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A SAMPLE ANALYSIS OF DOMAIN WALLS IN SIMPLE CUBIC PHASE OF C_{60}

P. SAINT-GRÉGOIRE

C.E.M.E.S. (UPR CNRS nr 8011), BP 4347, 31055 Toulouse Cedex, France

and

V. JANOVEC†‡ and V. KOPSKÝ‡

† *Technical University of Liberec, Hálkova 6, 461 17 Liberec 1, Czech Republic*
‡ *Institute of Physics, Acad. Sci., Na Slovance 2, 180 40 Praha 8, Czech Republic*

An analysis of possible structure of a domain wall (111) in rotational twin of fullerene C_{60} is performed with use of sectional layer groups. The eight possible domain states are described and it is shown that there exist only two types of domain pairs among the 46 possible combinations; one translational and one rotational. Possible orientation states of fullerene molecules in microscopic structure of the domain wall with orientation (111) are deduced.

Keywords: Fullerene, domains states, domain pairs, domain twins, structure of domain walls

1. INTRODUCTION

We shall consider here the same problem as in a parallel paper[1] so that the two studies intertwine. The subject of consideration is also the same - the structure of some feasible domain walls in simple cubic phase of fullerene C_{60}. While the twin paper concentrates on the group-theoretical aspects of the problem, especially on the use of "*scanning tables*" of the sectional layer groups in deciphering the local symmetries in domain walls, we shall emphasize here the geometrical aspect in application to a concrete case of fullerene C_{60}. Domain states and their symmetries are described on the basis of a previous study[2], the results of which, in particular the labelling and geometrical presentation, are adjusted for better clarity. At this point we stress the necessity of a precise description of the symmetries of domains states in terms of space groups which must be exactly specified, including their orientation and location in space. There exist two classes of equivalent domain pairs, the translational pair and the rotational pair, the scanning for which is performed in the twin paper. These results are then applied to analyze the structure of the (111) wall in the rotational domain twin in detail. A complete analysis of all possible domain walls on the same ground will be published elsewhere.

2. THE FUNCTION OF SCANNING TABLES

The standard approach to the study of domain walls consists of the following steps.
1. First we determine possible domain states. If $\mathcal{G}$ is the symmetry of parent struc-
ture S, $\mathcal{F}_1$ the symmetry of one of the domains states S_1, then the remaining domain
states $S_i = g_i S_1$ are obtained by the action of coset representatives in the resolution
$\mathcal{G} = \bigcup_i g_i \mathcal{F}_1$ of $\mathcal{G}$ versus $\mathcal{F}_1$ and the symmetry $\mathcal{F}_i = g_i \mathcal{F} g_i^{-1}$ of each of the states
S_i is obtained by conjugation. With the use of first normalizers we then determine
which symmetries are common for individual states. In the case we shall consider,
the low symmetry $\mathcal{F}_1$ is a self-normalizer and hence each domain state S_i has its own
symmetry group $\mathcal{F}_i$. 2. In the second step we determine the classes of equivalent
domain pairs. The latter are abstract aiding structures and an ordered domain pair
(S_i, S_j) is distinguished from an unordered domain pair $\{S_i, S_j\}$. The symmetry of an
ordered domain pair (S_i, S_j) contains elements $g \in \mathcal{G}$ for which $(G s_i, G s_j) = (S_i, S_j)$
and it is therefore an intersection $\mathcal{F}_{ij} = \mathcal{F}_i \cap \mathcal{F}_j$ of symmetries of the two individual
states. Since $\{S_i, S_j\} = \{S_j, S_i\}$, the symmetry of an unordered pair is a group
$\mathcal{J}_{ij} = \mathcal{F}_{ij} \cup g\mathcal{F}_{ij}$ of which $\mathcal{F}_{ij}$ is a subgroup of index two and $g\mathcal{F}_{ij}$ contains those
elements which transform S_i to S_j and back. 3. The next step involves the intro-
duction of domain twin and the use of scanning tables. For a given section plane in
space we assume that the structure on one side of the plane is S_i while on the other
it is the structure S_j. At this point we perform the scanning of the group $\mathcal{J}_{ij}$ for
sectional layer groups; each such layer group describes the symmetry of the domain
wall, the orientation and location of which is identical with that of the sectional plane.

2. DOMAIN STATES IN FULLERENE C_{60}

In consideration of domain states of solid fulleren C_{60} we embark from the parent
symmetry group $\mathcal{G} = Fm\bar{3}m$ in which molecules are assumed to behave like spheres
located in the positions of fcc cubic lattice. In the low symmetry phase of space
symmetry $Pa\bar{3}$, the molecules still occupy the same positions. Each molecule is now
an object of icosahedral symmetry which can fit the site point symmetries of cubic
groups in two ways:
    1. There are two so-called standard orientations of fullerene molecules with ref-
erence to cubic coordinate system, denoted as A and B. In both these orientations,
the molecules have in common with the cube the point symmetry operations of the
point group $m\bar{3}$. These include the rotations and rotoinversions about all four ro-
toinversion axes $\bar{3}_p$, $\bar{3}_w$, $\bar{3}_u$, $\bar{3}_v$ (subscripts p, w, u, and v correspond to orientations
$[111]$, $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$, and $[\bar{1}1\bar{1}]$, respectively), the main twofold axes 2_x, 2_y, and 2_z and
the respective mirror planes m_x, m_y, and m_z.
    If all molecules of C_{60} would occupy the positions of fcc cubic lattice with one of
the orientations A or B, then the resulting space symmetry will be $Fm\bar{3}$. The two
orientations will correspond to two domain states. Elements of the coset of $Fm\bar{3}$
in $Fm\bar{3}m$ will transform one of these states to the other. As a representative of
such transforming operations we shall take the mirror plane $m_{x\bar{y}}$. The phase with
the symmetry $Fm\bar{3}$ is not observed but the two domains can be distinguished as
secondary domains by components of electrogyration tensor $A_{14} = A_{25} = A_{36}$, which
is a tensor of type $\varepsilon V[V^2]$ or by the components $q_{23} = q_{31} = q_{12}$ of the antisymmetric
part $q \approx \{[V^2]^2\}$ of tensor $Q \approx [V^2]^2$ which represents tensor of electrostriction,

elastooptic or piezooptic tensor. These components are seen at once from tables of tensorial covariants[3].

2. It is known that the transformation from the orientation A to orientation B can be performed also by a rotation about the threefold cubic axes[4]. Any of the axes can be used and the rotation is noncrystallographic; it is a rotation through an angle $2\phi_o \approx 44.48°$ about [111] cubic axis which sends the molecule from standard orientation A to a standard orientation B. We shall now consider a rotation from standard orientation A only through the angle ϕ_o. This rotation brings the molecule to an orientation in which the icosahedral mirror planes coincide with cubic mirror planes $m_{x\bar{y}}$, $m_{y\bar{z}}$, and $m_{z\bar{x}}$. In other words, a common symmetry of the molecule and of the cube is now $\bar{3}_p m$. Analogous rotations about the other three cubic threefold axes will bring the molecule to states where common symmetries will be the other three rhombohedral groups.

Domain states and domain pairs were already analyzed[2]. The results of the analysis in an amended labelling is given below. We use the same labels as before to distinguish domain states in which the angle ϕ is positive and hence from the symmetric orientation towards standard orientation A (label 1) or negative and hence towards the standard orientation B (label 2). Unit cells of the domains are schematically shown in fig. 1. where letters p, w, u, and v are axial vectors representing rotations about the axes labelled by these letters.

$$1_1 \qquad 1_2 \qquad 1_3 \qquad 1_4$$

$$Pa\bar{3} \qquad Pa\bar{3}\ (a+b)/2 \qquad Pa\bar{3}\ (b+c)/2 \qquad Pa\bar{3}\ (c+a)/2$$

$$2_1 \qquad 2_2 \qquad 2_3 \qquad 2_4$$

$$Pb\bar{3} \qquad Pb\bar{3}\ (c+a)/2 \qquad Pb\bar{3}\ (a+b)/2 \qquad Pb\bar{3}\ (b+c)/2$$
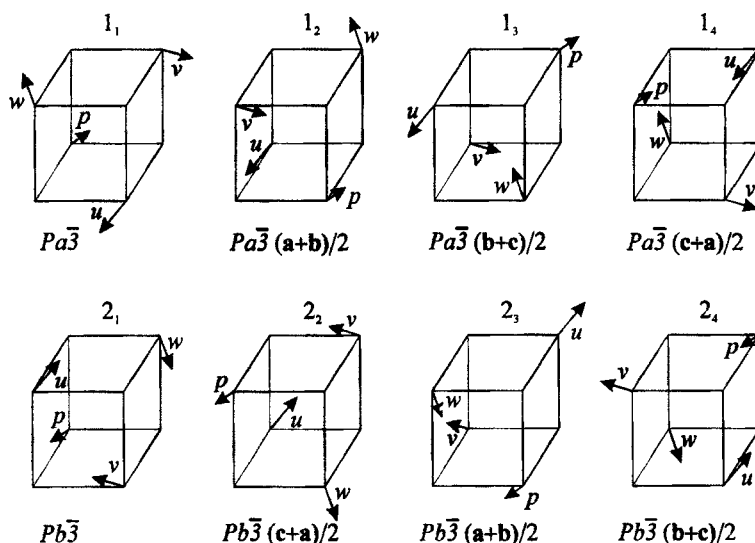
FIGURE 1 The eight domain states of fullerene

The labels 1_1, and 1_2, 1_3, 1_4 are chosen in such a way that the molecule rotated about the cubic axis 3_p is located respectively at the origin P and at points $P + (a + b)/2$, $P + (b + c)/2$, $P + (c + a)/2$. Equivalently, this means that at the origin P are located molecules rotated about 3_p and 3_u, 3_v, 3_w, respectively. The labels 2_1, and 2_2, 2_3, 2_4 are used for corresponding states in which the rotation about

the same axes (which are correlated with subscripts) as in previous cases is executed towards the standard orientation B, so that the angle ϕ is negative. The symmetries of individual states are given in a little table:

$\mathcal{F}(1_1) = Pa\overline{3}$,	$\mathcal{F}(2_1) = Pb\overline{3}$,
$\mathcal{F}(1_2) = Pa\overline{3}\ [(a+b)/2]$,	$\mathcal{F}(2_2) = Pb\overline{3}\ [(a+b)/2]$,
$\mathcal{F}(1_3) = Pa\overline{3}\ [(b+c)/2]$,	$\mathcal{F}(2_3) = Pb\overline{3}\ [(b+c)/2]$,
$\mathcal{F}(1_4) = Pa\overline{3}\ [(c+a)/2]$.	$\mathcal{F}(2_4) = Pb\overline{3}\ [(c+a)/2]$.

The symbol $Pb\overline{3}$ is a nonstandard symbol; we found it in the latest edition of *Vol. A* of the *International Tables for Crystallography* only on the bottom of page 67 in the part by Bertaut: *"Synoptic tables of space group symbols and their use"* without exact specification. The symbol logically denotes another setting of the group of the type T_h^6. In consideration of domain walls it is mandatory to specify the space and layer groups exactly, including their location and orientation in space. In case of the group $Pa\overline{3}$ we take the symmetry diagram from *Vol. A* as the standard location and the shifts behind this symbol denote the shift of the origin so that $Pa\overline{3}\ [(a+b)/2]$ means the group, the symmetry elements of which are located with reference to the origin at $P + [(a+b)/2]$ in the same way as the symmetry elements of the group $Pa\overline{3}$ with reference to the origin P.

It seems that the logical choice for the meaning of the group $Pb\overline{3}$ would correspond to the same diagram rotated by 90°. We choose, however, the standard location of the group $Pb\overline{3}$ in such a way that the three-fold axis 3_p passes again through the origin as in the case of the group $Pa\overline{3}$. The group $Pa\overline{3}$ rotated by 90° (conjugate by 4_z) is then the group $Pb\overline{3}\ [(a+b)/2]$ while $Pb\overline{3}$ is obtained from $Pa\overline{3}$ by reflection through the plane $m_{x\overline{y}}$. The advantage of this choice from the viewpoint of standardization of Hermann-Mauguin symbols is that the systems of nonprimitive translations of the four groups $Pm\overline{3}$, $Pn\overline{3}$, $Pa\overline{3}$, and $Pb\overline{3}$ of the arithmetic class $m\overline{3}P$ constitute a group.

3. SYMMETRY AND CLASSES OF DOMAIN PAIRS

The consideration of intersections $\mathcal{F}_{ij}$ show that there are only two classes of domain pairs in fullerene:

Translational pair: It is seen directly form the symmetry diagram of the group $Pa\overline{3}$ that:

$$\mathcal{F}(1_i, 1_j) = Pbca, \qquad\qquad \mathcal{F}(2_i, 2_j) = Pcab$$

whatever the indices $i \neq j$. The space group $Pbca$ is therefore common for all ordered translational pairs $(1_i, 1_j)$, the space group $Pcab$ is common for all ordered translational pairs $(2_i, 2_j)$.

Rotational pair: The domain states 1_1 and 2_1 are chosen so that their common symmetry would be:

$$\mathcal{F}(1_1, 2_1) = R\overline{3}_p.$$

The symmetry of the (unordered) pair $(1_1, 1_2)$ is obtained if we add the translation

$(\mathbf{a}+\mathbf{b})/2$ to the group *Pbca* which results in the space group *Cmca*. The symmetry of the pair $(1_1, 2_1)$ is obtained if we add the mirror plane $m_{x\bar{y}}$ to the group $\bar{3}_p$ which results in the space group $\bar{3}_p m$. Thus we have to consider only the following two representative cases:

$$\mathcal{J}(1_1, 1_2) = Cmca, \qquad\qquad \mathcal{J}(1_1, 2_1) = R\bar{3}_p m.$$

These are the groups to be scanned to obtain the sectional layer groups used for an analysis of respective domain walls.

4. THE SYMMETRY AND STRUCTURE OF DOMAIN TWINS

The analysis of sections through the two domain pair is performed in the twin paper on the ground of scanning tables for the sectional layer groups. We will choose for illustration the section of orientation (111) in the pair $(1_1, 2_1)$. In fig. 2. are described the positions of molecules for the domain states 1_1 and 2_1 in hexagonal coordinate system whose conventional basis $(\hat{\mathbf{a}}, \hat{\mathbf{b}}, \hat{\mathbf{c}})$ is related to the cubic basis $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ by $\hat{\mathbf{a}} = \mathbf{a} - \mathbf{c}$, $\hat{\mathbf{b}} = \mathbf{b} - \mathbf{a}$, $\mathbf{d} = \hat{\mathbf{c}} = \mathbf{a} + \mathbf{b} + \mathbf{c}$, where the last vector determines the scanning direction. Below we drop the hat, so that $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c} = \mathbf{d}$ are the hexagonal conventional vectors. The points denote the location of molecules and the letters refer to the axes about which the molecule will be rotated in the domain state. The vertices of triangles lie in the plane through the origin, the points inside shaded triangles represent the first layer on the level $\frac{1}{3}\mathbf{d}$, the points inside empty triangles represent the second layer on the level $\frac{2}{3}\mathbf{d}$.
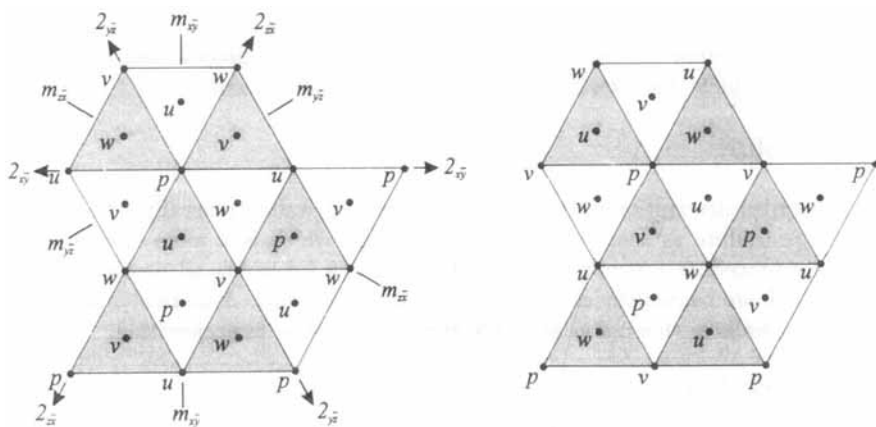

FIGURE 2 Hexagonal view of domain states 1_1 and 2_1.

The group of the pair is $R\bar{3}_p m$ and the sectional layer groups are $p\bar{3}_p m1$ on the level $0\mathbf{d}$, $p\bar{3}_p m1[(\mathbf{a} + 2\mathbf{b})/3]$ on the level $\frac{1}{3}\mathbf{d}$, and $p\bar{3}_p m1[(2\mathbf{a} + \mathbf{b})/3]$ on the level $\frac{2}{3}\mathbf{d}$. The location of layer groups on the two latter levels are exchanged with reference to the scanning table from the twin paper because our figures correspond to the reverse setting while obverse setting of the group $R\bar{3}_p m$ is used in .Vol. A and hence also in scanning tables. On these three levels are located planes of the same translational orbit. The planes of the other orbit with the same respective sectional layer groups

are at levels $\frac{1}{2}$d, $\frac{5}{6}$d, and $\frac{1}{6}$d. The first planes are those in which molecules are located, the second set of planes is not occupied. The *"floating"* [6] layer group is the group $p3_pm1$.

We shall consider the domain wall passing through the origin with domain state 1_1 in the upper space. The molecules corresponding to positions (p, w, v, u) in domain 1_1 must meet the molecules (p, u, w, v) in the central plane of the wall. Molecules in position p meet at the site point symmetry $\bar{3}_pm$ and the rotation ϕ is of opposite sign for the two domains. Hence this angle must be zero for molecules in the central plane. As we go into the domain 1_1, positions p have site point symmetry 3_p and the angle develops from zero to its value in the domain state 1_1. Analogously, as we go into domain 2_1, the angle develops towards the same value in opposite direction.

There exist another two chains of molecules in position p generated by molecules which lie off the central plane, one on a line passing through $P + (a + 2b)/3$, the other on a line passing through $P + (2a + b)/3$. On both these chains the angle ϕ again develops towards its value in the domains beginning from some finite angle.

These chains are repeated periodically with periodicity (a, b) in the plane. Inversion in the centre maps the first set of chains generated by molecules in the central plane onto itself and exchanges the two other sets of chains generated by molecules off the central plane (but still in the wall). The dependence of the angle ϕ on the distance from the central plane is therefore the same for both the latter chains.

Molecules in positions w, v, and u in domain 1_1 meet the molecules in positions u, w, and v of the domain 2_1 and the respective site-point symmetries are $2_{z\bar{x}}/m_{z\bar{x}}$, $2_{y\bar{z}}/m_{y\bar{z}}$, and $2_{x\bar{y}}/m_{x\bar{y}}$. The site point symmetries $2/m$ require that the molecules in central plane are oriented symmetrically with reference to respective planes m. As we go into the domains, the site point symmetries are trivial and the molecules rotate towards their orientations in domain states. A more precise description needs parameters which characterize arbitrary orientation of molecules.

CONCLUSION

A detailed description of the structure of domain wall is generally rather sophisticated procedure as seen from our consideration which is a mere example. The scanning procedure provides a systematic approach by which all geometrical relations which are consequences of symmetry can be revealed. A more complete study of domain walls in this material by the same approach is in preparation.

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