Table 9.7.1.2. *Space groups arranged by arithmetic crystal class and degree of symmorphism (cont.)*

(*b*) Tetragonal space groups. For *, † see Subsection 9.7.4.1.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Fully antimorphic
$4P$	$*P4^{(0)}$	$P4_2^{(1)}$	...	...	$P4_{1,3}\dagger^{(40)}$
$4I$	...	...	$I4_1\dagger^{(3)}$	$*I4^{(3)}$	...
$\bar{4}P$	$*P\bar{4}\dagger^{(0)}$	...	...	...	...
$\bar{4}I$	...	...	$*I\bar{4}\dagger^{(7)}$	...	...
$4/mP$	$*P4/m^{(0)}$	$P4_2/m^{(0)}\ P4/n^{(1)}$	$P4_2/n\dagger^{(20)}$	...	...
$4/mI$	...	...	...	$*I4/m^{(0)}\ I4_1/a\dagger^{(29)}$	...
$422P$	...	$*P422^{(0)}$	$P42_12^{(0)}$	$P4_{1,3}2_12\dagger^{(49)}$	...
		$P4_222^{(0)}$	$P4_{1,3}22^{(1)}$	$P4_22_12^{(1)}$	
$422I$	...	...	$I4_122\dagger^{(0)}$	$*I422^{(0)}$	...
$4mmP$	...	$*P4mm^{(0)}$	$P4bm^{(0)}$	$P4_2cm^{(0)}$	...
				$P4_2nm^{(0)}$	
				$P4cc^{(0)}$	
				$P4nc^{(0)}$	
				$P4_2mc^{(0)}$	
				$P4_2bc\dagger^{(1)}$	
$4mmI$	...	...	...	$*I4mm^{(0)}$	...
				$I4cm^{(0)}$	
				$I4_1md^{(0)}$	
				$I4_1cd\dagger^{(5)}$	
$\bar{4}2mP$	...	$*P\bar{4}2m^{(0)}$	$P\bar{4}2c^{(0)}$	$P\bar{4}2_1c\dagger^{(12)}$	...
			$P\bar{4}2_1m^{(0)}$		
$\bar{4}m2P$	...	$*P\bar{4}m2^{(0)}$	$P\bar{4}c2^{(0)}$	...	...
			$P\bar{4}b2^{(0)}$		
			$P\bar{4}n2^{(0)}$		
$\bar{4}m2I$	...	...	$*I\bar{4}m2^{(0)}$	$I\bar{4}c2\dagger^{(0)}$	...
$\bar{4}2mI$	...	...	$*I\bar{4}2m^{(0)}$	$I\bar{4}2d\dagger^{(0)}$	...
$4/mmmP$	...	$*P4/mmm^{(0)}$	$P4/mcc^{(0)}$	$P4/nbm^{(0)}$	...
		$P4_2/mmc^{(0)}$	$P4/nmm^{(0)}$	$P4/nnc^{(0)}$	
		$P4_2/mcm^{(0)}$		$P4/mbm^{(0)}$	
				$P4/mnc^{(0)}$	
				$P4/ncc^{(0)}$	
				$P4_2/nbc^{(0)}$	
				$P4_2/nnm^{(0)}$	
				$P4_2/mbc^{(0)}$	
				$P4_2/mnm^{(0)}$	
				$P4_2/nmc^{(0)}$	
				$P4_2/ncm^{(0)}$	
$4/mmmI$	...	$*I4/mmm^{(0)}$	...	$I4/mcm^{(0)}$	
				$I4_1/amd^{(0)}$	
				$I4_1/acd\dagger^{(0)}$	

empirical frequencies – it would be expected that there should be considerable correlation between them. All 'closest-packed' space groups are also 'fully antimorphic', and most of the 'limitingly close packed' and 'permissible' are 'tending to antimorphism'; a few requiring high molecular symmetry (222, *mm*2, *mmm*) and a couple of others are 'equally balanced'. Two 'fully antimorphic' groups, *Pc* and *Cc*, are merely 'permissible'. All 'fully symmorphic' space groups are 'impossible'.

9.7.1.4. *Relation to structural classes*

Structural classes (Belsky & Zorky, 1977, and papers cited there and below) are not an *a priori* classification of space groups but are a classification of structures within a space-group type in accordance with the number and kind of Wyckoff positions occupied by the molecules. As a considerable knowledge of the structures is required before their structural classes can be assigned, they form an *a posteriori* classification, and will be described (Section 9.7.5 below) after the empirical frequencies of space groups have been discussed.

9.7.2. Special positions of given symmetry

As noted by Kitajgorodskij, in many crystal structures molecules with inherent symmetry may occupy Wyckoff special positions, so that molecular and crystallographic symmetry elements coincide, and this may affect the relative frequencies of occurrence of structures with particular space groups. Tables of the frequency of occurrence of space groups have been published by many authors, from Nowacki (1942) onwards. Some typical recent papers are Brock & Dunitz (1994), Donohue (1985), Mighell, Himes & Rodgers (1983), Padmaya, Ramakumar & Viswamitra (1990), Wilson (1988, 1990,

Table 9.7.1.2. *Space groups arranged by arithmetic crystal class and degree of symmorphism (cont.)*

(*c*) Trigonal space groups. For *, † see Subsection 9.7.4.1.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Fully antimorphic
$3P$	$*P3^{(0)}$	...	...	...	$P3_{1,2}\dagger^{(33)}$
$3R$	...	...	...	$*R3\dagger^{(11)}$	...
$\bar{3}P$	$*P\bar{3}\dagger^{(1)}$	...	...	...	...
$\bar{3}R$	...	...	...	$*R\bar{3}\dagger^{(30)}$	...
$312P$ $321P$	...	$*P312^{(0)}$ $*P321^{(0)}$	...	$P3_{1,2}12\dagger^{(0)}$ $P3_{1,2}21\dagger^{(10)}$	...
$32R$	...	...	...	$*R32\dagger^{(0)}$	...
$3m1P$ $31mP$	...	$*P3m1^{(0)}$ $*P31m^{(0)}$	...	$P3c1\dagger^{(0)}$ $P31c\dagger^{(0)}$	...
$3mR$	...	...	...	$*R3m^{(0)}$ $R3c\dagger^{(7)}$	...
$\bar{3}m1P$ $\bar{3}1mP$	...	$*P\bar{3}m1^{(0)}$ $*P\bar{3}1m^{(0)}$	...	$P\bar{3}c1\dagger^{(0)}$ $P\bar{3}1c\dagger^{(0)}$	...
$\bar{3}mR$	...	...	...	$*R\bar{3}m^{(0)}$ $R\bar{3}c\dagger^{(0)}$	...

(*d*) Hexagonal space groups. For *, † see Subsection 9.7.4.1.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Fully antimorphic
$6P$	$*P6^{(0)}$	...	$P6_{2,4}^{(1)}$ $P6_3^{(0)}$	...	$P6_{1,5}\dagger^{(22)}$
$\bar{6}P$	$*P\bar{6}\dagger^{(0)}$	...	...	...	...
$6/mP$	$*P6/m^{(0)}$	...	$P6_3/m\dagger^{(0)}$	...	...
$622P$	...	$*P622^{(0)}$ $P6_{2,4}22^{(0)}$	...	$P6_322^{(1)}$ $P6_{1,5}22\dagger^{(2)}$	...
$6mmP$	...	$*P6mm^{(0)}$	...	$P6cc^{(0)}$	...
				$P6_3cm^{(0)}$ $P6_3mc^{(0)}$	
$\bar{6}m2P$ $\bar{6}2mP$	...	$*P\bar{6}m2^{(0)}$ $*P\bar{6}2m^{(0)}$	...	$P\bar{6}c2\dagger^{(0)}$ $P\bar{6}2c\dagger^{(0)}$	
$6/mmmP$	...	$*P6/mmm^{(0)}$	...	$P6/mcc\dagger^{(0)}$	...
				$P6_3/mcm^{(0)}$ $P6_3/mmc^{(0)}$	

(*e*) Cubic space groups. For *, †, see Subsection 9.7.4.1. No examples with one molecule in general position were found, so the frequencies are omitted.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Antimorphic except for 3
$23P$	...	$*P23$	...	...	$P2_13\dagger$
$23F$	...	...	$*F23\dagger$	...	...
$23I$	...	...	$*I23$ $I2_13\dagger$	...	...
$m\bar{3}P$	...	$*Pm\bar{3}$	$Pn\bar{3}$	...	$Pa\bar{3}\dagger$
$m\bar{3}F$	...	...	$*Fm\bar{3}$	$Fd\bar{3}\dagger$	...
$m\bar{3}I$	...	...	$*Im\bar{3}$	$Ia\bar{3}\dagger$	...
$432P$	...	$*P432$	...	$P4_232\dagger$ $P4_{1,3}32\dagger$	...
$432F$	...	...	$*F432$	$F4_132\dagger$	...
$432I$	...	...	$*I432$	$I4_132\dagger$	...
$\bar{4}3mP$	...	$*P\bar{4}3m$	...	$P\bar{4}3n\dagger$	...
$\bar{4}3mF$	...	...	$*F\bar{4}3m$	$F\bar{4}3c\dagger$	...
$\bar{4}3mI$	...	...	$*I\bar{4}3m$	$I\bar{4}3d\dagger$	...
$m\bar{3}mP$	...	$*Pm\bar{3}m$	$Pm\bar{3}n$ $Pn\bar{3}m$	$Pn\bar{3}\dagger$	...
$m\bar{3}mF$	...	$*Fm\bar{3}m$	...	$Fm\bar{3}c$ $Fd\bar{3}m$	$Fd\bar{3}c\dagger$
$m\bar{3}mI$	...	$*Im\bar{3}m$	...	$Ia\bar{3}d\dagger$	...

1993*b*,*c*), but many of them hardly go beyond recognizing the fact that structures frequently made use of molecular symmetry – Wilson (1988) explicitly chose to ignore it. The early work of Belsky, Zorky and their colleagues did not attract much attention outside Russian-speaking areas. Recently, however, there has been a spate of interest (Wilson, 1991, 1993*b*,*c*,*d*; Brock & Dunitz, 1994; Belsky, Zorkaya & Zorky, 1995). Earlier lack of results is partly due to the fact that the Cambridge Structural Database (Section 9.7.3) did not provide a search program that would distinguish between occupation of a general position and multiple occupation of special positions of the required symmetry (Wilson, 1993*d*, Section 3). Belsky, Zorkaya & Zorky (1995) were able to make this distinction, and their paper is the source of many of the statistics quoted without special citation here.

It would be interesting to know which space groups possess positions with the symmetry of each of the 32 point groups 1, $\bar{1}$, 2, m, $2/m$, ..., $m\bar{3}m$. Volume A of *International Tables for Crystallography* (Hahn, 1995) enumerates the symmetry of all the special positions of a given space group, but does not readily

answer the reverse question: which space groups contain special positions of given point group $\mathcal{G}$? Some general points may be noted.

(i) Special positions of symmetry $\mathcal{G}$ will be found in the symmorphic, but not other, space groups of the geometric class $\mathcal{G}$. Thus, for example, there are special positions of symmetry *mmm* in *Pmmm*, *Cmmm*, *Fmmm*, *Immm*, but not in any other space group in the geometric class *mmm*.

(ii) A 'family tree' of point groups is given in Fig. 10.3.2 of Volume A of *International Tables for Crystallography* (Hahn, 1995). Special positions of symmetry $\mathcal{G}$ may be sought in space groups of the geometric classes linked to $\mathcal{G}$ by a line (possibly zigzag) having a generally upwards direction. Thus, to take the same example, special positions of symmetry *mmm* are found in certain space groups of $4/mmm$ ($P4/mmm$, $P4/mbm$, $4_2/mmc$, $P4_2/mcm$, $P4_2/mmm$, $I4/mmm$, $I4/mcm$), in $\bar{6}/mmm$ ($P6/mmm$), in $m\bar{3}$ ($Pm\bar{3}$, $Im\bar{3}$), and in $m\bar{3}m$ ($Pm\bar{3}m$, $Fm\bar{3}m$).

(iii) Obviously, the higher up the tree the symmetry $\mathcal{G}$ is, the fewer will be the space groups in which it can occur – special positions of symmetry $m\bar{3}m$ can occur only in the three symmorphic space groups of the corresponding geometric class. The lower symmetries (2, m, $\bar{1}$, $\bar{3}$), with nothing below them but 1, can be traced upwards along many branches, and so can occur in many space groups, but not all are equally favoured. Special positions of symmetry 2 can be sought in all higher geometric classes except $\bar{6}$, $3m$, and $\bar{3}$, but those of symmetry 3 could occur only in the classes of the trigonal, hexagonal, and cubic systems. An approximate count* (Table 9.7.2.1) shows that special positions of symmetry 2 occur in 167 space groups, of m in 99, of $\bar{1}$ in 38, and of 3 in 57. The only other special positions with space-group frequencies of this order are $2/m$ (39), 222 (30), and *mm* (57).

9.7.3. Empirical space-group frequencies

Empirical space-group frequencies are based on two major collections of structural data for organic substances, in Cambridge and Moscow, respectively.

The Cambridge Structural Database (Allen *et al.*, 1991) contains assignments of space groups for a variety of different types of organic compounds. The file can be computer searched in many ways; it is easy, for example, to trace all structures having a particular space group, or those having a particular space group and a particular number of formula units per unit cell. For the present purpose, a selection has to be made, omitting space groups not substantiated by a full structure determination or dubious because of disorder in the crystal. The packing considerations discussed in previous paragraphs would not apply to crystals in which the intermolecular binding was ionic rather than van der Waals or the like, so that space groups of ionic structures (for example salts of organic acids) are also rejected. Unfortunately, as it is implemented at present (early 1995), it is not possible to search for structures with molecules occupying general positions or specified special positions, so that, in particular, the frequency data of Wilson (1993*d*) are inflated by the inability to distinguish between single occupation of a general position and multiple occupation of special positions.

The file compiled by V. A. Belsky at the L. Ya. Karpov Institute of Physical Chemistry in Moscow is the source of the data used by Belsky, Zorkaya & Zorky (1995). This file differs in objective from the Cambridge file; the latter includes all reasonably established organic structures short of proteins and high polymers, whereas the former concentrates on structures containing only a single type of molecule ('homomolecular structures'). It thus contains appreciably fewer entries than the Cambridge file, even if structures of the types mentioned in the previous paragraph are excluded from the latter. The Moscow file is, of course, the primary source for the data of Belsky, Zorkaya & Zorky (1995), in which the occupation of general and special positions is explicitly presented.

9.7.4. Use of molecular symmetry

It has long been recognized that in many crystal structures molecules with inherent symmetry occupy Wyckoff special positions, so that molecular and crystallographic symmetry elements coincide, but until recently systematic data have been lacking. Now the occurrence of molecules of particular symmetry in structures of various space-group types can be traced in the data of Belsky, Zorkaya & Zorky (1995), and will be discussed briefly.

9.7.4.1. *Positions with symmetry 1*

The empirical results for 'homomolecular structures' with one molecule in the general position are given in Table 9.7.1.2. The classification by arithmetic crystal class and degree of symmorphism follows Wilson (1993*d*); the numerical data are taken from Belsky, Zorkaya & Zorky (1995). Space groups symmorphic in the technical sense (Wilson, 1993*d*) are prefixed by an asterisk (∗), and in each arithmetic crystal class the space group most nearly antimorphic is followed by an obelus (†). The number of known structures having precisely one molecule in the general Wyckoff position is given as a superscript in brackets. It will be noticed immediately that structures with space groups 'fully symmorphic' or 'tending to symmorphism' are extremely rare. Most have no examples; three ($P4_2$, $P4/n$ and $P\bar{3}$) are credited with a single example each. The frequency of space groups increases rapidly with increasing antimorphism. In the monoclinic system, the 'fully symmorphic' space group $P2/m$ has no examples with one molecule in the general position, the 'equally balanced' $P2/c$ has 11 examples, the 'tending to antimorphism' $C2/c$ has 587, and the 'fully antimorphic' $P2_1/c$ has 5951. Other systems have fewer examples, but the trend is the same; the really popular space groups are the 'fully antimorphic' plus $P1$ and $P\bar{1}$.

All space groups, of course, possess general positions of symmetry 1, and the data in Table 9.7.2.1 show that 116 of them exhibit structures of some kind, and that 57 exhibit structures in which one or more general positions are used. 13 space groups ($P1$, $P2_1$, Pc, Cc, $P2_12_12_1$, $Pca2_1$, $Pna2_1$, $P4_{1,3}$, $P3_{1,2}$, $P6_{1,5}$) have no positions with symmetry higher than 1. These space groups contain no syntropic symmetry elements, and all are relatively popular.

9.7.4.2. *Positions with symmetry $\bar{1}$*

Many space groups are centrosymmetric (all those in the geometric classes $\bar{1}$, $2/m$, *mmm*, $4/m$, $4/mmm$, $\bar{3}$, $\bar{3}m$, $6/m$, $6/mmm$, $m\bar{3}$, $m\bar{3}m$), but comparatively few of them possess special positions of symmetry $\bar{1}$, as the centres of symmetry are often encumbered by other symmetry elements. All centres of symmetry in $P\bar{1}$, $P2_1/c$ and *Pbca* are free, as are some of those in $P\bar{3}$ and $R\bar{3}$. When the encumbrance is an antitropic symmetry element, the special position can still be occupied by a molecule of symmetry $\bar{1}$ only, but when the encumbrance is syntropic or atropic the position cannot accommodate such a molecule. Table

* Such counts are tedious and subject to error, but the table should be correct within a few units.

references