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LAYER GROUPS, SCANNING TABLES AND THE STRUCTURE OF DOMAIN WALLS

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Symmetry of possible domain walls of orientations (111) and (100) in fulleren is considered as an example of the use of scanning tables which should appear in a scheduled *Vol. E: "Subperiodic Groups"* of the *International Tables for Crystallography*. Fullerene molecules have icosahedral symmetry. Possible orientation states of molecules of C_{60}, compatible with the symmetry $Pa\bar{3}$, are those in which one of the three-fold axes of icosahedron coincides with one of the cubic three-fold axes. The orientation in each position is characterized by an angle ϕ by which it deviates from the orientation in which the icosahedral mirror planes passing through the axes also coincide with respective cubic mirror planes. Domain states and domain pairs are described in terms of these orientations. There exist only two sets of equivalent domain pairs; a translational pair with symmetry $Cmce$ and a rotational pair with symmetry $R\bar{3}m$. Sectional layer groups of these space symmetries are determined with use of scanning tables. These layer groups determine the site point symmetries in respective walls and hence the possible orientation states of C_{60} molecules within the wall as well as their modulation towards the region of domain states.

1. INTRODUCTION

The symmetry of a planar section of a crystal is a layer group just if the section has a crystallographic orientation. In this connection, it is called a sectional layer group, a term introduced by Holser[1] in consideration of twinning. Such groups can be introduced without reference to particular crystal structures. The sectional layer group contains exactly those operations of the space group which leave the sectional plane invariant. For a given space group, the sectional layer groups depend on the orientation of the sectional plane and on its location which can be determined by intersection of the plane with a complementary straight line. The procedure of the determination and presentation of the dependence of sectional layer symmetry on the location of the sectional plane of a given orientation along a straight line in a direction **d** complementary to this orientation received the name of the "scanning of space groups for sectional layer groups"[2]. The direction **d** is called the "scanning direction" and it has been shown how to solve the problem systematically with use of so-called "scanning groups" on the ground of the "scanning theorem".

The scanning process is a part of the search for the structure of feasible domain walls[3,4,5]. As a planar edifice, a wall has the symmetry of a layer group which predetermines tensor properties of the wall and its microscopic structure. This structure

depends on the orientation and location of the wall. An analogous procedure can be applied to consideration of grain boundaries[6]; in this connection the term *"bicrystallography"* is coined for problems of planar junctions between two various orientations of the same phase[7].

The intention to treat the scanning problem systematically motivated standardization of Hermann-Mauguin symbols of layer groups in conjunction with other subperiodic groups. Such standards are now prepared in *Vol E: "Subperiodic Groups"* of the *International Tables for Crystallography*[8] which will include so-called *"Scanning Tables"*. While particular cases have been analyzed in the literature [9,10] a complete description of the scanning of sectional layer groups is now therefore available.

As an example of its use, the symmetries of possible domain walls of orientations (111) and (001) in a simple cubic phase of fullerene C_{60} will be found and conclusions about consequences for microscopic structure of walls will be discussed.

2. ORIENTATION STATES OF FULLERENE MOLECULES IN CUBIC ENVIRONMENT

Carbon atoms in the molecule of fullerene C_{60} are arranged on vertices of a body which is close to Archimedean truncated icosahedron. In its solid cubic form, the centres of molecules C_{60} are located at points of the face centred cubic lattice. At higher temperatures, the molecules are assumed to rotate so they can be considered as spheres with resulting space symmetry $Fm\bar{3}m$. To discuss possible locations and orientations of these molecules in lower symmetry $Pa\bar{3}$, intermediate symmetry $Fm\bar{3}$ and in feasible domain walls we overview briefly the relationship of icosahedral symmetry to the cubic.

An icosahedron can be inscribed into a cube as shown on fig. 1. from the book by Altmann and Herzig[11]. The circles in this figure represent corresponding carbon atoms of buckminster fullerene C_{60}. The common symmetry of the icosahedron and of the cube is the point group $T_h = m\bar{3}$, the symmetry of an inscribed tetrahedron. Like tetrahedron, the icosahedron can be inscribed into the cube in two ways. Rotation of the icosahedron through 90° about any of the fourfold axes, reflection in the mirror planes (110), (101), (011) or any other operation of the coset to $m\bar{3}$ in $m\bar{3}m$ swaps the two orientations.
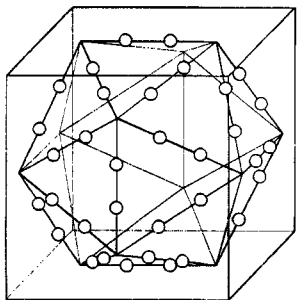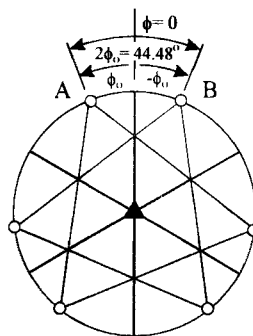

FIGURE 1 Buckminster fullerene in cubic environment.

FIGURE 2 Definition of angular parameter

It is important for present consideration to see that the conversion from one standard orientation of the icosahedron to another can also be performed by rotation about the cubic threefold axes through an angle $2\phi_o \approx 44.48°$ or through an angle $\approx 75.52°$ which complements $2\phi_o$ to $120°$ depending on the axis and direction of the rotation and on the original and final orientation. These angles or their trigonometric functions are universal geometric constants which express the relationship between cube and inscribed icosahedron. To define uniquely the orientations of fulleren molecules in cubic structure, we denote the two standard orientations by A and B in the same manner as in the paper of Brooks Harris[12]. The orientation in fig. 1 is the standard orientation B and it can be obtained from the standard orientation A by rotation through $2\phi_o$ about the axis [111] in the negative (clockwise) direction.

If we look now down the threefold axis [111], then the two triangles in fig.2. represent the (111) face of icosahedron in the two standard orientations A and B. In these orientations three mutually perpendicular mirror planes of the icosahedron coincide with cubic mirror planes (100), (010), and (001). We allow the icosahedron to rotate freely about the axis [111]. In the middle between standard orientations A and B there is an orientation in which the icosahedral mirror planes containing the axis [111] coincide with the cubic mirror planes $(1\bar{1}0)$, $(\bar{1}01)$, and $(01\bar{1})$. We set the angle which describes the orientation of icosahedron at zero in this position. Every possible orientation of the icosahedron in which its threefold axis coincides with the cubic [111] axis is then described by an angle ϕ in the margins $60° \geq \phi \geq -60°$. The values $\phi = \phi_o = 22.24°$, $-\phi_o = -22.24°$ correspond to standard orientations A and B, respectively. Analogously, the orientations of icosahedron, in which its threefold axis coincides with one of the cubic axes $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, are described by one angle ϕ through which the icosahedron is rotated from the orientation in which its mirrors coincide with respective mirrors of the cube.

The marginal angle $\phi = 60°$ corresponds to an orientation of icosahedron in which its mirror planes again coincide with the cubic mirror planes. This orientation is also obtained when the icosahedron in orientation with an angle $\phi = 0°$ is reflected through the plane perpendicular to the three-fold axis. The angles with absolute value $|\phi| > 60°$ are equivalent to angles within the margin $60° \geq \phi \geq -60°$.

Thus the orientation states of icosahedron and consequently of the molecule of fullerene are described by the rotation axis which is one of the cubic axes 3_p, 3_w, 3_u, 3_v and by the rotation angle ϕ. If this angle is ϕ_o, then the orientation is the standard orientation A, if it is $-\phi_o$, then the orientation is the standard orientation B, independently of the rotation axis.

3. THE SECTIONAL LAYER GROUPS

Domain states and domain pairs were already considered[13] and it was found that there exist only two classes of domain pairs: a translational and a rotational pair. We assign a label 1_1 to the first domain state in which the origin P of coordinate system is occupied by a molecule rotated through positive angle ϕ, which means from the central orientation towards the standard A orientation, about 3_p-axis. The label 1_2 is assigned to the domain state in which molecule of this orientation is located at $P + (a + b)/2$ and the label 2_1 to the domain state in which the molecule at the origin P is rotated about 3_p-axis through negative angle of the same magnitude

which means towards the standard B orientation.

The symmetries of these states are $\mathcal{F}(1_1) = Pa\bar{3}$, $\mathcal{F}(1_2) = Pa\bar{3}$ [(a + b)/2], $\mathcal{F}(2_1) = Pb\bar{3}$. The symmetry $Pa\bar{3}$ is a standard space group described by the diagram in *Vol. A* of the *International Tables for Crystallography*. The symbol $Pa\bar{3}$ [(a+b)/2] has the meaning of the same group shifted in space by [(a+b)/2], so that its symmetry elements are located in the same way with reference to the origin at $P + [(a + b)/2]$ as the elements of $Pa\bar{3}$ are located with reference to origin at P. The symbol $Pb\bar{3}$ is nonstandard and we choose it for the group which is conjugate to $Pa\bar{3}$ by a mirror $\{m_{x\bar{y}}|0\}_P$ which is Seitz symbol for a mirror of orientation $(1\bar{1}0)$, passing through the origin P.

The symmetries of ordered pairs are then the intersections $\mathcal{F}(1_1, 1_2) = Pbca$ and $\mathcal{F}(1_1, 2_1) = R\bar{3}_p$. Adding the operations which transform the domain states between themselves, which is the translation [(a + b)/2] in the first case and the reflection $\{m_{x\bar{y}}|0\}_P$ in the second case, we receive the symmetry groups of pairs (unordered):

$$\mathcal{J}(1_1, 1_2) = Cmce \quad \text{(new symbol for } Cmca\text{)} \quad \text{and} \quad \mathcal{J}(1_1, 2_1) = R\bar{3}_pm.$$

These two groups are to be scanned now for the sectional layer groups. The first table below is the scanning table for orthogonal scanning of the group $Cmce$; for the group $R\bar{3}m$ we display only the line necessary for our case.

No. 64   Group type $Cmce \approx D_{2h}^{18}$

Space Group $\mathcal{G} = C\frac{2}{m}\frac{2}{c}\frac{2_1}{a}$

Orientation orbit (*hkl*)	Conventional basis of the scanning group a' b' d			Scanning group $\mathcal{H}$	Translation orbit *sd*	Sectional layer group $\mathcal{L}(sd)$
(001)	a	b	c	$Cmca$	$[0d, \frac{1}{2}d]$ $[\frac{1}{4}d, \frac{3}{4}d]$ $[\pm sd, (\pm s + \frac{1}{2})d]$	$c2/m11$ $cm2a$ (a/4) $cm11$
(100)	b	c	a	$Bbcm$	$[0d, \frac{1}{2}d]$ $[\frac{1}{4}d, \frac{3}{4}d]$ $[\pm sd, (\pm s + \frac{1}{2})d]$	$pbam$ $pbaa$ (a'/4) $pba2$
(010)	c	a	b	$Abma$	$[0d, \frac{1}{2}d]$ $[\frac{1}{4}d, \frac{3}{4}d]$ $[\pm sd, (\pm s + \frac{1}{2})d]$	$pbmn$ $pbma$ (b'/4) $pbm2$ [(a' + b')/4]

An excerption from scanning table of the space group $\mathcal{G} = R\bar{3}m$						
(0001)	a	b	c	$R\bar{3}m$	$[0d, \ [\frac{1}{2}d,$ $\frac{1}{3}d, \ \| \ \frac{5}{6}d,$ $\frac{2}{3}d] \quad \frac{1}{6}d]$ $[\pm sd, (\pm s + \frac{1}{3})d,$ $(\pm s + \frac{2}{3})d]$	$p\bar{3}m1$ $p\bar{3}m1$ [(2a + b)/3] $p\bar{3}m1$ [(a + 2b)/3] $p3m1$

The heading of each table is the space group $\mathcal{G}$ to be scanned. The first row specifies the orientation of the set of planes among which we choose the domain wall. The second column defines a conventional basis of the scanning group $\mathcal{H}$ in terms of the conventional basis of the group $\mathcal{G}$. The scanning group, given in the third column, is the equitranslational subgroup of the scanned group $\mathcal{G}$, the point group H of which is that subgroup of the point group G of $\mathcal{G}$ which leaves the chosen orientation of planes invariant. The scanning group $\mathcal{H}$ is therefore defined by the scanned group $\mathcal{G}$ and by the orientation of planes. According to the scanning theorem, the scanning of the group $\mathcal{G}$ for the sectional layer groups with given orientation of sections is identical with the scanning of the group $\mathcal{H}$ for the sectional layer groups with this orientation of section planes[2].

The fourth column refers to the location of the section plane along the scanning line $P + s\mathbf{d}$ and the last column indicates the respective sectional layer group in the basis $\mathbf{a}'$, $\mathbf{b}'$ and with reference to the origin at $P + s\mathbf{d}$. Thus we have a set of coordinate systems in section planes with the same basis and with the origin on the scanning line. The section planes are grouped into translational orbits under the action of the scanning group $\mathcal{H}$. The sectional layer groups which refer to two planes of the same orbit are conjugate by those operations of $\mathcal{H}$ which move one plane of the orbit to the other. The structure is related in the same way to planes of the same orbit, in different ways to planes of different orbits. The orbits are distinguished in tables by square brackets.

4. THE SYMMETRY AND THE STRUCTURE OF DOMAIN WALLS

There is a close relationship between location properties of sectional layer groups and of domain walls. Groups themselves have certain location properties[15]. In particular, a nontrivial layer group can be localized by its plane as are the groups of special translational orbits. If the location of domain wall coincides with such plane, the respective sectional layer group is the symmetry of its central plane and determines the symmetry of the twin. Trivial layer groups are plane groups in three dimensions and they cannot be localized in the direction orthogonal to the orientation of the plane. There exists one such group for each orientation and it is "floating" in the scanning direction. This group is always the intersection of sectional layer groups for special locations and it corresponds to a general translational orbit. From the scanning tables we retrieve the following information:

Domain pair $(1_1, 1_2)$, orientation (001): 1. At the level 0d: Sectional layer group is $c2/m11$. The symmetry of twin is $p2/b11$ $[(\mathbf{a} + \mathbf{b})/4]$. 2. At the level $\frac{1}{4}$d: Sectional layer group is $cm2a$ $(\mathbf{a}/4)$. The symmetry of twin is $pb2b$ $(\mathbf{a}/4)$. 3. At the general level sd: The floating layer group is $cm11$. The symmetry of twin is $pb11$ $(\mathbf{a}/4)$.

Domain pair $(1_1, 2_1)$, orientation (111): 1. At the level 0d: Sectional layer groups is $p\bar{3}_pm1$. The twin symmetry is $p3_p21$. 2. At the general level sd: The floating layer group is $p3_pm1$. The symmetry of twin is $p3_p$.

The site point symmetries at locations of molecules of C_{60} in the low temperature phase of fullerene are $\bar{3}m$ and the angle ϕ completely determines the state; the orientation of each of the four molecules of the unit cell must be given be the same angle ϕ about different axes. The symmetry of domain wall relaxes this condition and

the molecules have more degrees of freedom, depending on their location. Generally, the molecule can isotropically expand or shrink and it has three rotational degrees of freedom: Two parameters which determine the orientation of its threefold axis and one parameter, the angle ϕ, which determines the orientation of the molecule.

The site point symmetries at the location of molecules control their orientation in the central plane and in the wall. The sectional layer group is the symmetry of the central plane and from respective site point symmetries we determine the orientations of molecules in this plane. As we go into the domains, the site point symmetries are determined by the symmetry of the twin. The molecules are allowed to rotate towards their values in the two domain states. At the same time the lattice parameter in the scanning direction changes towards its value in single domain state. The symmetry of twin contains operations which correlate the orientations of molecules in the two domains; these are the operations which change simultaneously the normal to the wall and exchange the domain states.

The use of this information for analysis of domain wall of orientation (111) between domains 1_1 and 2_1 is briefly described in the twin paper[14]. A complete description of structures of all possible walls in this material is in preparation.

CONCLUSION

The function of scanning tables and of standards of layer groups is not only the facilitation of scanning procedure. The final analysis of the structure of a domain wall requires meticulous description of orientation and location of involved space and layer symmetries. The standards should guarantee unique description. Latex files of the scanning for individual cases are available on request.

ACKNOWLEDGEMENT

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