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Introduction to the crystallographic space groups

Some object has the symmetry of some group of transformations – what it means?

The choice of some set of properties of the object, which may be transformed, has been made. If the result of the transformation is identical with the object before the transformation, we sad, that the object has the symmetry of this transformation, or that it is invariant under this transformation.

The objects under our interest: crystals

The transformations under our interest: isometric (preserving the distance between two points) transformations of the Euclidean space (motions) – symmetry operations: translations, n-fold rotations (proper rotations), reflections, inversion; rotoinversions (improper rotations), screw rotations, glide reflections.
The *Nomenclature Report* of IUC defined also the geometric element – a geometric item, which allows the fixed points of the symmetry operation (after removal of any intrinsic glide or screw translation), and symmetry element – the combination of a geometric element with the set of symmetry operations having this geometric element in common: rotation axis, screw axis, reflection planes (mirror planes), glide planes, inversion centre.
For all symmetry operations the printed symbols and for all symmetry elements the graphical symbols are defined.
In given coordinate system each symmetry operation has two types of algebraic representations: (W, w), where W is an (n x n) matrix and w an (n x 1) column; **W** is (n+1) x (n+1) "augmented" matrix.

Crystal – in classical crystallography – any solid state object invariant under some set of translations.
Different crystals have different additional symmetry operations under which they are invariant.
The set of symmetry operations under which given crystal is invariant are related, and form some special set named the group.

The group is named the set $\{g_k\}$, which fulfill the following conditions:

The "group multiplication" is defined, inner in the set

$$g_i \circ g_j = g_n$$

This multiplication is associative

$$g_i \circ (g_j \circ g_k) = (g_i \circ g_j) \circ g_k$$

Exists in the set the identity element $e \in G$
$g_i \circ e = e \circ g_i = g_i$
To each element $g_i \in G$ exists the inverse element $g_i^{-1} \in G$
$g_i \circ g_i^{-1} = g_i^{-1} \circ g_i = e$

The minimal quantity of elements, which multiplication gives all group are named the generators of the group. Different set of group elements may by chosen as generators of the group. The number of elements in the group is named as the order of the group.

The set P is the subgroup of group G:

G: |G| , $\{g_i \in G\}$

P: |P|, $\{p_i \in P\}$ $\{p_i \in G\}$ but exist such $g_i \notin P$, so: |P| < |G| **=>**

P must to be a group. Than we note:

$P \subset G$

Group G is the direct product of its subgroups G_1 and G_2:

Each of elements $g \in G$ may be done as $g = g_1 \circ g_2$ where $g_1 \in G_1; g_2 \in G_2$ and elements of the group G_1 commute with elements of group G_2. Elements of each of subgroups need not commute between themselves.

$$G = G_1 \times G_2$$

Group G is cyclic:

All set of G elements may be received by multiplication of one element by itself $\{g_i\} : g_i = g^{ni}, g^n = e$ n denotes the order of the group. The cyclic group has only one generator.

Group is abelan (commutative):

All elements of the group commute between themselves
$g_i \circ g_j = g_j \circ g_i$

Mappings of groups

Homomorphism F on G

1) $\forall$ $f_i \in F \rightarrow$ exactly one $g_i \in G$

2) $\forall$ $g_i \in G \rightarrow$ (exactly) one $f_i \in F$ (**Isomorphism**)

3) (picture f_i)(picture f_j) = picture (f_i f_j)
   $f_i \rightarrow g_i$, $f_j \rightarrow g_j$
   $f_i f_j = f_k$, $g_i g_j \rightarrow g_k$ $\qquad f_k \rightarrow g_k$
   $\{f_i\} \rightarrow E_g$ then $\{f_i\}$ is named the (kernel?) of the mapping $F \rightarrow G$
   (E_g – unite element of G)

Group G' is the extension G by H if exists such homomorphism G' on G for which H is the kernel ($H \subset G'$, the set of elements of G' related to the identity element of G)

Examples of some special groups

Euclidean group: The set of all symmetry operations in the Euclidean space.

Vector group V: The set of all vectors with addition as the group multiplication. This group is continuous. The discrete vector group may be defined, which is the subgroup of general vector group, when exists such positive number *d*, that each vector length (except zero one) is biggest then *d* or equal *d*.
In the three dimensional Euclidean space each element of this group may be written as:

$$t = n_1 a_1 + n_2 a_2 + n_3 a_3$$

n_i are the real numbers for general V
n_i are the integer numbers for discrete V
a_i are the primitive basis vectors

Translation group T – the group of translation operators, isomorfic to the vector group (with vector addition as the group multiplication). This group is the subgroup of the Euclidean group ($T \subset E$).The general translation group **T** is continuous and infinite.

Some subgroup $\mathbf{T_d}$ of $\mathbf{T}$ may be defined, which is isomorfic to discrete vector group.
The discrete set of space points, isomorfic with discrete vector group and invariant under the action of corresponding discrete translation group is named the crystal lattice. Then set of a_i are named primitive lattice vectors. Three dimensional T group is the direct product of three one dimensional T groups.

Two vector groups (crystal lattices) are the same type, if one may be getting from the second by continuous deformation.
In Euclidean space 14 different crystal lattices may be defined. They are named the Bravais lattices.

For each lattice exists the primitive cell – build on the primitive lattice vectors. Another choice of crystallographic basis vectors follow to another crystallographic cell- named elementary cell. The choice of the crystallographic basis vectors according to the International Tables for Crystallography follow to the cell named "conventional".

To each lattice the reciprocal lattice may be defined. Vector b_i is the elementary vector of the reciprocal lattice, related to the a_i direct lattice elementary vector, when a_i and b_i vectors are connected by the relation: $a_i \cdot b_j = 2\pi\,\delta_{ij}$. The reciprocal elementary cell chosen in this way, that the lattice node is in the cell centre, is named the first Brillouine zone. The symmetry of reciprocal lattice is the same as the symmetry of corresponding direct lattice.

Rotation group R – group of all rotation operators. It is the subgroup of the Euclidean group. ($R \subset E$)

Inversion group I – group consisting with two elements only- identity and inversion operator (e, I); It is the subgroup of the Euclidean group. ($I \subset E$)

Symmetric group– set of all permutations of m elements. The order of symmetric group equals $m!$

Unimodular group– set of matrices with determinants 1 (±1) with matrix multiplication as group multiplication.

Point group *P* – set of symmetry operations, which leave at least one point invariant. Rotation group may be a point group, as good as inversion group and direct product of inversion and rotation groups.

Crystallographic point group P- it is such point group, which leaves the crystallographic lattice invariant. Each crystallographic point group is a subgroup of general point group. Only identity, 2-fold, 3-fold, 4-fold and 6-fold rotations (C_1, C_2, C_3, C_4 i C_6) may be the symmetry operations of crystallographic lattices. There are only 32 different crystallographic point groups. Between them are 7 maximal groups, which are not related by group – subgroup relation (holoedr).

Space group G – set of all symmetry operations of a crystal structure. To those operations belong translations, rotations and rotoinversions (crystallographic), reflections, inversions (symmorfic space groups), and additionally screw rotations and glide reflections (nonsymmofric space groups). There are 230 different crystallographic space groups.

Space group is the extension some point group by translation group.
The elements of space group and the multiplication rule of its elements may be written by using the Saitz notation:

$g_i\, g_j = \{h_i \,|\, \mathbf{t}_i + \boldsymbol{\tau}_i\}\{h_j \,|\, \mathbf{t}_j + \boldsymbol{\tau}_j\} = \{h_i h_j \,|\, h_i(\mathbf{t}_j + \boldsymbol{\tau}_j) + (\mathbf{t}_i + \boldsymbol{\tau}_i)\}$ where

$$h_i = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \qquad \vec{\tau}_i = \begin{bmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{bmatrix} \qquad \vec{t}_i = \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix}$$

or in the notation of four-dimensional matrices:

$$g_i = \begin{pmatrix} a_{11i} & a_{12i} & a_{13i} & n_{1i} + \tau_{1i} \\ a_{21i} & a_{22i} & a_{23i} & n_{2i} + \tau_{2i} \\ a_{31i} & a_{32i} & a_{33i} & n_{3i} + \tau_{3i} \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Full description of crystallographic space groups is given in International Tables for Crystallography (A).

Schoenflies Symbols of crystallographic point groups:
(Identity element, which must belong to each group, will not be mentioned)

C_i - comprise only inversion.
C_n - comprise only one n-fold rotation axis. It is the n-order, cyclic group.

C_{nv} – comprise n-fold rotation axis and n reflection planes including this axis. The angle between two neighboring planes equals π/n.

C_{nh} - comprise n-fold rotation axis and reflection planes perpendicular to the axis. All groups with n even comprise the inversion.

S_n - comprise improper n-fold rotation axis (inversion axis). At the case if n is the odd number, groups S_n and C_{nh} are identical ($S_1 = C_{1h} = C_s$). If n is the even number, these groups are different, and $C_{n/2}$ is the subgroup of S_n. (Different then C_{2h}, C_{4h} and C_{6h} correspondingly are groups $S_2 = C_i$, S_4 and S_6).

D_n - comprise n-fold rotation axis and n 2-fold rotation axis perpendiculars to this n-fold axis.

D_{nd} - comprise all elements of group D_n and additionally reflection planes including the highest symmetry axis and bisectors of angles between 2-fold rotation axis perpendiculars to this highest symmetry axis.

D_{nh} - comprise all elements of group D_n and additionally reflection planes perpendiculars to the highest symmetry axis.

T - comprise all 12 rotation axis, which are the symmetry elements of tetrahedron.

T_d - comprise all symmetry elements of tetrahedron (rotation axis and reflection planes). There are 24 such elements. T_d group apart from elements of group T comprise 6 improper rotations S_4 and 6 reflection planes.

T_h - is the direct product of the T and S_2 groups (or T and C_i). It also has 24 elements.

O - comprise all rotation axis, which are the symmetry elements of cube and octahedron. There are 24 such elements.

O_h - is the highest point group, comprising 48 elements. It is the direct product of O and S_2 groups.

Among the crystallographic point groups the groups written down are the direct products of its subgroups:
For n =2, 4, 6 groups $C_{nh} = C_n$ x C_i or $C_{nh} = C_n$ x C_s and $D_{nh} = D_n$ x C_i or $D_{nh} = D_n$ xC_s
For n = 3 groups $C_{3h} = C_3$ x C_s, $D_{3h} = D_3$ x C_s and $D_{3d} = D_3$ x C_i
$T_h = T$ x C_i, $O_h = O$ x C_i

The discrete vector groups are collected in the 7 crystallographic systems.

To the given crystallographic system belong these discrete vector groups (crystallographic lattices) which are invariant under the same maximal point group (holoedr).

7 crystallographic systems and their symmetry point groups							
triclinic	C_1	**C_i**					
	1	**I**					
monoclinic	C_2	C_s	**C_{2h}**				
	2	m	**2/m**				
ortorhombic	D_2	C_{2v}	**D_{2h}**				
	222	mm2	**mmm**				
tetragonal	C_4	S_{4i}	C_{4h}	D_4	C_{4v}	D_{2d}	**D_{4h}**
	4	$\bar{4}$	4/m	442	4mm	$\bar{4}2m$	**4/mmm**
trigonal (rhombohedral)	C_3	C_{3i}	D_3	C_{3v}	**D_{3d}**		
	3	$\bar{3}$	32(1)	3m	**$\bar{3}m$**		
hexagonal	C_6	C_{3h}	C_{6h}	D_6	C_{6v}	D_{3h}	**D_{6h}**
	6	$\bar{6}$	6/m	622	6mm	$\bar{6}m2$	**6/mmm**
cubic	T	T_4	O	T_d	**O_h**		
	23	m$\bar{3}$	432	$\bar{4}3m$	**m3m**		

In the table for each point group below the Schoenflies symbol the international symbol (Hermann-Mauguin) is given. Holoedr is mentioned by bold font.

In the lattice, which is invariant under the given point group strictly given relations between the elementary lattice vectors and angles between them must be fulfilled.
These relations often are quoted as the criterion for appurtenance to given crystallographic system (for example, for the lattice belonging to the orthorhombic system a≠ b ≠c i $\alpha = \beta = \gamma = 90^0$), but should be mentioned, that for centered lattices it concerns non primitive, but conventional settings.

<u>14 different types of crystallographic Bravais lattices and their</u> <u>appurtenance</u> **<u>to crystallographic systems:</u>**

Triclinic: **P –** primitive lattice

Monoclinic: **P** - primitive lattice; **C, A** or **B** – face cantered lattice (with translation centering correspondingly the cell face perpendicular to z, x or y axis)
Orthorhombic: **P** - primitive lattice; **C, A** or **B** - face cantered lattice; **F** – all-face centered lattice (with translation centering all cell faces); **I** – body-cantered lattice (with translation centering the cell volume

Tetragonal: P - primitive lattice; **I** - body-cantered lattice

Trigonal (rhombohedral): **P** - primitive lattice

Hexagonal: **P** - primitive lattice

Cubic: **P** - primitive lattice; **F** - all-face cantered lattice; **I** - body-cantered lattice

The crystal structure created by introduction to the elementary cell some structural elements may be invariant under the point group, which is not the holoedr (as the lattice), but which is the subgroup of given holoedr.

<u>International symbols (Hermann-Mauguin) of 230 crystallographic space groups</u>

The definition of symmetry directions of given lattice play a important part in the understanding of the space group symbols. They are presented in the Table quoted below:

Lattice	Symmetry directions		
	primary	secondary	Tertiary
Triclinic	no exists		
Monoclinic	[010] ("unique axis b") [001] ("unique axis c")		
Orthorhombic	[100]	[010]	[001]
Tetragonal	[001]	[100] [010]	[1-10] [110]
Hexagonal	[001]	[100] [010] [-1-10]	[1-10] [120] [-2-10]

Rhombohedral (hexagonal axis)	[001]	[100] [010] [-1-10]	
Rhombohedral (rhombohedral axis)	[111]	[1-10] [01-1] [-101]	
Cubic	[100] [010] [001]	[111] [1-1-1] [-11-1] [-1-11]	[1-10] [110] [01-1] [011] [-101] [101]

A symbol of each group consists from two parts:

(i) The lattice letter designating the Bravais-lattice type.

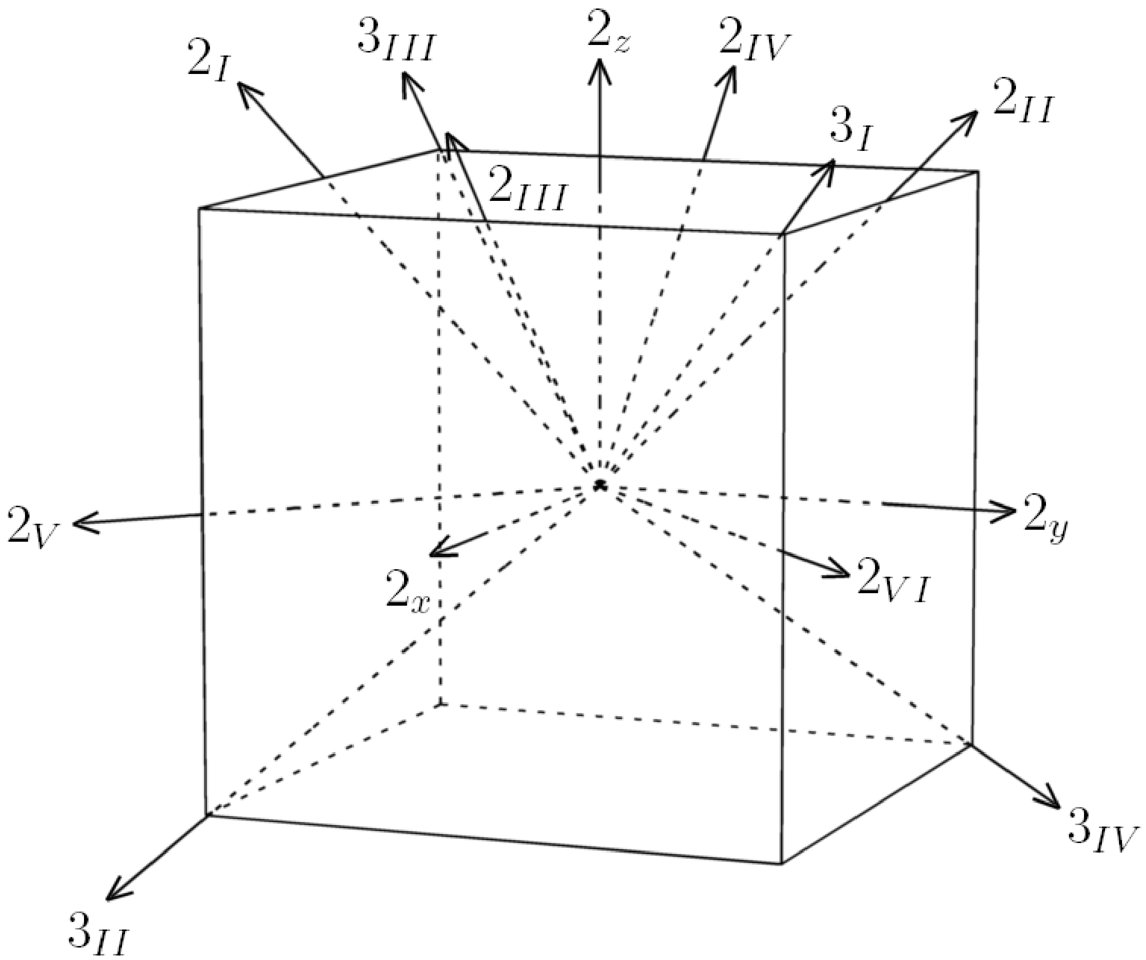
(ii) The one, two or three entries after to lattice letter refer to the one, two or three kinds of symmetry directions of the lattice belonging to the space group. Symmetry directions occur either as singular direction (as in the monoclinic and orthorhombic crystal systems) or as set of symmetrically equivalent symmetry directions (as in higher-symmetrical crystal systems). The symmetry directions and their sequence for the different lattices are summarized in the table quoted above. According to their position in this sequence, the symmetry directions are referred to as “primary”, “secondary” and “tertiary” directions. The symbols of space group elements related to given symmetry directions are written in the Herman-Mauguin in the sequence as these directions are. Each position contains one or two (separated by a slash) characters designating symmetry elements (axis- parallel to the direction and planes – perpendicular to the direction).
The international space group symbol depends on the choice of coordinate system.

Point group of the space group

To each space group G the point group G_P is subscribed, getting by omitting all (lattice and non-lattice) translations in the symmetry elements of the group G. The group G_P sometimes is not the subgroup of G.

In the Schoenflies symbol of space group the symbol of corresponding point group is used, with addition of the number, which distinguished different space groups having the same point group. Such notation is independent on the choice of crystallographic system.

Elements of *O* group are shown on the picture.



4-fold rotations along x, y, z directions appear along 2_x, 2_y, 2_z.

Site symmetry group is the set of symmetry operations which leave given site invariant.

Set of equivalent positions in given space group

Set of Euclidean space points invariant under one of the crystallographic space group may be biggest that this, which include only given group lattice points. Each of such sets is named the set of equivalent positions, or the Wyckoff positions, or the orbit of the group.

Each of the Wyckoff positions is described by the number indicating its multiplicity (number of equivalent positions in the elementary cell). The

Wyckoff positions may be general, or – if some from symmetry elements transform this position to itself – special one. Behind the multiplicity number the Latin letter describes the given Wyckoff position in given space group.

Each point belonging to given set of equivalent positions, after the choice of crystallographic coordinate system, may be presented by its coordinate triplets. From coordinate triplets of all points belonging to the set of general Wyckoff position the matrices representing all symmetry elements of given group may be followed by a simple way.

Conjugate groups (symmetrically equivalent)

If P_1 and P_2 are the subgroups of G, and there is some element $c \in G$ such, as:
$P_2 = c\, P_1\, c^{-1}$ (it means each element of P_1 is multiply in this way, and as the result follows the element P_2), then these groups are coniugate (equivalent)

Example:

$G = D_3 = \{ E, 3_I , 3_I^{-1} , 2_I , 2_{IV} , 2_V\}$
$P_1 = D_2 = \{ E, 2_I \}$; $c = 3_I$
$P_2 = \{ 3_I E 3_I^{-1}, 3_I 2_I 3_I^{-1}\} = \{ E, 2_V\} = D_2'$

Groups D_2 and D_2' are conjugate (equivalent) subgroups of group D_3.

Site symmetry groups of the positions belonging to the same Wyckoff position are equivalent subgroups of given space group.

The class of conjugate elements:
$a, b \in G$ are conjugate if $\exists\ c \in G$,such, as:

$$b = c\, a\, c^{-1}$$

Class of the elements conjugated with a: the set of all different elements $g_i \in G$ conjugated with a.

Coset decomposition of group G under the H subgroup.

$\{h_i\} \in H$, $H \subset G$, $s_\sigma \in G$ $s_\sigma \notin H$ (except identity element)

The left coset : $s_\sigma H = s_\sigma h_1 \oplus s_\sigma h_2 \oplus \ldots \oplus s_\sigma h_n$

The right coset: $H s_\sigma = h_1 s_\sigma \oplus h_2 s_\sigma \oplus \ldots \oplus h_n s_\sigma$

s_σ is named the coset representant.

If | H | is the order of subgroup H, and | G | is the order of subgroup G the number $|s_\sigma| = {}^{|G|}/_{|H|}$ is named the index of subgroup H in the group G.

The cosets under the H subgroup in the G group are either separated or coincidete. So the group G may be done as the direct sum of the cosets (and the creating subgroup H

$$G = \sum_{1}^{|S\sigma|} \oplus\, s_\sigma H$$

The number of cosets of H in the decomposition of G is equal to the index of H in G. The group H may have a few supergroups and in each of them may have another index.

The subgroup with minimal index in given group G is named the maximal subgroup of the G group.

<u>Example:</u>

$G = C_{3V}$

$H = C_3 = \{ E, C_3, C_3^2\}$ $s_\sigma \in \{ \sigma_a, \sigma_b, \sigma_c \}$

The left cosets:

$\sigma_a H = \sigma_a\{ E, C_3, C_3^2 \}$

$\sigma_a E = \sigma_a$

$$\underset{\sigma_a}{\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}} \underset{C_3}{\begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}} = \underset{\sigma_c}{\begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}}$$

$$\underset{\sigma_a}{\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}} \underset{C_3^2}{\begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}} = \underset{\sigma_b}{\begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}}$$

$\sigma_a H = \{ \sigma_a, \sigma_c, \sigma_b \}$

In the similar way:

$\sigma_b H = \{ \sigma_b, \sigma_a, \sigma_c \}$
$\sigma_c H = \{ \sigma_c, \sigma_b, \sigma_a \}$

Each of these planes may be the representant of the coset, because the getting sets coincident.

$G = C_{3V} = \{ E , C_3 , C_3^2 \} + \sigma_a\{ E , C_3 , C_3^2 \}$
or
$C_{3V} = \{ E , C_3 , C_3^2 \} + \sigma_b\{ E , C_3 , C_3^2 \}$
or
$C_{3V} = \{ E , C_3 , C_3^2 \} + \sigma_c\{ E , C_3 , C_3^2 \}$

The another subgroup in C_{3V} group is

$H = S_1 = \{E, \sigma_a\}$, coset representants $s_\sigma \in \{C_3 , C_3^2 \}$

$C_3H = \{C_3, \sigma_b\}$

$$\begin{array}{ccccc} C_3 & & \sigma_a & & \sigma_b \\ \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} & & \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & = & \begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array}$$

$C_3^2H = \{ C_3^2, \sigma_c \}$

$$\begin{array}{ccccc} C_3^2 & & \sigma_a & & \sigma_c \\ \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} & & \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & = & \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array}$$

$G = C_{3V} = \{ E , \sigma_a \} + C_3\{ E , \sigma_a \} + C_3^2\{ E , \sigma_a \}$

The same set of cosets follow from the choice of another represents - $s_\sigma \in \{ \sigma_b, \sigma_c\}$.

The similar decompositions may be done for right cosets.
In the "International Tables for Crystallography" the space groups are decomposed in the cosets under the translation group, which is the subgroup of each of space groups:

G = H + aH + bH + ...

G – space group H =T – translation group { a , b , ...} – coset representants. Just these coset representants are written down in the block "Symmetry operations" at each space group tables.