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Geometric Units in Hexagonal and Rhombohedral Space Groups

BY CHUNG CHIEH

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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Abstract

Hexagonal space groups, *i.e.* those with an *hP* lattice, are classified from the geometric-unit viewpoint by considering hexagonal crystal structures as combinations and permutations of some basic hexagonal prisms. Geometric units are the Dirichlet domains of the Wyckoff positions with the highest point-group symmetry in the space group. In this classification, there are six types of hexagonal space groups. Type *h*1 consists of two independent geometric units of the same symmetry per crystallographic cell; in type *h*2, the two units are identical, but differently oriented. Type *h*3 has six independent geometric units, again of the same point-group symmetry, but the six units can be made up of three pairs, each consisting of two identical units, thus giving rise to type *h*4. There are subclasses in types *h*1 and *h*3. Centers of geometric units in *h*1(*a*) and *h*3(*a*) are uniquely defined by intersections of point-group symmetry elements, whereas those in *h*1(*b*) and *h*3(*b*) are not because the space groups in these subtypes are hemimorphic. Therefore, the two units along the polar axis may be combined as one. Type *h*5 consists of three units, each turned 120° from its neighbors owing to the screw axis 3_1, 3_2, 6_2 and 6_4. Similarly, type *h*6 has six units due to screw axes 6_1 and 6_5, and adjacent units are 60° apart. Rhombohedral space groups show two types of patterns: type *r*1 has two independent, and type *r*2 two identical, units. The h.c.p. and related structures are used to demonstrate the application of geometric units to crystal-structure descriptions.

Introduction

A recurring problem in finding a model for the solution of a crystal structure and its interpretation is to identify some convenient units that, by easy symmetry operations, will enable the construction of the entire structure. In this respect, asymmetric units, topological units (Wells, 1977), crystal chemical units, symmetry-related units (Kennard, Speakman & Donnay, 1967), building units (Lima-de-Faria & Figueiredo, 1976) and crystallographic cells have been used. For cubic crystal structures, Chieh (1979) suggested geometric units based on the construction of polyhedra, a proposal which differs from the previous ones in that it deals mainly with the symmetrical distribution of the atoms in the structure, rather than their connectivity or framework. The classification and description of cubic space groups in terms of geometric units were later given by Chieh, Burzlaff & Zimmermann (1982). The concept of geometric units was extended to tetragonal space groups by Chieh (1983), and some advantages were pointed out.

Applications of geometric units to cubic crystal structures have been given in previous publications (Chieh, 1980, 1982, 1983). Their application to the solution of a crystal structure and its subsequent interpretation was exemplified by the paper on anhydrous zinc bromide (Chieh & White, 1984). The present paper deals with the hexagonal and rhombohedral space groups.

Early work on the classification of cubic space groups by geometric units was somewhat intuitive. As more work on the theoretical aspects of space groups developed (see Gubler, 1982; Fischer & Koch, 1983; Burzlaff & Zimmermann, 1980) it became apparent that the classification follows the results of Euclidean normalizers of space groups. The purpose of geometric units is to divide a crystal structure into polyhedral units that have the same shape, volume and point-group symmetry.

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Dirichlet domains in hexagonal and rhombohedral lattices

All hexagonal lattices are primitive *hP*, but when hexagonal coordinate axes are used for a rhombohedral lattice, the cell *hR* contains three lattice points. If the rhombohedral coordinates are used, the cell is primitive *rP*. In terms of geometric units, the rhombohedral lattice is different from the hexagonal one.

In a rhombohedral lattice the Dirichlet (1850) domains, which are sometimes referred to as Wigner–Seitz (1933) cells, have two shapes depending on the rhombohedral angle α, if we ignore the special cases of $\alpha = 60$ and 90°. Since geometric units are derived from the Dirichlet domains of Wyckoff sites of the highest symmetry in a space group, we shall explain the variation in shape of the Dirichlet polyhedron as the angle α varies. In the special case of $\alpha = 60°$, the 'rhombohedral' lattice is metrically a cubic *F* lattice. Therefore the Dirichlet domain has the shape of a rhombic dodecahedron. This well known polyhedron, which was mentioned by Chieh (1983), is also related to a special case of a tetragonal lattice. For $60 < \alpha < 90°$, the rhombic dodecahedron deforms along one of the threefold axes, as shown in Fig. 1(*a*). For $\alpha = 90°$, the lattice is pseudo-cubic *P* and metrically the Dirichlet domain is a cube. For $\alpha > 90°$, the neighbor along the [111] axis becomes nearest, and the planes between the lattice points in this direction will take part in shaping the Dirichlet domain, as shown in Fig. 1(*b*). This polyhedron can be derived from the truncated octahedron by compressing it along a threefold axis. At the other extreme, for $\alpha = 120°$, the lattice is a hexagonal net. The Dirichlet domain for a hexagonal lattice is a hexagonal prism as shown in Fig. 1(*c*).

Geometric units in hexagonal and rhombohedral space groups

The translations of any rhombohedral space group generate a site 1/2, 1/2, 1/2 (the body center of the *rP* cell), which has the same point-group symmetry as the origin. The same groups, referred to the *hR* cell, generate a site 0, 0, 1/2, which has the same symmetry as in the corresponding hexagonal space groups. Since there is no unique point in polar groups, an equivalent origin of this type does not stand out, but it is there. In space groups such as *P*312, $P\bar{6}$, $P\bar{6}m2$ *etc.*, sites 1/3, 2/3, 0 and 2/3, 1/3, 0 also have the same point-group symmetry as the origin, and these sites, together with those halfway along **c**, are very special Wyckoff positions whose Dirichlet domains may serve as convenient geometric units.

The geometric units for hexagonal and rhombohedral space groups bear certain similarity to those of the tetragonal system. The analysis of the hexagonal space groups results in five categories (*a*, *b*, *c*, *d* and *e* in Fig. 2). For the (*a*) category, the Dirichlet domain of the hexagonal lattice is divided into two geometric units by a plane half way in the [001] direction. The units for the (*c*) category are similar to those of (*a*), but they have 1/3 of the volume of the Dirichlet domain of the lattice, and units in the (*d*) category have 1/6 of the volume (shortened along the *c* direction). Units in the (*b*) category have 1/6 of the volume of the cell, as their area in the *ab* plane is 1/3 of the mesh (Fig. 3) in addition to the division of *c* by 2. In all categories, the overall shape of the geometric units remains as a hexagonal prism. In the rhombohe-

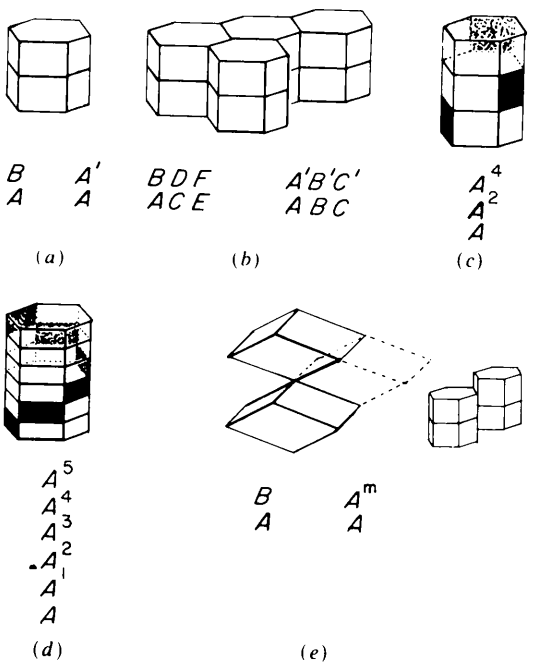

Fig. 2. Geometric units and packing patterns for hexagonal space groups (*a*, *b*, *c* and *d*) and rhombohedral space groups (*e*).

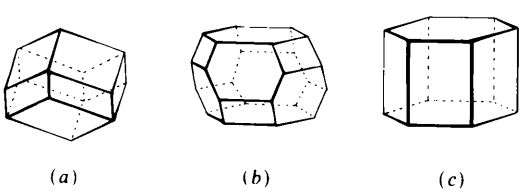

Fig. 1. Dirichlet domains for (*a*) a rhombohedral lattice with $\alpha < 90°$, (*b*) a rhombohedral lattice with $\alpha > 90°$, and (*c*) a hexagonal lattice.

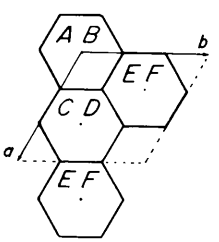

Fig. 3. Relationship between geometric unit in category (*b*) and crystallographic cell.

Table 1. *Classification of hexagonal space groups by packing pattern of geometric units*

Type, no. of pattern unit, orientation		Space-group number Space-group symbol Wyckoff positions as geometric unit center, site symmetry							
*h*1(*a*)	*B*	147	150	162	164	175	177	189	191
	A	*P*3	*P*321	$P\bar{3}1m$	$P\bar{3}m1$	*P*6/*m*	*P*622	$P\bar{6}2m$	*P*6/*mmm*
	A:	1(*a*) $\bar{3}$..	1(*a*) 32.	1(*a*) $\bar{3}$.*m*	1(*a*) $\bar{3}m$.	1(*a*) 6/*m*..	1(*a*) 622	1(*a*)$\bar{6}2m$	1(*a*) 6/*mmm*
	A:	1(*b*) $\bar{3}$..	1(*b*) 32.	1(*b*) $\bar{3}$.*m*	1(*b*) $\bar{3}m$.	1(*b*) 6/*m*..	1(*b*) 622	1(*b*)$\bar{6}2m$	6/*mmm*
*h*1(*b*)		157				168	183		
		*P*31*m*				*P*6	*P*6*mm*		
	AB:	1(*a*) 3.*m*				1(*a*) 6..	1(*a*) 6*mm*		
*h*2	*A*′	159	163	165		173	176	182	184
	A	*P*31*c*	$P\bar{3}1c$	$P\bar{3}c1$		$P6_3$	$P6_3/m$	$P6_322$	*P*6*cc*
	A:	2(*a*) 3..	2(*b*) $\bar{3}$..	2(*b*) $\bar{3}$..		2(*a*) 3..	2(*b*) $\bar{3}$..	2(*a*) 32.	2(*a*) 6..
	′:	*m**	*m**	*m*		6	6	6	*m*
						185	186	190	192
						$P6_3cm$	$P6_3mc$	$P\bar{6}2c$	*P*6/*mcc*
	A:					2(*a*) 3.*m*	2(*a*) 3*m*.	2(*a*) 32.	2(*b*) 6/*m*..
	′:					6	6	*m**	*m*
						193	194		
						$P6_3/mcm$	$P6_3/mmc$		
	A:					2(*b*) $\bar{3}$.*m*	2(*a*) $\bar{3}m$.		
	′:					6	6		
*h*3(*a*)	*BDF*	149				174	187		
	ACE	*P*312				$P\bar{6}$	$P\bar{6}m2$		
	A:	1(*a*) 3.2				1(*a*) $\bar{6}$..	1(*a*) $\bar{6}m2$		
	B:	1(*b*) 3.2				1(*b*) $\bar{6}$..	1(*b*) $\bar{6}m2$		
	C:	1(*c*) 3.2				1(*c*) $\bar{6}$..	1(*c*) $\bar{6}m2$		
	D:	1(*d*) 3.2				1(*d*) $\bar{6}$..	1(*d*) $\bar{6}m2$		
	E:	1(*e*) 3.2				1(*e*) $\bar{6}$..	1(*e*) $\bar{6}m2$		
	F:	1(*f*) 3.2				1(*f*) $\bar{6}$..	1(*f*) $\bar{6}m2$		
*h*3(*b*)		143	156						
		*P*3	*P*3*m*1						
	AB:	1(*a*) 3..	1(*a*) 3*m*.						
	CD:	1(*b*) 3..	1(*b*) 3*m*.						
	EF:	1(*c*) 3..	1(*c*) 3*m*.						
*h*4	*A*′*B*′*C*′	158				188			
	A B C	*P*3*c*1				$P\bar{6}c2$			
	A:	2(*a*) 3..				2(*a*) 3.2	or 2(*b*) $\bar{6}$..		
	B:	2(*b*) 3..				2(*c*) 3.2	2(*d*) $\bar{6}$..		
	C:	2(*c*) 3..				2(*e*) 3.2	2(*f*) $\bar{6}$..		
	′:	*m**				*m**			
*h*5	A^4	144	145	151	152	171	172	180	181
	A^2	$P3_1$	$P3_2$	$P3_112$	$P3_121$	$P6_2$	$P6_4$	$P6_222$	$P6_422$
	A *A*:	3(*a*) 1	3(*a*) 1	3(*a*)..2	3(*a*) .2.	3(*a*) 2..	3(*a*) 2..	3(*a*) 222	3(*a*)222
		153	154						
		$P3_212$	$P3_221$						
	A:	3(*a*) ..2	3(*a*) .2.						
*h*6	A^5					169	170	178	179
	A^4					$P6_1$	$P6_5$	$P6_122$	$P6_522$
	A^3 *A*:					6(*a*) 1	6(*a*) 1	6(*a*) .2.	6(*a*) .2.
	A^2								
	A^1								
	A								

Orientation notations 6, *m*, *m** represent six-fold rotation axis, mirror perpendicular to **a** and mirror perpendicular to **a***, respectively. In that order, the first one will be given in cases where all three or any two are present. Superscript to pattern letter *A*, in types *h*5 and *h*6, refers to number of 60° rotations.

dral case (Fig. 2*e*), the units generally have the shape of a dodecahedron or distorted truncated octahedron, but in the special case where $\alpha = 90°$, the units are metric cubes. The units shown in the figure are cubes for clarity, but the packing is perhaps easier to understand if we use the hexagonal prisms in a staggered arrangement (shown in the inset). The transformation of shapes has been discussed in connection with the geometric units in the tetragonal system (Chieh, 1983). All categories, except (*c*) and (*d*), have two types.

Classification of hexagonal and rhombohedral space groups by geometric units

In the classification of hexagonal and rhombohedral space groups (Tables 1 and 2), the symbols of *International Tables for Crystallography* (1983) are used. The method of classification is similar to that applied to tetragonal space groups (Chieh, 1983).

Like the tetragonal system, there are hemimorphic hexagonal space groups for which the origins are not uniquely defined because there are no symmetry axes

Table 2. *Geometric units in rhombohedral space groups*

Type, no. of pattern unit, orientation			Space-group number Space-group symbol Wyckoff positions as geometric unit center, site symmetry		
*r*1	*B*		148	155	166
	A		$R\bar{3}$	*R*32	$R\bar{3}m$
		A:	1(*a*) $\bar{3}$.	1(*a*) 32	1(*a*) $\bar{3}m$
		B:	1(*b*) $\bar{3}$.	1(*b*) 32	1(*b*) $\bar{3}m$
*r*1(*b*)			146	160	
			*R*3	*R*3*m*	
		AB:	1(*a*) 3.	1(*a*) 3*m*	
*r*2	*A*′		161	167	
	A		*R*3*c*	$R\bar{3}c$	
		A:	2(*a*) 3.	2(*b*) $\bar{3}$	
		′:	*m**	6	

See note in Table 1 for meaning of symbols.

intersecting at any point. The two units that could have been used for space groups that have a unique point as their origin may be combined along the [001] direction, and be considered as a single unit. These space groups are placed in subtypes *h*1(*b*) and *h*3(*b*) (Table 1).

When units *A* and *B* are combined, they actually form a one-unit period in the [001] direction. For hexagonal space groups, the axes 6, 6_1 (6_5), 6_2 (6_4) and 6_3 give rise to the possibility of having one, six, three and two geometric units, respectively, in one [001] period. Type *h*5 has the sequence AA^2A^4 (^{2} and ^{4} refer to 6^2 and 6^4 operations), and all space groups in this type contain one of the screw axes 3_1, 3_2, 6_2, 6_4. Space groups $P6_1$, $P6_5$, $P6_122$ and $P6_522$ are classified under type *h*6, with six geometric units per cell, in a manner similar to that of type *h*5. The point-group symmetries of the geometric units are 1 or .2. When the geometric unit has symmetry 1, it is also the asymmetric unit. Symmetry in the geometric unit reduces the volume of the asymmetric unit to 1/2, 1/3, 1/6 or 1/12 that of the geometric unit.

There are two independent units *A* and *B* for types *h*1(*a*) and *h*3(*a*) stacked in the [001] direction, whereas both units for space groups in types *h*2 and *h*4 are the same. They are differently oriented, and thus the representations such as *A* and *A*′ are used. The prime indicates one of the following symmetry operations: repeated 60° rotations ($' = 6^{1,2,\ldots,5}$), reflection in a mirror perpendicular to *a* ($' = m$), and reflection in a mirror perpendicular to *a** ($' = m^*$).

Discussion

A geometric unit in a crystal structure is a building block possessing point-group symmetry of the Wyckoff site which serves as its center. Such units in crystal structures usually consist of simple easily recognizable polyhedral arrangements of atoms, molecules or ions. There are common arrangements of these units for crystals of many space groups (see Table 1 for examples). Thus the analysis of geometric units for the abstract space groups is of fundamental importance for the study of relationships between crystal structures, especially in the aspect of symmetrical distribution of atoms. For ease of application, adjacent units may be divided in such a way that they have bumps and craters fitting into each other, but the overall arrangement of the units remains the same.

The classification, in which most geometric units have non-trivial crystallographic point-group symmetry, shows that the description of space groups by geometric units is applicable not only to symmorphic groups (*i.e.* those generated by combining point groups with Bravais lattices), but also to nonsymmorphic groups. In retrospect, had a type with four units in the [001] direction period been added to the classification of tetragonal space groups (Chieh, 1983), no geometric units in that system would have sections of screw axes 4_1 or 4_3.

If oriented symbols such as 3*m*. and 3.*m* are used to differentiate symmetry directions, the descriptions using geometric-unit patterns for the space groups are unique, and there is a one-to-one correspondence between the descriptions and the space groups. The symbols used in this paper are those given by Donnay & Turrell (1974). They have been adopted by *International Tables for Crystallography* (1983). Enantiomorphic space groups with 6_1, 6_2 *etc.* are distinguished by the handed screws, these must be employed in order to distinguish their stacking patterns. Although symbols such as 6^{-1} and 6^1 could have been employed, no effort has been made to distinguish them at this point in time.

Although the classification of space groups by geometric units follows the principle of Cheshire groups (Hirshfeld, 1968; Fischer & Koch, 1983), there is a minor difference in that the latter deals with only the symmetry elements whereas the former includes the metric geometric properties. Let us make a few comparisons between the classification of space groups by geometric units and that by Cheshire groups. In simple terms, the Cheshire group is the symmetry group of the symmetry elements of the space group. Two independent sites, such as 1(*a*) 0, 0, 0 and 1(*b*) 0, 0, 1/2 in *P*6/*m*, are not equivalent from a geometry viewpoint but are equivalent from the symmetry viewpoint; both have point-group symmetry 6/*m*. Similarly, equivalent sites 2(*b*) 0, 0; 0, 0, 0, 1/2 in $P6_3/m$ have the same symmetry 3, the symmetry elements are similarly oriented, although not the geometric units. These two space groups thus have the same Cheshire group *P*6/*mmm*, with a cell reduced to $a \times b \times (1/2)c$. Yet, they are classified under types *h*1 and *h*2 in Table 1.

The Cheshire groups of space groups with polar axes such as 3, 4, 6 and 6*mm* are continuous groups with *Z*-type lattices. Thus *P*6 and $P6_3$ have the same

Cheshire group $Z^{1}6/mmm$, but they are classified in types $h1(b)$ and $h2$, respectively. The combined (AB) geometric unit for $P6$ (Table 1) belongs to point group 6.., but the geometric unit in $P6_3$ belongs to point group 3. Here is a case where two space groups belonging to the same Cheshire group are placed in different types when classified by geometric unit owing to the fact that translation $c/2$ is not equivalent in $P6$ to what it is in $P6_3$. Note, however, that the geometric units in $P6_3$, contrary to those in $P6_3/m$, have no unique points to define their centers, and these two space groups, although belonging to different Cheshire groups, are placed in the same type in the present treatment.

Geometric units are particularly useful for the description of complicated structures such as those cubic ones given by Chieh (1980, 1982). Atoms belonging to the same Wyckoff positions form concentric polyhedra around the center of the geometric unit. These polyhedra are listed in ascending order of the distances of the atoms from the center. The number of vertices of a polyhedron is given as a subscript to the chemical symbol of the element occupying those vertices. Atoms on the surfaces, edges of vertices of the geometric unit are shared by neighboring units; the number of units sharing an atom is given as a divisor of that subscript. For example, $E_{6/6}$ represents a polyhedron with six vertices, in which each atom is shared by six units.

The h.c.p. and related structures are not complicated but their descriptions by geometric units may serve as examples illustrating the method. These structures (Pearson symbol $hP2$) belong to space group $P6_3/mmc$, which is in type $h2$ (Table 1). A [001] period of these structures consists of two identical units rotated 60° apart. This space group has four Wyckoff positions of multiplicity 2: $2(a)$ $\bar{3}m.$, $2(b)\bar{6}m2$, $2(c)$ $\bar{6}m2$ and $2(d)$ $\bar{6}m2$. Obviously, the symmetry of the environment of atoms is not $3m.$ but $\bar{6}m2$. The origin chosen in *International Tables for Crystallography* is on an (a) site, with symmetry $\bar{3}m.$, which is the octahedral 'hole' of the closest packed spheres. In this choice, the geometric units, represented for example by $Mg_{6/6}$, are the shared octahedra whose vertices are occupied by atoms, and units A and A' share a face to give the proper orientation. If one chooses $2(b)$ as the geometric unit centers, the units would consist of shared equilateral triangles. In this case, the unit should be represented by $Mg_{3/3}$. Unlike $2(a)$ and $2(b)$, one $2(c)$ site is above one $2(d)$ site, the other $2(c)$ site is below a $2(d)$ site (**c** vector pointing up). Therefore, they are not suitable centers for geometric units. Either $2(c)$ or $2(d)$ are possible sites for atoms when a center of $\bar{3}m.$ is chosen as the origin. The reason why they are not suitable for geometric unit centers can also be seen from the fact that atoms are not directly one above each other, whereas the centers of the triangles and those of octahedral 'holes' are.

Both Wyckoff positions $2(a)$ and $2(b)$ of space groups $p31c$, $P6_3$ and $P6_3mc$ appear to have the same (but unequivalent) site symmetry. For reasons as given previously for the h.c.p. structures, only sites $2(a)$ are suitable for geometric unit centers in the present scheme of classification.

The NiAs ($hP4$) structure is derived from the h.c.p. structure, but only Ni atoms are located at $\bar{3}m.$ symmetry centers. For simplicity the location of Ni is used as the origin; using the notation described above, we may represent the geometric unit by $NiAs_{6/6}$. As examples for geometric units consisting of three and four atoms $B_{12/6}Re_{6/6}$ and $CCr_{12/6}Al_{6/6}$ are used for B_2Re ($hP6$) and $AlCCr_2$ ($hP8$), respectively. Knowing the point-group symmetry to be $\bar{3}m.$, it is easy to construct such a geometric unit without having to use coordinates. Thus the geometric unit concept may be used to simplify the notation of structural data.

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