Acta Cryst. (1976). A**32**, 380

Study of Principal Subgroups and of their General Positions in *C* and *I* Groups of Class *mmm* — D_{2h}

BY E. F. BERTAUT

CNRS, Laboratoire des Rayons-X, B.P. 166, 38042 *Grenoble*; *CEN-G, Laboratoire de Diffraction Neutronique, DRF, B.P.* 85, 38041 *Grenoble, France*

(*Received* 28 *April* 1975; *accepted* 30 *October* 1975)

Once the symmetry operations and the general positions of the *C* and *I* groups of class *mmm* are given in the form of ordered standard blocks, their principal subgroups can be presented in such a way that their general point positions are easily recognized. New full standard symbols are proposed.

Scope and outline

We are here concerned with centred groups *C* and *I* of class *mmm*. It often happens in phase transitions in which the symmetry is lowered that only one symmetry element is lost, either the inversion (*C* and *I* subgroups) or the centring (*P* subgroups). One is interested not only in recognizing all possible maximal subgroups, but also in knowing the general positions of a chosen subgroup.

Thus our main problem is not the mere derivation of subgroups, a question which has been solved by several authors (see for instance Neubüser & Wondratschek, 1966), but a subgroup tabulation presented in such a way that from the knowledge of the general positions of the group the general positions of a chosen subgroup can be recognized at once.

To make the point clear, we start with the result obtained for space group $Cmcm-D_{2h}^{17}$. We reproduce in Table 1 the general positions of *Cmcm* in some convenient order. Table 1 is a 4×4 block of the coordinate triplets which are in a one-to-one correspondence with the symmetry operations listed in the 4×4 block of Table 2.

One recognizes of course the planes m,c,m of the Hermann–Mauguin symbol, but also other planes b,n,n [already listed in the symbols of *International Tables for X-ray Crystallography* (1952)] and binary axes which will be considered later. The point on which we particularly insist is the one-to-one correspondence of the coordinate triplets in Table 1 and the symmetry operations of Table 2. Thus if the subgroup tabulation is able to show *all* the symmetry operations of a specific subgroup the above one-to-one correspondence enables one to read at once the coordinate triplets of the general positions of the specific subgroup. This is exactly the purpose of Table 3.

Table 2. *Block of symmetry operations*

C	*m*	*c*	$m-D_{2h}^{17}$
	x	y	z
e	2	2	2_1
i	m	c	m
t	2_1	2_1	$2_1^{(t)}$
ti	b	n	n

The subgroup Table 3 has two parts; the upper one contains the *P* subgroups, the lower one the *C* (and *A*) subgroups.

P subgroups. Here the division into columns and lines is essential. The first line contains the *P* subgroups of class 222. The second line contains those *P* subgroups of class *mmm* which have the symmetry centre (i_1) at 000, *i.e.* the image of *xyz* is $\bar{x}\bar{y}\bar{z}$.

The third line contains those *P* subgroups of class *mmm* which have the symmetry centre (i_2) at $\frac{1}{4}\frac{1}{4}0$, *i.e.* the image of *xyz* is $\frac{1}{2}-x,\frac{1}{2}-y,\bar{z}$.

We now consider the columns. In each column the two *P* groups listed of class *mmm* have in common the *P* subgroup of class 222 in the first line. By now, we know all the symmetry elements of a maximal *P* subgroup of class *mmm* and thus we can read from Table 1 the corresponding coordinate triplets.

Example 1: Subgroup *Pbnm*; centre i_1 at 000. The eight symmetry elements are: the identity (e), the two-fold axes $2_1,2_1,2_1$, the inversion i_1 and the planes b,n,m. For the sake of clarity we reproduce in Table 4

Table 1. *Block of coordinate triplets* $Cmcm-D_{2h}^{17}$

$x,\ y,\ z$	$x,\ \bar{y},\ \bar{z}$	$\bar{x},\ y,\ \frac{1}{2}-z$	$\bar{x},\ \bar{y},\ \frac{1}{2}+z$
$\bar{x},\ \bar{y},\ \bar{z}$	$\bar{x},\ y,\ z$	$x,\ \bar{y},\ \frac{1}{2}+z$	$x,\ y,\ \frac{1}{2}-z$
$\frac{1}{2}+x,\ \frac{1}{2}+y,\ z$	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ \bar{z}$	$\frac{1}{2}-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$	$\frac{1}{2}-x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$
$\frac{1}{2}-x,\ \frac{1}{2}-y,\ \bar{z}$	$\frac{1}{2}-x,\ \frac{1}{2}+y,\ z$	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$	$\frac{1}{2}+x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$

Table 3. *Subgroups of* $C^{mcm}_{bnn} = Cmcm - D^{17}_{2h}$

Subgroups			
$P222_1 - D^2_2$	$P2_12_12_1(\frac{1}{4}00) - D^4_2$	$P22_12_1^{(t)}(\frac{1}{4}00) \doteqdot D^3_2$	$P2_122_1^{(t)}(0\frac{1}{4}\frac{1}{4}) \doteqdot D^3_2$
$Pmcm \doteqdot D^5_{2h}$	$Pbnm \doteqdot D^{16}_{2h}$	$Pmnn \doteqdot D^{12}_{2h}$	$Pbcn - D^{14}_{2h}$
$^*Pbnn \doteqdot D^6_{2h}$	$Pmcn \doteqdot D^{16}_{2h}$	$Pbcm - D^{11}_{2h}$	$Pmnm - D^{13}_{2h}$
$C222_1 - D^5_2$	$C^{mc2_1}_{bn2_1} -$ $Cmc2_1 - C^{12}_{2v}$	$C^{2cm}_{2_1nn}(z \rightleftarrows x)$ $Ama2 - C^{16}_{2v}$	$C^{m2m}_{b2_1n}(x \to y \to z \to x)$ $Amm2 - C^{14}_{2v}(\frac{1}{4}00)$

* The centre of inversion is at $\frac{1}{4}\frac{1}{4}0$ for this line.

Table 2 with the corresponding symmetry elements asterisked. We read at once from Table 1 the corresponding coordinate triplets of the subgroup *Pbnm*, given in the same order as the symmetry elements above:

$$xyz;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,\bar{z};\ \tfrac{1}{2}-x,\tfrac{1}{2}+y,\tfrac{1}{2}-z;\ \bar{x},\bar{y},\tfrac{1}{2}+z;$$
$$\bar{x}\bar{y}\bar{z};\ \tfrac{1}{2}-x,\tfrac{1}{2}+y,z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,\tfrac{1}{2}+z;\ x,y,\tfrac{1}{2}-z\,.$$

Table 4. *Symmetry elements and subgroups*

The symmetry elements of *Pbnm* are asterisked. The coordinate triplets are read from Table 1 in corresponding positions.

e^*	2	2	2_1^*
i^*	m	c	m^*
t	2_1^*	2_1^*	$2_1^{(t)}$
ti	b^*	n^*	n

Example 2: Subgroup *Pbcm*; centre i_2 at $\frac{1}{4}\frac{1}{4}0$. The eight symmetry elements are: the identity, the twofold axes $2, 2_1, 2_1^{(t)}$, the inversion i_2 and the planes b, c, m.

We read, by the same method, from Table 1 the corresponding coordinate triplets

$$x,y,z;\ x,\bar{y},\bar{z};\ \tfrac{1}{2}-x,\tfrac{1}{2}+y,\tfrac{1}{2}-z;\ \tfrac{1}{2}-x,\tfrac{1}{2}-y,\tfrac{1}{2}+z;$$
$$\tfrac{1}{2}-x,\tfrac{1}{2}-y,\bar{z};\ \tfrac{1}{2}-x,\tfrac{1}{2}+y,z;\ x,\bar{y},\tfrac{1}{2}+z;\ x,y,\tfrac{1}{2}-z\,.$$

Remark. In *International Tables* (I.T.) the centre of symmetry is chosen at 000. For shifting the origin from $\frac{1}{4}\frac{1}{4}0$ to 000, apply the following rule: leave $+x$ and $+y$ coordinates as they stand and make the substitutions

$$-x \rightleftarrows \tfrac{1}{2}-x;\quad -y \rightleftarrows \tfrac{1}{2}-y\,,$$

in order to obtain the coordinate triplets of *Pbcm*; centre at 000:

$$xyz;\ x,\tfrac{1}{2}-y,\bar{z};\ \bar{x},\tfrac{1}{2}+y,\tfrac{1}{2}-z;\ \bar{x},\bar{y},\tfrac{1}{2}+z;$$
$$\bar{x}\bar{y}\bar{z};\ \bar{x},\tfrac{1}{2}+y,z;\ x,\tfrac{1}{2}-y,\tfrac{1}{2}+z;\ x,y,\tfrac{1}{2}-z\,.$$

Other symbols. $-D^j_{2h}$ means 'same setting as in I.T.' while $\doteqdot D^j_{2h}$ means 'equivalent to D^j_{2h}, but with another setting'. The parentheses in the first line after the space group symbol of the *P* subgroups of class 222 indicate the shift of origin with respect to the standard notation in I.T.

C subgroups. Here the first *C* subgroup is the (only) one of class 222, followed by those of class *mm*2. Note that in I.T. the twofold axis of centred groups of class *mm*2 is always taken along the **z** direction. Thus *C* groups of settings 2*mm* or *mm*2 are written as *A* groups in I.T.

The prescription for finding coordinates is particularly simple. The identity and (any) three symbols after *C* produce already four coordinate triplets; the four others are obtained by adding the translation $\frac{1}{2}\frac{1}{2}0$ of *C*.

Example 3: $C^{m2m}_{b2_1n}$. Four symmetry elements are identity *e*, *m*, 2, *m*. From Table 1 one has:

$$x,y,z;\ \bar{x},y,z;\ \bar{x},y,\tfrac{1}{2}-z;\ x,y,\tfrac{1}{2}-z$$

plus four triplets formed by adding $\frac{1}{2}\frac{1}{2}0$.

If one wants to get the *A* setting of I.T. one has first to perform the permutation $x \to y \to z \to x$ indicated in Table 3, with the result:

$$(000;\ 0\tfrac{1}{2}\tfrac{1}{2}) + xyz;\ x\bar{y}z;\ \tfrac{1}{2}-x,\bar{y},z;\ \tfrac{1}{2}-x,y,z\,.$$

This is, say, the positions of I.T., but with a shift $\frac{1}{4}00$ of the origin, also indicated in Table 3 in parentheses after the space-group symbol *Amm*2.

Other ordering schemes. Of course it is natural to think of other ordering schemes. For instance let us number from 1 to 16 the coordinate triplets of Table 1. The subgroup *Pbnm* is entirely specified by the numbers 1, 4, 5, 8, 10, 11, 14, 15.

Another ordering scheme is obtained by a matrix notation a_{ij} for the symmetry elements and b_{ij} for the corresponding coordinate triplets (*i* for lines, *j* for columns in Tables 1 and 2). Thus *Pbnm* is entirely specified by the following indices *ij*: 11, 32, 33, 14; 21, 42, 43, 24.

However none of these schemes has the power of the synthetic Table 3 which shows how the subgroups are correlated. For instance one has from Table 3 at once

$$P222_1 \times \bar{1}_1 = Pmcm$$
$$P222_1 \times \bar{1}_2 = Pbnn\,.$$

Here $\bar{1}_1$ is the group formed by the identity and the inversion centre i_1 at 000, $\bar{1}_2$ is the group formed by the identity and the inversion centre i_2 at $\frac{1}{4}\frac{1}{4}0$.

Having described the use and hopefully the usefulness of the subgroup Table 3, we devote the main part of the paper (§§ 1 and 2) to the derivation of such subgroup tables. Some other results are noteworthy.

We shall see (§ 2·4) that *C* and *I* groups of class *mmm* naturally fall into two categories: (*a*) those in which simple (non-helical) binary axes 2_x and 2_y intersect, the maximal subgroups of class 222 being respectively $C222$ and $I222$, (*b*) those in which simple binary axes 2_x and 2_y do not intersect, the maximal subgroups of class 222 being respectively $C222_1$ and $I2_12_12_1$.

In the course of this paper we have developed a very simple block-algebra which is able to indicate the results of the multiplication of any symmetry elements of the present space groups without referring to an explicit representation $(\alpha|\tau_\alpha)$ of the space-group elements involved (§ 2·5).

Finally we come up (§ 3) with the proposal of using 'standardized' full symbols for the C and I groups of class *mmm*, *i.e.* symbols which at a glance show the eight maximal P subgroups of class *mmm with* their position of inversion centres.

For the reader already aware of group theory, the following considerations summarize in an abstract way the subgroup part of the paper but may be omitted in a first reading.

Considerations of group theory

Let $\mathscr{G}$ be a space group of lattice C or I of class *mmm*. Let $\mathscr{H}$ be a subgroup of class 222 or *mm*2 and of lattice P. The coset expansion of $\mathscr{G}$ can be written:

$$\mathscr{G}=\mathscr{H}+i\mathscr{H}+t\mathscr{H}+ti\mathscr{H} .$$

Each term of the second member corresponds to a line of the block (*cf.* § 2.2). $\mathscr{H}+i\mathscr{H}$ is a centrosymmetric subgroup of $\mathscr{G}$ of class *mmm* and lattice P. One can write:

$$\mathscr{G}=(\mathscr{H}+i\mathscr{H})+t(\mathscr{H}+i\mathscr{H}) .$$

$\mathscr{H}+ti\mathscr{H}$ is also a centrosymmetric subgroup of $\mathscr{G}$ of class *mmm* and lattice P (ti is a centre of inversion). One can write:

$$\mathscr{G}=(\mathscr{H}+ti\mathscr{H})+t(\mathscr{H}+ti\mathscr{H})$$

with $t^2 \doteqdot e$. $\mathscr{H}+t\mathscr{H}$ is a (non-centrosymmetric) subgroup of $\mathscr{G}$, belonging to the class 222 or *mm*2 and to a multiple lattice C or I. One may write:

$$\mathscr{G}=(\mathscr{H}+t\mathscr{H})+i(\mathscr{H}+t\mathscr{H})$$

with $it \doteqdot ti$ (modulo a non-fractional lattice translation).

Our study corresponds to finding: all subgroups of class *mmm* and lattice P of the forms $\mathscr{H}+i\mathscr{H}$ and $\mathscr{H}+ti\mathscr{H}$; all subgroups of class 222 and *mm*2 with a multiple cell C or I of the form $\mathscr{H}+t\mathscr{H}$; all subgroups of class 222 and *mm*2 with a primitive lattice P, say $\mathscr{H}$. All these subgroups are invariant.

Block algebra

In order to make the concepts clear we start with block algebra (symmetry elements, choice of generators, subgroups and relations with general positions) in simple P lattices before considering C and I lattices of class *mmm*. (*cf.* Bertaut & Wondratschek, 1971).

1. Primitive lattices

The block of symmetry operations has the following form

$$\begin{array}{cccc} & x & y & z \\ \underline{e} & \underline{2} & \underline{2} & 2 \\ \underline{i} & m & m & m\,. \end{array} \qquad (1\text{–}1a)$$

Here e means the identity operation, 2 is a twofold axis, i is the inversion centre, $m=i\,.\,2$ a plane of symmetry. Although we use here point-group notations, it is understood that 2 means the symbol of a space-group element, translations being included, as for instance in $(2_x|\tau_x)$. In the same spirit m is written for the corresponding symmetry plane which may be a mirror or a glide plane. We illustrate by the space group *Pbnm* (D_{2h}^{16}) the possible structure of the block of symmetry operations (1–2) and the corresponding triplets of point coordinates, already given under Example 1.

$$\begin{array}{cccc} \underline{e} & \underline{2_{1x}} & \underline{2_{1y}} & 2_{1z} \\ \underline{i} & b & n & m\,. \end{array} \qquad (1\text{–}2)$$

Here

$2_{1x}=(2_x|\tfrac{1}{2}\tfrac{1}{2}0)$ is a screw axis 2_1 at $x\tfrac{1}{4}0$
$2_{1y}=(2_y|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})$ – – – – 2_1 at $\tfrac{1}{4}y\tfrac{1}{4}$
$2_{1z}=(2_z|00\tfrac{1}{2})$ – – – – 2_1 at $00z$
$i=(\bar{1}|000)$ is a symmetry centre at the origin.

1.1 *Structure of the block*

The symmetry operations in the block are not independent and generators are underlined. For instance, in the first line of block (1–1*a*) the operation 2 under z is the product 2·2 of the operations under x and y. The second line of the block is obtained by multiplying each term of the first line by i. An important property of the block is that any one of the four terms in a line is the product of the three other terms.

Example 4: According to the multiplication rule

$$(\alpha|\tau_\alpha)\,(\beta|\tau_\beta)=(\alpha\beta|\alpha\tau_\beta+\tau_\alpha)$$

one has

$$(2_x|\tfrac{1}{2}\tfrac{1}{2}0)\,(2_y|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})=(2_x\,.\,2_y|\tfrac{1}{2}\tfrac{\bar{1}}{2}\tfrac{\bar{1}}{2}+\tfrac{1}{2}\tfrac{1}{2}0)=(2_z|10\tfrac{\bar{1}}{2}) \doteqdot (2_z|00\tfrac{1}{2})$$

or

$$2_{1x}\,.\,2_{1y}=2_{1z}\,.$$

The sign $\doteqdot$ means 'equivalent modulo a lattice translation'. One easily checks that $n=(m_y|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})$ is equal to $i\,.\,2_{1y}(\doteqdot 2_{1y}\,.\,i)$ *etc*. Here m_y is the mirror perpendicular to Oy at xOz, represented by the matrix

$$m_y=\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}=i\,.\,2_y\,.$$

The reader may check that $n \doteqdot ibm$, $i \doteqdot bnm$ *etc.*

Some subgroup relations are immediately evident from block (1–1*a*). Lines 1+2 contain the symmetry operations of the P groups of class $mmm-D_{2h}$. Line 1 corresponds to the P groups of class 222–D_2. The columns $1+2$, $1+3$, $1+4$ correspond to P groups of class $2/m-C_{2h}$. Also $P2$ is contained in the first line and $P\bar{1}$ in the first column.

1.1.1 *Choice of generators.* However the choice of the generators is somewhat arbitrary. For simplicity we keep constant the first column containing the generators e and i. We can still freely choose any two other generators provided they are in different columns. We restrict our choice to the two columns under x and y (a term in the last column is the product of the three other terms in the same line) so that we have $2\times2=4$ possible structures of the block (1–1a, b, c, d)

$$\begin{array}{cccc} \underline{e} & \underline{2} & m & m \\ \underline{i} & m & \underline{2} & 2 \end{array} \qquad (1\text{–}1b)$$

$$\begin{array}{cccc} \underline{e} & m & \underline{2} & m \\ \underline{i} & \underline{2} & m & 2 \end{array} \qquad (1\text{–}1c)$$

$$\begin{array}{cccc} \underline{e} & \underline{m} & \underline{m} & 2 \\ \underline{i} & 2 & 2 & m\,. \end{array} \qquad (1\text{–}1d)$$

Thus we obtain in the first lines of these blocks three subgroups of the class $mm2-C_{2v}$ and three subgroups of class $m-C_s$ (equivalencies included).

Example 5: In $Pbnm$ there are three non-centrosymmetric orthorhombic subgroups $P2_1nm\doteqdot Pmn2_1-C_{7v}^2$, $Pb2_1m\doteqdot Pmc2_1-C_{2v}^2$ and $Pbn2_1\doteqdot Pna2_1-C_{2v}^9$ and the three monoclinic subgroups $Pm-C_s^1$, Pb–C_s^2 and $Pn\doteqdot Pb-C_s^2$.

It is an easy matter to construct the general positions of the desired subgroup once the correspondence between the symmetry elements and the point triplets is established.

Example 6: $Pbn2_1$: one has from block (1–2) and Example 1

$$xyz;\ \tfrac{1}{2}-x,\tfrac{1}{2}+y,z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,\tfrac{1}{2}+z;\ \bar{x},\bar{y},\tfrac{1}{2}+z\,.$$

Remark. One recognizes that all the subgroups found in this way can be obtained at a glance from the full symbol of I.T. which is given in our example as $P2_1/b$ $2_1/n$ $2_1/m$ by taking various combinations of operations present in the symbol and corresponding to the classes mmm, 222, $mm2$, $2/m$, 2 and m.

The reason why we have spent so much time on the block structure is to prepare for the treatment of the case of multiple cells where the space-group symbol does not give immediate information on all possible subgroups.

2. Multiple lattices *C* and *I*

2.1 *Associated symmetry elements*

In C and I lattices we have two translational generators $t_1=(e|000)$ and $t_2=(e|\tfrac{1}{2}\tfrac{1}{2}0)$ for C, $t_2=(e|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})$ for I. For simplicity we write $t_2=(e|t)$. With each element $(\alpha|\tau_\alpha)$ we can form an associated symmetry element

$$t_2(\alpha|\tau_\alpha)=(\alpha|\tau_\alpha+t)\ . \qquad (2\text{–}1)$$

Thus for $t=\tfrac{1}{2}\tfrac{1}{2}0$ screw axes along x and y are always coexistent with ordinary binary axes, the nature of the axis along Oz being unchanged. For $t=\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}$ there will be screw axes *and* ordinary binary axes in the three directions x,y,z. Likewise glide planes are associated with mirrors or glide planes of a different nature; for instance a glide plane a perpendicular to Oz changes to b in the multiplication by t_2.

If $i_1=(\bar{1}|000)$ is the inversion operation at the origin, $i_2=(t_2\,.\,i=(\bar{1}|t)$ is the symbol of the inversion centre at $\tfrac{1}{2}t$, say at $\tfrac{1}{4}\tfrac{1}{4}0$ in a C lattice, at $\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4}$ in an I lattice.

2.2 *Block structure*

In space groups of class mmm and lattices C or I, we can now construct a block of symmetry operations in a form similar to the block (1–1a). Generators are underlined.

$$\begin{array}{cccc} & x & y & z \\ \underline{e} & \underline{2} & \underline{2} & 2 \\ \underline{i} & m & m & m \\ \underline{t} & t2 & t2 & t2 \\ ti & tm & tm & tm\,. \end{array} \qquad (2\text{–}2)$$

The third and fourth lines result from multiplying the first line by the operations, translation t and inversion ti.

The block contains the symmetry operations of:

a P group of class 222 (line 1),

a P group of class mmm (lines $1+2$) as already discussed,

a C or I group of class 222 (lines $1+3$),

a P group of class mmm (lines $1+4$) with the origin displaced to the inversion centre at $\tfrac{1}{2}t$.

The property that each term is equal (modulo a non-fractional lattice translation) to the product of the three other terms on the same line is conserved. Thus the last column is a consequence of the three other ones. *Keeping always constant the first column* which contains the generators e, i and t, we can confine our choice of the two other generators to any couple of terms in the second (x) and third (y) column. Thus we can write $4\times4=16$ different 'first lines' (2–3).

Once the first line is fixed, the structure of the whole block is fixed. Consequently we can construct 16 different blocks of symmetry operations for a given I or C group. We shall not write down all of them, because all the relevant properties can be read from a standard form of *one* block which we shall specify later.

	x	y	z		x	y	z
e	2	2	2	e	t2	2	t2
e	2	m	m	e	t2	m	tm
e	2	t2	t2	e	t2	t2	2
e	2	tm	tm	e	t2	tm	m

e	m	2	m	e	tm	2	tm	
e	m	m	2	e	tm	m	$t2$	
e	m	$t2$	tm	e	tm	$t2$	m	
e	m	tm	$t2$	e	tm	tm	$2.$	(2–3)

2.3 *Enumeration of subgroups*

We enumerate here the subgroups contained in the blocks (including equivalencies) and corresponding to classes mmm, $mm2$ and 222. From (2–3) one has:

Line 1: four P groups of class 222:

$$P222;\ P2,t2,t2;\ Pt2,2,t2;\ Pt2,t2,2;$$

twelve groups of class $mm2$ say, four groups P, setting $mm2$:

$$Pmm2;\ Ptm,m,t2;\ Pm,tm,t2;\ Ptm,tm,2;$$

four groups P, setting $2mm$:

$$P2mm;\ Pt2,m,tm;\ Pt2,tm,m;\ P2,tm,tm;$$

four groups P, setting $m2m$:

$$Pm2m;\ Ptm,t2,m;\ Pm,t2,tm;\ Ptm,2,tm\ .$$

Lines $1+2$: four P groups of class mmm; inversion centre i_1 at 000:

$$Pmmm;\ Pm,tm,tm;\ Ptm,m,tm;\ Ptm,tm,m\ .$$

Lines $1+3$: one C group of class 222:

$$C222=C2,t2,t2=Ct2,2,t2=Ct2,t2,2=C^{2}_{t2}{}^{2}_{t2}{}^{2}_{t2}\ ;$$

one C group of class $mm2$:

$$Cmm2=Ctm,m,t2=Cm,tm,t2=Ctm,tm,2=C^{m}_{tm}{}^{m}_{tm}{}^{2}_{t2};$$

one C group of class $2mm$:

$$C2mm=Ct2,m,tm=Ct2,tm,m=C2,tm,tm=C^{2}_{t2}{}^{m}_{tm}{}^{m}_{tm};$$

one C group of class $m2m$:

$$Cm2m=Cm,t2,tm=Ctm,t2,m=Ctm,2,tm=C^{m}_{tm}{}^{2}_{t2}{}^{m}_{tm}\ .$$

The two last group are written in I.T. as A groups, the twofold axis being chosen along Oz.

Remark. There is only one maximal C group of each class because for $(\alpha|\tau_\alpha)$ contained in the C group the associated element $t(\alpha|\tau_\alpha)$ is contained too as shown in the 'full' symbol.

Lines $1+4$: four P groups of class mmm; inversion centre i_2 at $\frac{1}{2}t=\frac{1}{4}\frac{1}{4}0$:

$$Ptm,tm,tm;\ Pm,m,tm;\ Pm,tm,m;\ Ptm,m,m\ .$$

The same enumeration is true for the subgroups of I groups of class mmm, replacing C by I and $\frac{1}{2}t$ by $\frac{1}{4}\frac{1}{4}\frac{1}{4}$.

Remark. Each P subgroup of class mmm and each C (or I) subgroup occurs four times in the 16 blocks.

Important remark. For a given P group we shall define as 'associated group' the group which has the associated symmetry symbols. Thus, Ptm,tm,m (inversion centre at 000) and Pm,m,tm (inversion centre at $\frac{1}{2}t$) are associated groups.

Associated P groups of class mmm have the important property of having the same subgroup of class 222. Indeed

$$(tm,tm,m)\times i=t2,t2,2$$

and also

$$(m,m,tm)\times ti=t2,t2,2$$

according to the rule

$$tm\times i_1 \doteq mti_1=m\times i_2\ .$$

Examples of associated groups are found in the columns of Table 3.

Conversely the same P subgroup of class 222, multiplied by the groups $\bar{1}_1$ and $\bar{1}_2$ (see under *Scope and outline*) gives rise to two associated P groups of class mmm. It is for this reason that in the title of this paper we use the word 'principal' subgroups (and not just 'maximal') to mean a wider range of subgroups. Thus the indication of the P subgroups of class 222 in Table 3 is an immediate aid for getting the general positions of the 'maximal' P subgroups of class mmm.

2.4 *Choice of the standard block*

We propose to choose always *ordinary* twofold axes along Ox and Oy as generators in the first line of the standard block. There are two cases to be considered.

Case (*a*). The twofold axes of the generators 2_x and 2_y intersect. Consequently the twofold axis 2_z along O_z as well as $t2_z$, noted $2_z^{(t)}$ is an ordinary twofold axis. The P subgroups of class 222 are:

$$P222-D_2^1;\ P2_12_12-D_2^3;$$
$$P22_12^{(t)}\text{ and }P2_122^{(t)}\doteq P222_1-D_2^2\ .$$

The C subgroups of class 222 (lines $1+3$) are all equivalent to $C222-D_2^6$.

The I subgroups of class 222 are all equivalent to $I222-D_2^8$.

Case (*b*). The twofold axes of the generators 2_x and 2_y do not intersect. The twofold axis along Oz is always a screw axis 2_{1z}, as well as $t2_{1z}$, noted $2_{1z}^{(t)}$.

The P subgroups of class 222 are

$$P222_1-D_2^2;\ P2_12_12_1-D_2^4;$$
$$P22_12_1^{(t)}\text{ and }P2_122_1^{(t)}\doteq P2_12_12-D_2^3\ .$$

The C subgroups of class 222 are all equivalent to $C222_1-D_2^5$.

The I subgroups of class 222 are all equivalent to $I2_12_12_1-D_2^9$.

Example 7: $Cmcm-D_{2h}^{17}$

We take the following generators:

$$\mathbf{e};\ \mathbf{2_x}=(2_x|000);\ \mathbf{2_y}=(2_y|00\tfrac{1}{2});\ \mathbf{i}=(\bar{1}|000);\ \mathbf{t}=(e|\tfrac{1}{2}\tfrac{1}{2}0)\ .$$

The twofold axes do not intersect [case (*b*)]. One constructs easily the other symmetry elements (2–4) by using the multiplication rule given under § 1.1, the block itself (Table 2) and the corresponding point positions (Table 1).

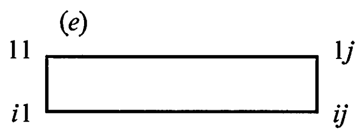
$$\begin{array}{llll}
\mathbf{2_z}=(2_z|00\tfrac{1}{2}) & \text{corresponds to} & 2_1 \text{ at } 00z & \\
\mathbf{m_x}=(m_x|000) & - & - \; m \text{ at } 0yz & \\
\mathbf{m_y}=(m_y|00\tfrac{1}{2}) & - & - \; c \text{ at } x0z & \\
\mathbf{m_z}=(m_z|00\tfrac{1}{2}) & - & - \; m \text{ at } xy\tfrac{1}{4} & \\
\mathbf{t2_x}=(2_x|\tfrac{1}{2}\tfrac{1}{2}0) & - & - \; 2_1 \text{ at } x\tfrac{1}{4}0 & \\
\mathbf{t2_y}=(2_y|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}) & - & - \; 2_1 \text{ at } \tfrac{1}{4}y\tfrac{1}{4} & \\
\mathbf{t2_z}=(2_z|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}) & - & - \; 2_1^t \text{ at } \tfrac{1}{4}\tfrac{1}{4}z & \\
\mathbf{tm_x}=(m_x|\tfrac{1}{2}\tfrac{1}{2}0) & - & - \; b \text{ at } \tfrac{1}{4}yz & \\
\mathbf{tm_y}=(m_y|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}) & - & - \; n \text{ at } x\tfrac{1}{4}z & \\
\mathbf{tm_z}=(m_z|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}) & - & - \; n \text{ at } xy\tfrac{1}{4}\,. & (2\text{–}4)
\end{array}$$

2.5 *Further properties of the block structure*

Each term a_{ij} of line i and column j is equal to the product of the term of the first line and same column j by the term of the first column and same line i

$$a_{ij}=a_{i1}\,.\,a_{1j}\;. \qquad (2\text{–}5)$$

This relation is illustrated by the following scheme of indices



For instance, $m=a_{22}$, $i=a_{12}$ and $2=a_{21}$ are uniquely correlated by

$$m=i\,.\,2\,.$$

Of course, m being a simple mirror and 2 a simple binary axis, the twofold axis 2 intersects the plane m at the centre i. Also

$$tm=ti\,.\,2(\doteq i\,.\,t2)$$

uniquely correlates the elements tm, ti and 2 (or tm, i and $t2$).

In view of the binary nature of the operation one has also

$$a_{i1}=a_{ij}\,.\,a_{1j} \text{ for each } j\,.$$

More generally

$$a_{ij}\,.\,a_{kj}=a_{i1}\,.\,a_{1j}\,.\,a_{k1}\,.\,a_{1j}=a_{i1}\,.\,a_{k1}\,.$$

Thus the product of two terms in the same column is equal to the product of terms in the first column and on the same lines.

Example 8: One wants to know what inversion centre (i_1 or i_2) correlates the plane c with the axis 2_{1y} in the block of *Cmcm*. One has

$$2_{1y}\,.\,c=ti=i_2\,.$$

Likewise, the product of two terms in the same line is equal to the product of terms in the first line and on the same columns.

Example 9: In the *Cmcm* block of Table 2 one has

$$n_y\,.\,n_z=2_y\,.\,2_{1z}=2_x\,.$$

More generally, once the block of symmetry elements is written down, any product of operations may be reduced by (2–5) without need of the explicit expressions of the operators $(\alpha|\tau_\alpha)$.

Examples:

$$m_x\,.\,2^t_{1z}=i2_x\,.\,t2_{1z}=it2_y=n_y$$
$$2_{1x}\,.\,n_z=t2_x\,.\,ti2_{1z}=i2_y=c$$
$$2_{1x}\,.\,c_y\,.\,n_z=e\,,\quad 2_{1x}\,.\,n_y\,.\,m_z=e \text{ etc.}\,.$$

3. Search of subgroups

In the example of *Cmcm*, the twofold axes 2_x and 2_y do not intersect. Consequently the subgroups of class 222 are those of case (*b*) under § 2.4 (*cf.* Table 3).

Maximal P and C subgroups are easily derived from § 2.3. We propose however another alternative which is the use of an *ordered* full symbol.

3.1. *The use of a full standard symbol in C and I groups*

We propose to use with the standard block convention (simple twofold axes along Ox and Oy as generators in the first line of the block of operators) the resulting full symbol indicating the symmetry planes *and* associated planes, with the following order: the first two upper indices are those planes which are the products of simple twofold axes 2_x and 2_y with the inversion i_1 at the origin 000. For instance the full standard symbol for $Cmcm-D^{17}_{2h}$ is C^{mcm}_{bnn}, for $Cmca-D^{18}_{2h}$ it is C^{mna}_{bcb} (see Table 5).

Table 5. *Full standard and I.T. symbols for C and I groups of class mmm*

To category *a* belong those groups which admit $P222$ as subgroup (or $C222$ in the C groups, $I222$ in the I groups listed here). To category *b* belong those groups which admit $P2_12_12_1$ as subgroup (or $C222_1$ in the C groups, $I2_12_12_1$ in the I groups listed here).

I.T.	Full standard symbol	Category
$Cmcm-D^{17}_{2h}$	C^{mcm}_{bnn}	*b*
$Cmca-D^{18}_{2h}$	C^{mna}_{bcb}	*b*
$Cmmm-D^{19}_{2h}$	C^{mmm}_{ban}	*a*
$Cccm-D^{20}_{2h}$	C^{ccm}_{nnn}	*b*
$Cmma-D^{21}_{2h}$	C^{maa}_{bmb}	*a*
$Ccca-D^{22}_{2h}$	C^{ncb}_{cna}	*a*
$Immm-D^{25}_{2h}$	I^{mmm}_{nnn}	*a*
$Ibam-D^{26}_{2h}$	I^{ccm}_{ban}	*a*
$Ibca-D^{27}_{2h}$	I^{caa}_{bcb}	*b*
$Imma-D^{28}_{2h}$	I^{mna}_{nmb}	*b*

From the knowledge of the full symbol it is easy to write down at a glance all the maximal P subgroups with the position of their inversion centre. In the present case P subgroups of class *mmm* with the inversion centre at 000 are those in which an odd number (three or one) of the upper indices of the full symbol is conserved. In Table 3 they are in the second line. In the example of *Cmca* they would be: *Pmna*, *Pbca*, *Pmcb*, *Pbnb*.

P groups of class *mmm* with the origin at $\frac{1}{4}\frac{1}{4}0$ are the complementary ones, formed with the associated planes. In the example of *Cmcm* they are found in the third line of Table 3. In the example of *Cmca* they would be: *Pbcb*, *Pmnb*, *Pbna*, *Pmca*.

We have listed in Table 5 the 'full standard symbol' and the symbol used in the I.T. for *C* and *I* groups of class *mmm*. It is easy to guess that the redactors of I.T. (1935) in their choice of a minimum number of symbols have avoided the symbol *n*, giving their preference to symbols in the following order *m*, *a*, *b* and *c* (with one exception $Ibca - D^{27}_{2h}$ which could have been consequently labelled *Ibaa*).

3.1.1. *Symmetry of the full symbol.* If in the full symbol we permute two planes of the lower indices with two planes of the upper indices, we do not change the foregoing subgroup scheme of *P* groups of class *mmm*, with respect to the origins. For instance (*cf.* Table 2)

$$C^{ccm}_{nnn} \doteqdot C^{nnm}_{ccn} \doteqdot C^{cnn}_{ncm} \doteqdot C^{ncn}_{cnm} \doteqdot Cccm - D^{20}_{2h};$$
$$I^{mna}_{nmb} \doteqdot I^{nma}_{mnb} \doteqdot I^{mmb}_{nna} \doteqdot I^{nnb}_{mma} \doteqdot Imma - D^{28}_{2h}.$$

The inversion of one upper (or all upper) with one lower (or all lower) indices is equivalent to a change of origin in the scheme of maximal *P* subgroups.

Thus $C^{ncm}_{cnn} - D^{20}_{2h}$ will still represent the group $Cccm - D^{20}_{2h}$, but the subgroups *Pncm*, *Pnnn* will now have the origin at 000 while in the full standard symbol their origin was at $\frac{1}{4}\frac{1}{4}0$.

3.1.2. *Remark.* In I.T. one finds under 'symbols for various settings', symbols generally equivalent to the above permuted symbols, sometimes with and sometimes without inversion of upper and lower indices. In fact the upper indices are those of the I.T. standard label, the lower indices the associated planes. If one may still predict possible *P* subgroups of class *mmm* from these I.T. symbols, one does not recognize their respective origins nor the positions of the planes with respect to the binary axes.

3.2. *C Subgroups*

The maximal *C* subgroups of the classes *mm*2, *m*2*m* and 2*mm* are also gained from the knowledge of the full symbol. One has only to replace a couple of associated planes by two associated twofold axes.

Example: C^{mcm}_{bnn} gives rise to (see Table 3)

$$C^{mc2_1}_{bn2_1^{(t)}} - C^{2}_{2v};\quad C^{2cm}_{2_1nn} \doteqdot C^{16}_{2v};\quad C^{m2m}_{b2_1n} \doteqdot C^{14}_{2v},$$

the last two groups being found in I.T. as *A* groups.

Note that in the upper indices the twofold axis is the product of the two accompanying planes; $m\,.\,c = 2_{1z}$ *etc.*

3.2.1. *P subgroups of class mm*2. They are not listed in Table 3; they are easily obtained from the full symbol (see above) of maximal *C* subgroups of class *mm*2, each full symbol giving rise to four such *P* subgroups. In the example of *Cmcm* the 12 subgroups are:

$$Pmc2_1 - C^{2}_{2v};\ Pmn2_1^{(t)} - C^{2}_{7v};$$
$$Pbc2_1^{(t)} \doteqdot Pca2_1 - C^{5}_{2v};\ Pbn2_1 \doteqdot Pna2_1 - C^{9}_{2v}.$$

$$P2cm \doteqdot Pma2 - C^{4}_{2v};\ P2_1cn \doteqdot Pna2_1 - C^{9}_{2v};$$
$$P2_1nm \doteqdot Pmn2_1 - C^{7}_{2v};\ P2nn \doteqdot Pnn2 - C^{10}_{2v}.$$

$$Pm2m \doteqdot Pmm2 - C^{1}_{2v};\ Pm2_1n \doteqdot Pmn2_1 - C^{2}_{7v};$$
$$Pb2_1m \doteqdot Pmc2_1 - C^{2}_{2v};\ Pb2n \doteqdot Pnc2 - C^{6}_{2v}.$$

Note that the three operators following *P* in the group symbol are not independent. For instance, in $Pmn2_1^{(t)}$ one has $mn = 2_1^{(t)}$ or $m2_1^{(t)} = n$ which one easily finds from the block algebra.

As an exercise the reader may derive these groups also from the full symbol of the *P* groups of class *mmm*

Table 6. *Block of symmetry operations*

Generators: e, t, i and $(2_x|00\frac{1}{2})$; $(2_y|00\frac{1}{2})$.

$Ibam - D^{26}_{2h}$

	x	*y*	*z*
e	2	2	2
i	*c*	*c*	*m*
t	2_1	2_1	2_1
ti	*b*	*a*	*n*

Coordinates

$x,\ y,\ z;$	$x,\ \bar{y},\ \frac{1}{2}-z;$	$\bar{x},\ y,\ \frac{1}{2}-z;$	$\bar{x},\ \bar{y},\ z;$
$\bar{x},\ \bar{y},\ \bar{z};$	$\bar{x},\ y,\ \frac{1}{2}+z;$	$x,\ \bar{y},\ \frac{1}{2}+z;$	$x,\ y,\ \bar{z};$
$\frac{1}{2}+x,\ \frac{1}{2}+y,\ \frac{1}{2}+z;$	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ \bar{z};$	$\frac{1}{2}-x,\ \frac{1}{2}+y,\ \bar{z};$	$\frac{1}{2}-x,\ \frac{1}{2}-y,\ \frac{1}{2}+z;$
$\frac{1}{2}-x,\ \frac{1}{2}-y,\ \frac{1}{2}-z;$	$\frac{1}{2}-x,\ \frac{1}{2}+y,\ z;$	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ z;$	$\frac{1}{2}+x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$

Subgroups

$P222(00\frac{1}{4}) \doteqdot D^{1}_{1}$	$P2_12_12 - D^{3}_{2}$	$P22_12_1(\frac{1}{4}0\frac{1}{4})$	$P2_122_1(0\frac{1}{4}\frac{1}{4})$
$Pccm - D^{3}_{2h}$ * $Pban - D^{4}_{2h}$	$Pbam - D^{9}_{2h}$ $Pccn - D^{10}_{2h}$	$Pcan \doteqdot D^{14}_{2h}$ $Pbcm - D^{11}_{2h}$	$Pbcn - D^{14}_{2h}$ $Pcam \doteqdot D^{11}_{2h}$
$I222(00\frac{1}{4}) - D^{8}_{2}$	$I^{cc2}_{ba2_1}$ $Iba2 - C^{21}_{2v}$	$I^{2cm}_{2_1an}(z \rightleftarrows x)$ $Ima2 - C^{22}_{2v}(\frac{1}{4}00)$	$I^{c2m}_{b2_1n}(x \to y \to z \to x)$ $Ima2 - C^{22}_{2v}(\frac{1}{4}00)$

* The centre of inversion is at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ for this line.

(see § 1) and show that one finds 24 subgroups, each one occuring twice.

Remark on tabulation

Table 6 shows what the tabulation of the symmetry block, general positions and subgroups look like for $I_{ban}^{ccm} = Ibam - D_{2h}^{26}$. The author has tabulated in a similar way all the C groups (D_{2h}^{17} to D_{2h}^{22}) and I groups (D_{2h}^{25} to D_{2h}^{28}).*

* These tables are available as photocopies which may be purchased from the author or obtained from the deposit with the British Library Lending Division (Supplementary Publication No. SUP 31500: 14 pp., 1 microfiche) through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

In the tables deposited under the IUCr auxiliary publication scheme, the reader will also find the corresponding tables for the two F groups $Fmmm - D_{2h}^{23}$ and $Fddd - D_{2h}^{24}$ with self-explanatory notations.

References

BERTAUT, E. F. & WONDRATSCHEK, H. (1971). *Acta Cryst.* A**27**, 298–300; (erratum) *Acta Cryst.* A**28**, 355.

Internationale Tafeln zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.

International Tables for X-ray Crystallography (1952). Vol. I. p. 548. Birmingham: Kynoch Press.

NEUBÜSER, J. & WONDRATSCHEK, H. (1966). *Kristall und Technik*, **1**, 529–543.

Acta Cryst. (1976). A**32**, 387

Determination by X-ray Diffraction of Interstitial Concentrations of Vanadium Ions in Disordered VO_x

BY M. MORINAGA AND J. B. COHEN

Department of Materials Science and Engineering, The Technological Institute, Northwestern University, Evanston, Illinois 60201, *U.S.A.*

(*Received* 9 *October* 1975; *accepted* 2 *December* 1975)

Integrated intensities were measured from VO_x single crystals with $x = 0{\cdot}80$, 0·94, 1·01, 1·11 and 1·25. A least-squares refinement was carried out for the scale factor and the isotropic temperature factors of vanadium and oxygen ions for each composition, for a range of interstitial vanadium contents. The R values after the refinement were 0·04–0·05. There are vanadium ions at tetrahedral interstitial sites, the concentration of which changes from 0–0·5% to 3% with composition x; this confirms quantitatively previous studies which employed dynamical electron diffraction effects. The temperature factors of vanadium (B_V) and oxygen (B_O) increase with x; $B_V = 1{\cdot}02$–$1{\cdot}38$ Å^2 and $B_O = 0{\cdot}58$–$1{\cdot}24$ Å^2. The composition dependence of the overall temperature factor is similar to that of the lattice parameter. The 002 structure factor for electrons U_{002} and the critical voltage E_c at which the second-order Kikuchi line disappears were calculated for $VO_{0{\cdot}82}$ and $VO_{1{\cdot}20}$, using the individual temperature factors determined by this study. The 002 structure factors measured by the critical-voltage and the intersecting-Kikuchi-line method [Watanabe, Andersson, Gjønnes & Terasaki (1974). *Acta Cryst.* A**30**, 772–776] were in agreement within less than 2%. The results support the idea that the ionic state of the cation lies between neutral and singly ionized.

Introduction

Vanadium monoxide is stable over a wide range of compositions at high temperature from $VO_{0{\cdot}8}$ to $VO_{1{\cdot}3}$ (Schönberg, 1954; Andersson, 1954; Westman & Nordmark, 1960; Stenström & Westman, 1968). Its structure is that of NaCl with a large number of vacancies on both vanadium and oxygen sublattices. The concentration of vanadium and oxygen vacancies changes with composition (Banus & Reed, 1970; Banus, Reed & Strauss, 1972). Even at stoichiometry about 15% of both sublattices are vacant. The existence of interstitial (tetrahedral) vanadium ions for oxygen-rich compositions has been reported (Høier & Andersson, 1974). Thus the defect structure is quite complicated. The observed diffuse scattering exhibits a composition dependence (Andersson & Gjønnes, 1970; Andersson & Taftø, 1970; Bell & Lewis, 1971; Hayakawa, Morinaga & Cohen, 1973; Andersson, Gjønnes & Taftø, 1974) which appears to be related to the Fermi surface of VO_x (Hayakawa *et al.*, 1973). At high temperatures it has been suggested that in $VO_{1{\cdot}23}$ there are vacancy clusters each involving one interstitial vanadium surrounded by four vanadium vacancies (Andersson *et al.*, 1974). Quantitative comparisons of scattering of such defects to measured data have not yet been made. It is interesting to note that this proposed defect structure is quite similar to that for wüstite, Fe_xO (Koch & Cohen, 1969; Cheetham, Fender & Taylor, 1971). An ordered structure near $VO_{1{\cdot}2-1{\cdot}3}$ has been