

Chapter 2: Crystal Structures and Symmetry

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January 13, 2008

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A theory of the physical properties of solids would be practically impossible if the most stable elements were not regular crystal lattices. The N-body problem is reduced to manageable proportions by the existence of translational symmetry. This means that there exist a set of basis vectors ($\mathbf{a}, \mathbf{b}, \mathbf{c}$) such that the atomic structure remains invariant under translations through any vector which is the sum of integral multiples of these vectors. As shown in Fig. 1 this means that one may go from any location in the lattice to an identical location by following path composed of integral multiples of these vectors.

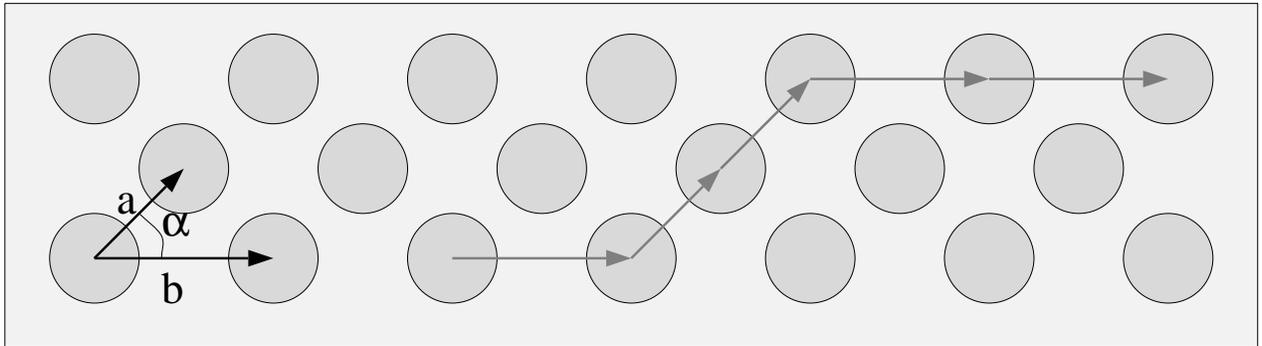


Figure 1: *One may go from any location in the lattice to an identical location by following path composed of integral multiples of the vectors \mathbf{a} and \mathbf{b} .*

Thus, one may label the locations of the "atoms"¹. which compose the lattice with

$$\mathbf{r}_n = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \quad (1)$$

¹we will see that the basic building blocks of periodic structures can be more complicated than a single atom. For example in NaCl, the basic building block is composed of one Na and one Cl ion which is repeated in a cubic pattern to make the NaCl structure

where n_1, n_2, n_3 are integers. In this way we may construct any periodic structure.

1 Lattice Types and Symmetry

1.1 Two-Dimensional Lattices

These structures are classified according to their symmetry. For example, in 2d there are 5 distinct types. The lowest symmetry is an oblique lattice, of which the lattice shown in Fig. 1 is an example if $a \neq b$ and α is not a rational fraction of π . Notice that it is invari-

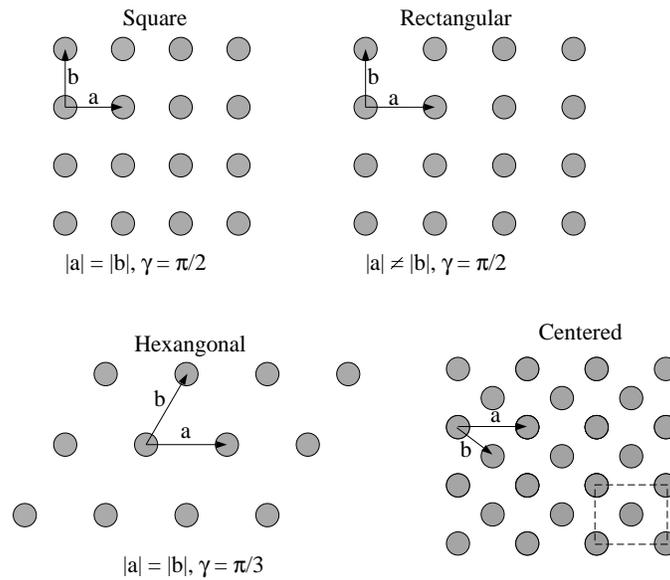


Figure 2: *Two dimensional lattice types of higher symmetry. These have higher symmetry since some are invariant under rotations of $2\pi/3$, or $2\pi/6$, or $2\pi/4$, etc. The centered lattice is special since it may also be considered as lattice composed of a two-component basis, and a rectangular unit cell (shown with a dashed rectangle).*

ant only under rotation of π and 2π . Four other lattices, shown in Fig. 2 of higher symmetry are also possible, and called special lattice types (square, rectangular, centered, hexagonal). A Bravais lattice is the common name for a distinct lattice type. The primitive cell is the parallel piped (in 3d) formed by the primitive lattice vectors which are defined as the lattice vectors which produce the primitive cell with the smallest volume ($\mathbf{a} \cdot (\mathbf{c} \times \mathbf{c})$). Notice that the primitive cell does not always capture the symmetry as well as a larger cell, as is the case with the centered lattice type. The centered lattice is special since it may also be considered as lattice composed of a two-component basis on a rectangular unit cell (shown with a dashed rectangle).

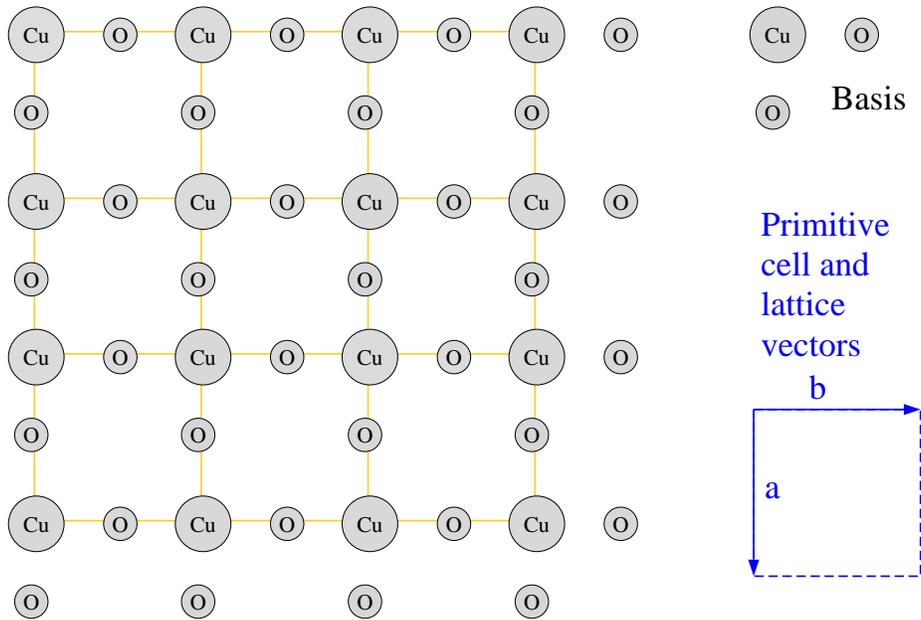


Figure 3: A square lattice with a complex basis composed of one Cu and two O atoms (c.f. cuprate high-temperature superconductors).

To account for more complex structures like molecular solids, salts, etc., one also allows each lattice point to have structure in the form of a basis. A good example of this in two dimensions is the CuO_2 planes which characterize the cuprate high temperature superconductors (cf. Fig. 3). Here the basis is composed of two oxygens and one copper atom laid down on a simple square lattice with the Cu atom centered on the lattice points.

1.2 Three-Dimensional Lattices

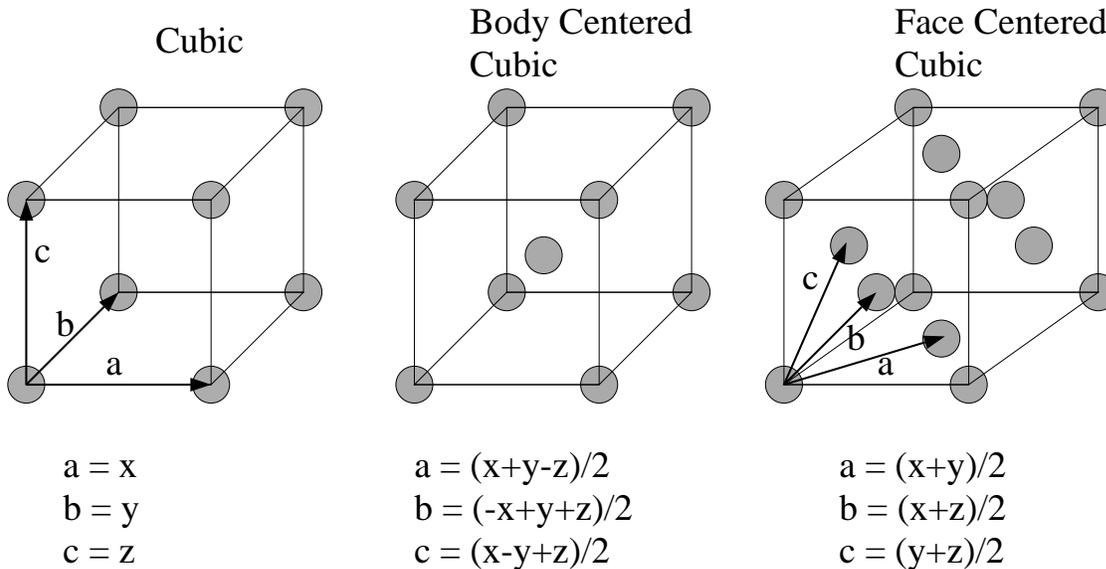


Figure 4: *Three-dimensional cubic lattices. The primitive lattice vectors ($\mathbf{a}, \mathbf{b}, \mathbf{c}$) are also indicated. Note that the primitive cells of the centered lattice is not the unit cell commonly drawn.*

The situation in three-dimensional lattices can be more complicated. Here there are 14 lattice types (or Bravais lattices). For example there

are 3 cubic structures, shown in Fig. 4. Note that the primitive cells of the centered lattice is not the unit cell commonly drawn. In addition, there are triclinic, 2 monoclinic, 4 orthorhombic ... Bravais lattices, for a total of 14 in three dimensions.

2 Point-Group Symmetry

The use of symmetry can greatly simplify a problem.

2.1 Reduction of Quantum Complexity

If a Hamiltonian is invariant under certain symmetry operations, then we may choose to classify the eigenstates as states of the symmetry operation and H will not connect states of different symmetry.

As an example, imagine that a symmetry operation R leaves H invariant, so that

$$RHR^{-1} = H \quad \text{then} \quad [H, R] = 0 \quad (2)$$

Then if $|j\rangle$ are the eigenstates of R , then $\sum_j |j\rangle\langle j|$ is a representation of the identity, and we expand $HR = RH$, and examine its elements

$$\sum_k \langle i|R|k\rangle\langle k|H|j\rangle = \sum_k \langle i|H|k\rangle\langle k|R|j\rangle . \quad (3)$$

If we recall that $R_{ik} = \langle i|R|k\rangle = R_{ii}\delta_{ik}$ since $|k\rangle$ are eigenstates of

R , then Eq. 3 becomes

$$(R_{ii} - R_{jj}) H_{ij} = 0. \quad (4)$$

So, $H_{ij} = 0$ if R_i and R_j are different eigenvalues of R . Thus, when the states are classified by their symmetry, the Hamiltonian matrix becomes Block diagonal, so that each block may be separately diagonalized.

2.2 Symmetry in Lattice Summations

As another example, consider a Madelung sum in a two-dimensional square centered lattice (i.e. a 2d analog of NaCl). Here we want to calculate

$$\sum_{ij} \frac{\pm}{p_{ij}}. \quad (5)$$

This may be done by a brute force sum over the lattice, i.e.

$$\lim_{n \rightarrow \infty} \sum_{i=-n, n} \sum_{j=-n, n} \frac{(-1)^{i+j}}{p_{ij}}. \quad (6)$$

Or, we may realize that the lattice has some well defined operations which leave it invariant. For example, this lattice is invariant under inversion $(x, y) \rightarrow (-x, -y)$, and reflections about the x $(x, y) \rightarrow (x, -y)$ and y $(x, y) \rightarrow (-x, y)$ axes, etc. For these reasons, the eight points highlighted in Fig. 5(a) all contribute an identical amount to the sum in Eq. 5. In fact all such interior points have a degeneracy of 8. Only special points like the point at the origin (which is unique) and points along the symmetry axes (the xy and x axis, each with a degeneracy of

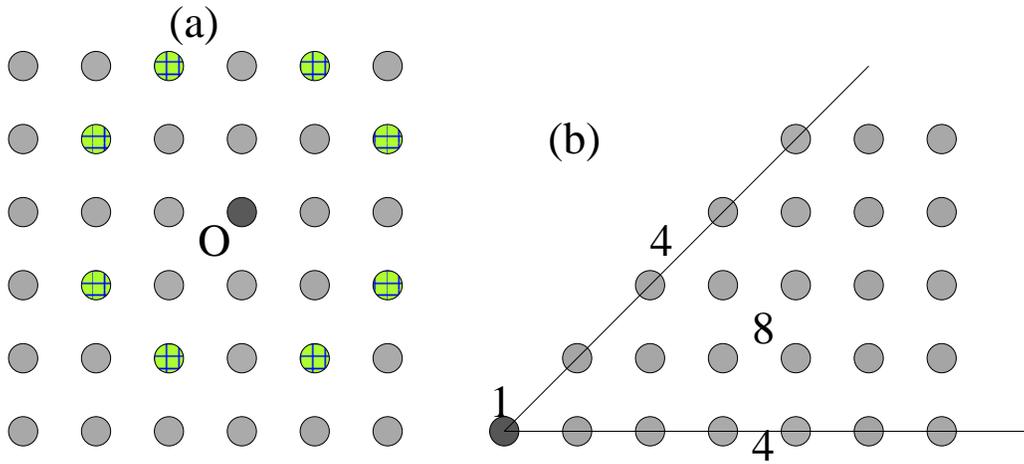


Figure 5: *Equivalent points and irreducible wedge for the 2-d square lattice. Due to the symmetry of the 2-d square lattice, the eight patterned lattice sites all contribute an identical amount to the Madelung sum calculated around the solid black site. Due to this symmetry, the sum can be reduced to the irreducible wedge (b) if the result at each point is multiplied by the degeneracy factors indicated.*

four) have lower degeneracies. Thus, the sum may be restricted to the irreducible wedge, so long as the corresponding terms in the sum are multiplied by the appropriate degeneracy factors, shown in Fig. 5(b). An appropriate algorithm to calculate both the degeneracy table, and the sum 5 itself are:

```

c First calculate the degeneracy table
c
do i=1,n
do j=0,i
  if(i.eq.j.or.j.eq.0) then

```

```

        deg(i,j)=4
    else
        deg(i,j)=8
    end if
end do
end do
deg(0,0)=1
c
c  Now calculate the Madelung sum
c
sum=0.0
do i=1,n
do j=0,i
    p=sqrt(i**2+j**2)
    sum=sum+((-1)**(i+j))*deg(i,j)/p
end do
end do

```

By performing the sum in this way, we saved a factor of 8! In fact, in three-dimensions, the savings is much greater, and real band structure calculations (eg. those of F.J. Pinski) always make use of the point group symmetry to accelerate the calculations.

The next question is then, could we do the same thing for a more complicated system (fcc in 3d?). To do this, we need some way of

classifying the symmetries of the system that we want to apply. Group theory allows us to learn the consequences of the symmetry in much more complicated systems.

A group S is defined as a set $\{E, A, B, C \dots\}$ which is closed under a binary operation $*$ (ie. $A * B \in S$) and:

- the binary operation is associative $(A * B) * C = A * (B * C)$
- there exists an identity $E \in S : E * A = A * E = A$
- For each $A \in S$, there exists an $A^{-1} \in S : AA^{-1} = A^{-1}A = E$

In the point group context, the operations are inversions, reflections, rotations, and improper rotations (inversion rotations). The binary operation is any combination of these; i.e. inversion followed by a rotation.

In the example we just considered we may classify the operations that we have already used. Clearly we need $2!2^2$ of these (ie we can choose to take (x,y) to any permutation of (x,y) and choose either \pm for each, in D -dimensions, there would be $D!2^D$ operations). In table. 1, all of these operations are identified The reflections are self inverting as is the inversion and one of the rotations and inversion rotations. The set is clearly also closed. Also, since there are 8 operations, clearly the interior points in the irreducible wedge are 8-fold degenerate (w.r.t. the Madelung sum).

This is always the case. Using the group operations one may always reduce the calculation to an irreducible wedge. They the degeneracy of

Operation	Identification
$(x, y) \rightarrow (x, y)$	Identity
$(x, y) \rightarrow (x, -y)$	reflection about x axis
$(x, y) \rightarrow (-x, y)$	reflection about y axis
$(x, y) \rightarrow (-x, -y)$	inversion
$(x, y) \rightarrow (y, x)$	reflection about $x = y$
$(x, y) \rightarrow (y, -x)$	rotation by $\pi/2$ about z
$(x, y) \rightarrow (-y, -x)$	inversion-reflection
$(x, y) \rightarrow (-y, x)$	inversion-rotation

Table 1: *Point group symmetry operations for the two-dimensional square lattice. All of the group elements are self-inverting except for the sixth and eight, which are inverses of each other.*

each point in the wedge may be determined: Since a group operation takes a point in the wedge to either itself or an equivalent point in the lattice, and the former (latter) does (does not) contribute the the degeneracy, the degeneracy of each point times the number of operations which leave the point invariant must equal the number of symmetry operations in the group. Thus, points with the lowest symmetry (invariant only under the identity) have a degeneracy of the group size.

2.3 Group designations

Point groups are usually designated by their Schönflies point group symbol described in table. 2 As an example, consider the previous ex-

Symbol	Meaning
C_j	(j=2,3,4, 6) j-fold rotation axis
S_j	j-fold rotation-inversion axis
D_j	j 2-fold rotation axes \perp to a j-fold principle rotation axis
T	4 three-and 3 two-fold rotation axes, as in a tetrahedron
O	4 three-and 3 four-fold rotation axes, as in a octahedron
C_i	a center of inversion
C_s	a mirror plane

Table 2: *The Schönflies point group symbols. These give the classification according to rotation axes and principle mirror planes. In addition, their are suffixes for mirror planes (h: horizontal=perpendicular to the rotation axis, v: vertical=parallel to the main rotation axis in the plane, d: diagonal=parallel to the main rotation axis in the plane bisecting the two-fold rotation axes).*

ample of a square lattice. It is invariant under

- rotations \perp to the page by $\pi/2$
- mirror planes in the horizontal and vertical (x and y axes)
- mirror planes along the diagonal (x=y, x=-y).

The mirror planes are parallel to the main rotation axis which is itself a 4-fold axis and thus the group for the square lattice is C_{4v} .

3 Simple Crystal Structures

3.1 FCC

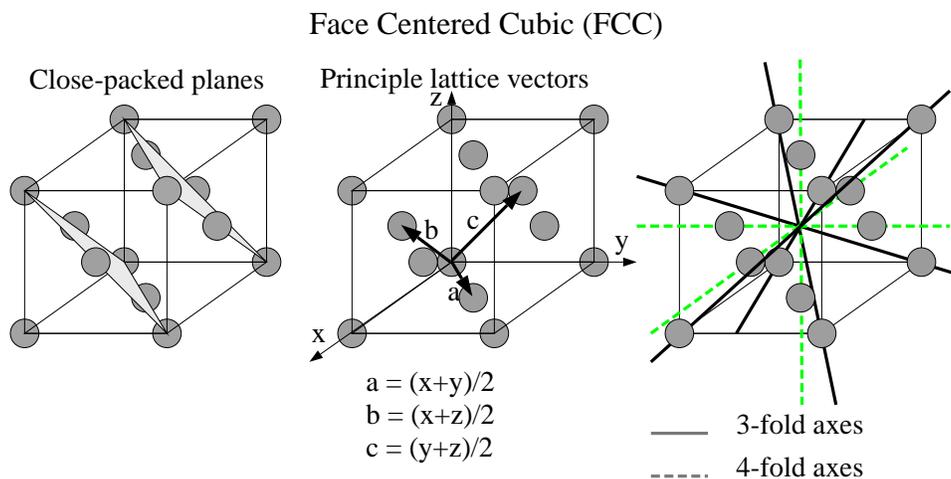


Figure 6: *The Bravais lattice of a face-centered cubic (FCC) structure. As shown on the left, the fcc structure is composed of parallel planes of atoms, with each atom surrounded by 6 others in the plane. The total coordination number (the number of nearest neighbors) is 12. The principle lattice vectors (center) each have length $1/\sqrt{2}$ of the unit cell length. The lattice has four 3-fold axes, and three 4-fold axes as shown on the right. In addition, each plane shown on the left has the principle 6-fold rotation axis \perp to it, but since the planes are shifted relative to one another, they do not share 6-fold axes. Thus, four-fold axes are the principle axes, and since they each have a perpendicular mirror plane, the point group for the fcc lattice is O_h .*

The fcc structure is one of the close packed structures, appropriate for metals, with 12 nearest neighbors to each site (i.e., a coordination number of 12). The Bravais lattice for the fcc structure is shown in Fig. 6 It is composed of parallel planes of nearest neighbors (with six

nearest neighbors to each site in the plane)

Metals often form into an fcc structure. There are two reasons for this. First, as discussed before, the s and p bonding is typically very long-ranged and therefore rather non-directional. (In fact, when the p-bonding is short ranged, the bcc structure is favored.) This naturally leads to a close packed structure. Second, to whatever degree there is a d-electron overlap in the transition metals, they prefer the fcc structure. To see this, consider the d-orbitals shown in Fig. 7 centered on one of the face centers with the face the xy plane. Each lobe of the d_{xy} , d_{yz} , and d_{xz} orbitals points to a near neighbor. The xz,xy,yz triplet form rather strong bonds. The $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals do not since they point away from the nearest neighbors. Thus the triplet of states form strong bonding and anti-bonding bands, while the doublet states do not split. The system can gain energy by occupying the triplet bonding states, thus many metals form fcc structures. According to Ashcroft and Mermin, these include Ca, Sr, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Al, and Pb.

The fcc structure also explains why metals are ductile since adjacent planes can slide past one another. In addition each plane has a 6-fold rotation axis perpendicular to it, but since 2 adjacent planes are shifted relative to another, the rotation axes perpendicular to the planes are 3-fold, with one along the each main diagonal of the unit cell. There are also 4-fold axes through each center of the cube with mirror planes

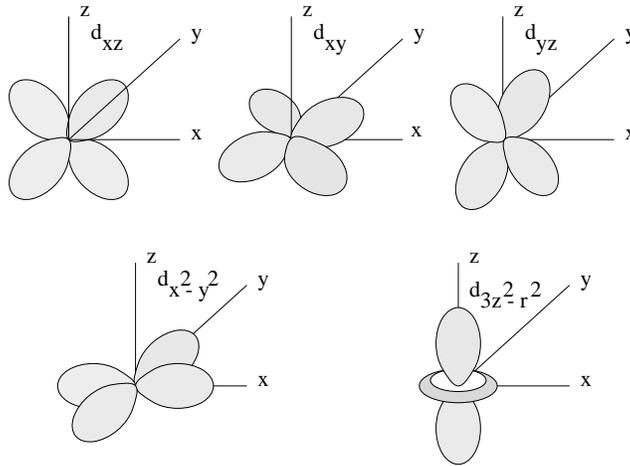


Figure 7: *The d-orbitals. In an fcc structure, the triplet of orbitals shown on top all point towards nearest neighbors; whereas, the bottom doublet point away. Thus the triplet can form bonding and antibonding states.*

perpendicular to it. Thus the fcc point group is O_h . In fact, this same argument also applies to the bcc and sc lattices, so O_h is the appropriate group for all cubic Bravais lattices and is often called the cubic group.

3.2 HCP

As shown in Fig. 8 the Hexagonal Close Packed (HCP) structure is described by the D_{3h} point group. The HCP structure (cf. Fig. 9) is similar to the FCC structure, but it does not correspond to a Bravais lattice (in fact there are five cubic point groups, but only three cubic Bravais lattices). As with fcc its coordination number is 12. The simplest way to construct it is to form one hexagonal plane and then add two identical ones top and bottom. Thus its stacking is ABABAB...

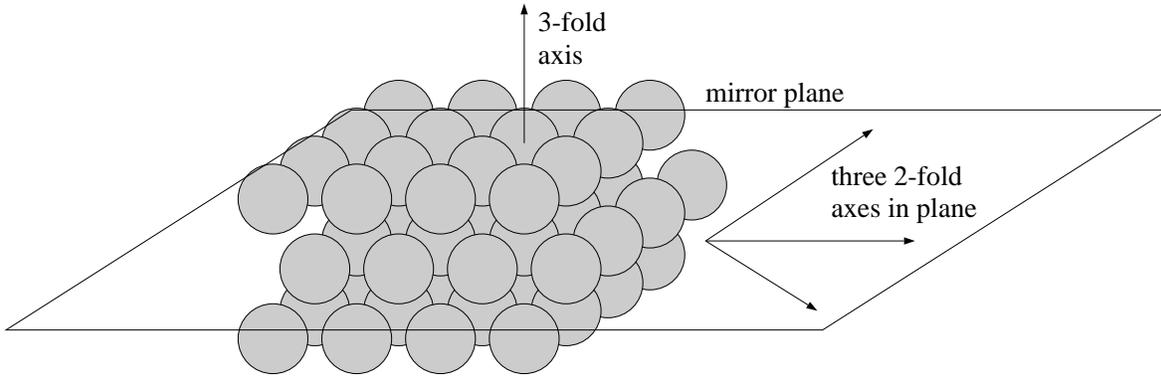


Figure 8: *The symmetry of the HCP lattice. The principle rotation axis is perpendicular to the two-dimensional hexagonal lattices which are stacked to form the hcp structure. In addition, there is a mirror plane centered within one of these hexagonal 2d structures, which contains three 2-fold axes. Thus the point group is D_{3h} .*

of the planes. This shifting of the planes clearly disrupts the d-orbital bonding advantage gained in fcc, nevertheless many metals form this structure including Be, Mg, Sc, Y, La, Ti, Zr, Hf, Tc, Re, Ru, Os, Co, Zn, Cd, and Tl.

3.3 BCC

Just like the simple cubic and fcc lattices, the body-centered cubic (BCC) lattice (cf. Fig. 4) has four 3-fold axes, 3 4-fold axes, with mirror planes perpendicular to the 4-fold axes, and therefore belongs to the O_h point group.

The body centered cubic structure only has a coordination number of 8. Nevertheless some metals form into a BCC lattice (Ba V Nb, Ta W M, in addition Cr and Fe have bcc phases.) Bonding of p-orbitals is

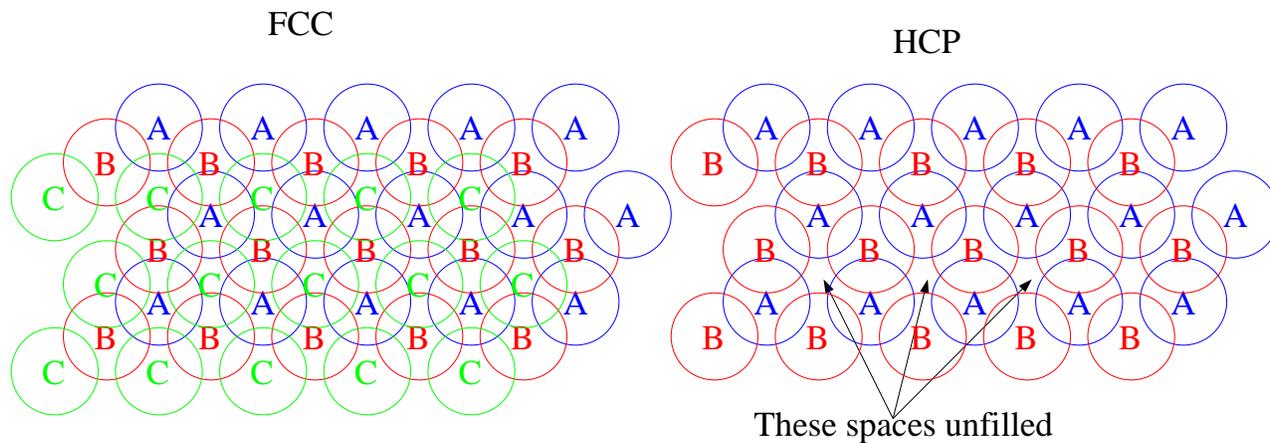


Figure 9: A comparison of the FCC (left) and HCP (right) close packed structures. The HCP structure does not have a simple Bravais unit cell, but may be constructed by alternately stacking two-dimensional hexagonal lattices. In contrast, the FCC structure may be constructed by sequentially stacking three shifted hexagonal two-dimensional lattices.

ideal in a BCC lattice since the nnn lattice is simply composed of two interpenetrating cubic lattices. This structure allows the next-nearest neighbor p-orbitals to overlap more significantly than an fcc (or hcp) structure would. This increases the effective coordination number by including the next nearest neighbor shell in the bonding (cf. Fig. 10).

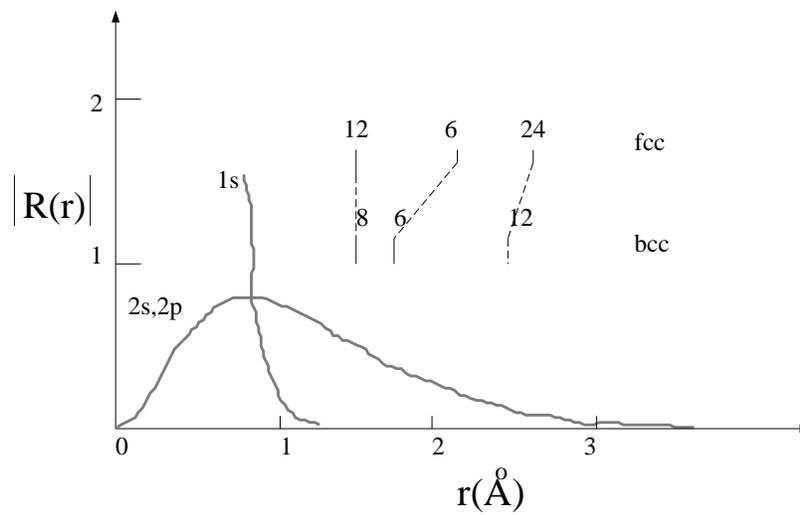


Figure 10: *Absolute square of the radial part of the electronic wavefunction. For the bcc lattice, both the 8 nearest, and 6 next nearest neighbors lie in a region of relatively high electronic density. This favors the formation of a bcc over fcc lattice for some elemental metals (This figure was lifted from I&L).*