February 6, 2007

LECTURE #09

Examples of Space Groups
Space Group Tables
Copper consists of Cu at the 4a sites or just at the lattice points. For NaCl, consists of Na at 4a and Cl at 4b, or vice versa. For CaF₂, the basis is Ca at 4a and F at 8c. Again we note that the general equivalent point is 192f, and there can be a crystal structure with this space group with atoms just at 192f (4 x 48 = 192). Of course, there are only 48 such atoms in the primitive unit cell. For the structures shown in Fig. 3-5 the coordination numbers are: Cu-12; NaCl-6; CaF₂-8.4.

A number of elements have the face-centered cubic (fcc) structure, and they are listed in Table 3-1. This means only the 4a sites are occupied as in the Cu example. The fcc structure is one of the two so-called close-packed structures. These are discussed in Section 3-7, but suffice it to say this structure can be obtained by the packing of hard spheres (billiard balls).

![Copper, NaCl, CaF₂ structures](image)

Fig. 3-5 Several structures with the \( \text{O}_h^{\text{d}}(\text{Fm}3\text{m}) \) space group.

Zn at the 4a site at (0, 0, 0) and S at the 4c site at \((1/4, 1/4, 1/4)\) plus the equivalent positions due to the F-lattice. Figure 3-7c shows the structure. Unlike diamond, this structure does not have a screw axis or center of symmetry owing to the dissimilarity of the atoms. The lack of an \( \text{I}1(1) \) symmetry operation allows materials with this crystal structure to be piezoelectric (Chapter 5), while diamond is not.

### 3-4 Point Group of a Space Group

So far in this chapter we have avoided mentioning the meaning of the term the point group of a space group and how it can be determined, although it was mentioned briefly in Chapter 1. Let us define it now. Consider all the symmetry operations of a space group. These operations include the lattice translations as in Eq. 2-1, point symmetry operations like \( \mathbf{R}_{10} \), and glide and screw operations \( \mathbf{R}_1 \mathbf{r} \). All three types may be written, in the Seitz notation, as \( \mathbf{R}_1 \mathbf{t} \) where \( \mathbf{t} \) is a lattice translation (Eq. 2-1) or a fraction of a unit cell translation \( \mathbf{r} \) as in Eq. 1-11. The point group of a space group is defined as the group of operations obtained if we take the space group symmetry operations and set all translations to zero. We are then left with a set of operations \( \mathbf{R}_{10} \). Note that for nonsymmorphic space groups some of these operations will not be symmetry operations of the crystal (as discussed in Section 1-3), so we might ask what is the use of the definition. The answer is that it is extremely useful and important. There is a one-to-one correspondence (an isomorphism) between the set of operations of the point group of the space group and the set of operations of one of the 32 crystallographic point groups; this leads to ways to classify the wave functions of the crystal. (This point will not be discussed here.) Also the macroscopic properties of crystal are determined by the operations \( \mathbf{R}_{10} \) because small translations such as \( \mathbf{t} \) will not be noticed on a macroscopic scale.

(Heuwe's Principle)
**Copper**

**Symmorphically related structures**

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**CHAPTER 3**  SIMPLE CRYSTAL STRUCTURES

**Fm 3m**  No. 225  F 4/m 3 2/m

**Origin at centre (m3m)**

**Number of positions, Special positions, and point symmetry**

<table>
<thead>
<tr>
<th>Position</th>
<th>Symmetry</th>
<th>Coordinates of equivalent positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>192</td>
<td></td>
<td>(0,0,0; 0.5,0; 0.5,0.5,0; 0.5,0.5,0.5)</td>
</tr>
</tbody>
</table>

**Conditions limiting possible reflections**

**General:**

- All reflections are allowed.

**Special:**

- As above, plus no extra conditions.

---

**Fig. 3-6**  $O_h^*$ ($Fm 3m$)

- Will not be noticed on a macroscopic scale (Neumann's principle, discussed in Chapter 5).

Given a space group symbol it is very easy to determine the point group of the space group. In the Schoenflies notation the space group symbol is just a point group symbol with a superscript. If the superscript is ignored then we have the point group of the space group. In the International notation the space group symbol is a lattice type followed by a description of the point symmetry operations as well as
Sodium (at the a-sites)

CHAPTER 3  SIMPLE CRYSTAL STRUCTURES

Im3m-O\textsubscript{h}\textsuperscript{9}

- 6b sites
- 12d sites
- 24h sites

Fig. 3-3 Some of the positions of the \(O_\text{h}^9(1m\text{mm})\) space groups. The very large circles represent spheres at the 2a site at \((0, 0, 0)\) and \((1/2, 1/2, 1/2)\).

Several Metals

Symmorphic

CHAPTER 3  SIMPLE CRYSTAL STRUCTURES

Im3m

No. 229  \(14/m\ 3\ 2/m\)

Origin at centre (m\text{nn})

\begin{align*}
\text{Co-ordinates of equivalent points} \\
(0,0,0) & \quad (1,1,1) \quad (0,0,1) \\
(1,0,0) & \quad (1,1,0) \quad (0,1,1) \\
(0,1,0) & \quad (1,0,1) \quad (1,1,1) \\
(1,0,1) & \quad (0,1,1) \quad (1,1,0) \\
(0,1,1) & \quad (1,0,1) \quad (0,1,0) \\
(1,1,1) & \quad (0,0,1) \quad (1,0,0) \\
\end{align*}

\text{Condition limiting}
\text{possible reflections}

General:

Add: \(h + k + l = 2n\)
Add: \((h + l = 2n); C\)
Add: \((k + l = 2n); C\)

Special: as above, plus

no extra conditions

\begin{align*}
\text{Add: } & \quad h + k + l = 2n \\
\text{Add: } & \quad (h + l = 2n); C \\
\text{Add: } & \quad (k + l = 2n); C \\
\end{align*}

no extra conditions

Fig. 3-4 \(O_\text{h}^9(1m\text{mm})\).
### Example $\text{BaTiO}_3$

The crystal structure of $\text{BaTiO}_3$ belongs to the space group $Pm\bar{3}m$ (No. 221) with the origin at the centre. The Wyckoff notation, number of positions, co-ordinates of equivalent positions, and conditions limiting possible reflections are as follows:

<table>
<thead>
<tr>
<th>Number of positions</th>
<th>Wyckoff notation, and point symmetry</th>
<th>Co-ordinates of equivalent positions</th>
<th>Conditions limiting possible reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>$n$</td>
<td>$x,y,z; x,z,y; y,z,x; y,x,z; z,y,x; z,x,y$</td>
<td>General: No conditions</td>
</tr>
<tr>
<td>24</td>
<td>$m$</td>
<td>$x,x,x; x,y,y; x,z,z; y,x,x; y,y,y; y,z,z; z,x,x; z,y,y; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>24</td>
<td>$l$</td>
<td>$x,x,x; x,y,y; x,z,z; y,x,x; y,y,y; y,z,z; z,x,x; z,y,y; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>24</td>
<td>$k$</td>
<td>$x,x,x; x,y,y; x,z,z; y,x,x; y,y,y; y,z,z; z,x,x; z,y,y; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>12</td>
<td>$j$</td>
<td>$x,x,x; x,x,x; x,y,y; x,y,y; x,z,z; x,z,z; y,x,x; y,y,y; y,z,z; y,z,z; z,x,x; z,y,y; z,z,z; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>12</td>
<td>$i$</td>
<td>$x,x,x; x,x,x; x,y,y; x,y,y; x,z,z; x,z,z; y,x,x; y,y,y; y,z,z; y,z,z; z,x,x; z,y,y; z,z,z; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>12</td>
<td>$h$</td>
<td>$x,x,x; x,x,x; x,y,y; x,y,y; x,z,z; x,z,z; y,x,x; y,y,y; y,z,z; y,z,z; z,x,x; z,y,y; z,z,z; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>8</td>
<td>$g$</td>
<td>$x,x,x; x,x,x; x,y,y; x,y,y; x,z,z; x,z,z; y,x,x; y,y,y; y,z,z; y,z,z; z,x,x; z,y,y; z,z,z; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>6</td>
<td>$f$</td>
<td>$x,x,x; x,x,x; x,y,y; x,y,y; x,z,z; x,z,z; y,x,x; y,y,y; y,z,z; y,z,z; z,x,x; z,y,y; z,z,z; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>6</td>
<td>$e$</td>
<td>$x,x,x; x,x,x; x,y,y; x,y,y; x,z,z; x,z,z; y,x,x; y,y,y; y,z,z; y,z,z; z,x,x; z,y,y; z,z,z; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>3</td>
<td>$d$</td>
<td>$x,x,x; x,x,x; x,y,y; x,y,y; x,z,z; x,z,z; y,x,x; y,y,y; y,z,z; y,z,z; z,x,x; z,y,y; z,z,z; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>3</td>
<td>$c$</td>
<td>$x,x,x; x,x,x; x,y,y; x,y,y; x,z,z; x,z,z; y,x,x; y,y,y; y,z,z; y,z,z; z,x,x; z,y,y; z,z,z; z,z,z$</td>
<td>No conditions</td>
</tr>
<tr>
<td>1</td>
<td>$b$</td>
<td>$x,x,x$</td>
<td>No conditions</td>
</tr>
<tr>
<td>1</td>
<td>$a$</td>
<td>$x,x,x$</td>
<td>No conditions</td>
</tr>
</tbody>
</table>

**Fig. 3-2** $O_h^1(Pm\bar{3}m)$. 

![Diagram of $\text{BaTiO}_3$ crystal structure]

- **Face-centred sites c**
- **b-sites**
- **a-sites**
3-3 Diamond and Zinc Blende Structures

In this section we discuss the last two simple, important, cubic crystal structures. Figures 3-7a and 3-7b show the diamond structure, space group O_h^7(Fd3m). This is the first nonsymmorphic structure discussed in this chapter. It has an F-lattice with atoms at the 8a positions (0, 0, 0), (1/4, 1/4, 1/4) and the face-centering positions, i.e., the coordinates of equivalent positions are the same for all F-lattices as in Fig. 3-6. The full space group symbol is F4_1/d32/m and Fig. 3-7b shows the 41 axis at x = 1/2 and y = 1/4. Note that there is a center of inversion at (1/8, 1/8, 1/8) and (1/8, 3/8, 3/8). Besides diamond and gray tin, the technologically important elements silicon (Si) and germanium (Ge) have this crystal structure.

The zinc blende structure is closely related to that of diamond. ZnS, GaAs, and many other binary compounds have the zinc blende structure. The symmorphic space group is T_d^2(F43m) and the basis is...

(a) Diamond

(b) Diamond (Projection)

(c) ZnS or GaAs

Fig. 3-7 On page 148 these structures are shown with an emphasis on the tetrahedral bonding.