small molecules starting from the phases obtained by the CEDA, together with the results from the PIP illustrate *ab initio* phase determination and subsequent phase refinement. These were obtained using restraints currently employed in DMM. The results are encouraging, although the usefulness of the proposed method in routine structure determination requires further thought and investigation.

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Space Groups Rare for Organic Structures. II. Analysis by Arithmetic Crystal Class

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Abstract

Twelve arithmetic crystal classes contain only one space-group type; others contain various numbers up to sixteen (*mmmP* and 4/*mmmP*). In the multimember classes the number N_{sg} of substances having a particular space-group type can be modelled quantitatively (unweighted $R_2 \gtrsim 0{\cdot}05$) by

$$N_{sg} = A_{cc} \exp \{\sum (X_i)_{cc}[x_i]_{sg}\},$$

where A_{cc} is a normalizing constant for the arithmetic crystal class, $[x_i]_{sg}$ is the number of symmetry elements $[2, 2_1, m, a, b, c, d, n, 3, \bar{3}, 3_1, 3_2, 4, \ldots]$ of type x_i in the unit cell of the space-group type, $(X_i)_{cc}$ is a parameter characteristic of the arithmetic crystal class and the symmetry element, and the summation is over all the elements x_i that are to be considered. In many cases the parameters X_i are equal, within their estimated standard deviations, throughout a cohort larger than the arithmetic crystal class (such as a geometric crystal class or an entire crystal system). The above equation can then be applied to the larger cohort, with arithmetic crystal class included as an additional 'symmetry element' in the sum in the exponent. There is at present no theory to account for the different popularities of different arithmetic crystal classes.

1. Introduction

The space-group type $P2_1/c$ accounts for about one-third of all known molecular organic structures, whereas the space-group type $P2/m$ has no certain example. Why? Ultimately the space group of a crystal of a particular substance is determined by the minimum (or a local minimum) of the thermodynamic potential (Gibbs free energy) of the van der Waals and other forces, but a very simple model goes a long way towards 'explaining' the relative frequency of the

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various space-group types within a crystal class. The basic idea that the space-group frequency is determined by packing considerations was introduced by Kitaigorodsky (1945, 1955), who pointed out that the most frequent space-group types are those that permit the close packing of triaxial ellipsoids. Wilson (1987, 1988*a*, *b*) used the complementary idea that space-group types are rare when they contain symmetry elements - notably rotation axes and mirror planes - that prevent the molecules from freely choosing their positions within the unit cell. A twofold axis excludes molecular centres from a column of diameter equal to some molecular diameter (say M), a mirror plane from a layer of thickness M, and a centre of symmetry from a sphere of diameter M. One thus expects that in any arithmetic* crystal class the symmorphic space-group type will have very few examples, and that one of the non-symmorphic space groups will have the greatest number.

The Cambridge Structural Database (Allen *et al.*, 1979) contains assignments of space groups for a variety of different types of organic compound. The data vary widely in quality. For the present purpose a selection was made, rejecting space groups not substantiated by a full structure determination or dubious because of disorder in the crystal. The simple packing considerations discussed in the previous paragraph 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 were also rejected. The data in Wilson (1988*a*) relate to the database as it was in January 1987; those in Wilson (1988*b*) and in this paper to January 1988.

The object of statistical analysis is to model the frequency of occurrence of the space-group types within some arbitrary but possibly significant selection from the 219 effectively distinct space-group types (compare Donohue, 1985, and references cited therein). The selection may be smaller than a geometric crystal class, or larger, up to a crystal system or beyond. Most names for 'group' have a technical meaning in crystallography, but 'cohort' does not seem to have been pre-empted. The selection under discussion at any time will here be called the 'current cohort' (cc), or simply 'cohort'. The number of occurrences of a space-group type in various cohorts of the monoclinic and orthorhombic crystal systems could be represented semi-quantitatively by

$$N_{sg} = A_{cc} \exp\left(-B_{cc}[2]_{sg} - C_{cc}[m]_{sg}\right), \qquad (1)$$

where N_{sg} is the number of occurrences of the space-group type in the cohort, A_{cc} is a normalizing constant related to the size of the cohort, B_{cc} and C_{cc} are parameters characteristic of the cohort, $[2]_{sg}$ is the number of twofold axes and $[m]_{sg}$ is the number of mirror planes in one unit cell of the space-group type. The gross effect of multiple cells (C, I, F and in the trigonal system R) is allowed for by dividing the actual number of symmetry elements in the multiple cell by two, four or three to obtain the number in a volume-equivalent cell. In order to obtain quantitative agreement between the observed and calculated values of N_{sg}, it is necessary in most cohorts to allow for properties of the space-group type other than [2] and [m]. Equation (1) then becomes

$$N_{sg} = A_{cc} \exp\left\{\sum (X_i)_{cc}[x_i]_{sg}\right\}, \qquad (2)$$

where $[x_i]_{sg}$ is the number of symmetry elements of type x_i in the unit cell of the space-group type, $(X_i)_{cc}$ is a parameter characteristic of the cohort and the symmetry element, and the summation is over all the elements x_i that are to be considered.

In addition to 2 and m, Wilson allowed (i) for the geometric crystal class, (ii) for the type of cell (P, C, I, F, R), (iii) for the orientation of the space-group type relative to the point group in the six crystal classes (mm, $\bar{4}m$, 32, $3m$, $\bar{3}m$, $\bar{6}m$)* for which it is relevant, (iv) in the more symmetric crystal systems for the numbers of the various threefold, fourfold and sixfold axes, and (v) for a distinction between 'free' symmetry elements (not lying on, but possibly intersecting, other symmetry elements) and 'encumbered' symmetry elements (lying on other symmetry elements that affect a larger fraction of the unit cell). The first three of these, at the level of the cohort equal to a geometric crystal class, are exactly equivalent to classifying the space-group types by arithmetic crystal class. At coarser levels, and in particular at the level of the cohort equal to a crystal system, arithmetic crystal class as a single factor† gives better agreement than using (i)-(iii) as three factors. Ramakumar (1988) has suggested that the number of molecules in the asymmetric unit and the type of molecule (for example, small molecule *versus* protein) may affect the space-group distribution significantly. Terms corresponding to these factors could be included in the sum in (2) if desired.

There are twelve arithmetic crystal classes ($1P$, $\bar{1}P$, $2C$, $222F$, $\bar{4}P$, $\bar{4}I$, $3R$, $\bar{3}P$, $\bar{3}R$, $32R$, $\bar{6}P$, $23F$) that

* Arithmetic crystal classes are treated from an abstract viewpoint by Wondratschek (1987, pp. 719 and 728). A descriptive treatment is planned for Chapter 1.4 of Volume C of *International Tables for Crystallography.*

* It is convenient to use the 'short' symbols *mm*, $\bar{4}m$ *etc.* instead of the 'full' symbols *mm*2, $\bar{4}m2$ *etc.* when it is desired to emphasize that the question of orientation is deliberately held open.

† Statistical modelling programs distinguish between variates and factors. The values of variates are ordinary numbers; [2], [m], ... fall into this category. Factors are qualitative; they include type of cell, geometric crystal class, metal-organic compound, protein, ... The programs allow appropriately for both variates and factors; see Baker & Nelder (1978), sections 1.2.1, 8.5.2, 22.1 and 22.2.1.

contain only one space-group type, and are necessarily fitted exactly by a model based on arithmetic classes. They thus provide no evidence for or against the model. They include three ($P\bar{1}$, $P\bar{3}$, $R\bar{3}$) of the five space-group types with 'free' centres of symmetry, but the two others ($P2_1/c$ and $Pbca$) are also fitted exactly by a model allowing for free centres. Enantiomorphous space-group types ($P3_1$, $P3_2$ *etc.*) must be combined; there are thus $(230-12-2-11)=205$ space groups that can provide evidence for the general correctness of the model and for the magnitude of the coefficients B_{cc}, C_{cc}, ..., $(X_i)_{cc}$ in (1) and (2). However, the number of structures having the more symmetric space-group types is very limited ($P4_12_11$ has 167 examples, $R\bar{3}$ has 132, $I4_1$ has 100, all others under 100), and the parameters corresponding to many of the symmetry elements are much smaller than their program-estimated standard deviations. There are two cases to be considered. (i) The parameter is small, as well as being much smaller than its program-estimated standard deviation. In such cases it could be set equal to zero, usually without appreciable detriment to the fit and with reduced program-estimated standard deviations for the remaining parameters. (ii) The parameter is large and negative, with a very large program-estimated standard deviation. Such cases arise when the space-group types containing the corresponding symmetry element have very few or no examples. The parameter must then be retained, but with the realization that its numerical value has little or no significance. In practice, $\bar{3}$, $\bar{4}$, $\bar{6}$, 4_2, $6_{2,4}$ and 6_3 dropped out, either because of linear relationships (§ 1.1) or because their coefficients were negligibly small.

The best (in some sense) values of the parameters in equations like (1) or (2) can be fitted to the observations by various techniques embodied in statistical programs available on all but the smallest computers. The program used for the tables presented here was *GLIM* [generalized linear interactive modelling (Baker & Nelder, 1978)], which gives maximum-likelihood estimates of the parameters for a wide range of functional forms. To use the program it is necessary to specify not only the form of the function – (1) or (2) in this case – but also the variance of the observations. The model treats the frequency of occurrence of a space-group type as a binomial sample from a population represented by the number of structures in the current cohort, with the variance discussed in Appendix *A* of Wilson (1988*a*); the mean of the observed and calculated values of N_{sg} was used as the best available estimate of the space-group frequency. [A weighted mean might be preferable, but an analysis of bias comparable with that of Wilson (1976) for parameters of a different type is lacking.] In the accompanying tables two measures of agreement are given: the first is the unweighted R_2 familiar in crystallography; and the second is the scaled deviance, frequently used in statistics.* If the scaled deviance does not exceed the number of degrees of freedom by more than three standard deviations, the model may be regarded as satisfactory (Wilson, 1980). The statistical properties of R_2 have not been investigated in detail, but a rough calculation shows that the expected value of $(R_2)^2$ is approximately

$$\langle (R_2)^2 \rangle = (n-p)(\sum N_{sg})/[n \sum (N_{sg})^2], \qquad (3)$$

where n is the number of space-group types in the cohort and p is the number of parameters evaluated (Wilson, 1988*b*). This can become large when $\sum N_{sg}$ is small, even if the difference between the observed and calculated values of N_{sg} is within one or two units. In the following text and tables the square root of the quantity given by (3) is denoted by R_{rms}.

It should be stated that counting equivalent symmetry elements is to some extent arbitrary. Does the unit cell of $P2_1/c$ have one or eight 'free' centres of symmetry? Does $P2$ have one or four twofold axes? Does Pm have one or two mirror planes? It makes no difference to the statistical fit, provided that the counting is done consistently throughout the current cohort; if $[m]$ is halved or doubled, C_{cc} is doubled or halved, and the calculated values of N_{sg} are unaffected. The numbers actually used in the calculations are, of course, always indicated in the comparative tables.

1.1. *Linear relationships*

Within an arithmetic crystal class there are 'laws of conservation' of symmetry elements. For example, in $222P$ the numbers of twofold axes and of twofold screw axes are different in different space-group types, but their sum remains constant:

$$[2]+[2_1]=3. \qquad (4)$$

The same 'law' holds for $222C$, $222I$ and $222F$ if the actual numbers of axes are divided by 2 or 4 to give the numbers in a volume-equivalent cell. The same equation holds for *mmmP*, and in addition

$$[m]+[a]+[b]+[c]+[n]=3. \qquad (5)$$

Equations (4) and (5) also hold for *mmmC*, *mmmI* and *mmmF* when the actual numbers are divided by 2 or 4 and the *d* glides are included in the last case.

Equations (3) and (4) are simple examples of what statistical texts call linear relationships. In the present context the general linear relationship could be written

$$\sum a_i[x_i]=k, \qquad (6)$$

where the a_i's and k are integers constant within an arithmetic crystal class, and ordinarily within a

* In the tables of this paper the scaled deviance quoted is the actual value of $\sum(\text{obs.}-\text{calc.})^2/\sigma^2$, not the quantity given by the program *GLIM* (presumably $-2\ln L_{max}$).

Table 1. *Observed and calculated frequencies of space-group types in the monoclinic system; the cohort is the entire system*

Space group No.	Space group Symbol	Arithmetic class	[2]		Frequency Observed	Frequency Calculated
3	$P2$	3	1	0	6	4
4	$P2_1$		0	0	2488	2489
5	$C2$	4	0·5	0	296	296
6	Pm	5	0	1	1	0
7	Pc		0	0	133	133
8	Cm	6	0	0·5	17	18
9	Cc		0	0	355	354
10	$P2/m$	7	1	1	0	0
11	$P2_1/m$		0	1	192	191
13	$P2/c$		1	1	120	121
14	$P2_1/c$		0	0	13 877	13 877
12	$C2/m$	8	0·5	0·5	118	120
15	$C2/c$		0·5	0	2354	2353

Parameter values with program-estimated standard deviations

Coefficient of	Value	E.s.d.	
[2]	−6·41	0·20	
$[m]$	−5·96	0·17	
$[\bar{1}]$	−1·67	0·18	
Arithmetic class 3	−3·39	0·18	
4	−2·31	0·12	
5	−6·32	0·20	
6	−5·34	0·18	
7	Set to zero		
8	−0·24	0·10	
R_2	0·000	—	$R_{rms} = 0·005$
Scaled deviance	1·05	2·83	
Degrees of freedom	4	—	

geometric crystal class after the gross adjustment of dividing the $[x_i]$'s by 2, 4 or 3 has been made. The exceptions are in the geometric crystal classes (mm, $\bar{4}m$, 32, $3m$, $\bar{3}m$, $\bar{6}m$) in which the unit cells can use the point groups in two orientations; they are automatically allowed for when the arithmetic crystal classes are used as factors in the calculations.

When such linear relationships exist the effects of the symmetry elements related by them cannot be determined unambiguously; their combined effect can be divided among them in an infinity of different ways. The program *GLIM* adopts the procedure of using the elements in the order in which they occur in the fitting instructions, and rejects any superfluous ones; in other words, it attributes maximum effect to the symmetry elements first encountered and zero effect to those related to elements already encountered. One must, therefore, take care to place the elements in terms of which one wishes the analysis to be carried out at the beginning of the fitting instructions. One peculiar linear relationship should be noticed: that between the normalizing constant A_{cc} and the arithmetic crystal classes. By default, the coefficient for the arithmetic class first encountered is put equal to zero. It is usually convenient, however, to alter the fitting instructions so that the coefficient for the class with the largest number of members is zero. Exactly the same fit is obtained.

The above features of the program are particularly helpful in the more symmetric crystal classes, where many of the linear relationships are far from obvious. One can list as many symmetry elements as one likes, in the knowledge that the program will test them for linear relationships, use as many as are necessary from the beginning of the list, and report the rest as 'aliased'. Another difficulty in the more symmetric classes is the actual counting of the symmetry elements; not all elements are represented in *International Tables for Crystallography* (Hahn, 1987), and some minor anomalies may have arisen from undetected miscounts. A few gross miscounts revealed themselves immediately through major anomalies.

2. The triclinic system

The two triclinic arithmetic crystal classes contain only one space-group type each, and are thus of no interest at the present stage of the model. For the record, at the time of the search $P1$ had 448 examples and $P\bar{1}$ had 5864.

3. The monoclinic system

The monoclinic and orthorhombic systems were discussed in some detail by Wilson (1988*a*), and the recalculations with the more recent sample and with arithmetic crystal class as the basic unit need only a brief presentation. The data for the monoclinic system are given in Table 1. A cohort equal to the entire system is fitted satisfactorily with one set of

Table 2. *Parameters evaluated for various cohorts in the monoclinic system*

Program-estimated standard deviations are given in parentheses.

Cohort	Coefficient of [2]	Coefficient of [m]	Coefficient of [$\bar{1}$]
All space groups			
in geometric class 2	−6·0 (0·4)	—	—
in geometric class m	—	−6·0 (0·5)	—
in geometric class $2/m$	−6·5 (0·2)	−6·0 (0·2)	−1·7 (0·2)
with [m] = 0	−6·0 (0·4)	—	−1·3 (0·5)
with [2] = 0	—	−6·0 (0·5)	−1·8 (0·5)
in system	−6·4 (0·2)	−6·0 (0·2)	−1·7 (0·2)

parameters, listed at the bottom of the table. As in Wilson (1988*a*), the calculated frequencies are rounded to the nearest integer, but the residuals R_2 are based on the unrounded frequencies. Two space-group types ($C2$ and $P2_1/c$) are necessarily fitted exactly, as explained above, but the biggest discrepancy between the observed and the calculated values for the eleven others is two units. Unweighted R_2 is zero to three decimal places, and the scaled deviance (1·05) is actually less than the number of degrees of freedom (4). It will be noted that the coefficient of [2] and the coefficient of [m] are more or less equal, that of [2] being slightly the larger. Approximate consistency of these coefficients throughout the system can be checked by evaluating them for various cohorts smaller than the entire system. Details are given in Table 2.

4. The orthorhombic system

The orthorhombic crystal system has many more space-group types than the monoclinic, and a satisfactory fit could not be obtained for the whole system. The data for the geometric crystal class 222 are given in Table 3. Though for one space-group type the discrepancy between the observed and calculated values of N_{sg} is five units, with $R_2 = 0{\cdot}002$ and the scaled deviance (6·8) within one estimated standard deviation of the number of degrees of freedom (4) the fit can be regarded as very satisfactory. The fit for the geometric crystal class *mm* (Table 4) is also satisfactory, with $R_2 = 0{\cdot}028$ and the scaled deviance (24) within two estimated standard deviations of the number of degrees of freedom (13). It may be noted that over half of the scaled deviance arises from the single space-group type $Pmn2_1$ (31), for which the number of examples observed is over double the number calculated. For the geometric crystal class *mmm* (Table 5) the fit is not satisfactory. Though $R_2 = 0{\cdot}029$ is about the same as for *mm*, the scaled deviance (112) exceeds the number of degrees of freedom (19) by fifteen estimated standard deviations, and the coefficient of [2_1], though not large, has an unexpected sign. There are four space-group types for which the observed frequency is about twice that calculated. The discrepancies could undoubtedly be reduced by differentiating between differing types of 'encumbering'; intuition suggests, for example, that a twofold axis lying in a mirror plane may exhibit very little independent effect, whereas one lying in a glide plane may be 'encumbered' only to a small extent. The estimates of the coefficients of [2] and [m] are reasonably consistent throughout the orthorhombic system; for no obvious reason they are about half those found for the monoclinic system.

5. The tetragonal system

Tetragonal space-group types contain a fourfold axis of some kind, in addition to symmetry elements found in the monoclinic and orthorhombic groups, and these present new problems. One is the coincidence of axes of different types. Fourfold rotation axes and fourfold rotoinversion axes are also twofold axes; should the twofold axes be counted? They are not shown as symmetry elements in the drawings in Volume A of *International Tables for Crystallography* (Hahn, 1987), but appear in the list of *Symmetry Operations*. The non-directed fourfold screw axis 4_2 is also 2 and 2_1; should these be counted? The twofold axes appear in the list of *Symmetry Operations*; the screw axes do not. In a similar fashion, 4_1 and 4_3 may hide 2_1, and $4/m$ and $4_2/m$ may hide $\bar{4}$. For brevity, the symmetry elements represented in the drawings are called the visible symmetry elements.

There seems to be no physical reason to treat the lower-order symmetry axis as having any effect additional to that of the higher-order axis with which it coincides, and this accords with the drawings in Volume A; only the higher-order axis is shown. It was decided to count only the visible axes; any additional ones listed under *Symmetry Operations* or in the preliminary chapters of Volume A were ignored. On the other hand, geometrical intuition suggests that coincident reflexion and glide planes (which occur fairly frequently in centred cells) may have an effect other than that of the visible reflexion plane only, though possibly not simply the sum of the effects that the two planes would have if they were not coincident. It was decided to count coincident planes as if they were separate; no ill effects arose from this procedure for space-group types of the type $C2--$ in the geometric crystal class *mm* (Wilson, 1988*a*, § 5.3).

The enantiomorphous screw axes 4_1 and 4_3 need special consideration. As has been pointed out by Donohue (1985), if one stereoisomer crystallizes in a space-group type with one of these axes, its enantiomorph is practically certain to crystallize in the enantiomorphous space-group type with the other axis. One thus gets two space-group determinations from one structure determination in such cases.

Table 3. *Observed and calculated frequency of occurrence of space-group types in the orthorhombic geometric crystal class 222; the cohort is the geometric class*

Space group No.	Symbol	Arithmetic class	[2]	Frequency Observed	Calculated
16	$P222$	9	3	4	0
17	$P222_1$		2	3	6
18	$P2_12_12$		1	163	158
19	$P2_12_12_1$		0	4466	4466
20	$C222_1$	10	1	58	58
21	$C222$		2	2	2
22	$F222$	11	1·5	0	0
23	$I222$	12	1·5	3	2
24	$I2_12_12_1$		1·5	1	2

Parameter values with program-estimated standard deviations

Coefficient of	Value	E.s.d.	
[2]	−3·34	0·07	
Arithmetic class 9	Set to zero		
10	−1·00	0·15	
11	−9·09	109	
12	−2·79	0·66	
R_2	0·002	—	$R_{rms} = 0·010$
Scaled deviance	6·78	2·83	
Degrees of freedom	4	—	

Note. The large and poorly determined parameter for arithmetic class 11 reflects the fact that there are no observed examples.

Table 4. *Observed and calculated frequency of occurrence of space-group types in the orthorhombic geometric crystal class mm; the cohort is the geometric class*

Space group No.	Symbol	Arithmetic class	$[2]_{free}$	$[2]_{enc}$	$[2_1]_{free}$	$[m]$	Frequency Observed	Calculated
25	$Pmm2$	13	0	1	0	2	0	0
26	$Pmc2_1$		0	0	0	1	8	12
27	$Pcc2$		0	1	0	0	0	2
28	$Pma2$		0	1	0	1	0	0
29	$Pca2_1$		0	0	0	0	275	278
30	$Pnc2$		0	1	0	0	3	2
31	$Pmn2_1$		0	0	0	1	28	12
32	$Pba2$		1	0	0	0	11	10
33	$Pna2_1$		0	0	1	0	600	600
34	$Pnn2$		1	0	0	0	9	10
35	$Cmm2$	14	0	1	0	1	0	0
36	$Cmc2_1$		0	0	0	0·5	60	61
37	$Ccc2$		0	1	0	0	5	2
38	$C2mm$	15	0	0·5	0	1	0	2
39	$C2mb$		0	0·5	0	0·5	4	7
40	$C2cm$		0	0·5	0	0·5	9	7
41	$C2cb$		0	0·5	0	0	39	35
42	$Fmm2$	16	0	0·5	0	0·5	8	8
43	$Fdd2$		0·5	0	0·5	0	135	135
44	$Imm2$	17	0	0·5	0	1	1	1
45	$Iba2$		0	0·5	0	0	32	28
46	$Ima2$		0	0·5	0	0·5	3	6

Parameter values with program-estimated standard deviations

Coefficient of	Value	E.s.d.	
$[2]_{free}$	−3·32	0·52	
$[2]_{enc}$	−4·99	0·44	
$[2_1]_{free}$	0·77	0·06	
$[m]$	−3·15	0·20	
Arithmetic class 13	Set to zero		
14	0·06	0·16	
15	0·43	0·26	
16	0·55	0·14	
17	0·22	0·28	
R_2	0·028	—	$R_{rms} = 0·040$
Scaled deviance	24·1	5·1	
Degrees of freedom	13		

Table 5. *Observed and calculated frequency of occurrence of space-group types in the orthorhombic geometric crystal class mmm; the cohort is the geometric class*

Space group No.	Symbol	Arithmetic class	$[2]_{free}$	$[2]_{enc}$	$[2_1]_{free}$	$[m]$	Frequency Observed	Calculated
47	*Pmmm*	18	0	3	0	3	0	0
48	*Pnnn*		3	0	0	0	2	0
49	*Pccm*		0	3	0	1	0	0
50	*Pban*		1	2	0	0	1	0
51	*Pmma*		0	2	0	2	2	0
52	*Pnna*		1	1	1	0	20	5
53	*Pmna*		0	2	0	1	4	1
54	*Pcca*		1	1	0	0	10	12
55	*Pbam*		1	0	0	1	8	18
56	*Pccn*		0	1	2	0	134	152
57	*Pbcm*		0	1	0	1	36	37
58	*Pnnm*		1	0	0	1	18	18
59	*Pmmn*		0	1	0	2	9	2
60	*Pbcn*		0	1	1	0	347	326
61	*Pbca*		0	0	0	0	1645	1645
62	*Pnma*		0	0	1	1	502	499
63	*Cmcm*	19	0	1	0	1	40	12
64	*Cmca*		0	1	0	0·5	44	54
65	*Cmmm*		0	2	0	1·5	0	0
66	*Cccm*		0	2	0	0·5	2	2
67	*Cmma*		0	2	0	1	1	0
68	*Ccca*		0	2	0	0	6	8
69	*Fmmm*	20	0	1·5	0	0·75	1	5
70	*Fddd*		1·5	0	1·5	0	19	5
71	*Immm*	21	0	1·5	0	1·5	0	0
72	*Ibam*		0	1·5	0	0·5	14	1
73	*Ibca*		0	1·5	0	0	4	6
74	*Imma*		0	1·5	0	1	3	0

Parameter values with program-estimated standard deviations

Coefficient of	Value	E.s.d.	
$[2]_{free}$	−4·08	0·16	
$[2]_{enc}$	−3·37	0·16	
$[2_1]_{free}$	−0·76	0·07	
$[m]$	−2·94	0·36	
$[\bar{1}]$	−2·51	0·24	
Arithmetic class 18	Set to zero		
19	−1·09	0·16	
20	−0·97	0·35	
21	−3·01	0·40	
R_2	0·029	—	$R_{rms} = 0·025$
Scaled deviance	112	6·2	
Degrees of freedom	19	—	

The sign of the coefficient of $[2_1]_{free}$ is unexpected.

Should the total number of structures in the two space-group types be attributed to each? Or should the two space-group types be added together and treated as a single space-group type? In the calculations here the latter procedure was chosen, since it does not give double statistical weight to structures in these space-group types.

5.1. *Linear relationships*

As already noted for the monoclinic and orthorhombic systems, within each point group there is a certain 'conservation of symmetry elements'; the different space-group types interchange reflexion planes and the various types of glide plane, but the total number of planes remains constant (within the complication already mentioned for centred cells, and a special complication arising from the two orientations, $\bar{4}2m$ and $\bar{4}m2$, of the point group $\bar{4}m$). Similarly, the various types of axis interchange, but the total number remains constant. This 'conservation' gives rise to linear relations between the symmetry elements, the most obvious of which is

$$[4]+[4_1]+[4_2]+[4_3]=C, \tag{7}$$

where $[\ldots]$ indicates the number of symmetry elements within the volume-equivalent cell of the type indicated between the square brackets and C is a constant for the geometric crystal class. A less-obvious relation is

$$[2]+[2_1]+[\bar{4}]=A, \tag{8}$$

where A is a constant within a geometric crystal class. For planes the relation is

$$[m]+[g]=P, \tag{9}$$

Table 6. *Observed and calculated frequencies of space-group types in the simpler tetragonal classes; the cohort is the combined geometrical classes* 4, $\bar{4}$ *and* 422

Space group No.	Symbol	Arithmetic class	[2]	[4]	$[4_{1,3}]$	Frequency Observed	Calculated
75	$P4$	22	1	1	0	1	0
76	$P4_1$		0	0	1	83	84
77	$P4_2$		1	0	0	6	5
78	$P4_3$					Included in 76	
79	$I4$	23	0	0·5	0	11	11
80	$I4_1$		1	0	0	15	15
81	$P\bar{4}$	24	1	0	0	4	4
82	$I\bar{4}$	25	0	0	0	27	27
89	$P422$	28	3	1	0	0	0
90	$P42_12$		1	1	0	0	0
91	$P4_122$		2	0	1	3	3
92	$P4_12_12$		0	0	1	167	166
93	$P4_222$		3	0	0	0	0
94	$P4_22_12$		1	0·5	0	8	9
95	$P4_322$					Included in 91	
96	$P4_32_12$					Included in 92	
97	$I422$	29	1	0·5	0	0	0
98	$I4_122$		2	0	1	1	1

Parameter values with program-estimated standard deviations

Coefficient of	Value	E.s.d.	
[2]	−2·00	0·32	
[4]	−4·63	1·03	
$[4_{1,3}]$	0·91	0·43	
Arithmetic class 22	−0·69	0·11	
23	0·51	0·38	
24	−0·81	0·62	
25	−0·91	0·47	
28	Set to zero		
29	−1·25	1·60	
R_2	0·012	—	$R_{rms} = 0·060$
Scaled deviance	1·19	3·46	
Degrees of freedom	6	—	

where again P is a constant within a geometric crystal class, provided that all planes, and not merely the visible ones, are included in the enumeration. For two or three space-group types, for which the invisible glide planes could not be deduced with certainty from either the paragraph *Symmetry Operations* or the introductory material of Volume A, (9) was accepted as an article of faith and $[g]$ was deduced from $[m]$.

5.2. *Comparison of observed and calculated frequencies*

The observed numbers of structures in the space-group types of the tetragonal system are given in Tables 6–10, together with the numbers calculated from (2) including the tetragonal symmetry elements.

Agreement is in general good, though space groups $P\bar{4}n2$ (118) and possibly $P4_2/mnm$ (136) are exceptions. For the simpler geometric crystal classes the maximum discrepancy is one unit, and in fact the geometric classes without mirror planes (4, $\bar{4}$, 422) can be combined in a single cohort (Table 6). With $R_2 = 0·012$ and the scaled deviance (1·3) much less than the number of degrees of freedom (6) the agreement is very satisfactory. The same is true for $4/m$ (Table 7, $R_2 = 0·008$, scaled deviance = 0·66, DF = 1). In $4mm$ (Table 8) there is one discrepancy of three units, but overall the agreement is as good as can be expected statistically [scaled deviance (5·2) less than the number of degrees of freedom (7); $R_2 = 0·24$, value expected from (3) 0·29]. In $\bar{4}m$ (Table 9) there is a discrepancy of 6 units for $P\bar{4}n2$ (118), but overall the agreement is not bad ($R_2 = 0·13$, scaled deviance = 14·2 with e.s.d. 4·0, DF = 8). The value of R_{rms} from (3) is 0·14. In $4/mmm$ (Table 10) the maximum discrepancy is 4 units for $P4_2/mnm$ (136), and overall the agreement is as good as can be expected for such a sparsely populated class – a total of 48 examples, with the result that several of the parameters are less than their program-estimated standard deviations. The value of $R_2 = 0·31$ is high, but (3) indicates that 0·30 is to be expected with so few examples. The scaled deviance of 13·1 with e.s.d. of 5·3 is less than the number of degrees of freedom (14).

6. The trigonal system

The trigonal system contains only 402 structures, distributed over 24 space-group types, or 22 when enantiomorphous groups are combined. The number of space-group types in each arithmetic crystal class,

Table 7. *Observed and calculated frequencies of occurrence of space-group types in the geometric crystal class 4/m; the cohort is the geometric class*

Space group No.	Space group Symbol	Arithmetic class	[2]	[4]	[$4_{1,3}$]	[m]	Frequency Observed	Frequency Calculated
83	$P4/m$	26	1	1	0	1	1	0
84	$P4_2/m$	26	1	0	0	1	0	0
85	$P4/n$	26	0	1	0	0	4	4
86	$P4_2/n$	26	0	0	0	0	61	61
87	$I4/m$	27	0	0·5	0	0·5	12	12
88	$I4_1/a$	27	0	0	1	0	100	100

Parameter values with program-estimated standard deviations

Coefficient of	Value	E.s.d.	
[2]	−6·55	12·8	
[4]	−2·72	0·56	
[$4_{1,3}$]	0·494	0·12	
[m]	−0·528	0·79	
R_2	0·008	—	$R_{rms}=0·46$
Scaled deviance	0·68	1·41	
Degrees of freedom	1	—	

Note. The arithmetic class is not a significant factor in this cohort. The large negative coefficient of [2] and its large e.s.d. reflect the fact that the two space groups with diad axes are rare in comparison with those without diads.

Table 8. *Observed and calculated frequencies of occurrences of space-group types in the geometric crystal class 4mm; the cohort is the geometric class*

Space group No.	Space group Symbol	Arithmetic class	[2]	[4]	[$4_{1,3}$]	[m]	Frequency Observed	Frequency Calculated
99	$P4mm$	30	1	1	0	4	0	0
100	$P4bm$	30	1	1	0	2	0	0
101	$P4_2cm$	30	1	0	0	2	0	1
102	$P4_2nm$	30	1	0	0	2	2	1
103	$P4cc$	30	1	1	0	0	0	1
104	$P4nc$	30	1	1	0	0	4	1
105	$P4_2mc$	30	1	0	0	2	1	1
106	$P4_2bc$	30	1	0	0	0	5	5
107	$I4mm$	31	0	0·5	0	2	0	0
108	$I4cm$	31	0	0·5	0	1	1	1
109	$I4_1md$	31	1	0	1	1	4	4
110	$I4_1cd$	31	1	0	1	0	12	12

Parameter values and program-estimated standard deviations

Coefficient of	Value	E.s.d.	
[4]	−1·41	0·84	
[$4_{1,3}$]	0·83	0·43	
[m]	−1·03	0·36	
R_2	0·24	—	$R_{rms}=0·29$
Scaled deviance	5·2	4·0	
Degrees of freedom	8	—	

Note. Diad axes and arithmetic class are not significant.

however, is small (two contain only a single space-group type), and the model gives a good fit to a cohort consisting of the entire system. Several of the symmetry elements are rejected by linear relationships, and others are small in comparison with their program-estimated standard deviations. The fit obtained with twofold axes, threefold screw axes and mirror planes as the significant symmetry elements is given in Table 11, along with the values of the parameters. With $R_2=0·029$ and the scaled deviance (5·7 with e.s.d. = 3·7) less than the number of degrees of freedom (7) the fit may be regarded as very satisfactory.

7. The hexagonal system

The hexagonal system contains only 125 structures, even fewer than the trigonal system. They are distributed over 27 space-group types, or 23 when enantiomorphous groups are combined. The number of space-group types in each arithmetic crystal class, however, is not large (one contains only a single space-group type), and the model gives a good fit to a cohort consisting of the entire system. Several of the symmetry elements are rejected by linear relationships, and others are small in comparison with their

Table 9. *Observed and calculated frequencies of occurrence of space-group types in the geometric crystal class $\bar{4}m$; the cohort is the geometric class*

Space group No.	Space group Symbol	Arithmetic class	$[2]_{free}$	$[2]_{enc}$	$[m]$	Frequency Observed	Frequency Calculated
111	$P\bar{4}2m$	32	0	3	2	0	0
112	$P\bar{4}2c$	32	0	3	0	0	1
113	$P\bar{4}2_1m$	32	0	1	2	9	10
114	$P\bar{4}2_1c$	32	0	1	0	55	54
115	$P\bar{4}m2$	33	0	3	2	1	0
116	$P\bar{4}c2$	33	0	3	0	0	1
117	$P\bar{4}b2$	33	3	0	0	2	3
118	$P\bar{4}n2$	33	3	0	0	6	3
119	$I\bar{4}m2$	34	0	2	1	0	0
120	$I\bar{4}c2$	34	0	2	0	0	0
121	$I\bar{4}2m$	35	0	1	1	9	5
122	$I\bar{4}2d$	35	1	0	0	12	14

Parameter values and program-estimated standard deviations

Coefficient of	Value	E.s.d.	
$[2]_{free}$	−1·60	0·23	
$[2]_{enc}$	−1·87	0·43	
$[m]$	−0·83	0·15	
Arithmetic class 33	Set to zero		
34	−10·41	1299	
35	−1·60	0·35	
R_2	0·11	—	$R_{rms}=0·12$
Scaled deviance	8·0	3·5	
Degrees of freedom	6	—	

Note. Distinguishing between free and encumbered axes, as in certain orthorhombic classes, considerably improves the fit. The large negative value, with very large e.s.d., for the coefficient for the arithmetic class 34 arises because the class has no examples.

Table 10. *Observed and calculated frequency of occurrence of space-group types in the geometric crystal class $4/mmm$; the cohort is the geometric class*

The cohort is sparsely populated, and only the coefficients of $[4_{1,3}]$ and $[m]$ are statistically significant. Retaining arithmetic crystal class as a factor gives a better fit, though the coefficient is smaller than its program-estimated standard deviation.

Space group No.	Space group Symbol	Arithmetic class	$[4_{1,3}]$	$[m]$	Frequency Observed	Frequency Calculated
123	$P4/mmm$	36	0	5	1	0
124	$P4/mcc$	36	0	1	2	2
125	$P4/nbm$	36	0	2	0	1
126	$P4/nnc$	36	0	0	3	3
127	$P4/mbm$	36	0	3	0	0
128	$P4/mnc$	36	0	1	1	2
129	$P4/nmm$	36	0	4	1	0
130	$P4/ncc$	36	0	0	3	3
131	$P4_2/mmc$	36	0	3	1	0
132	$P4_2/mcm$	36	0	3	1	0
133	$P4_2/nbc$	36	0	0	2	3
134	$P4_2/nnm$	36	0	2	2	1
135	$P4_2/mbc$	36	0	1	2	2
136	$P4_2/mnm$	36	0	3	5	0
137	$P4_2/nmc$	36	0	3	2	0
138	$P4_2/ncm$	36	0	2	0	1
139	$I4mmm$	37	0	3	2	0
140	$I4/mcm$	37	0	2	0	1
141	$I4_1/amd$	37	2	2	3	4
142	$I4_1/acd$	37	2	0	17	16

Parameter values with program-estimated standard deviations

Coefficient of	Value	E.s.d.	
$[4_{1,3}]$	1·21	0·92	
$[m]$	−0·63	0·19	
Arithmetic class 37	Set to zero		
38	−0·73	1·85	
R_2	0·30	—	$R_{rms}=0·32$
Scaled deviance	13·9	5·7	
Degrees of freedom	16	—	

Table 11. *Observed and calculated frequencies of space-group types in the trigonal system; the cohort is the entire system*

Space group No.	Symbol	Arithmetic class	[2]	[$3_{1,2}$]	[m]	Frequency Observed	Calculated
143	$P3$	38	0	0	0	5	2
144	$P3_1$	38	0	3	0	52	53
145	$P3_2$	38	0	3	0	Included in 144	
146	$R3$	39	0	2	0	57	57
147	$P\bar{3}$	40	0	0	0	26	26
148	$R\bar{3}$	41	0	2	0	132	132
149	$P312$	42	6	0	0	0	0
150	$P321$	43	3	0	0	0	2
151	$P3_112$	42	6	3	0	2	2
152	$P3_221$	43	3	3	0	38	37
153	$P3_212$	42	6	3	0	Included in 151	
154	$P3_221$	43	3	3	0	Included in 152	
155	$R32$	44	6	2	0	3	3
156	$P3m1$	45	0	0	6	1	0
157	$P31m$	46	0	0	3	0	0
158	$P3c1$	45	0	0	0	2	2
159	$P31c$	46	0	0	0	1	1
160	$R3m$	47	0	2	3	7	8
161	$R3c$	47	0	2	0	41	40
162	$P\bar{3}1m$	48	6	0	3	0	1
163	$P\bar{3}1c$	48	6	0	0	5	4
164	$P\bar{3}m1$	49	3	0	6	1	0
165	$P\bar{3}c1$	49	3	0	12	4	4
166	$R\bar{3}m$	50	6	2	3	6	4
167	$R\bar{3}c$	50	6	2	6	19	20

Parameter values with program-estimated standard deviations

Coefficient of	Value	E.s.d.
[2]	−0·312	0·037
[$3_{1,2}$]	1·06	0·22
[m]	−0·534	0·107
Arithmetic class 38	−1·97	0·25
39	−0·840	0·142
40	0·489	0·477
41	Set at zero	
42	−3·38	0·91
43	−1·40	0·27
44	−1·91	0·69
45	−2·04	0·94
46	−2·84	1·51
47	−1·19	0·16
48	0·567	0·695
49	−0·419	0·700
R_2	0·029	—
Scaled deviance	5·65	3·7
Degrees of freedom	7	—

program-estimated standard deviations. The fit obtained with twofold axes and sixfold screw axes $6_{1,5}$ as the significant symmetry elements is given in Table 12, along with the values of the parameters. The value $R_2 = 0{\cdot}094$ may be regarded as adequate for such a small number of structures [(3) gives $R_{rms} = 0{\cdot}14$]; the maximum difference between the observed and calculated frequencies is 3 units. The scaled deviance (10·3 with e.s.d. = 5·1) is less than the number of degrees of freedom (13), and is thus satisfactory.

8. The cubic system

The present sample has very few structures in the cubic system; they are listed in Table 13. With so few examples it is obviously useless to try to fit a detailed statistical model. The only space-group type having two-figure frequency is $Pa\bar{3}$ with 19 examples, so it was thought that a cohort consisting of the geometrical crystal class $m\bar{3}$ might be worth investigating. A trial with [2], [m] and arithmetic crystal class gave practically perfect agreement, but all parameters were smaller than their program-estimated standard deviations, the coefficient of [2] being the best determined. The fit with [2] as the only variate is shown in Table 14. Statistically it is satisfactory, with $R_2 = 0{\cdot}12$, $R_{rms} = 0{\cdot}22$, scaled deviance 2·7 with e.s.d. 3·2 and five degrees of freedom. The numbers are so small, however, that one can only say that the cubic system gives no evidence against the model.

Table 12. *Observed and calculated frequencies of space-group types in the hexagonal system; the cohort is the entire system*

Space group No.	Symbol	Arithmetic class	[2]	$[6_{1,5}]$	Frequency Observed	Calculated
168	$P6$	51	3	0	0	0
169	$P6_1$	51	0	1	42	43
170	$P6_5$	51	0	1	Included in 169	
171	$P6_2$	51	3	0	3	0
172	$P6_4$	51	3	0	Included in 171	
173	$P6_3$	51	0	0	14	14
174	$P\bar{6}$	52	0	0	1	1
175	$P6/m$	53	3	0	0	1
176	$P6_3$	53	0	0	37	37
177	$P622$	54	9	0	0	0
178	$P6_122$	54	6	1	9	8
179	$P6_522$	54	6	1	Included in 178	
180	$P6_222$	54	9	0	2	0
181	$P6_422$	54	9	0	Included in 180	
182	$P6_322$	54	6	0	1	3
183	$P6mm$	55	3	0	0	0
184	$P6cc$	55	3	0	0	0
185	$P6_3cm$	55	0	0	2	3
186	$P6_3mc$	55	0	0	5	3
187	$P\bar{6}m2$	56	3	0	0	0
188	$P\bar{6}c2$	56	3	0	0	0
189	$P\bar{6}2m$	57	3	0	0	2
190	$P\bar{6}2c$	57	3	0	4	2
191	$P6/mmm$	58	9	0	1	0
192	$P6/mcc$	58	9	0	1	0
193	$P6_3/mcm$	58	6	0	1	2
194	$P6_3/mmc$	58	6	0	2	2

Parameter values with program-estimated standard deviations

Coefficient of	Value	E.s.d.	
[2]	−1·12	0·38	
$[6_{1,5}]$	1·14	0·27	
Arithmetic class 51	Set to zero		
52	−2·61	1·67	
53	0·99	0·28	
54	5·04	2·30	
55	−1·36	0·51	
56	−11	Large	
57	1·43	1·33	
58	4·53	2·42	
R_2	0·094	—	$R_{rms} = 0·14$
Scaled deviance	10·3	5·1	
Degrees of freedom	13	—	

Table 13. *Observed frequency of occurrence of space-group types in the cubic system*

Space group No.	Symbol	Frequency	Space group No.	Symbol	Frequency
195	$P23$	0	213	$P4_132$	2
196	$F23$	0	214	$I4_132$	0
197	$I23$	2	215	$P\bar{4}3m$	0
198	$P2_13$	3	216	$F\bar{4}3m$	0
199	$I2_13$	0	217	$I\bar{4}3m$	7
200	$Pm\bar{3}$	0	218	$P\bar{4}3n$	4
201	$Pn\bar{3}$	0	219	$F\bar{4}3c$	4
202	$Fm\bar{3}$	1	220	$I\bar{4}3d$	3
203	$Fd\bar{3}$	0	221	$Pm\bar{3}m$	0
204	$Im\bar{3}$	2	222	$Pn\bar{3}n$	2
205	$Pa\bar{3}$	19	223	$Pm\bar{3}n$	1
206	$Ia\bar{3}$	3	224	$Pn\bar{3}m$	1
207	$P432$	0	225	$Fm\bar{3}m$	3
208	$P4_232$	0	226	$Fm\bar{3}c$	0
209	$F432$	0	227	$Fd\bar{3}m$	1
210	$F4_132$	0	228	$Fd\bar{3}c$	0
211	$I432$	0	229	$Im\bar{3}m$	5
212	$P4_332$	Included in 213	230	$Ia\bar{3}d$	1

Table 14. *Observed and calculated frequencies of space-group types in the cubic geometric class $m\bar{3}$; the cohort is the geometric class*

Space group No.	Symbol	Arithmetic class	[2]	[m]	Frequency Observed	Calculated
200	$Pm\bar{3}$	62	3	3	0	0
201	$Pn\bar{3}$	62	3	0	0	0
202	$Fm\bar{3}$	63	2	2	1	1
203	$Fd\bar{3}$	63	2	0	0	1
204	$Im\bar{3}$	64	2	2	2	1
205	$Pa\bar{3}$	62	0	0	19	19
206	$Ia\bar{3}$	64	2	0	3	1

Parameter value with program-estimated standard deviation

	Value	E.s.d.	
Coefficient of [2]	−1·82	0·37	
R_2	0·12	—	$R_{rms} = 0·22$
Scaled deviance	2·7	3·2	
Degrees of freedom	5	—	

The coefficients of [m] and of arithmetic class are not significant.

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X-ray Birefringence and Dichroism in Lithium Niobate, $LiNbO_3$

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Abstract

Accurate synchrotron-radiation X-ray transmission measurements have been carried out on hexagonal $LiNbO_3$ in the vicinity of the Nb K-absorption edge ($E = 18·986$ keV). The experiments were performed on the two-axis diffractometer at HASYLAB in dedicated mode of DORIS II (3·7 GeV). Single-crystal wafers cut perpendicular to [10.0] were rotated around the monochromatized beam using an experimental set up analogous to the optical polarizing microscope. Both the horizontally and vertically polarized components of the transmitted radiation were recorded at the same time and analysed in terms of a classical optical model derived from the Jones calculus. Fits to the observations yielded agreement indices between 0·013 and 0·052 supporting the applicability of the model to X-ray energies. X-ray

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