Chapter III

Space Group Symmetry

III.1 Introduction

Thus far the treatment of symmetry has been restricted to the proper rotational and reflection symmetries of space lattices. The discussion of the symmetry of crystalline solids does not end with the presentation of the 14 Bravais lattice types because the symmetry of a solid is the symmetry of its three-dimensionally periodic particle density, and there are more symmetries available to such periodic patterns than to the lattices which characterize their translational symmetries. This is because of the existence of symmetry operations appropriate to such patterns but not to their lattices, for example the pattern need not be centrosymmetric while the lattice must be.

III.2 Proper and Improper Rotations

The symmetry operations of crystalline solids can be viewed in terms of their effect upon x, y, z in 3-dimensional space. For example, a two-fold axis through the origin and parallel to the c axis takes x, y, z into \(\bar{x}, \bar{y}, \bar{z}\) and thus can be represented by the matrix

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix} =
\begin{pmatrix}
\bar{x} \\
\bar{y} \\
\bar{z}
\end{pmatrix},
\]

and similarly the \(3 \times 3\) matrices for all the proper rotations of the groups \(O_h\) and \(D_{6h}\) can be written down (Tables III.1 and III.2). Matrices for all proper rotations of all space groups are contained in these tables. Figure III.1 clarifies the perhaps not immediately obvious relationship of x, y, z and the point related to it by a \(C_{6z}\) operation (x - y, x, z) in a hexagonal lattice.

![Illustration of relationship of positional parameters under \(C_{6z}\) in a hexagonal lattice](image)

Fig. III.1. Illustration of relationship of positional parameters under \(C_{6z}\) in a hexagonal lattice
The proper rotational symmetry operations of a crystalline solid form a closed set (in fact a group). This implies that if two such operations are members of the set then the combined operation is also. For example, in $O_h$, the $90^\circ$ rotation along $z$ together with the $120^\circ$ rotation along the body diagonal ($C_{3(x+y+z)}$) combine according to

\[
\begin{pmatrix}
0 & \tilde{1} & 0 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
0 & 0 & 1 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
= \begin{pmatrix}
\tilde{1} & 0 & 0 \\
0 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix}
\]  

(III.2)

\begin{table}
<table>
<thead>
<tr>
<th>Operation</th>
<th>Matrix</th>
<th>Symmetry Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 0 0$</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>$1$</td>
</tr>
<tr>
<td>$0 1 0$</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>$C_{2x}$</td>
</tr>
<tr>
<td>$0 0 1$</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 0 &amp; 0 &amp; 1 \ 1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>$C_{3(x+y+z)}$</td>
</tr>
<tr>
<td>$1 0 0$</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>$C_{3(x-y+z)}$</td>
</tr>
<tr>
<td>$0 1 0$</td>
<td>$\begin{pmatrix} 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>$C_{3(y-x+z)}$</td>
</tr>
<tr>
<td>$0 0 1$</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>$C_{4y}$</td>
</tr>
<tr>
<td>$0 1 0$</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>$C_{4_1}$</td>
</tr>
<tr>
<td>$0 0 1$</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 0 &amp; 0 &amp; 1 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>$C_{4_2}$</td>
</tr>
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<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>$C_{2(x+y)}$</td>
</tr>
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<td>$1 0 0$</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>$1$</td>
</tr>
<tr>
<td>$0 0 0$</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \end{pmatrix}$</td>
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<td>$0 0 0$</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>$1$</td>
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<td>$0 0 0$</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>$1$</td>
</tr>
</tbody>
</table>

\textbf{Table III.1. Proper Rotational Symmetry Operations of $O_h$}
\end{table}