

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	Space-group symbol	Space-group No.	Frequency	Space-group symbol	Space-group No.	Frequency	Space-group symbol	Space-group No.	Frequency
P1	1	305	Pmmn	59	23	P4̄b2	117	2	P6/m	175	1
P1̄	2	3986	Pbcn	60	341	P4n2	118	4	P6 ₂ /m	176	75
P2	3	11	Pbca	61	1261	I4m2	119	1	P622	177	2
P2 ₁	4	1957	Pnma	62	548	I4c2	120	2	P6 ₃ 22	178	6
C2	5	273	Cmcm	63	61	I42m	121	12	P6 ₄ 22	179	1
Pm	6	1	Cmca	64	96	I42d	122	22	P6 ₅ 22	180	4
Pc	7	102	Cmmm	65	4	P4/mmm	123	0	P6 ₆ 22	181	1
Cm	8	22	Cccm	66	12	P4/mcc	124	8	P6 ₇ 22	182	6
Cc	9	277	Cmma	67	2	P4/nbm	125	4	P6mm	183	0
P2/m	10	5	Ccca	68	14	P4/nnc	126	1	P6cc	184	0
P2 ₁ /m	11	239	Fmmm	69	3	P4/mbm	127	2	P6 ₈ cm	185	1
C2/m	12	189	Fddd	70	30	P4/mnc	128	14	P6 ₉ mc	186	15
P2/c	13	141	Immm	71	4	P4/nmm	129	19	P6m2	187	0
P2 ₁ /c	14	10450	Ibam	72	27	P4/ncc	130	16	P6c2	188	0
C2/c	15	1930	Ibca	73	8	P4 ₂ /mnc	131	3	P62m	189	0
P222	16	7	Inma	74	5	P4 ₂ /mcm	132	1	P62c	190	9
P222 ₁	17	9	P4	75	1	P4 ₂ /nbc	133	2	P6 ₃ /mmm	191	1
P2 ₁ 2 ₁ 2	18	187	P4 ₁	76	47	P4 ₂ /nmm	134	2	P6/mcc	192	7
P2 ₁ 2 ₁ 2 ₁	19	3359	P4 ₂	77	3	P4 ₂ /mbe	135	1	P6 ₄ /mcm	193	0
C222 ₁	20	86	P4 ₃	78	7	P4 ₂ /mnm	136	17	P6 ₅ /mnc	194	9
C222	21	5	I4	79	12	P4 ₂ /nmc	137	8	P23	195	0
F222	22	0	I4 ₁	80	9	P4 ₂ /ncm	138	3	F23	196	0
I222	23	7	P4̄	81	7	I4/mmm	139	17	I23	197	3
I2 ₁ 2 ₁ 2 ₁	24	5	I4̄	82	59	I4/mcm	140	4	P2 ₁ 3	198	15
Pmm2	25	2	P4/m	83	6	I4 ₁ /amd	141	11	I2 ₁ 3	199	0
Pmc2 ₁	26	12	P4 ₁ /m	84	3	I4 ₂ /acd	142	19	Pm3	200	2
Pcc2	27	0	P4/n	85	37	P3	143	10	Pn3	201	0
Pma2	28	1	P4 ₂ /n	86	48	P3 ₁	144	21	Fm3	202	0
Pca2 ₁	29	242	I4/m	87	28	P3 ₂	145	10	Fd3	203	1
Pnc2	30	3	I4 ₁ /a	88	98	R3	146	40	Im3	204	3
Pmn2 ₁	31	37	P422	89	1	P3	147	26	Pa3	205	36
Pba2	32	9	P4 ₂ 2	90	4	R3̄	148	188	Ia3	206	5
Pna2 ₁	33	513	P4 ₂ 22	91	3	P312	149	0	P432	207	0
Pnn2	34	14	P4 ₁ 2 ₁ 2	92	101	P321	150	5	P4 ₃ 32	208	0
Cmm2	35	2	P4 ₂ 22	93	2	P3 ₁ 12	151	0	F432	209	1
Cmc2 ₁	36	56	P4 ₂ 2 ₁ 2	94	7	P3 ₂ 12	152	27	F4 ₃ 32	210	3
Ccc2	37	6	P4 ₂ 22	95	1	P3 ₃ 12	153	0	I432	211	0
Anm2	38	0	P4 ₂ 2 ₁ 2	96	44	P3 ₂ 21	154	8	P4 ₄ 32	212	1
Abm2	39	5	I422	97	2	R32	155	23	P4 ₅ 32	213	1
Ama2	40	14	I4 ₂ 22	98	1	P3m1	156	1	I4 ₁ 32	214	0
Aba2	41	47	P4mm	99	0	P31m	157	4	P43m	215	7
Fmm2	42	8	P4hm	100	0	P3c1	158	3	F43m	216	1
Fdd2	43	115	P4 ₁ cm	101	0	P31c	159	5	I43m	217	18
Imm2	44	3	P4 ₂ nm	102	4	R3m	160	21	P43n	218	6
Iba2	45	31	P4cc	103	0	R3c	161	39	F43c	219	2
Ima2	46	5	P4nc	104	3	P31m	162	0	I43d	220	4
Pmmm	47	4	P4 ₁ mc	105	0	P31c	163	13	Pm3m	221	3
Pnnn	48	3	P4 ₂ bc	106	1	P3m1	164	15	Pn3n	222	0
Pccm	49	1	I4mm	107	2	P3c1	165	17	Pm3n	223	5
Pban	50	2	I4cm	108	1	R3m	166	20	Pn3m	224	1
Pmma	51	9	I4 ₁ md	109	6	R3c	167	36	Fm3m	225	22
Pnna	52	23	I4 ₂ cd	110	9	P6	168	0	Fm3c	226	0
Pmna	53	15	P42m	111	1	P6 ₁	169	14	Fd3m	227	1
Pcca	54	13	P42c	112	0	P6 ₂	170	16	Fd3c	228	4
Pham	55	12	P4 ₂ 1m	113	17	P6 ₃	171	5	Im3m	229	8
Pccn	56	101	P4 ₂ 1c	114	68	P6 ₄	172	0	Ia3d	230	0
Pbcn	57	64	P4m2	115	1	P6 ₅	173	33			
Pnnn	58	30	P4c2	116	0	P6̄	174	1			

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.

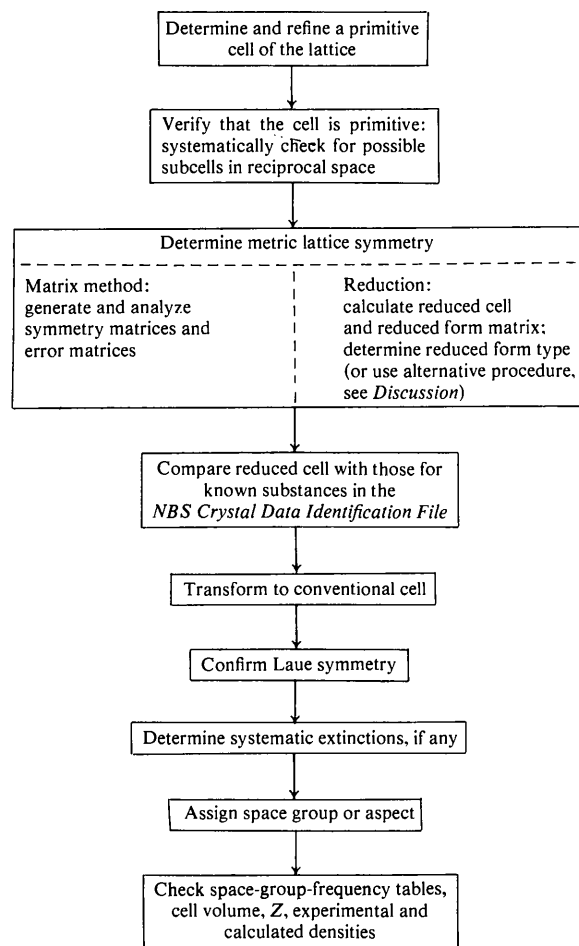
It is a serious error in strategy for the experimentalist not to check explicitly for the highest metric symmetry. This can lead to an assignment of a space group in the wrong crystal system. Traditionally, one of the first steps in assigning a space group for a compound is to select unit-cell parameters 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 $\beta = 121.01(2)^\circ$, can be described in the rhombohedral space group *R3c*, with $a = 18.274$ Å and $\alpha = 64.07^\circ$. A transformation matrix relating the *C*-centered monoclinic cell to the primitive rhombohedral cell (=reduced cell) is $(0\ 0\ -1/\frac{1}{2}\ \frac{1}{2}\ 0/\frac{1}{2}\ -\frac{1}{2}\ 0)$. 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 rhombo-

hedral 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 Ni₃Al. 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 Ni₃Al 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 Ni₃Al 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 Ni₃Al-type precipitate par-

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