+a/2)^2 + (y+a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$

$$x x b_m \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$-e^{-1k(1/2,-1/2,-1/2)a} \int b^*_1 \left(\left[(x+a/2)^2 + (y-a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$

$$x x b_m \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$-e^{-1k(-1/2,1/2,-1/2)a} \int b^*_1 \left(\left[(x-a/2)^2 + (y+a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$

$$x x b_m \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+e^{-1k(-1/2,-1/2,1/2)a} \int b^*_1 \left(\left[(x-a/2)^2 + (y-a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$

$$x x b_m \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

Making the usual transformation $x \longrightarrow -x$, $y \longrightarrow -y$, $z \longrightarrow -z$ gives

$$\langle M \rangle_{mnx1} = K(e^{1k1a/2}(e^{1(k_2+k_3a/2} + e^{-1(k_2+k_3a/2)} +$$

$$+e^{-1k_1 a/2}(e^{1(k_2-k_3)a/2} + e^{-1(k_2-k_3)a/2} +)$$

$$= 4K(\cos k_1 a/2 \cos k_2 a/2 \cos k_3 a/2 - i \sin k_1 a/2 \sin k_2 a/2 \cos k_3 a/2$$

$$= V_{mn} q_n$$

$$\langle M \rangle_{mny1} = -e^{1k(a/2,a/2,a/2)a} \int b^*_1 \left(\left[(x+a/2)^2 + (y+a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$

$$x y b_m \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+e^{1k(a/2,-a/2,-a/2)a} \int b^*_1 \left(\left[(x+a/2)^2 + (y-a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$

$$x y b_m \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+e^{1k(-a/2,a/2,-a/2)a} \int b^*_1 \left(\left[(x-a/2)^2 + (y+a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$

$$x y b_m \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+e^{1k(-a/2,-a/2,a/2)a} \int b^*_1 \left(\left[(x-a/2)^2 + (y-a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$

$$x y b_m \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

Making the usual transformation we get:

$$\langle M\rangle_{xav1} = K\{e^{ik(a/2,a/2,a/2)} - e_1(a/2,-a/2,-a/2) - e_{ik}(-a/2,a/2,-a/2)$$

$$+ e_{ik}(-a/2,-a/2,a/2)$$

$$= 4K(-\sin k_1 a/2 \sin k_2 a/2 \cos k_3 a/2 + i \cos k_1 a/2 \cos k_2 a/2 \sin k_3 a/2$$

$$= V_{uv} q_x$$

$$\langle M\rangle_{xax1} = -e^{ik(a/2,a/2,a/2)} a \int b^*_1 \left(\left[(x+a/2)^2 + (y+a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$

$$x z b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+ e^{ik(a/2,-a/2,-a/2)} a \int b^*_1 \left(\left[(x+a/2)^2 + (y-a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$

$$x z b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+ e^{ik(-a/2,a/2,-a/2)} a \int b^*_1 \left(\left[(x-a/2)^2 + (y+a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$

$$x z b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+ e^{ik(-a/2,-a/2,a/2)} a \int b^*_1 \left(\left[(x-a/2)^2 + (y-a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$

$$x y b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

Making the usual transformation we get:

$$\langle M\rangle_{xax1} = K\{e^{ik(a/2,a/2,a/2)} - e_1(a/2,-a/2,-a/2) + e_{ik}(-a/2,a/2,-a/2)$$

$$- e_{ik}(-a/2,-a/2,a/2)$$

$$= 4K(-\sin k_1 a/2 \cos k_2 a/2 \sin k_3 a/2 + i \cos k_1 a/2 \sin k_2 a/2 \cos k_3 a/2$$

$$= V_{uv} q_z$$

$$\langle M\rangle_{yax1} = -e^{ik(a/2,a/2,a/2)} a \int b^*_1 \left((x+a/2)^2 + (y+a/2)^2 + (z+a/2)^2 \right)^{1/2}$$

$$y b_n (x^2+y^2+z^2+)^{1/2} \, dx dy dz$$

$$- e^{ik(a/2,-a/2,-a/2)} a \int b^*_1 \left((x+a/2)^2 + (y-a/2)^2 + (z-a/2)^2 \right)^{1/2}$$

$$y b_n (x^2+y^2+z^2+)^{1/2} \, dx dy dz$$

$$- e^{ik(-a/2,a/2,-a/2)} a \int b^*_1 \left((x-a/2)^2 + (y+a/2)^2 + (z-a/2)^2 \right)^{1/2}$$

$$y b_n (x^2+y^2+z^2+)^{1/2} \, dx dy dz$$

$$- e^{ik(-a/2,-a/2,a/2)} a \int b^*_1 \left(\left[(x-a/2)^2 + (y-a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$

$$y b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

Making the usual transformation we get:

$$\langle M\rangle_{yax1} = -K\{e^{ik(a/2,a/2,a/2)} - e_1(a/2,-a/2,-a/2) + e_{ik}(-a/2,a/2,-a/2)$$

$$-e^{ik(-a/2,-a/2,a/2)}$$

$$=-4K(-\sin k_1 a/2\cos k_2 a/2\sin k_3 a/2+i\cos k_1 a/2\sin k_2 a/2\cos k_3 a/2$$

$$= V_{sing_z}$$

$$\langle M\rangle_{vav_1} = e^{ik(a/2,a/2,a/2)} a \int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$

$$y_a x b_a\left((x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

$$+e^{ik(a/2,-a/2,-a/2)} a \int b^*_1\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$

$$y_a x b_a\left((x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

$$+e^{ik(-a/2,a/2,-a/2)} a \int b^*_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$

$$y_a x b_a\left((x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

$$+e^{ik(-a/2,-a/2,a/2)} a \int b^*_1\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$

$$y_a x b_a\left((x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

Making the usual transformation $x\rightarrow -x$, $y\rightarrow -y$ and $z\rightarrow -z$ we get:

$$\langle M\rangle_{vav_1} = K(e^{ik(a/2,a/2,a/2)}-e_1(a/2,-a/2,-a/2)+e_{ik}(-a/2,a/2,-a/2)$$

$$+e_{ik}(-a/2,-a/2,a/2)$$

$$= 4K(-\sin k_1 a/2\sin k_2 a/2\cos k_3 a/2+i\cos k_1 a/2\cos k_2 a/2\sin k_3 a/2)$$

$$= V_{uv}g_x$$

$$\langle M\rangle_{vav_1} = -e^{ik(a/2,a/2,a/2)} a \int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$

$$yyb_a\left((x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

$$+e^{ik(a/2,-a/2,-a/2)} a \int b^*_1\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$

$$yyb_a\left((x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

$$+e^{ik(-a/2,a/2,-a/2)} a \int b^*_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$

$$yyb_a\left((x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

$$+e^{ik(-a/2,-a/2,a/2)} a \int b^*_1\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$

$$yyb_a\left((x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

Making the usual transformation we get:

$$\langle M\rangle_{vav_1} = K(e^{ik(a/2,a/2,a/2)}+e_1(a/2,-a/2,-a/2)+e_{ik}(-a/2,a/2,-a/2)$$

$$+e_{ik}(-a/2,-a/2,a/2)$$

$$= 4K(\cos k_1 a/2 \cos k_2 a/2 \cos k_3 a/2 - i \sin k_1 a/2 \sin k_2 a/2 \sin k_3 a/2)$$

$$= V_{vv} g_0$$

$$\langle M \rangle_{vox1} = e^{ik(a/2,a/2,a/2)a} \int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right) yz b_0\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

$$+e^{ik(a/2,-a/2,-a/2)a} \int b^*_1\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right) yz b_0\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

$$+e^{ik(-a/2,a/2,-a/2)a} \int b^*_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right) yz b_0\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

$$+e^{ik(-a/2,-a/2,a/2)a} \int b^*_1\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right) yz b_0\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

Making the usual transformation we get:

$$\langle M \rangle_{vox1} = K(e^{ik(a/2,a/2,a/2)} + e^{ik(a/2,-a/2,-a/2)} - e^{ik(-a/2,a/2,-a/2)} - e^{ik(-a/2,-a/2,a/2)}$$

$$= 4K(-\cos k_1 a/2 \sin k_2 a/2 \sin k_3 a/2 + i \sin k_1 a/2 \cos k_2 a/2 \cos k_3 a/2)$$

$$= V_{vx} g_1$$

$$\langle M \rangle_{xox1} = -e^{ik(a/2,a/2,a/2)a} \int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right) z b_0\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

$$-e^{ik(a/2,-a/2,-a/2)a} \int b^*_1\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right) z b_0\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

$$-e^{ik(-a/2,a/2,-a/2)a} \int b^*_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right) z b_0\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

$$-e^{ik(-a/2,-a/2,a/2)a} \int b^*_1\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right) z b_0\left((x^2+y^2+z^2+)^{1/2}\right) dxdydz$$

Making the usual transformation we get:

$$\langle M \rangle_{xox1} = -K(e^{ik(a/2,a/2,a/2)} - e^{ik(a/2,-a/2,-a/2)} - e^{ik(-a/2,a/2,-a/2)} + e^{ik(-a/2,-a/2,a/2)}$$

$$= -4K(-\sin k_1 a/2 \sin k_2 a/2 \cos k_3 a/2 + i \cos k_1 a/2 \cos k_2 a/2 \sin k_3 a/2)$$

$$= V_{vx} g_1$$

$$\langle \hat{M} \rangle_{xox_1} = e^{ik(a/2,a/2,a/2)a} \int b^*_1 \left(\left[(x+a/2)^2 + (y+a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$

$$x z b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+ e^{ik(a/2,-a/2,-a/2)a} \int b^*_1 \left(\left[(x+a/2)^2 + (y-a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$

$$x z b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+ e^{ik(-a/2,a/2,-a/2)a} \int b^*_1 \left(\left[(x-a/2)^2 + (y+a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$

$$x z b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+ e^{ik(-a/2,-a/2,a/2)a} \int b^*_1 \left(\left[(x-a/2)^2 + (y-a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$

$$x z b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

After the usual transformation we get:

$$\langle \hat{M} \rangle_{xox_1} = K \left(e^{ik(a/2,a/2,a/2)} - e^{ik(a/2,-a/2,-a/2)} + e^{ik(-a/2,a/2,-a/2)} \right.$$

$$\left. - e^{ik(-a/2,-a/2,a/2)} \right)$$

$$= 4K(-\sin k_1 a/2 \cos k_2 a/2 \sin k_3 a/2 + i \cos k_1 a/2 \sin k_2 a/2 \cos k_3 a/2)$$

$$= V_{xx} g_z$$

$$\langle \hat{M} \rangle_{xoy_1} = e^{ik(a/2,a/2,a/2)a} \int b^*_1 \left((x+a/2)^2 + (y+a/2)^2 + (z+a/2)^2 \right)^{1/2}$$

$$y z b_n (x^2+y^2+z^2+)^{1/2} \, dx dy dz$$

$$+ e^{ik(a/2,-a/2,-a/2)a} \int b^*_1 \left(\left[(x+a/2)^2 + (y-a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$

$$y z b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+ e^{ik(-a/2,a/2,-a/2)a} \int b^*_1 \left(\left[(x-a/2)^2 + (y+a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$

$$y z b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

$$+ e^{ik(-a/2,-a/2,a/2)a} \int b^*_1 \left(\left[(x-a/2)^2 + (y-a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$

$$y z b_n \left((x^2+y^2+z^2+)^{1/2} \right) dx dy dz$$

Making the usual transformation we get:

$$\langle \hat{M} \rangle_{xoy_1} = K \left(e^{ik(a/2,a/2,a/2)} + e^{ik(a/2,-a/2,-a/2)} - e^{ik(-a/2,a/2,-a/2)} \right.$$

$$\left. - e^{ik(-a/2,-a/2,a/2)} \right)$$

$$= 4K(-\cos k_1 a/2 \sin k_2 a/2 \sin k_3 a/2 + i \sin k_1 a/2 \cos k_2 a/2 \cos k_3 a/2)$$

$$= V_{yx} g_1$$

$$\langle M\rangle_{xox_1} = e^{ik(a/2,a/2,a/2)a}\int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$z z b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$
$$+e^{ik(a/2,-a/2,-a/2)a}\int b^*_1\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$z z b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$
$$+e^{ik(-a/2,a/2,-a/2)a}\int b^*_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$z z b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$
$$+e^{ik(-a/2,-a/2,a/2)a}\int b^*_1\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$z z b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$

After the usual transformation we get:

$$\langle M\rangle_{xox_1} = K\left(e^{ik(a/2,a/2,a/2)}+e^{ik(a/2,-a/2,-a/2)}+e^{ik(-a/2,a/2,-a/2)}\right.$$
$$\left.+e^{ik(-a/2,-a/2,a/2)}\right)$$
$$= 4K\left(\cos k_1 a/2\cos k_2 a/2\cos k_3 a/2 - i\sin k_1 a/2\sin k_2 a/2\sin k_3 a/2\right)$$
$$= V_{xx} g_n$$

$$\langle M\rangle_{x_1 x_n} = e^{-ik(a/2,a/2,a/2)a}\int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$x b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$
$$+e^{-ik(a/2,-a/2,-a/2)a}\int b^*_1\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$x b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$
$$+e^{-ik(-a/2,a/2,-a/2)a}\int b^*_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$x b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$
$$+e^{-ik(-a/2,-a/2,a/2)a}\int b^*_1\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$x b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big)dxdydz$$

Making the usual transformation we get:

$$\langle M\rangle_{x_1 x_n} = K\left(e^{-ik(a/2,a/2,a/2)}+e^{-ik(a/2,-a/2,-a/2)}-e^{-ik(-a/2,a/2,-a/2)}\right.$$
$$\left.-e^{-ik(-a/2,-a/2,a/2)}\right)$$
$$= 4K\left(-\cos k_1 a/2\sin k_2 a/2\sin k_3 a/2 - i\sin k_1 a/2\cos k_2 a/2\cos k_3 a/2\right)$$
$$= V_{xn} g_1$$

$$\langle M\rangle_{\mu 1\nu a}=e^{-1k(a/2,a/2,a/2)a}\int b^{*}_{1}\left([(x+a/2)^2+(y+a/2)^2+(z+a/2)^2]^{1/2}\right)$$
$$x x b_a\left(i x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+e^{-1k(a/2,-a/2,-a/2)a}\int b^{*}_{1}\left([(x+a/2)^2+(y-a/2)^2+(z-a/2)^2]^{1/2}\right)$$
$$x x b_a\left(i x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+e^{-1k(-a/2,a/2,-a/2)a}\int b^{*}_{1}\left([(x-a/2)^2+(y+a/2)^2+(z-a/2)^2]^{1/2}\right)$$
$$x x b_a\left(i x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+e^{-1k(-a/2,-a/2,a/2)a}\int b^{*}_{1}\left([(x-a/2)^2+(y-a/2)^2+(z+a/2)^2]^{1/2}\right)$$
$$x x b_a\left(i x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$

After the usual transformation we get:

$$\langle M\rangle_{\mu 1\nu a}= K(e^{-1k(a/2,a/2,a/2)}+e^{-1k(a/2,-a/2,-a/2)}+e^{-1k(-a/2,a/2,-a/2)}$$
$$+e^{-1k(-a/2,-a/2,a/2)}$$
$$= 4K(\cos k_1 a/2\cos k_2 a/2\cos k_3 a/2+i\sin k_1 a/2\sin k_2 a/2\sin k_3 a/2)$$
$$= V_{\mu\nu}g^{*}_{a}$$
$$\langle M\rangle_{\mu 1\nu a}= e^{-1k(a/2,a/2,a/2)a}\int b^{*}_{1}\left([(x+a/2)^2+(y+a/2)^2+(z+a/2)^2]^{1/2}\right)$$
$$x y b_a\left(i x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+e^{-1k(a/2,-a/2,-a/2)a}\int b^{*}_{1}\left([(x+a/2)^2+(y-a/2)^2+(z-a/2)^2]^{1/2}\right)$$
$$x y b_a\left(i x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+e^{-1k(-a/2,a/2,-a/2)a}\int b^{*}_{1}\left([(x-a/2)^2+(y+a/2)^2+(z-a/2)^2]^{1/2}\right)$$
$$x y b_a\left(i x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$
$$+e^{-1k(-a/2,-a/2,a/2)a}\int b^{*}_{1}\left([(x-a/2)^2+(y-a/2)^2+(z+a/2)^2]^{1/2}\right)$$
$$x y b_a\left(i x^2+y^2+z^2+\right)^{1/2}\,dx\,dy\,dz$$

Making the usual transformation we get:

$$\langle M\rangle_{\mu 1\nu a}= K(e^{-1k(a/2,a/2,a/2)}-e^{-1(a/2,-a/2,-a/2)}-e^{-1k(-a/2,a/2,-a/2)}$$
$$+e^{-1k(-a/2,-a/2,a/2)}$$
$$= 4K(-\sin k_1 a/2\sin k_2 a/2\cos k_3 a/2-i\cos k_1 a/2\cos k_2 a/2\sin k_3 a/2)$$
$$= V_{\mu\nu}g^{*}_{x}$$

$$\langle \hat{M} \rangle_{x1za} = e^{-ik(a/2,a/2,a/2)a} \int b^{*}_{1}\left(\left[(x+a/2)^2 + (y+a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$
$$xz\, b_a\left((x^2+y^2+z^2+)^{1/2} \right) dx\,dy\,dz$$
$$+ e^{-ik(a/2,-a/2,-a/2)a} \int b^{*}_{1}\left(\left[(x+a/2)^2 + (y-a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$
$$xz\, b_a\left((x^2+y^2+z^2+)^{1/2} \right) dx\,dy\,dz$$
$$+ e^{-ik(-a/2,a/2,-a/2)a} \int b^{*}_{1}\left(\left[(x-a/2)^2 + (y+a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$
$$xz\, b_a\left((x^2+y^2+z^2+)^{1/2} \right) dx\,dy\,dz$$
$$+ e^{-ik(-a/2,-a/2,a/2)a} \int b^{*}_{1}\left(\left[(x-a/2)^2 + (y-a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$
$$xz\, b_a\left((x^2+y^2+z^2+)^{1/2} \right) dx\,dy\,dz$$

After the usual transformation we get:

$$\langle \hat{M} \rangle_{x1za} = K\left(e^{-ik(a/2,a/2,a/2)} - e^{-ik(a/2,-a/2,-a/2)} + e^{-ik(-a/2,a/2,-a/2)} - e^{-ik(-a/2,-a/2,a/2)} \right)$$
$$= 4K(-\sin k_1 a/2 \cos k_2 a/2 \sin k_3 a/2 - i \cos k_1 a/2 \sin k_2 a/2 \cos k_3 a/2)$$
$$= V_{xz}\, g^{*}_{z}$$

$$\langle \hat{M} \rangle_{y1za} = e^{-ik(a/2,a/2,a/2)a} \int b^{*}_{1}\left(\left[(x+a/2)^2 + (y+a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$
$$y\, b_a\left((x^2+y^2+z^2+)^{1/2} \right) dx\,dy\,dz$$
$$+ e^{-ik(a/2,-a/2,-a/2)a} \int b^{*}_{1}\left(\left[(x+a/2)^2 + (y-a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$
$$y\, b_a\left((x^2+y^2+z^2+)^{1/2} \right) dx\,dy\,dz$$
$$+ e^{-ik(-a/2,a/2,-a/2)a} \int b^{*}_{1}\left(\left[(x-a/2)^2 + (y+a/2)^2 + (z-a/2)^2 \right]^{1/2} \right)$$
$$y\, b_a\left((x^2+y^2+z^2+)^{1/2} \right) dx\,dy\,dz$$
$$+ e^{-ik(-a/2,-a/2,a/2)a} \int b^{*}_{1}\left(\left[(x-a/2)^2 + (y-a/2)^2 + (z+a/2)^2 \right]^{1/2} \right)$$
$$y\, b_a\left((x^2+y^2+z^2+)^{1/2} \right) dx\,dy\,dz$$

Making the usual transformation we get:

$$\langle \hat{M} \rangle_{y1za} = K\left(e^{-ik(a/2,a/2,a/2)} - e^{-i(a/2,-a/2,-a/2)} + e^{-ik(-a/2,a/2,-a/2)} - e^{-ik(-a/2,-a/2,a/2)} \right)$$
$$= 4K(-\sin k_1 a/2 \cos k_2 a/2 \sin k_3 a/2 - i \cos k_1 a/2 \sin k_2 a/2 \cos k_3 a/2)$$
$$= V_{zz}\, g^{*}_{z}$$

$$\langle \hat{M} \rangle_{v1xa} = e^{-1k(a/2,a/2,a/2)a} \int b^{*}_{1}\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right) xyb_a\left(\left(x^2+y^2+z^2+\right)^{1/2}\right)dxdydz$$

$$+e^{-1k(a/2,-a/2,-a/2)a} \int b^{*}_{1}\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right) xyb_a\left(\left(x^2+y^2+z^2+\right)^{1/2}\right)dxdydz$$

$$+e^{-1k(-a/2,a/2,-a/2)a} \int b^{*}_{1}\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right) xyb_a\left(\left(x^2+y^2+z^2+\right)^{1/2}\right)dxdydz$$

$$+e^{-1k(-a/2,-a/2,a/2)a} \int b^{*}_{1}\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right) xyb_a\left(\left(x^2+y^2+z^2+\right)^{1/2}\right)dxdydz$$

After the usual transformation we get:

$$\langle \hat{M} \rangle_{v1xa} = K\left(e^{-1k(a/2,a/2,a/2)} - e^{-1k(a/2,-a/2,-a/2)} - e^{-1k(-a/2,a/2,-a/2)} + e^{-1k(-a/2,-a/2,a/2)}\right.$$

$$= 4K\left(-\sin k_1 a/2 \sin k_2 a/2 \cos k_3 a/2 - i \cos k_1 a/2 \cos k_2 a/2 \sin k_3 a/2\right)$$

$$= V_{wv} g^{*}_{x}$$

$$\langle \hat{M} \rangle_{v1ya} = e^{-1k(a/2,a/2,a/2)a} \int b^{*}_{1}\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right) yyb_a\left(\left(x^2+y^2+z^2+\right)^{1/2}\right)dxdydz$$

$$+e^{-1k(a/2,-a/2,-a/2)a} \int b^{*}_{1}\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right) yyb_a\left(\left(x^2+y^2+z^2+\right)^{1/2}\right)dxdydz$$

$$+e^{-1k(-a/2,a/2,-a/2)a} \int b^{*}_{1}\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right) yyb_a\left(\left(x^2+y^2+z^2+\right)^{1/2}\right)dxdydz$$

$$+e^{-1k(-a/2,-a/2,a/2)a} \int b^{*}_{1}\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right) yyb_a\left(\left(x^2+y^2+z^2+\right)^{1/2}\right)dxdydz$$

Making the usual transformation we get:

$$\langle \hat{M} \rangle_{v1ya} = K\left(e^{-1k(a/2,a/2,a/2)} + e^{-1(a/2,-a/2,-a/2)} + e^{-1k(-a/2,a/2,-a/2)} + e^{-1k(-a/2,-a/2,a/2)}\right.$$

$$= 4K\left(\cos k_1 a/2 \cos k_2 a/2 \cos k_3 a/2 + i \sin k_1 a/2 \sin k_2 a/2 \sin k_3 a/2\right)$$

$$= V_{vv} g^{*}_{a}$$

$$\langle M\rangle_{yiza}=e^{-ik(a/2,a/2,a/2)a}\int b^{*}_{1}\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$yzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(a/2,-a/2,-a/2)a}\int b^{*}_{1}\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$yzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(-a/2,a/2,-a/2)a}\int b^{*}_{1}\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$yzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(-a/2,-a/2,a/2)a}\int b^{*}_{1}\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$yzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

After the usual transformation we get:

$$\langle M\rangle_{yiza}=K(e^{-ik(a/2,a/2,a/2)}+e^{-ik(a/2,-a/2,-a/2)}-e^{-ik(-a/2,a/2,-a/2)}$$
$$-e^{-ik(-a/2,-a/2,a/2)}$$
$$=4K(-\cos k_1a/2\sin k_2a/2\sin k_3a/2-i\sin k_1a/2\cos k_2a/2\cos k_3a/2)$$
$$=V_{yz}g^{*}_{1}$$
$$\langle M\rangle_{ziza}=e^{-ik(a/2,a/2,a/2)a}\int b^{*}_{1}\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$zb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(a/2,-a/2,-a/2)a}\int b^{*}_{1}\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$zb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(-a/2,a/2,-a/2)a}\int b^{*}_{1}\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$zb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(-a/2,-a/2,a/2)a}\int b^{*}_{1}\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$zb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

Making the usual transformation we get:

$$\langle M\rangle_{xiza}=K(e^{-ik(a/2,a/2,a/2)}-e^{-i(a/2,-a/2,-a/2)}-e^{-ik(-a/2,a/2,-a/2)}$$
$$+e^{-ik(-a/2,-a/2,a/2)}$$
$$=4K(-\sin k_1a/2\sin k_2a/2\cos k_3a/2-i\cos k_1a/2\cos k_2a/2\sin k_3a/2)$$
$$=V_{xza}g^{*}_{x}$$

$$\langle M\rangle_{x1ya}=e^{-ik(a/2,a/2,a/2)a}\int b^{*}_{1}\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$xzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(a/2,-a/2,-a/2)a}\int b^{*}_{1}\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$xzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(-a/2,a/2,-a/2)a}\int b^{*}_{1}\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$xzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(-a/2,-a/2,a/2)a}\int b^{*}_{1}\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$xzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

After the usual transformation we get:

$$\langle M\rangle_{x1ya}=K(e^{-ik(a/2,a/2,a/2)}-e^{-ik(a/2,-a/2,-a/2)}+e^{-ik(-a/2,a/2,-a/2)}$$
$$-e^{-ik(-a/2,-a/2,a/2)}$$
$$=4K(-\sin k_1a/2\cos k_2a/2\sin k_3a/2-i\cos k_1a/2\sin k_2a/2\cos k_3a/2)$$
$$=V_{xy}g^{*}_{2}$$
$$\langle M\rangle_{x1ya}=e^{-ik(a/2,a/2,a/2)a}\int b^{*}_{1}\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$yzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(a/2,-a/2,-a/2)a}\int b^{*}_{1}\left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$yzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(-a/2,a/2,-a/2)a}\int b^{*}_{1}\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$yzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$
$$+e^{-ik(-a/2,-a/2,a/2)a}\int b^{*}_{1}\left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$yzb_a\left(i(x^2+y^2+z^2+)^{1/2}\right)dxdydz$$

Making the usual transformation we get:

$$\langle M\rangle_{x1ya}=K(e^{-ik(a/2,a/2,a/2)}+e^{-i(a/2,-a/2,-a/2)}-e^{-ik(-a/2,a/2,-a/2)}$$
$$-e^{-ik(-a/2,-a/2,a/2)}$$
$$=4K(-\cos k_1a/2\sin k_2a/2\sin k_3a/2-i\sin k_1a/2\cos k_2a/2\cos k_3a/2)$$
$$=V_{yx}g^{*}_{1}$$

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$$\langle \bar{M} \rangle_{x_1 x_2} = e^{-ik(a/2,a/2,a/2)\cdot a} \int b^*_1\left(\left[(x+a/2)^2+(y+a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$z z b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big) dx dy dz$$
$$+ e^{-ik(a/2,-a/2,-a/2)\cdot a} \int b^* \left(\left[(x+a/2)^2+(y-a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$z z b_n \left(x^2+y^2+z^2+\right)^{1/2}\Big) dx dy dz$$
$$+ e^{-ik(-a/2,a/2,-a/2)\cdot a} \int b^*_1\left(\left[(x-a/2)^2+(y+a/2)^2+(z-a/2)^2\right]^{1/2}\right)$$
$$z z b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big) dx dy dz$$
$$+ e^{-ik(-a/2,-a/2,a/2)\cdot a} \int b^* \left(\left[(x-a/2)^2+(y-a/2)^2+(z+a/2)^2\right]^{1/2}\right)$$
$$z z b_n\left(x^2+y^2+z^2+\right)^{1/2}\Big) dx dy dz$$

After the usual transformation we get:

$$\langle \bar{M} \rangle_{x_1 x_2} = K\left(e^{-ik(a/2,a/2,a/2)} + e^{-ik(a/2,-a/2,-a/2)} + e^{-ik(-a/2,a/2,-a/2)}\right.$$
$$\left. + e^{-ik(-a/2,-a/2,a/2)}\right)$$
$$= 4K\left(\cos k_x a/2 \cos k_y a/2 \cos k_z a/2 - i \sin k_x a/2 \sin k_y a/2 \sin k_z a/2\right)$$
$$= \bar{V}_{xx} g^n_n$$