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The Perils of *Cc*: Comparing the Frequencies of Falsely Assigned Space Groups with their General Population

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Abstract

A compilation of 221 space-group corrections from a false low symmetry (FS) to a higher true symmetry (TS) shows that higher symmetry is often overlooked in only a few space-group types. An incorrect lattice (false crystal class) is found most often for rhombohedral space-group types, and there especi-

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ally for $R\bar{3}m$ (TS) and $R\bar{3}c$ (TS), and for space group $Fdd2$ (TS). An inversion center is most often missed in space groups $C2/c$ (TS) and $Pnma$ (TS). The group which has the highest probability of being falsely assigned in a crystal structure determination is space group Cc (FS), both in absolute numbers and relative to its frequency among determined crystal structures. Possibly over 10% of all crystal structures reported in Cc (FS) should actually be described in a higher true symmetry ($C2/c$, $Fdd2$ or $R\bar{3}c$). For comparative purposes statistics of the frequency of space groups among inorganic crystal structures are given and compared with the corresponding distribution among organic compounds. Each space group appears to be occupied by at least one example. Inorganic substances are heavily concentrated in space groups of the most symmetric crystal classes of trigonal, tetragonal, hexagonal and cubic symmetry. Inorganic crystal structures are, compared to the organic structures, much more evenly distributed over the crystal systems. Surprisingly inversion centers are *not* much more common among inorganic substances when compared with organic compounds.

Introduction

When we determine a crystal structure there are four points at which we judge the symmetry of a previously undetermined structure:

(*a*) Before the diffraction experiment we do this on the basis of our knowledge of the physical properties of the substance. The simplest check along these lines is the visual inspection of the specimen. In some cases the available evidence may be meagre.

(*b*) Inspection of the geometry of the reciprocal lattice allows assignment of a crystal system. This is the point at which a mistake made at the beginning has a reasonable chance of being perpetuated. This can happen most easily when a preliminary orientation matrix obtained on a single-crystal diffractometer is accepted and not rechecked.

(*c*) After the intensity data have been collected we inspect their symmetry in reciprocal space. If a mistake was made in (*b*) above, we might overlook the symmetry of the intensity distribution. Intensity information may be abundant in a standard single-crystal investigation, especially if data were collected within the complete reflexion sphere, but are limited in the case of powder diffraction.

(*d*) After the crystal structure is determined and refined we have the possibility of studying the symmetry of the result in direct space. This means that we can check the lattice geometry and the distribution of atoms for inherent symmetries which previously might have been overlooked.

Because this last chance to check the symmetry is sometimes neglected, an appreciably large, but essentially unknown number of crystal structure determinations are described in incorrect space groups. The most common occurrence seems to be the assignment of space groups of too low symmetry (Schomaker & Marsh, 1979; Jones, 1984; Baur & Tillmanns, 1986; Marsh, 1986*a*) and we restrict ourselves to treating these cases only. In some instances refinement in a false space group can lead to incorrect chemistry being described for the compound studied (*e.g.* Marsh, 1986*b*; Müller, Bernet & Hoppe, 1991). Since the number of published space-group corrections is now sufficiently large to give meaningful statistics we have compiled the relevant data.

Reported space-group changes

We searched the literature for reported space-group changes from a lower false symmetry (FS) to true higher symmetries (TS) and identified 210 of them. The corresponding papers were published between 1964 and 1991 and more than half of them were authored by Marsh and coworkers. An additional 10 space-group changes are known in our laboratory, one was communicated to us by U. Müller, and these 11 remain unpublished so far. We thus count 221 separate entries whereby we disregard isostructural pairs or series: the count refers to distinctly different crystal structure types, see Table 1. The sample consists of crystal structures of organic molecules, organometallics, inorganic compounds and alloys. The nature of our literature search is such that it is difficult to be certain of having found all possible references. These 221 cases are only a fraction of the expected number if all incorrectly assigned space groups were corrected. This is based on the estimate made by Baur & Tillmanns (1986), according to which about 3% of all published crystal structures may have been described in too low a symmetry. We cannot be certain that all the reported space-group revisions themselves are correct. Some of them are based on new refinements of the original diffraction data, some on new data and some on a comparison of the e.s.d.'s of the positional coordinates with the shifts in the coordinates necessary to attain higher symmetry. All reported space-group changes are given with their observed frequencies in Table 2. They are sorted into the three categories of error already employed by Baur & Tillmanns (1986): (1) both Laue class and crystal system are wrong; (2) only the Laue class is wrong; (3) Laue class and crystal system are correct, but an inversion center is missing. Additionally another category covers cases in which (4) a centering was overlooked, or too large a cell chosen, sometimes because diffraction spots were not recognized as due to twinning problems.

Table 1. *References to space-group corrections*

Entries are in the sequence: count, original space group, FS, corrected space group, TS (all space groups entered as given in the literature, that is not necessarily in standard setting), number of category, original reference, reference for correction. References are given in the order: last name of author, but not more than nine characters, the last (or the ninth) character is a + if there are multiple authors, year of publication, abbreviation for the journal, volume number, page number. If several corrections were published, the last one is given, on the assumption that the previous ones are quoted there. Numbers 24*, 52*, 93*, 97*, 124* and 138* are not counted towards the total of 221 entries because they are isostructural with the entries preceding them.

	FS	TS	Category	Reference 1	Reference 2
1	*Ic*	*I*2/*c*	3	GARCIA-B + (1968). *ZK*, **127**, 145	BAUR + (1970). *ZK*, **131**, 213
2	*P*$\bar{1}$	*I*2/*m*	1	BAGIEU-B + (1975). *AC*, **B31**, 2264	BAUR + (1986). *AC*, **B42**, 95
3	$P2_1$	$A2_1ma$	1	FAURE + (1981). *CSC*, **10**, 515	BAUR + (1986). *AC*, **B42**, 95
4	*P*1	*A*2/*a*	1	GOSTOJIC + (1982). *CSC*, **11**, 1215	BAUR + (1986). *AC*, **B42**, 95
5	*P*1	*Cm*	1	COUSSON + (1983). *AC*, **C39**, 425	BAUR + (1986). *AC*, **B42**, 95
6	*P*1	*Cc*	1	RZAIGUI + (1983). *JSSC*, **50**, 240	BAUR + (1986). *AC*, **B42**, 95
7	*P*1	*Im*	1	PALCHIK + (1984). *DAN*, **278**, 108	BAUR + (1986). *AC*, **B42**, 95
8	*C*2/*c*	*R*$\bar{3}$*c*	1	MATSUNO + (1984). *BCSJ*, **57**, 593	BAUR + (1986). *AC*, **B42**, 95
9	*P*1	*P*$\bar{1}$	3	STEFANID + (1982). *ZK*, **159**, 255	BAUR + (1986). *AC*, **B42**, 95
10	*P*1	*P*$\bar{1}$	3	PRINCE + (1984). *AC*, **C40**, 1499	BAUR + (1986). *AC*, **B42**, 95
11	*Pba*2	*Pbam*	3	BRISSON + (1984). *AC*, **C40**, 1405	BAUR + (1986). *AC*, **B42**, 95
12	*P*$\bar{1}$	*C*2/*c*	1	STEFFEN + (1977). *IC*, **16**, 1119	MARSH + (1979). *IC*, **18**, 2331
13	*P*$\bar{1}$	*C*2/*c*	1	BERTRAND (1977). *IC*, **16**, 1484	MARSH + (1979). *IC*, **18**, 2331
14	*Aa*	*A*2/*a*	3	MOORE + (1977). *IC*, **16**, 1839	MARSH + (1979). *IC*, **18**, 2331
15	*P*1	*P*$\bar{1}$	3	CANNAS + (1977). *IC*, **16**, 228	MARSH + (1979). *IC*, **18**, 2331
16	*C*2	*C*2/*m*	3	KARIPIDE + (1977). *IC*, **16**, 3299	MARSH + (1979). *IC*, **18**, 2331
17	$Pna2_1$	*Pnma*	3	CLEARFIE + (1977). *IC*, **16**, 628	MARSH + (1979). *IC*, **18**, 2331
18	*P*1	*P*$\bar{1}$	3	CHIA + (1977). *IC*, **16**, 254	MARSH + (1979). *IC*, **18**, 2331
19	*P*$\bar{1}$	*C*2/*c*	1	TOUPET + (1984). *AC*, **C40**, 1490	MARSH + (1988). *AC*, **B44**, 77
20	*Bb*	*Fdd*2	1	GRIDUNOV + (1983). *SPC*, **28**, 166	MARSH + (1988). *AC*, **B44**, 77
21	*Cc*	*Fdd*2	1	HO + (1986). *AC*, **C42**, 1787	MARSH + (1988). *AC*, **B44**, 77
22	*Cc*	*Fdd*2	1	HERBSTEI + (1986). *AC*, **B42**, 575	MARSH + (1988). *AC*, **B44**, 77
23	*Bb*	*C*2/*c*	3	VOLIOTIS + (1975). *AC*, **B31**, 2607	MARSH + (1988). *AC*, **B44**, 77
24*	*Bb*	*C*2/*c*	3	VOLIOTIS + (1975). *AC*, **B31**, 2612	MARSH + (1988). *AC*, **B44**, 77
25	*Pa*	$P2_1/a$	3	FUJISAWA + (1982). *BCSJ*, **55**, 3424	MARSH + (1988). *AC*, **B44**, 77
26	*Pc*	$P2_1/a$	3	MERCIER + (1982). *AC*, **B38**, 1731	MARSH + (1988). *AC*, **B44**, 77
27	*Cm*	*C*2/*m*	3	LEFUR + (1982). *AC*, **B38**, 1431	MARSH + (1988). *AC*, **B44**, 77
28	*Cc*	*C*2/*c*	3	NIRMALA + (1982). *AC*, **B38**, 839	MARSH + (1988). *AC*, **B44**, 77
29	*Cc*	*C*2/*c*	3	REBBAH + (1979). *AC*, **B35**, 2197	MARSH + (1988). *AC*, **B44**, 77
30	$Cmc2_1$	*Cmcm*	3	JEFFS + (1983). *AC*, **C39**, 1205	MARSH + (1988). *AC*, **B44**, 77
31	$I4_1$	$I4_1/a$	3	EL-TOUK + (1984). *JACS*, **106**, 4596	MARSH + (1988). *AC*, **B44**, 77
32	*P*1	*P*$\bar{1}$	3	SOLANS + (1982). *CSC*, **11**, 1199	MARSH + (1988). *AC*, **B44**, 77
33	$Pna2_1$	*Pnam*	3	GERDIL + (1974). *HCA*, **57**, 489	MARSH + (1988). *AC*, **B44**, 77
34	$Pna2_1$	*Pnam*	3	ZANOTTI + (1982). *CSC*, **11**, 1329	MARSH + (1988). *AC*, **B44**, 77
35	$P2_1$	$P2_1/c$	3	SCHNEIDE + (1982). *CSC*, **11**, 1233	MARSH + (1988). *AC*, **B44**, 77
36	*Cc*	*C*2/*c*	3	BOCELLI, (1982), *CSC*, **11**, 2035	MARSH + (1988). *AC*, **B44**, 77
37	$Pna2_1$	*Pnam*	3	ALÉONARD + (1980). *JSSC*, **34**, 79	MARSH + (1988). *AC*, **B44**, 77
38	*P*1	*Cc*	1	MAIRESSE + (1978). *AC*, **B34**, 1771	MARSH (1980). *AC*, **B36**, 219
39	*R*$\bar{3}$	*R*$\bar{3}$	3	RANGE + (1984). *ZN*, **39**b, 118	JONES + (1987). *ZN*, **42**b, 1365
40	*P*$\bar{1}$	*C*2/*m*	1	WILLETT + (1988), *IC*, **27**, 614	MARSH (1988). *IC*, **27**, 2902
41	*P*$\bar{1}$	*C*2/*c*	1	OZAROWSK + (1988). *IC*, **27**, 628	MARSH (1988). *IC*, **27**, 2902
42	$Cmc2_1$	*Cmcm*	3	DARRIET + (1978). *AC*, **B34**, 3528	MARSH + (1983). *AC*, **B39**, 280
43	*Cmcm*	$P6_3/mcm$	1	MARSH + (1983). *AC*, **B39**, 280	LEPAGE + (1984). *AC*, **C40**, 1787
44	*P*$\bar{1}$	*P*$\bar{1}$	3	EMSLEY + (1981). *JINC*, **43**, 2243	GILMORE + (1982). *AC*, **B38**, 2809
45	*P*$\bar{1}$	*P*2/*n*	1	LEE + (1987). *JSSC*, **67**, 364	MARSH (1988). *JSSC*, **73**, 577
46	*I*$\bar{4}$	*I*$\bar{4}$2*m*	2	GASTALDE + (1987). *JSSC*, **66**, 251	MARSH + (1988). *JSSC*, **73**, 591
47	*P*3	*R*32	1	BOEYENS + (1985). *IC*, **24**, 2926	MARSH (1987). *AC*, **B43**, 174
48	$P2_1$	$P2_1/m$	3	BAVOSO + (1984). *AC*, **C40**, 2035	MARSH (1986). *AC*, **B42**, 193
49	$Pbc2_1$	*Pbcm*	3	PETT + (1983). *IC*, **22**, 3661	MARSH (1986). *AC*, **B42**, 193
50	*Pn*	*P*2/*n*	3	YAMAGUCH + (1984). *AC*, **C40**, 113	MARSH (1986). *AC*, **B42**, 193
51	*P*1	*P*$\bar{1}$	3	GALI + (1989). *AC*, **C45**, 1667	MARSH (1990). *AC*, **C46**, 2497
52*	*P*1	*P*$\bar{1}$	3	GALI + (1989). *AC*, **C45**, 1667	MARSH (1990). *AC*, **C46**, 2497
53	$Pna2_1$	*Pnma*	3	CASTELLA + (1989). *AC*, **C45**, 1207	MARSH (1990). *AC*, **C46**, 1761
54	*P*1	*P*$\bar{1}$	3	TOUPET + (1989). *AC*, **C45**, 1044	MARSH (1990). *AC*, **C46**, 1356
55	*C*2/*m*	*R*$\bar{3}$*m*	1	BHAN + (1969). *JLCM*, **19**, 121	CENZUAL + (1990). *ZK*, **193**, 217
56	*C*2/*m*	*R*$\bar{3}$*m*	1	AXEL + (1965). *ANC*, **77**, 379	SCHNERIN + (1980). *ZM*, **71**, 357
57	*C*2/*m*	*R*$\bar{3}$*m*	1	BHAN + (1969). *JLCM*, **19**, 121	CENZUAL + (1990). *ZK*, **193**, 217
58	*C*2/*m*	*R*$\bar{3}$*m*	1	EISENMAN + (1985). *ZN*, **40**b, 1419	EISENMAN + (1989). *ZN*, **44**b, 1228
59	*C*2/*m*	*R*$\bar{3}$*m*	1	MICHELET + (1976). *JLCM*, **45**, 185	CLAUSS + (1978). *NJMM*, 256
60	*C*2/*m*	*R*$\bar{3}$*m*	1	BHAN + (1969). *JLCM*, **19**, 121	CENZUAL (1990). *ZK*, **C193**, 217
61	*C*2/*m*	*R*$\bar{3}$*m*	1	ZALKIN + (1956). *JPC*, **60**, 1275	CENZUAL (1990). *ZK*, **C193**, 217
62	*C*2/*m*	*R*$\bar{3}$*m*	1	WELK + (1977). *ZN*, **32**b, 749	CENZUAL (1990). *ZK*, **C193**, 217
63	*C*2/*m*	*R*$\bar{3}$*m*	1	BELIN (1981). *AC*, **B37**, 2060	MARSH + (1983). *AC*, **B39**, 280
64	*C*2/*c*	*R*$\bar{3}$*m*	1	PETROV + (1987). *SPC*, **32**, 289	CENZUAL (1990). *ZK*, **C193**, 217
65	*C*2/*m*	*R*$\bar{3}$*m*	1	WELK + (1977). *ZN*, **32**b, 749	CENZUAL (1990). *ZK*, **C193**, 217
66	*C*2	*R*32	1	KLEE + (1979). *ZN*, **34**b, 657	CENZUAL (1990). *ZK*, **C193**, 217
67	*C*2/*c*	*R*$\bar{3}$*c*	1	BRONGER + (1982). *JLCM*, **83**, 29	BRONGER + (1983). *JLCM*, **95**, 275

Table 1 (*cont.*)

	FS	TS	Category	Reference 1	Reference 2
68	*Cm*	*R3m*	1	COLLIN + (1974). *AC*, **B30**, 1134	CENZUAL (1990). *ZK*, **C193**, 217
69	*Pnc2*	*Pnca*	3	SPEK (1977). *CSC*, **6**, 259	SPEK + (1990). *AC*, **C46**, 1357
70	*Cmmm*	*P4/mbm*	1	ABBA-TOU + (1990). *JSSC*, **84**, 245	MARSH (1990). *JSSC*, **87**, 467
71	$P\bar{1}$	*C2/m*	1	AKIMOTO + (1989). *JSSC*, **83**, 132	MARSH (1990). *JSSC*, **86**, 135
72	*Cc*	*C2/c*	3	BINO + (1979). *IC*, **18**, 2599	MARSH + (1981). *IC*, **20**, 299
73	$I\bar{4}$	*I4/m*	3	BAYON + (1979). *IC*, **18**, 3478	MARSH + (1981). *IC*, **20**, 299
74	$P2_1$	$Cmc2_1$	1	GINDEROW (1989). *AC*, **C45**, 185	MARSH (1989). *AC*, **C45**, 1840
75	*Cc*	*C2/c*	3	COTTON + (1980). *AC*, **B36**, 457	MARSH (1981). *AC*, **B37**, 1985
76	*C2/c*	$R\bar{3}c$	1	HALLER + (1983). *AC*, **C39**, 1559	MARSH (1984). *AC*, **C40**, 1632
77	*Pn*	$P2_1/n$	3	NOORDIK + (1982). *CSC*, **11**, 1335	HERBSTEI + (1984). *AC*, **C40**, 1633
78	*C2/c*	*Ibca*	1	BENAMARA + (1987). *AC*, **C43**, 616	MARSH (1987). *AC*, **C43**, 2470
79	*Pnn2*	*Pnna*	3	FORTIER + (1985). *AC*. **C41**, 1763	MARSH (1986). *AC*, **C42**, 1327
80	*Cc*	*C2/c*	3	LUEKENS + (1984). *IC*, **23**, 1718	MARSH + (1985). *IC*, **24**, 2114
81	*Pn*	$P2_1/n$	3	BURFORD + (1984). *IC*, **23**, 1946	MARSH + (1985). *IC*, **24**, 2114
82	*Cm*	*P6m2*	1	METIN + (1984). *JSSC*, **55**, 299	MARSH (1986). *JSSC*, **64**, 119
83	$P2_1$	$P2_1/n$	3	SATYANAR + (1981). *ZK*, **157**, 191	HERBSTEI + (1985). *ZK*, **173**, 249
84	$P\bar{1}$	*C2/c*	1	RATH + (1985). *IC*, **24**, 3934	SCHAEFER (1986). *IC*, **25**, 2665
85	*C2*	$P3_121$	1	HÄMÄLÄIN + (1978). *ACS*, **A32**, 549	DAVIES (1984). *AC*, **C40**, 903
86	$P4_1$	$P4_12_12$	2	KVICK + (1980). *AC*, **B36**, 734	HERBSTEI + (1982). *AC*, **B38**, 1051
87	$P6_3/m$	$P6_3/mmc$	2	ENDRES + (1979). *AC*, **B35**, 2880	HERBSTEI + (1982). *AC*, **B38**, 1051
88	$P6_3/m$	$P6_3/mmc$	2	MULLICA + (1980). *AC*, **B36**, 2561	HERBSTEI + (1982). *AC*, **B38**, 1051
89	$P\bar{1}$	*C2/c*	1	ENDRES + (1980). *AC*, **B36**, 2230	HERBSTEI + (1982). *AC*, **B38**, 1051
90	*C2/c*	$R\bar{3}c$	1	GALY + (1980). *AC*, **B36**, 392	HERBSTEI + (1982). *AC*, **B38**, 1051
91	*C2/c*	$R\bar{3}c$	1	BINO + (1976). *JACS*, **98**, 7093	HERBSTEI + (1982). *AC*, **B38**, 1051
92	*C2/m*	$R\bar{3}m$	1	HASSEL + (1958). *ACS*, **12**, 1146	HERBSTEI + (1982). *AC*, **B38**, 1051
93*	*C2/m*	$R\bar{3}m$	1	HASSEL + (1959). *ACS*, **13**, 1781	HERBSTEI + (1982). *AC*, **B38**, 1051
94	$P\bar{1}$	$P2_1/n$	1	BOIS + (1976). *AC*, **B32**, 1541	SCHOMAKE + (1979). *AC*, **B35**, 1094
95	$P\bar{1}$	*C2/c*	1	VANDERVE + (1984). *IC*, **23**, 146	MARSH (1984). *IC*, **23**, 3682
96	$P\bar{1}$	*C2/c*	1	CHIADMI + (1985). *AC*, **C41**, 811	MARSH (1986). *AC*, **C42**, 511
97*	$P\bar{1}$	*C2/c*	1	BRODALLA + (1980). *ZN*, **35b**, 403	MARSH (1986). *AC*, **C42**, 511
98	$Pna2_1$	*Pnam*	3	WEI + (1988). *AC*, **C44**, 77	WEI + (1988). *AC*, **C44**, 1866
99	$P2_1$	$P2_1/m$	3	COOKSLEY + (1974). *AC*, **B30**, 864	BAUR + (1987). Unpublished.
100	*P3m1*	$P\bar{3}m1$	3	BEAULIEU + (1982). *MC*, **113**, 415	BAUR + (1991). Unpublished.
101	*C2/c*	$P\bar{3}c1$	1	MASSA (1977). *ZAAC*, **436**, 29	MARSH + (1983). *AC*, **B39**, 280
102	$C222_1$	*Ccmm*	3	VILMINOT + (1978). *AC*, **B34**, 3308	MARSH + (1983). *AC*, **B39**, 280
103	$Pn2_1a$	*Pnma*	3	YANAGISA + (1979). *AC*, **B35**, 137	MARSH + (1983). *AC*, **B39**, 280
104	*C2*	*C2/c*	3	MACHIDA + (1982). *AC*, **B38**, 386	MARSH + (1983). *AC*, **B39**, 280
105	$Cmc2_1$	*Cmcm*	3	BAENZING + (1966). *IC*, **5**, 1399	MARSH + (1983). *AC*, **B39**, 280
106	*C2*	*C2/m*	3	KOZAREK + (1973). *IC*, **12**, 2129	MARSH + (1983). *AC*, **B39**, 280
107	*P4b2*	*P4/mbm*	3	PINTO + (1980). *JCSCC*, **13**	MARSH + (1983). *AC*, **B39**, 280
108	*Cc*	*C2/c*	3	LEADBETT + (1980). *MCLC*, **61**, 39	MARSH + (1983). *AC*, **B39**, 280
109	*P1*	*Cc*	1	BUROW + (1979). *ZAAC*, **459**, 59	JONES (1984). *CSR*, **13**, 157
110	$P2_1/m$	*Cmcm*	1	JANSEN (1978). *RCM*, **15**, 242	BODENSTE + (1983). *ZN*, **38b**, 172
111	$Pna2_1$	*Pnam*	3	CLEGG + (1985), *AC*, **C41**, 530	CLEGG (1986). *AC*, **C42**, 1463
112	$Pna2_1$	*Pnam*	3	KIHLBORG + (1971). *AC*, **B27**, 2066	KIHLBORG + (1972). *AC*, **B28**, 3097
113	$P3_2$	$P3_221$	2	FISCHER + (1983), *NJMM*, 49	FISCHER + (1987). *AC*, **C43**, 1852
114	*Cc*	*C2/c*	3	OZIMA (1986). *AC*, **C42**, 513	OZIMA (1987). *AC*, **C43**, 173
115	*Cc*	*C2/c*	3	CORDES + (1974). *AC*, **B30**, 1621	SINGH + (1978). *AC*, **B34**, 2956
116	$P4_2/n$	$P4_2/nmc$	2	KURODA + (1983). *IC*, **22**, 3620	MARSH (1984). *IC*, **23**, 2363
117	$P\bar{1}$	*C2/c*	1	SHIMIZU + (1983). *AC*, **C39**, 891	SHIMIZU + (1984). *AC*, **C40**, 902
118	$P2_1$	$P2_12_12_1$	1	SUGIO + (1983). *AC*, **C39**, 745	SUGIO + (1984). *AC*, **C40**, 712
119	*C2*	*Fdd2*	1	JABER + (1983). *AC*, **C39**, 485	MARSH (1983). *AC*, **C39**, 1473
120	$P\bar{1}$	*Immm*	1	SOLANS + (1983). *AC*, **C39**, 1510	MARSH (1984). *AC*, **C40**, 1110
121	*Cc*	*C2/c*	3	DUMORA + (1971). *MRB*, **6**, 561	WU + (1973). *MRB*, **8**, 593
122	*Cc*	*C2/c*	3	HOLT + (1977). *AC*, **B33**, 95	BAUR + (1991). Unpublished.
123	*Cc*	*C2/c*	3	GUILLEVI + (1974). *AC*, **B30**, 111	BAUR + (1991). Unpublished.
124*	*Cc*	*C2/c*	3	GUILLEVI + (1974). *AC*, **B30**, 111	BAUR + (1991). Unpublished.
125	*Cc*	*C2/c*	3	RODEK + (1980). *ZAAC*, **462**, 42	BAUR + (1991). Unpublished.
126	*Cc*	*C2/c*	3	LEE + (1969), *AC*, **B25**, 2497	EINSPAHR + (1971). *AC*, **B27**, 846
127	*Cm*	*C2/m*	3	NODA + (1986). *AC*, **B42**, 529	MARSH (1987). *AC*, **B43**, 415
128	$P\bar{4}$	$P\bar{4}2_1m$	2	BALL + (1985). *AC*, **C41**, 47	MARSH + (1985). *AC*, **C41**, 1383
129	$P\bar{1}$	*C2/c*	1	ALLAN + (1985). *AC*, **C41**, 58	MARSH + (1985). *AC*, **C41**, 1383
130	$P\bar{1}$	*C2/c*	1	OLSZAK + (1987). *AC*, **C43**, 2169	MARSH + (1988). *AC*, **C44**, 948
131	*P31c*	$P6_3/mmc$	1	SCHUSTER + (1980). *ZM*, **71**, 341	PARTHÉ + (1988). *AC*, **C44**, 774
132	*C2/c*	$R\bar{3}c$	1	AVERBUCH + (1987). *AC*, **C43**, 1653	MARSH (1988). *AC*, **C44**, 774
133	*P1*	$P\bar{1}$	3	FORNASINI (1987). *AC*, **C43**, 613	MARSH + (1988). *AC*, **C44**, 395
134	*C2*	*Fdd2*	1	CHARPIN + (1988). *AC*, **C44**, 1698	MARSH (1989). *AC*, **C45**, 980
135	$Pna2_1$	*Pnma*	3	HÖKELEK + (1988). *AC*, **C44**, 832	MARSH (1989). *AC*, **C45**, 694
136	$P\bar{1}$	*C2/c*	1	SAMEENA + (1988). *AC*, **C44**, 1047	MARSH (1989). *AC*, **C45**, 347
137	$P2_1/m$	*Cmcm*	1	MULLICA + (1989). *AC*, **C45**, 330	MARSH + (1989). *AC*, **C45**, 1270
138*	$P2_1/m$	*Cmcm*	1	MULLICA + (1988). *ICA*, **142**, 9	MARSH (1989). *ICA*, **157**, 1
139	*P1*	$P\bar{1}$	3	KITAJIMA + (1988). *AC*, **C44**, 1876	MARSH (1989). *AC*, **C45**, 1269
140	*P1*	$P\bar{1}$	3	BOCELLI + (1984). *AC*, **C40**, 679	BOCELLI + (1986). *AC*, **C42**, 127
141	*P1*	$P\bar{1}$	3	BOCELLI + (1984). *AC*, **C40**, 1391	BOCELLI + (1986). *AC*, **C42**, 127
142	*Cc*	*C2/c*	3	RAMANI + (1975). *FER*, **9**, 49	MARUMO + (1974). *AC*, **B30**, 1628

Table 1 (*cont.*)

	FS	TS	Category	Reference 1	Reference 2
143	*Cc*	*C*2/*c*	3	Matveeva + (1980). *SPD*, **25**, 321	Baur + (1991). Unpublished.
144	*Cc*	*C*2/*c*	3	Hanson (1962). *AC*, **15**, 930	Boese + (1990). *ZK*, **193**, 289
145	*Cc*	*C*2/*c*	3	Pascard (1955). *CR*, **240**, 2162	Yu + (1978). *JCMS*, **8**, 193
146	*Cc*	*C*2/*c*	3	Dittrich + (1969). *ZAAC*, **371**, 306	Hodeau + (1982). *JSSC*, **45**, 170
147	*Cc*	*C*2/*c*	3	Maksimov + (1974). *SPD*, **18**, 681	Metcalf − + (1976). *AC*, **B32**, 2553
148	$P2_1$	$P2_1/m$	3	Tzschach + (1985). *JCSR*, **15**, 423	Marsh (1986). *JCSR*, **16**, 797
149	$P\bar{1}$	$P\bar{1}$	3	Calestan + (1987). *JCSR*, **17**, 251	Marsh (1988). *JCSR*, **18**, 219
150	$P\bar{1}$	$P2_1/n$	1	Bois + (1976). *AC*, **B32**, 1541	Schomaker + (1979). *AC*, **B35**, 1094
151	*Cc*	*Fdd*2	1	Sakae + (1978). *AM*, **63**, 520	Baur + (1991). Unpublished.
152	*Cc*	*C*2/*c*	3	Staffel + (1988). *ZAAC*, **563**, 27	Marsh + (1990). *ZAAC*, **582**, 128
153	$I\bar{4}$	*I*4/*m*	3	Bino + (1979). *IC*, **18**, 2599	Marsh + (1981). *IC*, **20**, 299
154	*Cc*	*R*3*c*	1	Greiser + (1977). *CB*, **110**, 3388	Davies + (1982). *AC*, **B38**, 2251
155	$P2_1$	$P2_12_12_1$	1	Bernal + (1988). *ICA*, **142**, 235	Marsh (1989). *ICA*, **157**, 1
156	$Pna2_1$	*Pnam*	3	Zhongshe + (1988). *ICA*, **142**, 333	Marsh (1989). *ICA*, **157**, 1
157	*P*1	*R*3*m*	1	Araujo-M + (1988). *ICA*, **146**, 123	Marsh (1989). *ICA*, **161**, 1
158	*Cc*	*C*2/*c*	3	Leukens + (1984). *IC*, **23**, 1718	Marsh + (1985). *IC*, **24**, 2114
159	*Pn*	$P2_1/n$	3	Burford + (1984). *IC*, **23**, 1946	Marsh + (1985). *IC*, **24**, 2114
160	$P\bar{1}$	*C*2/*c*	1	Cotton + (1984). *IC*, **23**, 4033	Marsh + (1985). *IC*, **24**, 3487
161	*Cc*	*Fdd*2	1	Arif + (1987). *OM*, **6**, 506	Marsh + (1987). *OM*, **6**, 1996
162	*C*2	*C*2/*c*	3	Picard + (1987). *JSSC*, **69**, 380	Baur + (1991). Unpublished.
163	*I*2/*a*	*Fddd*	1	Searle + (1989). *ICA*, **156**, 57	Marsh (1989). *ICA*, **166**, 1
164	*R*3	$R\bar{3}$	3	Ouvrard + (1988). *JSSC*, **73**, 27	Marsh (1988). *JSSC*, **77**, 190
165	*Pb*2*n*	*Pbcn*	3	Leblanc + (1983). *JSSC*, **47**, 24	Marsh (1984). *JSSC*, **51**, 405
166	*Pc*	*Pmcm*	1	Aléonard + (1982). *JSSC*, **42**, 80	Marsh (1983). *JSSC*, **47**, 242.
167	$C222_1$	*Ccmm*	3	Rogers + (1979). *JCMS*, **9**, 45	Marsh (1980), *JCMS*, **10**, 163
168	*P*1	$P\bar{1}$	3	Brisse + (1983). *OM*, **2**, 878	Marsh + (1984). *OM*, **3**, 1118
169	*C*2/*c*	$R\bar{3}c$	1	Alder + (1983). *JCSCC*, 999	Schaefer + (1984). *JCSCC*, 1555
170	*C*2/*c*	$P\bar{3}1c$	1	Alder + (1983). *JCSCC*, 1000	Schaefer + (1984). *JCSCC*, 1555
171	*Cc*	*C*2/*c*	3	Nair + (1989). *IC*, **28**, 1582	Marsh (1990). *IC*, **29**, 572
172	*Cc*	*C*2/*c*	3	Reger + (1989). *IC*, **28**, 3092	Marsh (1990). *IC*, **29**, 1449
173	*Cc*	*C*2/*c*	3	Dahlstro + (1982). *IC*, **21**, 933	Marsh + (1983). *IC*, **22**, 1691
174	$P2_1$	$Cmc2_1$	1	Bandoli + (1988). *JCSR*, **18**, 679	Marsh (1990). *JCSR*, **20**, 197
175	*Pa*	*P*2/*a*	3	Suzuki + (1988). *OM*, **7**, 2243	Marsh (1989). *OM*, **8**, 1583
176	$P4_2mc$	$P4_2/nmc$	3	Okuda + (1990). *AC*, **C46**, 1755	Marsh (1991). *AC*, **C47**, 1775
177	$P\bar{1}$	*C*2/*c*	1	Xu + (1990). *AC*, **C46**, 1447	Marsh (1991). *AC*, **C47**, 1774
178	*I*4/*m*	*I*4/*mcm*	2	AbbaTour + (1990). *JSSC*, **87**, 229	Marsh (1991). *JSSC*, **92**, 594
179	*P*2/*c*	*C*2/*c*	4	Wandner + (1986). *RCM*, **23**, 520	Müller + (1990). *ZAAC*, **583**, 205
180	$P2_1/n$	*C*2/*c*	4	Wandner + (1988). *ZAAC*, **557**, 153	Müller + (1990). *ZAAC*, **V583**, **P153**
181	$P2_1$	$P2_1/c$	3	Stoll + (1988). *ZAAC*, **564**, 45	Müller + (1991). *ZAAC*. In the press.
182	$P2_1/a$	*C*2/*c*	4	Kirfel + (1979). *ZK*, **149**, 315	Kirfel + (1984). *ZK*, **167**, 287
183	$Pna2_1$	*Pnam*	3	Hoppe + (1987). *ZAAC*, **551**, 123	Müller, U. (1991). Personal communication.
184	*Iba*2	*Ibam*	3	Bednowit + (1966). *AC*, **20**, 100	Müller, (1978). *AC*, **B34**, 1044
185	*Pmna*	*Cmmm*	4	Avilov + (1972). *SPC*, **17**, 237	Cenzual + (1991). *AC*, **B47**, 433
186	*I*4*mm*	*I*4/*mm*	3	Iwasaki (1965). *JPSJ*, **20**, 89	Cenzual + (1991). *AC*, **B47**, 433
187	$I\bar{4}3m$	$Pm\bar{3}m$	4	Puselj + (1978). *CCA*, **51**, 75	Cenzual + (1991). *AC*, **B47**, 433
188	*Pnma*	*Cmcm*	4	Bruzzone + (1970). *JLCM*, **22**, 253	Cenzual + (1991). *AC*, **B47**, 433
189	*Bba*2	*Cmca*	3	Schubert + (1950). *ZM*, **41**, 433	Cenzual + (1991). *AC*, **B47**, 433
190	$P\bar{3}$	$P6_3/m$	2	Günzel + (1958). *ZM*, **49**, 124	Cenzual + (1991). *AC*, **B47**, 433
191	$P\bar{6}$	$P\bar{6}m2$	2	Schubert + (1955). *ZM*, **46**, 216	Cenzual + (1991). *AC*, **B47**, 433
192	*P*2/*m*	*C*2/*m*	4	Watanabe (1982). *JSSC*, **43**, 226	Cenzual + (1991). *AC*, **B47**, 433
193	$P\bar{4}2c$	$P4_2/mmc$	3	Bauer + (1980). *AC*, **C36**, 1540	Cenzual + (1991). *AC*, **B47**, 433
194	$P4_22_12$	$P4_2/mnm$	3	Yamane + (1987). *JSSC*, **71**, 1	Cenzual + (1991). *AC*, **B47**, 433
195	*P*222	*Pccm*	3	Juza + (1968). *ZAAC*, **356**, 253	Cenzual + (1991). *AC*, **B47**, 433
196	*P*321	$P\bar{3}m1$	3	Zalkin + (1956). *JPC*, **60**, 234	Cenzual + (1991). *AC*, **B47**, 433
197	*P*2/*m*	*P*2/*m*	4	Loebich + (1979). *JLCM*, **63**, 83	Cenzual + (1991). *AC*, **B47**, 433
198	$P\bar{6}$	$P\bar{6}m2$	2	Larson + (1965). *AC*, **18**, 906	Cenzual + (1991). *AC*, **B47**, 433
199	*Cm*2*m*	*Cmcm*	3	Burkhardt + (1965). *ZM*, **56**, 864	Cenzual + (1991). *AC*, **B47**, 433
200	*R*3	$R\bar{3}m$	2	Schubert + (1963). *ZM*, **54**, 422	Cenzual + (1991). *AC*, **B47**, 433
201	*C*222	*Cmmm*	3	Becher + (1966). *ZAAC*, **344**, 140	Cenzual + (1991). *AC*, **B47**, 433
202	*Pmmn*	*Cmcm*	4	Nowotny + (1951). *MC*, **82**, 513	Cenzual + (1991). *AC*, **B47**, 433
203	$P222_1$	*Pmma*	3	Andresen + (1972). *ACS*, **26**, 175	Cenzual + (1991). *AC*, **B47**, 433
204	$P222_1$	*Pmma*	3	Göbel + (1976). *PSS*, **A34**, 553	Cenzual + (1991). *AC*, **B47**, 433
205	*I*422	*I*4/*mmm*	3	Hoppe + (1964). *ZAAC*, **329**, 110	Cenzual + (1991). *AC*, **B47**, 433
206	$P\bar{1}$	*C*2/*c*	1	Kanishch + (1979). *JSC*, **20**, 122	Cenzual + (1991). *AC*, **B47**, 433
207	*R*3	*R*3*m*	2	Rouxel + (1971). *BSCF*, 3930	Cenzual + (1991). *AC*, **B47**, 433
208	*Pnnn*	*Cccm*	4	Somenkov + (1968), *SPSS*, **10**, 1076	Cenzual + (1991). *AC*, **B47**, 433
209	$P2_1/m$	$P2_1/m$	4	Giessen + (1964). *AC*, **17**, 615	Cenzual + (1991). *AC*, **B47**, 433
210	*P*2/*m*	*P*2/*m*	4	Giessen + (1964), *AC*, **17**, 615	Cenzual + (1991). *AC*, **B47**, 433
211	$P6_3/m$	$P6_3/mmc$	2	Toman + (1952). *AC*, **5**, 329	Cenzual + (1991). *AC*, **B47**, 433
212	$F\bar{4}3m$	$Fd\bar{3}m$	3	Kharkin + (1970). *SPC*, **14**, 779	Cenzual + (1991). *AC*, **B47**, 433
213	*Aba*2	*Ccca*	3	Schubert + (1950). *ZM*, **41**, 298	Cenzual + (1991). *AC*, **B47**, 433
214	$P\bar{4}b2$	*P*4/*nbm*	3	Boller (1978). *MC*, **109**, 975	Cenzual + (1991). *AC*, **B47**, 433
215	*P*622	*P*6/*mmm*	3	Boller + (1976). *JLCM*, **45**, 103	Cenzual + (1991). *AC*, **B47**, 433
216	*P*31*c*	$P6_3mc$	2	Schuster + (1984). *JSSC*, **53**, 260	Cenzual + (1991). *AC*, **B47**, 433
217	*Ama*2	*Cmcm*	3	Hatt + (1959). *AC*, **12**, 655	Cenzual + (1991). *AC*, **B47**, 433

Table 1 (*cont.*)

	FS	TS	Category	Reference 1	Reference 2
218	*Amm*2	*Cmcm*	3	STOLZ + (1962). *ZM*, **53**, 433	CENZUAL + (1991). *AC*, **B47**, 433
219	$P3_1$	$P3_112$	2	VENABLES + (1968). *PM*, **18**, 177	CENZUAL + (1991). *AC*, **B47**, 433
220	$P\bar{6}m2$	$P6_3/mmc$	3	SAITO (1959). *AC*, **12**, 500	CENZUAL + (1991). *AC*, **B47**, 433
221	*Pcc*2	*Pccm*	3	ASANO + (1973). *PSS*, **A15**, 267	CENZUAL + (1991). *AC*, **B47**, 433
222	$P6_1$	$P6_122$	2	ADAM + (1955). *AC*, **8**, 349	CENZUAL + (1991). *AC*, **B47**, 433
223	$P2_1$	$P2_1/m$	3	KUZMICHE + (1976). *RJIC*, **21**, 1565	CENZUAL + (1991). *AC*, **B47**, 433
224	$P\bar{6}$	$P6/mmm$	2	WILSON + (1960). *AC*, **13**, 56	CENZUAL + (1991). *AC*, **B47**, 433
225	$P31c$	$P6_3/mmc$	2	SCHUSTER + (1980). *ZM*, **71**, 341	CENZUAL + (1991). *AC*, **B47**, 433
226	*Cc*	*Fdd*2	1	SCHULZE + (1980). *ZAAC*, **471**, 59	BAUR + (1991). Unpublished.
227	$C\bar{1}$	$C2/c$	1	KATO + (1983). *MJ*, **11**, 261	BAUR + (1991). Unpublished.

Journal abbreviations: *AC Acta Cryst., ACS Acta Chem. Scand., AM Am. Mineral., ANC Angew. Chem., BCSJ Bull. Chem. Soc. Jpn, CCA Croat. Chem. Acta, CB Chem. Ber., CR C. R. Acad. Sci. (Paris), CSC Cryst. Struct. Commun., CSR Chem. Soc. Rev., DAN Dokl. Akad. Nauk SSSR, FER Ferroelectrics, HCA Helv. Chim. Acta, IC Inorg. Chem., ICA Inorg. Chim. Acta, JACS J. Am. Chem. Soc., JCMS J. Cryst. Mol. Struct., JCSCC J. Chem. Soc. Chem. Commun., JCSR J. Crystallogr. Spectrosc. Res., JINC J. Inorg. Nucl. Chem., JLCM J. Less-Common Met., JPC J. Phys. Chem., JPSJ J. Phys. Soc. Jpn, JSC J. Struct. Chem., JSSC J. Solid State Chem., MC Monatsh. Chem., MCLC Mol. Cryst. Liq. Cryst., MJ Mineral. J., MRB Mater. Res. Bull., NJMM Neues Jahrb. Mineral. Monatsh., OM Organometallics, PM Philos. Mag., PSS Phys. Status Solidi, RCM Rev. Chim. Minéral., RJIC Russ. J. Inorg. Chem., SPC Sov. Phys. Crystallogr., SPD Sov. Phys. Dokl., SPSS Sov. Phys. Solid State, ZAAC Z. Allg. Anorg. Chem., ZK Z. Kristallogr., ZM Z. Metallkd., ZN Z. Naturforsch.*

It is particularly difficult to diagnose incorrect symmetry caused by overlooked twinning, because the diffraction symmetry points clearly to a different, but false, symmetry. We must distinguish between cases where the twin individuals have more or less equal volumes and those where only a small part of the total intensity is diffracted by a contributing twin. Instances can occur where the true symmetry is:

(1) lower than originally suspected, because the Laue symmetry appears to be higher, due to overlap of nonequivalent, but for each individual twin observable, reflections;

(2) higher than originally suspected, because systematic extinctions (due to centering, glide planes or screw axes) are obscured by overlapping reciprocal lattices, that is by overlap of extinct reflections in one twin individual with observed reflections from another individual.

After a crystal structure is solved and refined such occurrences may be surmized because of the presence of unusual bond lengths, statistical occupancies or uncommonly large R values. Here we only treat instances where the true symmetry is higher than originally assumed, thus Table 1 only contains twinning cases of the second kind mentioned above. Our search for examples of this last category was the least thorough.

For further details concerning the crystal structure determination of crystals with twinning problems see Araki (1991), Bärnighausen (1985), Bärnighausen & Schiller (1985), Müller *et al.* (1991) and the literature cited therein.

Discussion

Table 2 addresses itself to the question of which space groups (FS) have the highest probability of being encountered as the result of an incorrect space-group assignment in a particular crystal structure determination. Table 3 presents those space groups (TS) which have the largest potential for being missed as the true description of the symmetry of a particular crystal structure which is instead reported as possessing unnecessarily low (false) symmetry. Such questions can only be discussed if we compare the observed frequencies of the space groups involved with the overall space-group frequencies found for known crystal structures. The percentages listed in Tables 2 and 3 under 'overall' refer to the space-group frequencies of 86 303 crystal structure determinations of organic molecules, organometallics, inorganic compounds and alloys (Padmaja, Ramakumar & Viswamitra, 1990; and see *Appendix*). Cases of space groups that occur three or fewer times are treated as statistical noise and are not discussed any further, but they are listed in Table 2. All errors of categories 2 (change in Laue class without change in crystal system) and 4 (overlooked centering or too large unit cells) fall into this class. When we compare the frequencies of the overall populations, which are based on individual crystal structure determinations, with the frequencies found for the wrongly assigned crystal structure *types*, we may be introducing a bias. However, we have no practical way of handling this problem, thus we must assume that the ratio of individual crystal structure determinations to crystal structure types is a constant for all space groups.

Only 14 space-group types (FS) occur in category 1. Each one of these represents a type which it is apparently easy to accept as the correct lattice without recognizing that a more highly symmetric lattice (TS) is called for. Space groups $P1$, Cc and $C2/m$ (FS) are clearly over represented compared with their frequencies among all space groups, while space

Table 2. *Frequencies of space-group revisions reported in the literature, subdivided by category of error (see text)*

The first entry is the original incorrectly assigned space group (FS), the second the corrected space-group (TS) assignment (all space groups are given in their standard setting), the number tells how often this type of false assignment occurs in our sample of 221 cases. The percentages of the falsely assigned space group in our sample and the frequency of the corresponding space group among all known structures are given last.

Incorrect	Corrected	No.	Sample (%)	Overall (%)	Incorrect	Corrected	No.	Sample (%)	Overall (%)
Category 1									
*P*1	*Cm*	2			*Cm*	*R*3*m*	1		
*P*1	*Cc*	3			*Cm*	$P\bar{6}m2$	1	1	0.13
*P*1	*R*3*m*	1	3	0.90	*Cc*	*Fdd*2	6		
$P\bar{1}$	*C*2/*m*	3			*Cc*	$R\bar{3}c$	1	3	0.86
$P\bar{1}$	*P*2/*c*	1			$P2_1/m$	*Cmcm*	2	1	0.92
$P\bar{1}$	$P2_1/c$	2			*C*2/*m*	$R\bar{3}m$	11	5	1.66
$P\bar{1}$	*C*2/*c*	17			*C*2/*c*	*Fddd*	1		
$P\bar{1}$	*Immm*	1	11	11.87	*C*2/*c*	*Ibca*	1		
$P2_1$	$P2_12_12_1$	2			*C*2/*c*	$P\bar{3}c1$	2		
$P2_1$	$Cmc2_1$	3	2	4.06	*C*2/*c*	$R\bar{3}c$	8	5	5.69
*C*2	*Fdd*2	2			*Cmcm*	$P6_3/mcm$	1	0.5	0.88
*C*2	*R*32	1			*Cmmm*	*P*4/*mbm*	1	0.5	0.12
C2	$R\bar{3}c$	1	2	0.72	*P*3	*R*32	1	0.5	0.06
Pc	*Pmma*	1	0.5	0.31	*P*31*c*	$P6_3/mmc$	1	0.5	0.07
Category 2									
$P4_1$	$P4_12_12$	1			*R*3	$R\bar{3}m$	1		
$P\bar{4}$	$P\bar{4}2_1m$	1			$P\bar{3}$	$P6_3/m$	1		
$I\bar{4}$	$I\bar{4}2m$	1			*P*31*c*	$P6_3mc$	1		
$P4_2/n$	$P4_2/nmc$	1			*P*31*c*	$P6_3/mmc$	1		
*I*4/*m*	*I*4/*mcm*	1			$P6_3$	$P6_322$	1		
$P3_1$	$P3_112$	1			$P\bar{6}$	$P\bar{6}m2$	2		
$P3_2$	$P3_221$	1			$P\bar{6}$	*P*6/*mmm*	1		
*R*3	*R*3*m*	1			$P6_3/m$	$P6_3/mmc$	3		
Category 3									
*P*1	$P\bar{1}$	14	6	0.90	*Amm*2	*Cmcm*	2	1	0.06
$P2_1$	$P2_1/m$	4			*Ama*2	*Cmcm*	1	0.5	0.06
$P2_1$	$P2_1/c$	3	3	4.06	*Aba*2	*Cmca*	1		
*C*2	*C*2/*m*	2			*Aba*2	*Ccca*	1	1	0.10
*C*2	*C*2/*c*	2	2	0.72	*Iba*2	*Ibam*	1	0.5	0.05
Pc	*P*2/*c*	2			$I4_1$	$I4_1/a$	1	0.5	0.02
Pc	$P2_1/c$	5	3	0.31	$I\bar{4}$	*I*4/*m*	2	1	0.26
Cm	*C*2/*m*	2	1	0.13	$P4_22_12$	$P4_2/mnm$	1	0.5	0.03
Cc	*C*2/*c*	28	13	0.86	*I*422	*I*4/*mmm*	1	0.5	0.02
*P*222	*Pccm*	1	0.5	0.02	$P4_2mc$	$P4_2/nmc$	1	0.5	0.01
$P222_1$	*Pmma*	2	1	0.02	*I*4*mm*	*I*4/*mmm*	1	0.5	0.04
$C222_1$	*Cmcm*	2	1	0.20	$P\bar{4}2c$	$P4_2/mmc$	1	0.5	0.01
*C*222	*Cmmm*	1	0.5	0.03	$P\bar{4}b2$	*P*4/*nbm*	1		
*Pcc*2	*Pccm*	1	0.5	0.00	$P\bar{4}b2$	*P*4/*mbm*	1	1	0.02
$Pca2_1$	*Pbcm*	1	0.5	0.57	*R*3	$R\bar{3}$	2	1	0.19
*Pnc*2	*Pbcn*	2	1	0.02	*P*321	$P\bar{3}m1$	1	0.5	0.09
*Pba*2	*Pbam*	1	0.5	0.05	*P*3*m*1	$P\bar{3}m1$	1	0.5	0.12
$Pna2_1$	*Pnma*	12	5	1.40	*P*622	*P*6/*mmm*	1	0.5	0.01
*Pnn*2	*Pnna*	1	0.5	0.05	$P\bar{6}m2$	$P6_3/mmc$	1	0.5	0.06
$Cmc2_1$	*Cmcm*	3	1	0.38	$F\bar{4}3m$	$Fd\bar{3}m$	1	0.5	0.41
Category 4									
*P*2/*m*	*P*2/*m*	2			*Pnnn*	*Cccm*	1		
*P*2/*m*	*C*2/*m*	1			*Pmna*	*Cmmm*	1		
$P2_1/m$	$P2_1/m$	1			*Pmmn*	*Cmcm*	1		
*P*2/*c*	*C*2/*c*	1			*Pnma*	*Cmcm*	1		
$P2_1/c$	*C*2/*c*	2			$I\bar{4}3m$	$Pm\bar{3}m$	1		

groups $P\bar{1}$, $P2_1$ and *C*2/*c* (FS) are under represented. Four of the seven rhombohedral groups occur in our sample of missed true symmetries. Apparently in most of these cases only one third of the rhombohedral symmetry was recognized and the space groups were taken to be monoclinic. 25 cases of the overlooked true symmetries in category 1 occur in rhombohedral space groups, that is 11% of the sample of 221 cases. In the total sample of 86 303 crystal structures only 3.23% are rhombohedral (see *Appendix*). Included among the rhombohedral space groups erroneously described in lower symmetry are the nine new cases found by Cenzual, Gelato, Penzo & Parthé (1990), who searched systematically among centered monoclinic unit cells of crystal structures of alloys for rhombohedral symmetry. In fact in our survey here we find one case each of *P*1 and *P*3 (FS), which really should be described in *R*3*m*

Table 3. *Space groups for which the correct symmetry has most often been missed*

The first entry gives the correct symmetry (TS), the second entry the original wrongly assigned lower-symmetry space group (FS). The overall percentage now refers to the correct space group. For other explanations see Table 2.

Corrected	Incorrect	No.	Sample (%)	Overall (%)	Corrected	Incorrect	No.	Sample (%)	Overall (%)
Category 1									
$C2/c$	$P\bar{1}$	17	8	5.69	$R\bar{3}c$	$C2$	1		
$Fdd2$	$C2$	2			$R\bar{3}c$	Cc	1		
$Fdd2$	Cc	6	4	0.35	$R\bar{3}c$	$C2/c$	8	5	0.60
$R\bar{3}m$	$C2/m$	11	5	1.02					
Category 3									
$P\bar{1}$	$P1$	14	6	11.87	$C2/c$	$C2$	2		
$P2_1/c$	$P2_1$	3			$C2/c$	Cc	28	14	5.69
$P2_1/c$	Pc	5	4	25.16	$Pnma$	$Pna2_1$	12	5	4.26

and $R32$ (TS), and two instances of $P\bar{3}c1$ (TS) mistaken for $C2/c$ (FS). The most common occurrence, however, in our sample is to mistake a rhombohedral cell for a centered monoclinic cell. An even more pronounced enrichment can be observed for space group $Fdd2$ (TS), where either one of the glide planes (Cc, FS) or the twofold axis ($C2$, FS) remain of the full symmetry (see Table 3). Space group $C2/c$ (TS) is often mistaken for $P\bar{1}$, but the absolute frequency of that occurrence must be partly due to the abundance of $C2/c$ in the total sample of 86 303 crystal structures (only three space groups are more common than $C2/c$, see Table 6). But on the whole, C-centered space groups are still over represented among the cases of missed lattice symmetry, while primitive and especially the body-centered space-group types are heavily under represented. All told it is quite clear that trigonal symmetry is more easily missed than tetragonal, hexagonal or cubic symmetry. Possibly trigonal symmetry in the rhombohedral setting is not easily recognized because it lacks a right angle between the directions of the cell constants, while in the hexagonal setting there are many systematic extinctions which can lead us astray in a sparsely populated reciprocal lattice. The latter reason may also be responsible for choosing C-centered monoclinic cells instead of $Fdd2$ or $Fddd$, because not only the F extinction, but also the glide planes are effective in diluting the population of the reciprocal lattice.

Thirty-five space-group types without an inversion center have been falsely assigned (category 3). The most frequently occurring ones are Cc, $Pna2_1$, $P1$, Pc and $P2_1$ (FS). In most cases of wrongly chosen space groups lacking the necessary inversion center the choice of origin is free in one, two or three directions. This means that the additional overlooked symmetry elements can only be recognized easily after a shift in origin by some irrational fraction or fractions parallel to one or other lattice vector. Put the other way around: one has to look for the symmetry elements somewhere within the unit cell and not just at the origin. In this regard it is telling that for both $P2_1/c$ and $C2/c$ (TS) it is more common to miss the proper space-group symmetry when its glide plane component has been encountered (two degrees of freedom in the choice of origin), than when rotation axes have been identified first (one degree of freedom only, see Table 3). Most cases of overlooked symmetry occur in space groups $C2/c$, $P\bar{1}$, $Pnma$ and $P2_1/c$ (TS). However, only for $C2/c$ is the enrichment within our sample large relative to the abundance of $C2/c$ within the total population of 86 303 cases.

More than a quarter of all crystalline compounds (21 883 of 86 303) are found in noncentrosymmetric space groups. However, only those where there is freedom in choosing the origin are likely to contain numerous cases where an inversion center has been overlooked. These are, except for $P1$, space groups belonging to the nine crystal classes 2, m, $mm2$, 4, $4mm$, 3, $3m$, 6 and $6mm$ (with 11 269 representatives). Among substances crystallizing in space groups of the other eleven noncentrosymmetric crystallographic point groups cases of overlooked inversion centers are much less likely to occur.

Space group Cc (FS) appears both in absolute numbers, and relative to its overall frequency of occurrence, to be the space group with the highest probability of having been falsely assigned in a crystal structure determination. In order to test this observation we searched the 1991 release of the Inorganic Crystal Structure Database (Bergerhoff, Hundt, Sievers & Brown, 1983) and the Metals Data File (Calvert, 1981) for entries relating to space group Cc. We encountered 244 hits, of which 18 were error sets or bibliographic entries that were useless for our purposes. Of the remaining 226 entries of crystal structures reported to crystallize in space group Cc no less than 88 (or 40%) were flagged by the computer program *MISSYM* (Le Page, 1988) as possibly having a higher symmetry. Of these four were double entries in the data set, leaving us with 84 crystal structures (not crystal structure types) in Cc. Of these 13 already had been corrected in the literature, for 11 more it was obvious that a description in a higher symmetry was correct (for a total of 24 out of 84 cases or 29%). In 28 cases (one third) it is very

Table 4. *Space groups with the highest probability of being wrongly assigned in a crystal structure determination*

The table shows the number of times the given group (FS) shows up as an error in category 1, in category 3 or in total, the percentages of the false space group in our sample and the frequency of this space group among all known crystal structures.

	No. in category 1	No. in category 3	Total	Sample (%)	Overall (%)
Cc	7	28	35	16	0.86
Pc	1	7	8	4	0.31
*P*1	6	14	20	9	0.90
*C*2	4	4	8	4	0.72
$Pna2_1$		12	12	5	1.40
*C*2/*m*	11		11	5	1.66
*C*2/*c*	12		12	5	5.69
$P2_1$	5	7	12	5	4.06
$P\bar{1}$	24		24	11	11.87

likely that the description in space group *Cc* stands. This leaves 32 doubtful cases which we cannot decide without further investigation. But even the 24 confirmed cases mean that about 11% (24 of 226 entries) of inorganic compounds reported in space group *Cc* should have a higher symmetry. If we apply this percentage to the 501 organic crystal structures reported by Padmaja *et al.* (1990) to crystallize in space group *Cc* there should be 55 incorrect assignments among them. This number happens to match the 55 entries in *Cc* identified by Padmaja *et al.* (1990) as having more than one formula unit per asymmetric unit. Such are the perils of space-group *Cc*.

Concluding remarks

One observation stands out: clearly it is difficult to miss cubic symmetry. Only two examples of overlooked cubic space groups seem to have been reported so far. This is particularly noteworthy, considering that rhombohedral symmetry, which is strongly related to cubic symmetry, has been frequently misidentified. The lack of a right angle in rhombohedral symmetry must be very important in this regard.

All told the eight space groups (TS) listed in Table 3 have a reasonably high probability that some of their symmetry might be overlooked. Of these eight space groups *Fdd*2, $R\bar{3}c$, $R\bar{3}m$ and *C*2/*c* are over represented in our sample of 221 cases by factors ranging from eleven to four relative to their frequency in the sample of 86 303 determined crystal structures. Space groups $P\bar{1}$, $P2_1/c$ and *Pnma* on the other hand show up in Table 3, mostly because they are very common space groups and thus have been misidentified more often in absolute numbers.

Conversely crystal structures (Table 4) reported to crystallize in space groups *Cc*, *P*1, *Pc*, *C*2, $Pna2_1$ and *C*2/*m* (FS) have in that sequence the highest probability of being cases were a higher symmetry has been missed (over represented by factors ranging from 19 to 3). Space groups *C*2/*c*, $P2_1$ and $P\bar{1}$ (FS) are similarly represented in our sample as in the general population. The frequency distribution shown in Table 4 is completely different from the distribution shown in Table 6 for the general population. It is biased heavily towards space groups were the fixing of the origin has at least one degree of freedom.

We can attempt an estimate of how many crystal structures described in the space groups listed in Table 4 have actually been reported in unnecessarily low symmetry by extrapolating from our experience with space group *Cc* (FS). Out of 84 questionable assignments of inorganic crystal structures to space group *Cc*, 24 almost certainly have a higher true symmetry, while 28 really belong into *Cc*. If we allocate the remaining 32 questionable cases in the same ratio, we obtain 39 instances were the symmetry should be revised upwards. Thirteen of these 39 cases have already been corrected in the extant literature, that amounts to 33%. We can scale the 142 reported changes of symmetry recorded in Table 4 up to about 430 cases of missed symmetry or to 1.8% of all 23 712 compounds crystallizing in these nine space groups. The estimate of incorrectly described structures (3%) given by Baur & Tillmanns (1986) would then have been too large. One can look at it in a more positive way as well: one third of all falsely assigned space-group symmetries have already been revised. Marsh and co-workers have obviously done a thorough job so far.

Recommendations

A number of ways in which one can guard at several points during the course of a crystal structure determination against choosing too low a symmetry have been recommended by Baur & Tillmanns (1986). The least that should be done, however, is:

(1) to check the metric of the lattice at the beginning of a structural study (see Himes & Mighell, 1982), and

(2) check the symmetry of the completed crystal structure after the determination is completed (Le Page, 1988).

Table 5. *Space-group frequencies of* 34 692 *crystal structures of inorganic compounds (including alloys) and of* 51 611 *crystal structures of organic and organometallic compounds (Padmaja et al.*, 1990)

Space-group No.	Space-group symbol	Frequency (inorganic)	Frequency (organic)	Space-group No.	Space-group symbol	Frequency (inorganic)	Frequency (organic)
1	$P1$	146	635	73	$Ibca$	15	15
2	$P\bar{1}$	1508	8733	74	$Imma$	140	5
3	$P2$	19	8	75	$P4$	18	2
4	$P2_1$	224	3278	76	$P4_1$	21	79
5	$C2$	156	463	77	$P4_2$	8	5
6	Pm	13	1	78	$P4_3$	4	24
7	Pc	74	196	79	$I4$	19	16
8	Cm	80	30	80	$I4_1$	5	13
9	Cc	244	501	81	$P\bar{4}$	12	11
10	$P2/m$	81	7	82	$I\bar{4}$	149	76
11	$P2_1/m$	462	332	83	$P4/m$	19	1
12	$C2/m$	1180	254	84	$P4_2/m$	20	8
13	$P2/c$	206	254	85	$P4/n$	58	54
14	$P2_1/c$	2827	18885	86	$P4_2/n$	56	87
15	$C2/c$	1326	3585	87	$I4/m$	149	29
16	$P222$	14	3	88	$I4_1/a$	179	153
17	$P222_1$	17	4	89	$P422$	1	1
18	$P2_12_12$	62	271	90	$P42_12$	5	3
19	$P2_12_12_1$	380	5679	91	$P4_122$	6	2
20	$C222_1$	53	117	92	$P4_12_12$	87	160
21	$C222$	18	4	93	$P4_222$	0	1
22	$F222$	6	0	94	$P4_22_12$	13	16
23	$I222$	8	14	95	$P4_322$	5	2
24	$I2_12_12_1$	2	1	96	$P4_32_12$	29	65
25	$Pmm2$	15	1	97	$I422$	12	1
26	$Pmc2_1$	55	11	98	$I4_122$	5	2
27	$Pcc2$	0	1	99	$P4mm$	82	0
28	$Pma2$	18	1	100	$P4bm$	23	0
29	$Pca2_1$	109	387	101	$P4_2cm$	0	1
30	$Pnc2$	6	8	102	$P4_2nm$	15	3
31	$Pmn2_1$	146	40	103	$P4cc$	8	0
32	$Pba2$	26	16	104	$P4nc$	0	6
33	$Pna2_1$	369	840	105	$P4_2mc$	4	1
34	$Pnn2$	25	18	106	$P4_2bc$	2	6
35	$Cmm2$	9	1	107	$I4mm$	31	2
36	$Cmc2_1$	237	93	108	$I4cm$	6	4
37	$Ccc2$	3	9	109	$I4_1md$	22	5
38	$Amm2$	52	1	110	$I4_1cd$	12	20
39	$Abm2$	9	6	111	$P\bar{4}2m$	23	2
40	$Ama2$	38	12	112	$P\bar{4}2c$	8	0
41	$Aba2$	40	46	113	$P\bar{4}2_1m$	95	20
42	$Fmm2$	13	11	114	$P\bar{4}2_1c$	41	76
43	$Fdd2$	126	176	115	$P\bar{4}m2$	9	2
44	$Imm2$	49	7	116	$P\bar{4}c2$	9	2
45	$Iba2$	3	44	117	$P\bar{4}b2$	17	4
46	$Ima2$	26	5	118	$P\bar{4}n2$	21	14
47	$Pmmm$	212	0	119	$I\bar{4}m2$	25	3
48	$Pnnn$	2	3	120	$I\bar{4}c2$	12	3
49	$Pccm$	2	1	121	$I\bar{4}2m$	86	19
50	$Pban$	10	2	122	$I\bar{4}2d$	229	26
51	$Pmma$	57	7	123	$P4/mmm$	259	2
52	$Pnna$	49	49	124	$P4/mcc$	21	8
53	$Pmna$	27	8	125	$P4/nbm$	5	0
54	$Pcca$	23	17	126	$P4/nnc$	8	9
55	$Pbam$	265	13	127	$P4/mbm$	179	4
56	$Pccn$	50	178	128	$P4/mnc$	84	3
57	$Pbcm$	121	78	129	$P4/nmm$	354	10
58	$Pnnm$	272	49	130	$P4/ncc$	49	16
59	$Pmmn$	119	26	131	$P4_2/mmc$	22	3
60	$Pbcn$	266	519	132	$P4_2/mcm$	4	0
61	$Pbca$	466	2189	133	$P4_2/nbc$	5	4
62	$Pnma$	2863	811	134	$P4_2/nnm$	15	1
63	$Cmcm$	677	86	135	$P4_2/mbc$	56	5
64	$Cmca$	218	77	136	$P4_2/mnm$	278	16
65	$Cmmm$	103	4	137	$P4_2/nmc$	43	10
66	$Cccm$	46	7	138	$P4_2/ncm$	11	3
67	$Cmma$	23	2	139	$I4/mmm$	1176	11
68	$Ccca$	16	13	140	$I4/mcm$	343	3
69	$Fmmm$	50	3	141	$I4_1/amd$	301	8
70	$Fddd$	111	47	142	$I4_1/acd$	56	27
71	$Immm$	190	3	143	$P3$	40	11
72	$Ibam$	99	25	144	$P3_1$	29	44

Table 5 (*cont.*)

Space-group No.	Space-group symbol	Frequency (inorganic)	Frequency (organic)	Space-group No.	Space-group symbol	Frequency (inorganic)	Frequency (organic)
145	$P3_2$	5	22	188	$P\bar{6}c2$	29	0
146	$R3$	89	77	189	$P\bar{6}2m$	237	1
147	$P\bar{3}$	78	51	190	$P\bar{6}2c$	40	11
148	$R\bar{3}$	500	235	191	$P6/mmm$	498	1
149	$P312$	14	0	192	$P6/mcc$	67	2
150	$P321$	76	5	193	$P6_3/mcm$	216	0
151	$P3_112$	12	1	194	$P6_3/mmc$	1254	11
152	$P3_121$	149	56	195	$P23$	16	0
153	$P3_212$	1	1	196	$F23$	49	1
154	$P3_221$	31	21	197	$I23$	56	3
155	$R32$	69	19	198	$P2_13$	163	31
156	$P3m1$	104	0	199	$I2_13$	45	1
157	$P31m$	31	2	200	$Pm\bar{3}$	27	0
158	$P3c1$	8	7	201	$Pn\bar{3}$	45	0
159	$P31c$	46	11	202	$Fm\bar{3}$	37	2
160	$R3m$	223	23	203	$Fd\bar{3}$	34	1
161	$R3c$	98	62	204	$Im\bar{3}$	100	3
162	$P\bar{3}1m$	55	0	205	$Pa\bar{3}$	210	49
163	$P\bar{3}1c$	50	21	206	$Ia\bar{3}$	60	3
164	$P\bar{3}m1$	586	9	207	$P432$	2	0
165	$P\bar{3}c1$	86	20	208	$P4_232$	12	0
166	$R\bar{3}m$	858	18	209	$F432$	6	2
167	$R\bar{3}c$	458	57	210	$F4_132$	7	1
168	$P6$	3	0	211	$I432$	5	0
169	$P6_1$	16	35	212	$P4_332$	34	2
170	$P6_5$	9	27	213	$P4_132$	17	3
171	$P6_2$	1	4	214	$I4_132$	10	0
172	$P6_4$	0	2	215	$P\bar{4}3m$	89	3
173	$P6_3$	189	34	216	$F\bar{4}3m$	352	1
174	$P\bar{6}$	100	1	217	$I\bar{4}3m$	144	15
175	$P6/m$	14	0	218	$P\bar{4}3n$	88	8
176	$P6_3/m$	419	89	219	$F\bar{4}3c$	24	7
177	$P622$	11	0	220	$I\bar{4}3d$	277	6
178	$P6_122$	4	9	221	$Pm\bar{3}m$	506	9
179	$P6_522$	0	4	222	$Pn\bar{3}n$	3	0
180	$P6_222$	61	3	223	$Pm\bar{3}n$	53	1
181	$P6_422$	11	0	224	$Pn\bar{3}m$	25	3
182	$P6_322$	36	2	225	$Fm\bar{3}m$	1532	10
183	$P6mm$	0	1	226	$Fm\bar{3}c$	28	0
184	$P6cc$	1	0	227	$Fd\bar{3}m$	1050	5
185	$P6_3cm$	48	1	228	$Fd\bar{3}c$	19	5
186	$P6_3mc$	308	15	229	$Im\bar{3}m$	91	10
187	$P\bar{6}m2$	56	0	230	$Ia\bar{3}d$	251	1

APPENDIX

In order to judge the significance of the observed frequencies of incorrectly assigned (FS) and corrected space groups (TS) in our sample of 221 cases we had to compare them with the frequencies of occurrence of these space groups in a larger population. For crystal structures of organic and organometallic compounds such statistics have recently been provided by Padmaja *et al.* (1990) using the Cambridge Structural Database (Allen *et al.*, 1979). However, the 221 cases of corrected symmetry include inorganic and alloy structures as well. It has already been shown by Mackay (1967) on the basis of 3782 crystal species that the distribution of organic and inorganic compounds among the space groups differs: they belong to distinct populations. Mighell & Rodgers (1980) reported the relative frequencies of occurrence of the most common 32 space groups for 11 641 inorganic compounds. However, several of the space groups in which we were interested, are not among these 32 front runners. Therefore we checked the space-group frequencies of 34 692 inorganic compounds compiled in the 1991 release of the Inorganic Crystal Structure Database (ICSD, Bergerhoff *et al.*, 1983) and in the Metals Data File (MDF, Calvert, 1981). The results of that survey are given in Tables 5, 6 and 7 together with the statistics compiled by Padmaja *et al.* (1990). The numbers given here are not for structure types, but for individual crystal structure determinations. It would be an extremely lengthy task to sort 34 692 entries for structure types. There are also numerous possibilities for errors creeping into compilations such as ICSD or MDF, whereby many of these errors are already present in the original literature. Actually, both surveys quoted (Mighell & Rodgers, 1980; Padmaja *et al.*, 1990) were performed in order to show ways in which such errors may be diagnosed. The space-group symmetries of the packing of organic molecules have been

Table 6. *The 32 most frequent space groups ranked according to their occurrence in the total sample*

Data given: space-group number, space-group symbol, rank, number and percentage for the inorganic data, the organic data and for their sum. All space groups with a joint frequency down to 0.39 are listed, as well as all inorganic frequencies down to 0.99% (rank 24), and all organics down to 0.46% (rank 18).

Space-group	Space-group	Inorganic			Organic			Sum of inorganic and organic		
No.	symbol	Rank	No.	%	Rank	No.	%	Rank	No.	%
14	$P2_1/c$	2	2827	8.15	1	18885	36.59	1	21712	25.16
2	$P\bar{1}$	4	1508	4.35	2	8733	16.92	2	10241	11.87
19	$P2_12_12_1$	20	380	1.10	3	5679	11.00	3	6059	7.02
15	$C2/c$	5	1326	3.82	4	3585	6.95	4	4911	5.69
62	$Pnma$	1	2863	8.25	8	811	1.57	5	3674	4.26
4	$P2_1$	38	224	0.65	5	3278	6.35	6	3502	4.06
61	$Pbca$	16	466	1.34	6	2189	4.24	7	2655	3.08
225	$Fm\bar{3}m$	3	1532	4.42	96	10	0.02	8	1542	1.79
12	$C2/m$	7	1180	3.40	16	254	0.49	9	1434	1.66
194	$P6_3/mmc$	6	1254	3.61	93	11	0.02	10	1265	1.47
33	$Pna2_1$	21	369	1.06	7	840	1.63	11	1209	1.40
139	$I4/mmm$	8	1176	3.39	89	11	0.02	12	1187	1.38
227	$Fd\bar{3}m$	9	1050	3.03	126	5	0.01	13	1055	1.22
166	$R\bar{3}m$	10	858	2.47	70	18	0.03	14	876	1.02
11	$P2_1/m$	17	462	1.33	14	332	0.64	15	794	0.92
60	$Pbcn$	30	266	0.77	10	519	1.01	16	785	0.91
1	$P\bar{1}$	54	146	0.42	9	635	1.23	17	781	0.90
63	$Cmcm$	11	677	1.95	28	86	0.17	18	763	0.88
9	Cc	34	244	0.70	11	501	0.97	19	745	0.86
148	$R\bar{3}$	14	500	1.44	18	235	0.46	20	735	0.85
5	$C2$	50	156	0.45	12	463	0.90	21	619	0.72
164	$P\bar{3}m1$	12	586	1.69	100	9	0.02	22	595	0.69
167	$R\bar{3}c$	18	458	1.32	37	57	0.11	23	515	0.60
221	$Pm\bar{3}m$	13	506	1.46	102	9	0.02	24	515	0.60
176	$P6_3/m$	19	419	1.21	26	89	0.17	25	508	0.59
191	$P6/mmm$	15	498	1.44	195	1	0.00	26	499	0.58
29	$Pca2_1$	62	109	0.31	13	387	0.75	27	496	0.57
13	$P2/c$	44	206	0.59	17	254	0.49	28	460	0.53
129	$P4/nmm$	22	354	1.02	94	10	0.02	29	364	0.42
216	$F\bar{4}3m$	23	352	1.01	200	1	0.00	30	353	0.41
140	$I4/mcm$	24	343	0.99	148	3	0.01	31	346	0.40
18	$P2_12_12$	86	62	0.18	15	271	0.53	32	333	0.39

discussed by Kitaigorodskii (1961). A statistical analysis of the frequency distribution of space groups of organic substances has recently been given by Wilson (1988, 1990). Analogous studies for inorganic compounds are unknown to us.

We thought that our compilation, especially in juxtaposition with the statistics on the organic compounds might be of general interest, and therefore we are presenting the results as an appendix to our paper. We wish to make several points.

(1) Between the organic and the inorganic compounds *all* space groups are occupied, even though there are seven space-group types without inorganic examples and 28 without organic examples. If one so wishes one could take this as experimental proof of space-group theory. However, one has to bear in mind that not all space-group assignments are necessarily correct. Before anybody announces that there are certainly examples available for all space groups one should check the experimental validity of the assignments to space groups with very few representatives. All one can say now is that within the experimental accuracy of the individual crystal structure determinations all space groups have at least one example. There are five space groups with one example each. How many examples would we need to be completely convinced?

(2) The distribution is much more skewed for the organic compounds than for the inorganic compounds (Fig. 1). This point was made by Mighell & Rodgers (1980) and is reinforced by the results from our larger database. The 18 most populous space groups of inorganic compounds comprise 56.86% of that sample, the corresponding 18 groups of the organic crystal structures contain 92.71% of that population. At the other end of the frequency distribution there are many more unoccupied space group types among the organics than among the inorganics, see above.

(3) Among the 18 most common groups of inorganic materials all crystal systems are represented. The corresponding 18 groups of organic substances belong with one exception to the triclinic, monoclinic and orthorhombic systems. The exception is $R\bar{3}$ which is ranked 18 (235 cases, 0.46%)! In all, groups of triclinic, monoclinic and orthorhombic symmetry amount to 95.38% of the organic sample, but only 48.92% of the inorganic sample (Fig. 2).

(4) Of the 18 most common space groups of the inorganic structures none lacks an inversion center,

Table 7. *Frequency distribution of the space groups over the* 32 *crystal classes and over the crystal systems*

Data given: crystal class, rank, frequency and percentage for the inorganic data, the organic data and for their sum.

Crystal class symbol	Inorganic			Organic			Sum of inorganic and organic		
	Rank	No.	%	Rank	No.	%	Rank	No.	%
$\underline{1}$	28	146	0.42	8	635	1.23	15	781	0.90
$\bar{1}$	7	1508	4.35	2	8733	16.92	3	10241	11.87
Σ Triclinic	7	1654	4.77	3	9368	18.15	3	11022	12.77
2	18	399	1.15	5	3749	7.26	5	4148	4.81
m	17	411	1.18	7	728	1.41	11	1139	1.32
2/*m*	2	6082	17.53	1	23317	45.18	1	29399	34.06
Σ Monoclinic	2	6892	19.87	1	27794	53.85	1	34686	40.19
222	12	560	1.61	3	6093	11.81	4	6653	7.71
*mm*2	8	1374	3.96	6	1734	3.36	8	3108	3.60
mmm	1	6492	18.71	4	4237	8.21	2	10729	12.43
Σ Orthorhombic	1	8426	24.29	2	12064	23.37	2	20490	23.74
$\underline{4}$	32	75	0.22	15	139	0.27	29	214	0.25
$\bar{4}$	27	161	0.46	21	87	0.17	28	248	0.29
4/*m*	15	481	1.39	9	332	0.64	14	813	0.94
422	25	163	0.47	11	253	0.49	21	416	0.48
4*mm*	24	205	0.59	23	48	0.09	27	253	0.29
$\bar{4}$2*m*	11	575	1.66	12	171	0.33	16	746	0.86
4/*mmm*	4	3269	9.42	14	143	0.28	7	3412	3.95
Σ Tetragonal	4	4929	14.21	4	1173	2.27	4	6102	7.07
$\underline{3}$	26	163	0.47	13	154	0.30	26	317	0.37
$\bar{3}$	10	578	1.67	10	286	0.55	13	864	1.00
32	21	352	1.01	18	103	0.20	20	455	0.53
3*m*	14	510	1.47	17	105	0.20	17	615	0.71
$\bar{3}$m	5	2093	6.03	16	125	0.24	9	2218	2.57
Σ Trigonal	5	3696	10.65	5	773	1.50	6	4469	5.18
$\underline{6}$	23	218	0.63	19	102	0.20	25	320	0.37
$\bar{6}$	30	100	0.29	32	1	0.00	31	101	0.12
6/*m*	16	433	1.25	20	89	0.17	19	522	0.60
622	29	123	0.35	27	18	0.03	30	141	0.16
6*mm*	20	357	1.03	28	17	0.03	23	374	0.43
$\bar{6}$*m*2	19	362	1.04	30	12	0.02	22	374	0.43
6/*mmm*	6	2035	5.87	29	14	0.03	10	2049	2.37
Σ Hexagonal	6	3628	10.46	6	253	0.49	7	3881	4.50
$\underline{23}$	22	329	0.95	26	36	0.07	24	365	0.42
m$\bar{3}$	13	513	1.48	22	58	0.11	18	571	0.66
432	31	93	0.27	31	8	0.02	32	101	0.12
$\bar{4}$3*m*	9	947	2.81	25	40	0.08	12	1014	1.17
m$\bar{3}$*m*	3	3558	10.26	24	44	0.09	6	3602	4.17
Σ Cubic	3	5467	15.76	7	186	0.36	5	5653	6.55

therefore none of them would admit enantiomorphism, and 12 of them contain a mirror plane. Of the 18 most common space groups of the organic structures eight lack an inversion center, five could be enantiomorphic, and only three have mirror planes.

(5) Almost four fifths (77.95%) of the inorganic crystal structures crystallize in centrosymmetric space groups. This is not that much higher than the 72.42% centrosymmetric organic crystal structures and in this regard the difference between the two populations is not pronounced.

(6) The most striking difference between the inorganic and organic populations [next to the distribution among the crystal systems, see point (3)] is the concentration of inorganic structures in the space groups of highest symmetry in the trigonal, tetragonal, hexagonal and cubic systems (Fig. 2). In groups belonging to the crystal classes 3*m*, 4/*mmm*, 6/*mmm* and *m*$\bar{3}$*m* 10 955 of 17 720 compounds crystallize in the tetragonal, trigonal, hexagonal and cubic systems. This amounts to 31.58% of the total inorganic sample, while for the organic population the corresponding numbers are 326 of 2059 compounds (or 0.63% of the total organic sample). This observation would seem to support the contention that in solid-state inorganic chemistry a symmetry principle is at work (Bärnighausen, 1980; Brunner, 1971).

(7) While generally the distributions observed by Mighell & Rodgers (1980) and by us for the inorganic compounds are similar, in detail there are distinct differences: the sequence and the percentages of individual space groups are not identical. Mighell & Rodgers found *Fm*$\bar{3}$*m* to be the most common space group for inorganic compounds (about 8.4%, or close to 1000 occurrences), we find it to rank third

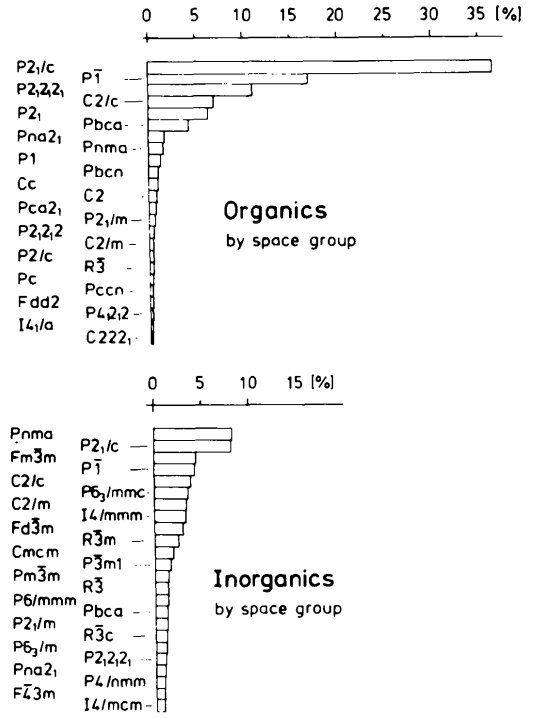

Fig. 1. The 24 most common space groups among organic and inorganic crystal structures shown as percentages of all organic or inorganic crystal structures.

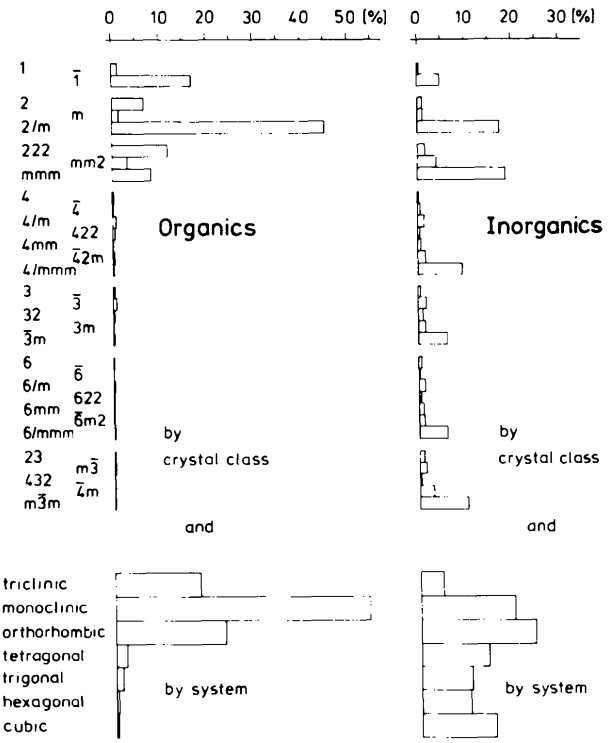

Fig. 2. Distribution of space groups of organic and inorganic crystal structures by crystal class and by crystal system.

behind *Pnma* and $P2_1/c$, with 4.42% and 1532 cases. This may be an artifact of the history of crystal structure determination. The older compilation was most likely more heavily weighted towards simpler more easily determined highly symmetric crystal structures. As time goes by their relative contribution should diminish ever further.

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