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Space-Group Frequencies for Organic Compounds

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Abstract

The space-group frequency for approximately 30 000 organic compounds in the *NBS Crystal Data Identification File* has been calculated for each of the 230 space groups. 75% of the compounds have been reported in only five space groups: $P2_1/c$ (36·0%), $P\bar{1}$ (13·7%), $P2_12_12_1$ (11·6%), $P2_1$ (6·7%) and $C2/c$ (6·6%). In contrast, there are 29 space groups with only one entry and 35 space groups with none at all. Although the space-group frequencies should be fairly representative of their distribution in nature, certain frequencies are over- or under-estimated. An analysis of the metric symmetry for about 30 000 lattices using a matrix technique has revealed that it is not uncommon for the metric symmetry to exceed the reported crystal symmetry. In many of these cases, the structures have been described in space groups of unnecessarily low symmetry. By explicitly checking for the highest possible metric symmetry during the space-group-determination procedure, errors of this type can be prevented.

Introduction

Using the *NBS Crystal Data Identification File* (1982), the frequency of occurrence has been calculated for each of the 230 space groups. The space-group frequencies presented in Table 1 were calculated for organic materials (*i.e.* carbon-containing compounds). Most of these compounds (~89·9%) correspond to entries that result from full structure determinations. The types of structures reported in the literature have been influenced by a variety of factors such as the techniques available to solve structures and special interest in selected categories of compounds. Nevertheless, since it was possible to tabulate space-group frequencies for 29 059 organic compounds that have been reported up to 1981, the results should be fairly representative of their distribution in nature.

The space-group-frequency table may be used in routine structure work. We have found it helpful to check a list of space-group frequencies as soon as a space group has been assigned or limited to a few possibilities. The frequencies may indicate that a space-group determination should be rechecked if the substance has been characterized by a rare or previously unoccupied space group. If the compound has, indeed, crystallized in a rare space group, the *NBS Crystal Data Identification File* may be used to find references for a structure comparison. For reasons discussed below, however, it is important not to have a false sense of security when a commonly reported space group has been determined.

Inspection of the data in Table 1 reveals that most organic compounds have been assigned to a relatively small number of space groups. In fact, 75% of the compounds have been described in only five space groups and 90% in 16 space groups. A comparison of the percent occupancy of the five most common space groups with corresponding data calculated earlier using a smaller sample of 21 051 compounds (Mighell & Rodgers, 1980) reveals that the percentages for the five most frequently occurring space groups are fairly constant. The percentages are as follows, with the earlier data given in parentheses: $P2_1/c$, 36·0% (35·5%); $P\bar{1}$, 13·7% (13·3%); $P2_12_12_1$, 11·6% (12·4%); $P2_1$, 6·7% (7·6%); $C2/c$, 6·6% (6·9%). In contrast, there are 117 space groups with very low frequencies (five or fewer compounds assigned to them). Of these 117 space groups, 29 space groups have one entry and 35 have no entry at all. Thus, it may be possible to develop theories which would explain why certain space groups are rare or uninhabited, or one may be able to correlate the molecular shape, physical properties, *etc.* with the probability that the compound crystallizes in a given space group.

As a further aid to experimental and theoretical work, space-group frequencies for the 86 chemical

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classes (steroids, silicon compounds, metal complexes, *etc.*) listed in *Molecular Structures and Dimensions* (1970–1982) are being prepared and will be submitted for publication.

Discussion

It is important to remember that the frequencies of occurrence are approximate since certain space-group frequencies may be under- or over-estimated. Detailed analyses of several cases in which crystal structures have been described in space groups of unnecessarily low symmetry have been carried out; examples are given in the following references: Davies, Kopf & Weiss (1982); Herbstein & Marsh (1982); Marsh & Schomaker (1980); Schomaker & Marsh (1979); Marsh & Schomaker (1979). These references demonstrate that what appears to be a satisfactory structural refinement does not necessarily imply a correct space-group determination. The errors in space-group assignments that are discussed in the above references can be divided into two categories: (1) incorrect space group but correct crystal system; (2) incorrect space group and incorrect crystal system. Errors of the second type can be prevented or detected by determin-

Table 1. *Space-group frequencies for* 29 059 *organic crystalline compounds*

Space-group symbol	Space-group No.	Frequency
$P1$	1	305
$P\bar{1}$	2	3986
$P2$	3	11
$P2_1$	4	1957
$C2$	5	273
Pm	6	1
Pc	7	102
Cm	8	22
Cc	9	277
$P2/m$	10	5
$P2_1/m$	11	239
$C2/m$	12	189
$P2/c$	13	141
$P2_1/c$	14	10450
$C2/c$	15	1930
$P222$	16	7
$P222_1$	17	9
$P2_12_12$	18	187
$P2_12_12_1$	19	3359
$C222_1$	20	86
$C222$	21	5
$F222$	22	0
$I222$	23	7
$I2_12_12_1$	24	5
$Pmm2$	25	2
$Pmc2_1$	26	12
$Pcc2$	27	0
$Pma2$	28	1
$Pca2_1$	29	242
$Pnc2$	30	3
$Pmn2_1$	31	37
$Pba2$	32	9
$Pna2_1$	33	513
$Pnn2$	34	14
$Cmm2$	35	2
$Cmc2_1$	36	56
$Ccc2$	37	6
$Amm2$	38	0
$Abm2$	39	5
$Ama2$	40	14
$Aba2$	41	47
$Fmm2$	42	8
$Fdd2$	43	115
$Imm2$	44	3
$Iba2$	45	31
$Ima2$	46	5
$Pmmm$	47	4
$Pnnn$	48	3
$Pccm$	49	1
$Pban$	50	2
$Pmma$	51	9
$Pnna$	52	23
$Pmna$	53	15
$Pcca$	54	13
$Pbam$	55	12
$Pccn$	56	101
$Pbcm$	57	64
$Pnnm$	58	30
$Pmmn$	59	23
$Pbcn$	60	341
$Pbca$	61	1261
$Pnma$	62	548
$Cmcm$	63	61
$Cmca$	64	96
$Cmmm$	65	4
$Cccm$	66	12
$Cmma$	67	2
$Ccca$	68	14
$Fmmm$	69	3
$Fddd$	70	30
$Immm$	71	4
$Ibam$	72	27
$Ibca$	73	8
$Imma$	74	5
$P4$	75	1
$P4_1$	76	47
$P4_2$	77	3
$P4_3$	78	7
$I4$	79	12
$I4_1$	80	9
$P\bar{4}$	81	7
$I\bar{4}$	82	59
$P4/m$	83	6
$P4_2/m$	84	3
$P4/n$	85	37
$P4_2/n$	86	48
$I4/m$	87	28
$I4_1/a$	88	98
$P422$	89	1
$P42_12$	90	4
$P4_122$	91	3
$P4_12_12$	92	101
$P4_222$	93	2
$P4_22_12$	94	7
$P4_322$	95	1
$P4_32_12$	96	44
$I422$	97	2
$I4_122$	98	1
$P4mm$	99	0
$P4bm$	100	0
$P4_2cm$	101	0
$P4_2nm$	102	4
$P4cc$	103	0
$P4nc$	104	3
$P4_2mc$	105	0
$P4_2bc$	106	1
$I4mm$	107	2
$I4cm$	108	1
$I4_1md$	109	6
$I4_1cd$	110	9
$P\bar{4}2m$	111	1
$P\bar{4}2c$	112	0
$P\bar{4}2_1m$	113	17
$P\bar{4}2_1c$	114	68
$P\bar{4}m2$	115	1
$P\bar{4}c2$	116	0
$P\bar{4}b2$	117	2
$P\bar{4}n2$	118	4
$I\bar{4}m2$	119	1
$I\bar{4}c2$	120	2
$I\bar{4}2m$	121	12
$I\bar{4}2d$	122	22
$P4/mmm$	123	0
$P4/mcc$	124	8
$P4/nbm$	125	4
$P4/nnc$	126	1
$P4/mbm$	127	2
$P4/mnc$	128	14
$P4/nmm$	129	19
$P4/ncc$	130	16
$P4_2/mmc$	131	3
$P4_2/mcm$	132	1
$P4_2/nbc$	133	2
$P4_2/nnm$	134	2
$P4_2/mbc$	135	1
$P4_2/mnm$	136	17
$P4_2/nmc$	137	8
$P4_2/ncm$	138	3
$I4/mmm$	139	17
$I4/mcm$	140	4
$I4_1/amd$	141	11
$I4_1/acd$	142	19
$P3$	143	10
$P3_1$	144	21
$P3_2$	145	10
$R3$	146	40
$P\bar{3}$	147	26
$R\bar{3}$	148	122
$P312$	149	0
$P321$	150	5
$P3_112$	151	0
$P3_121$	152	27
$P3_212$	153	0
$P3_221$	154	8
$R32$	155	23
$P3m1$	156	1
$P31m$	157	4
$P3c1$	158	3
$P31c$	159	5
$R3m$	160	21
$R3c$	161	39
$P\bar{3}1m$	162	0
$P\bar{3}1c$	163	13
$P\bar{3}m1$	164	15
$P\bar{3}c1$	165	17
$R\bar{3}m$	166	20
$R\bar{3}c$	167	36
$P6$	168	0
$P6_1$	169	14
$P6_5$	170	16
$P6_2$	171	5
$P6_4$	172	0
$P6_3$	173	33
$P\bar{6}$	174	1
$P6/m$	175	1
$P6_3/m$	176	75
$P622$	177	2
$P6_122$	178	6
$P6_522$	179	1
$P6_222$	180	4
$P6_422$	181	1
$P6_322$	182	6
$P6mm$	183	0
$P6cc$	184	0
$P6_3cm$	185	1
$P6_3mc$	186	15
$P\bar{6}m2$	187	0
$P\bar{6}c2$	188	0
$P\bar{6}2m$	189	0
$P\bar{6}2c$	190	9
$P6/mmm$	191	1
$P6/mcc$	192	7
$P6_3/mcm$	193	0
$P6_3/mmc$	194	9
$P23$	195	0
$F23$	196	0
$I23$	197	3
$P2_13$	198	15
$I2_13$	199	0
$Pm3$	200	2
$Pn3$	201	0
$Fm3$	202	0
$Fd3$	203	1
$Im3$	204	3
$Pa3$	205	36
$Ia3$	206	5
$P432$	207	0
$P4_232$	208	0
$F432$	209	1
$F4_132$	210	3
$I432$	211	0
$P4_332$	212	1
$P4_132$	213	1
$I4_132$	214	0
$P43m$	215	7
$F\bar{4}3m$	216	1
$I\bar{4}3m$	217	18
$P\bar{4}3n$	218	6
$F\bar{4}3c$	219	2
$I\bar{4}3d$	220	4
$Pm3m$	221	3
$Pn3n$	222	0
$Pm3n$	223	5
$Pn3m$	224	1
$Fm3m$	225	22
$Fm3c$	226	0
$Fd3m$	227	1
$Fd3c$	228	4
$Im3m$	229	8
$Ia3d$	230	0

ing the metric symmetry of the lattice. Using a matrix technique (Himes & Mighell, 1982) to analyze the metric symmetry of ~30 000 organic entries in the *NBS Crystal Data Identification File*, it has been found that many crystals reported in triclinic and monoclinic space groups have higher metric symmetry. Depending on the values used for 'reasonable' errors on the cell parameters, it was found that for 3 to 12% of the compounds the metric symmetry exceeds the crystal symmetry reported by the authors in the original reference. Inspection of samples from selected categories of these papers further revealed that, in many instances, the compounds have probably been described in space groups of too low symmetry.

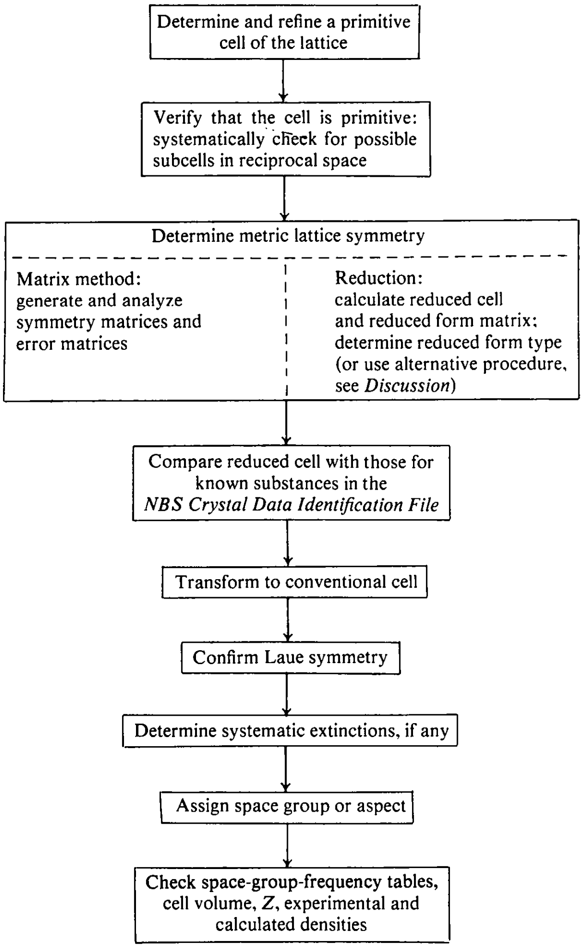
Many of the errors in space-group determination can be attributed to blind acceptance of the results of automated diffractometers, failure to inspect carefully the final structural parameters for possible higher symmetry, failure to ascribe unusual molecular or packing symmetry to a refinement in an incorrect space group, assuming that the e.s.d.'s on the cell parameters indicate accuracy rather than precision, and errors in space-group-determination strategy.

It is a serious error in strategy for the experimentalist not to check explicitly for the highest metric symmetry. This can lead to an assignment of a space group in the wrong crystal system. Traditionally, one of the first steps in assigning a space group for a compound is to select unit-cell parameters to be consistent with the observed intensity symmetry. The defect in this method is that the full intensity symmetry is not always easy to see. Thus, one could select a centered monoclinic cell consistent with the apparent Laue symmetry, check for systematic extinctions and conclude that everything is correct for the assignment of a centered monoclinic space group. However, the space group may be rhombohedral because the metric symmetry was not checked and the true Laue symmetry is higher. Our analysis of metric symmetry for organic compounds suggests that the rhombohedral system with approximately 300 reported compounds should have 10 to 20% more compounds assigned to it.

A detailed analysis of a typical example of missed rhombohedral symmetry has been reported by Davies, Kopf & Weiss (1982). In this case, it was shown that the structure of sodium *tert*-butoxide, which was originally reported in the monoclinic space group, Cc, with a = 30·995 (23), b = 19·378 (14), c = 18·269 (13) Å and β = 121·01 (2)°, can be described in the rhombohedral space group $R3c$, with a = 18·274 Å and α = 64·07°. A transformation matrix relating the C-centered monoclinic cell to the primitive rhombohedral cell (=reduced cell) is $(0\,0\,{-1}/\tfrac{1}{2}\,\tfrac{1}{2}\,0/\tfrac{1}{2}\,{-\tfrac{1}{2}}\,0)$. By using metric methods, one can immediately establish from the originally reported monoclinic cell parameters that the lattice is metrically rhombohedral. For example, the reduction method gives rhombohedral reduced form No. 2 (Mighell & Rodgers, 1980; *International Tables for X-ray Crystallography*, 1969), while the matrix technique, when applied to any primitive cell of the lattice, yields six matrices indicating the rhombohedral lattice symmetry.

In Table 2, we outline a procedure to help prevent errors in space-group determination. The procedure is similar to one presented earlier (Mighell & Rodgers, 1980) except that we have added a check using a matrix technique, a check of the *NBS Crystal Data Identification File*, and a check of the space-group-frequency table. As the table shows, the metric symmetry is determined as soon as a primitive unit cell of the lattice has been found. The metric symmetry may be determined using both matrix and reduction techniques. When using reduction techniques, the metric symmetry can be determined directly from the Niggli reduced form, or by alternative procedures recommended by Clegg (1981) and Le Page (1982). When assigning a space group, one should start by considering space groups consistent with the highest possible metric symmetry.

Table 2. *Space-group determination*



The compilation and evaluation of data for the *NBS Crystal Data Identification File* has been a collaborative effort between the NBS Crystal Data Center and the following data centers: Cambridge Crystallographic Data Centre (England), the Metals Data Center (Canada), and the Inorganic Structural Data Center (Germany). The authors wish to thank Drs Judith Stalick and Antonio Santoro for critical comment on the subject matter.

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The Local Atomic Order of a Ni–12·7 at.% Al Alloy Quenched from 1323 K*

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Abstract

High-angle X-ray diffuse scattering has been measured in a volume element in reciprocal space for a Ni–12·7 at.% Al alloy single crystal quenched from 1323 K. The Cowley–Warren order parameters were determined after separation of the first- and second-order size effects, using a procedure based on the Borie–Sparks quadratic approximation of atomic displacements. The experimental order coefficients were used to reconstruct the real-space locally ordered distribution of atoms, from which the spectrum of nearest-neighbor atomic configurations was determined. Some 61% of the Al atoms were found to be in a planar ordered configuration consisting of a nickel atom and four nearest-neighbor aluminum atoms, the basic structural unit of Ni_3Al. These planar elementary ordered units were, of course, distributed on the three equivalent {100} planes. While most of the ordered 'domains' consisted of from one to three Ni_3Al rings, a few domains were found to contain on the order of a hundred such elementary ordered units. The larger ordered domains may be thought of as embryos of the ordered Ni_3Al phase which have formed during quenching of the bulk alloy single crystal. There is evidence that the spatial distribution of ordered domains is not random.

Introduction

The α-phase Ni–Al alloys are classical examples of a precipitation hardening system; there is a marked decrease in solubility of Al in Ni with decreasing temperature; a second phase forms upon suitable low-temperature heat treatment. These alloys may also properly be considered as the prototype of a class of Ni-base superalloys whose commercially desirable mechanical properties are in a large part attributable to the presence of ordered Ni_3Al-*type* precipitate par-

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