Acta Cryst. (1970). A26, 409

Simple Algebra Derivation of the Cubic Space Groups O_h–$m3m$

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(*Received* 20 *October* 1969)

Two generators, a threefold rotation-inversion axis $(\bar{3} \mid 000)$ and a fourfold axis $(4_z \mid \tau)$ are sufficient to generate the O_h space groups. The possible values of the translation τ determine 10 different O_h groups.

It is well known that the relation (1) (Coxeter & Moser, 1965; Jaswon, 1965)

$$\mathbf{U}^4=\mathbf{R}^3=(\mathbf{UR})^2=e \tag{1}$$

defines a group of order 24, isomorphic with the cubic point group O if **U** represents a fourfold and **R** a threefold rotation and e the identity element. Adding a symmetry centre $\bar{1}$ to O, one obtains the point group O_h with 48 elements. Let us define the element **S** by

$$\mathbf{S}=\mathbf{R}\cdot\bar{1}=\bar{1}\cdot\mathbf{R}=\bar{3}\,. \tag{2}$$

Relation (3) is an immediate consequence of (1) (taking into account the commutation of $\bar{1}$ and **R** and the fact that $\mathbf{S}^3=\bar{1}$) and defines the O_h group

$$\mathbf{U}^4=\mathbf{S}^6=(\mathbf{US})^2=e\,. \tag{3}$$

Passing from the point group to space groups we require that the set of relations (3) are still true modulo a lattice translation **t**. Taking the centre of symmetry at the origin, we are concerned with the Koster symbols (Koster, 1957)

$$\mathbf{S}=(\bar{3}|000); \qquad \mathbf{U}=(4_z|\tau) \tag{3}$$

with the matrix elements

$$(\bar{3})=\begin{bmatrix} . & . & \bar{1} \\ \bar{1} & . & . \\ . & \bar{1} & . \end{bmatrix}; \quad (4_z)=\begin{bmatrix} . & -1 & . \\ 1 & . & . \\ . & . & 1 \end{bmatrix} \tag{4}$$

so that finally *we have only to determine the possible fractional translations* $\tau=\tau_x, \tau_y, \tau_z$ *associated with the fourfold axis.* From

$$\mathbf{U}^4=(e|\mathbf{t}_0) \tag{5}$$

we deduce that

'4 τ_z must be a lattice translation $\mathbf{t}_0$'. (*a*)

Thus the allowed values of τ_z are

$$\tau_z=0, \tfrac{1}{4}, \tfrac{1}{2}, \tfrac{3}{4}\,. \tag{6}$$

From

$$(\mathbf{US})^2=(e|\mathbf{t}_1) \tag{7}$$

one deduces that the vector

'2 τ_x, $\tau_y-\tau_z$, $\tau_z-\tau_y$ must be a lattice translation $\mathbf{t}_1$' (*b*)

(the condition $\mathbf{S}^6=e$ is always satisfied by our choice of the origin).

We get a third condition (*c*) by considering the operations of the fourfold axes $\mathbf{SUS}^{-1}$ and $\mathbf{S}^4\mathbf{US}^{-4}$ which have the same rotational part $(3\ 4_z\ 3^2)$ and thus can only differ by a lattice translation which yields the result that the vector

'2 τ_z, 2 τ_x, 2 τ_y must be a latticetranslation $\mathbf{t}_2$'. (*c*)

The method for deriving conditions (*a*) (*b*) and (*c*) is given in the Appendix. If we had started with a fourfold axis in the x direction, we would have found condition (6) for τ_x and similarly for τ_y so that finally we have to examine the conditions (*a*) (*b*) and (*c*) for the values 0, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the translations τ_x, τ_y and τ_z. As condition (*a*) is always satisfied for these values, we have only to evaluate $\mathbf{t}_1$ and $\mathbf{t}_2$ which must belong to the translations $P(000)$, $I(000; \frac{1}{2}\frac{1}{2}\frac{1}{2})$ or $F(000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0)$ up to integral translations.

This can be done in a systematic way by eliminating first forbidden vectors τ. For instance condition (*c*) excludes the triplet $\tau=\frac{1}{4}00$ because the corresponding vector $\mathbf{t}_2=\frac{1}{2}00$ is not a lattice vector. The same is true for $\tau=0\frac{1}{4}0$ and $00\frac{1}{4}$. Condition (*b*) excludes $\tau=\frac{1}{4}0\frac{1}{4}$ and $\frac{1}{4}\frac{1}{4}0$. Replacing in the foregoing triplets $\frac{1}{4}$ by $\frac{3}{4}$ and (or) a zero by $\frac{1}{2}$ still yields forbidden triplets such as $\frac{1}{4}\frac{1}{4}0$, $\frac{1}{4}0\frac{1}{2}, \frac{1}{4}\frac{1}{2}\frac{1}{2}, \frac{3}{4}00$ and so on. Note that $\tau=\frac{1}{4}\frac{1}{4}\frac{1}{4}$ is also forbidden.

Finally, we are left with only a few allowed combinations which are given in the first and last columns of Table 1. The second and third columns contain the vectors $\mathbf{t}_1$ and $\mathbf{t}_2$ wherefrom one deduces the lattice type given in the fourth column. For instance, for $\tau=00\frac{1}{2}$, one finds $\mathbf{t}_1=0\frac{1}{2}\frac{1}{2}$ so that the corresponding lattice must be F.

Next we have to show that the translation τ determines the space group in an unambiguous way. The first Hermann–Mauguin symbol is a symmetry plane perpendicular to (001) which in our notation is given

Table 1. *Construction of the cubic groups* O_h

τ	t_1	t_2	Lattice	τ'	τ''	Space group	Schoenflies notation	Equivalent vectors τ
000	000	000	P	000	000	$Pm3m$	O_h^1	
			F			$Fm3m$	O_h^5	$0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$
			I			$Im3m$	O_h^9	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$
$\frac{1}{2}00$	100	100	P	$\frac{1}{2}\frac{1}{2}0$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$Pn3n$	O_h^2	
$0\frac{1}{2}\frac{1}{2}$	000	101	P	$\frac{1}{2}\frac{1}{2}0$	000	$Pn3m$	O_h^4	
$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	100	111	P	000	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$Pm3n$	O_h^3	
$00\frac{1}{2}$	$0\frac{\bar{1}}{2}\frac{1}{2}$	100	F	000	$00\frac{1}{2}$	$Fm3c$	O_h^6	$0\frac{1}{2}0$; $\frac{1}{2}00$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
$0\frac{3}{4}\frac{3}{4}$	000	$\frac{3}{2}0\frac{3}{2}$	F	$\frac{1}{4}\frac{3}{4}\frac{1}{2}$	$\frac{1}{2}\frac{1}{2}0$*	$Fd3m$	O_h^7	$0\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{4}$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$
$0\frac{3}{4}\frac{1}{4}$	$0\frac{1}{2}\frac{\bar{1}}{2}$	$\frac{1}{2}0\frac{3}{2}$	F	$\frac{1}{4}\frac{3}{4}\frac{1}{4}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$†	$Fd3c$	O_h^8	$0\frac{1}{4}\frac{3}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$
$\frac{3}{4}\frac{1}{4}\frac{3}{4}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$\frac{3}{2}\frac{3}{2}\frac{1}{2}$	I	$\frac{1}{2}0\frac{1}{2}$	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$	$Ia3d$	O_h^{10}	$\frac{1}{4}\frac{3}{4}\frac{1}{4}$

* The vector $\frac{1}{2}\frac{1}{2}0$ is equivalent to 000 in an F lattice and implies the symbol m.
† The vector $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ is equivalent to $00\frac{1}{2}$ in an F lattice and implies the symbol c.

by

$$\mathbf{U}^{2}\cdot\bar{1}=(4_z^2\cdot\bar{1}|\tau') \tag{8}$$

with

$$\tau'=(4_z+e)\tau\ ; \tag{9}$$

$4_z^2\cdot\bar{1}=2_z\cdot\bar{1}$ is a mirror plane m. For instance, for $\tau=\frac{3}{4}\frac{1}{4}\frac{3}{4}$, one finds $\tau'=\frac{1}{2}0\frac{1}{2}$ so that the operation $(m|\tau')$ transforms $x\ y\ z$ into $\frac{1}{2}+x, y, \frac{1}{2}-z$ and thus represents a glide plane a in $x, y, \frac{1}{4}$.

The second Hermann–Mauguin symbol is the ternary axis 3 and the third symbol is the symmetry plane perpendicular to (110) which in our notation is given by

$$\mathbf{US}\cdot\mathbf{SU}\cdot\mathbf{US}=(m'|\tau'') \tag{10}$$

with

$$(m')=(4_z3^24_z^2\bar{3})=\begin{bmatrix}. & 1 & .\\ 1 & . & .\\ . & . & 1\end{bmatrix}\ ;\ \tau''=\tau+(4_z3^2)\tau'\ . \tag{11}$$

For instance, for $\tau=\frac{3}{4}\frac{1}{4}\frac{3}{4}$, one has $\tau''=\frac{1}{4}\frac{1}{4}\frac{1}{4}$ so that the operation $(m'|\tau'')$ (10) transforms $x\ y\ z$ into $\frac{1}{4}+y$, $\frac{1}{4}+x$, $\frac{1}{4}+z$ and represents a d plane. The vectors τ' and τ'' are tabulated in columns 5 and 6 of Table 1 and determine the nature of the symmetry planes in the space group symbols of column 7. Column 8 gives the corresponding Schoenflies notation.

The vector $\tau=000$ deserves special attention because it is compatible with lattices P, F and I. This gives rise to the symmorphic space groups $Pm3m$, $Fm3m$ and $Im3m$ which are semi-direct products of the translation group and the point group $m3m$.

Equivalent vectors

In non-primitive space groups, there are several equivalent τ vectors. For instance in F groups τ is equivalent to the vectors $\tau+(000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0)$ and in I groups τ is equivalent to $\tau+(000; \frac{1}{2}\frac{1}{2}\frac{1}{2})$. An equivalent τ vector may change τ' and τ'', but only modulo a lattice vector so that the space group symbols do not need any change.

Our derivation has the advantage over geometrical methods that it is complete: no group can be forgotten and equivalents can be easily detected. It also has the advantage over other algebraic methods, for instance the approach by dyadics (Zachariasen, 1945), of being simpler.

Comparison with *International Tables* (1952)

We have given in the first column of Table 1 the τ values adopted in *International Tables for X-ray Crystallography* (1952). For the space group O_h^6-$Fm3c$, the vector τ is $00\frac{1}{2}$. However the last column of the Table shows the equivalent vectors $\tau=\frac{1}{2}00$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, so that in this group one could have taken, below the fractional translations of F, the general positions as already listed under O_h^2-$Pn3n$ ($\tau=\frac{1}{2}00$) or those listed under O_h^3-$Pm3n$ ($\tau=\frac{1}{2}\frac{1}{2}\frac{1}{2}$) which would result in some typographical economy.

Also in O_h^7-$Fd3m$ the vector $\tau=0\frac{3}{4}\frac{3}{4}$ could be replaced by the simpler one $\tau=0\frac{1}{4}\frac{1}{4}$. The same is true for O_h^{10}-$Ia3d$ where the actual description with $\tau=\frac{3}{4}\frac{1}{4}\frac{3}{4}$ could be replaced by the slightly simpler one $\tau=\frac{1}{4}\frac{3}{4}\frac{1}{4}$.

Finally, from a pedagogical point of view it is possible to derive all the space groups (except the hexagonal ones) as subgroups of the O_h groups by a descent in symmetry.

The generation of the general positions, from a knowledge of **U** and **S**, will be described elsewhere (Bertaut, 1969).

APPENDIX

Writing the 4×4 matrices (Bienenstock & Ewald, 1962)

$$\mathbf{U}=\left[\begin{array}{cc|c} & & \tau_x\\ & 4_z & \tau_y\\ & & \tau_z\\ \hline 0 & 0 & 1\end{array}\right]\ ;\ \mathbf{S}=\left[\begin{array}{cc|c} & & 0\\ & \bar{3} & 0\\ & & 0\\ \hline 0 & 0 & 1\end{array}\right]$$

where (4_z) and $(\bar{3})$ are the 3×3 matrices (4), the operations $\mathbf{U}^4$ (5) $(\mathbf{US})^2$ (6), $\mathbf{SUS}^{-1}$ and $\mathbf{S}^4\mathbf{US}^{-4}$ are easily evaluated and give rise to the conditions (*a*), (*b*), (*c*) of

the text. The matrix used for the evaluation of τ' is

$$(4_z+e)=\begin{bmatrix}1 & -1 & .\\ 1 & 1 & .\\ . & . & 2\end{bmatrix}$$

τ'' (11) is evaluated by the same standard procedures.

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Acta Cryst. (1970). A**26**, 411

Diffraction des Electrons par les Cristaux Moléculaires. I. Effet de Diffraction Moléculaire

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(*Reçu le* 18 *septembre* 1969)

A formulation of the scattered intensity from molecular crystals explains the appearance of a molecular scattering effect at large scattering-parameter values.

Introduction

La détente d'un gaz dans le vide peut provoquer un phénomène de condensation, qui permet dans certaines conditions de former un jet moléculaire constitué par des cristaux (Audit & Rouault, 1967; Audit, 1969). Disposant ainsi dans le vide d'une sorte de poudre de cristaux moléculaires de tailles variables, on peut étendre à l'étude des cristaux les méthodes expérimentales classiques de diffraction électronique par les gaz. On parvient alors, en raison des valeurs de la longueur d'onde λ et du facteur de diffusion $f(s)$ des électrons rapides, à mesurer l'intensité diffractée pour des valeurs du paramètre de diffraction s ($s=4\pi \sin(\theta/2)/\lambda$; θ est l'angle des vecteurs d'onde incidente et diffusée), très supérieures aux valeurs accessibles par la diffraction des rayons X, qui est couramment utilisée pour l'étude des cristaux moléculaires.

Pour les valeurs autorisées du paramètre s, c'est à dire pour les valeurs inférieures au diamètre de la sphère d'Ewald $s_{\max}=4\pi/\lambda$, l'influence des vibrations thermiques sur les diagrammes de rayons X se traduit, dans l'approximation élastique, par une atténuation des réflexions de Bragg. Par contre pour des électrons de 50 keV ($s_{\max}=228$ Å^{-1}) l'influence des vibrations est plus rigoureuse: elle peut provoquer la disparition totale des réflexions de Bragg, qui correspondraient, aux grandes valeurs de s, à des distances interréticulaires de l'ordre de grandeur des amplitudes de vibration du réseau. Dans ce domaine de s, la diffraction collective due à la structure cristalline, peut s'effacer pour laisser apparaître une diffraction individuelle par les molécules du réseau. C'est l'apparition de cet effet de diffraction moléculaire que nous nous proposons d'expliquer.

Intensité diffractée par un cristal moléculaire

La position d'équilibre de l'atome j appartenant à la molécule m, située dans la maille élémentaire α sera définie par le vecteur:

$$\mathbf{r}_{\alpha mj}=\mathbf{r}_\alpha+\mathbf{r}_m+\mathbf{r}_j$$

tandis que la position à l'instant t de cet atome soumis aux vibrations sera:

$$\mathbf{r}_{\alpha mj}+\mathbf{u}_{\alpha mj}(t)\,.$$

En théorie cinématique, pour un vecteur d'onde incident $\mathbf{k}_0$, l'intensité diffractée dans la direction $\mathbf{k}=\mathbf{k}_0+\mathbf{s}$ a pour expression:

$$I(\mathbf{s})=\sum_{\alpha\beta}\sum_{mn}\sum_{jk} f_j f_k^* \exp\left[i\mathbf{s}\,.\,(\mathbf{u}_{\alpha mj}-\mathbf{u}_{\beta nk})\right]\exp\left[i\mathbf{s}\,.\,(\mathbf{r}_{\alpha mj}-\mathbf{r}_{\beta nk})\right]. \quad (1)$$

Les indices de sommation prenant les valeurs:

$$\alpha,\beta=1,2\ldots N$$
$$m,n=1,2\ldots p$$
$$j,k=1,2\ldots q\,,$$