

The zellengleichen Supergroups of the Space Groups

By L. L. BOYLE AND J. E. LAWRENSEN

University Chemical Laboratory, Canterbury, Kent, England

(Received 4 February 1972)

A complete list of the zellengleichen supergroups of the 230 Fedorov space groups is presented.

Recent progress in the measurement of the spectra of single crystals has sometimes been in advance of the theory of such spectra since fewer lines than would be expected on the basis of the space group symmetry have been observed. A possible explanation for the operation of a greater number of selection rules than would be expected is that in reality the crystal structure should be regarded as a distortion of a more symmetrical structure. The amount of the distortion is such that, although it is clearly measurable by diffraction methods, little intensity is imparted to those transitions which are due to the descent in symmetry. Interpretation of such spectra therefore requires a list of all the supergroups of the relevant space group.

Information about the supergroups of a given space group has only once been given explicitly and although this can in principle be derived from a list of subgroups, it is only in the last few years that serious attempts have been made to compile an accurate and complete list of either subgroups or supergroups. The construction of the 230 space groups led to a limited amount of information as the books by Hilton (1903) and Niggli (1919) show, but it was not until 1929 that a systematic theory was presented by Hermann (1929). Hermann's list first appeared in *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935) and corrections to this were given by Ascher, Gramlich & Wondratschek (1969). This list only comprised those which Hermann designated as *zellengleich*, i.e. those in which the descent in symmetry had only affected the rotations and reflexions but not the accompanying translations in the unit cell. The cases where only the translations and not the types of elements of symmetry of the crystal class are affected were designated *klassengleich* and will be considered by us in a companion paper. In general, however, a subgroup is not necessarily simply zellengleich or klassengleich, but as Hermann (1929) showed, it can always be regarded as a klassengleiche subgroup of a group which is a zellengleiche subgroup of the given group. In some cases it is also possible to regard the subgroup as a zellengleiche subgroup of a klassengleiche subgroup of the original group.

The two modes of descent in symmetry have different physical applications. The zellengleichen descents are particularly relevant to second-order phase transitions (Landau, 1937; Lifshitz, 1942; Ascher, 1966) and small distortions from energetically stable

structures. The klassengleichen descents are relevant to interpretation of the physical properties of crystals which have an inconveniently large number of molecules per unit cell. Both modes have been used by Neubüser & Wondratschek (1966) in rationalizations of the structures of some mineral varieties. This paper is also a useful review of the whole topic.

Ascher (1968) has produced a complete set of space-group correlation diagrams similar to the sample published a year earlier (Ascher, 1967). These are of the same form as the diagram for point groups presented by Hermann on p. 49 of *Internationalen Tabellen zur Bestimmung von Kristallstrukturen* (1935). We have only found four misprints in Ascher's (1968) work. Diagrams for the klassengleichen correlations have been prepared by Wondratschek, but at the time of writing these were still in manuscript form. A complete list of the maximal subgroups of the space groups was produced by Neubüser & Wondratschek (1969) from the results of computations using a program devised by Felsch & Neubüser (1963). Their results are in a full Hermann-Mauguin notation to give information about orientation and it is hoped that this paper will not only fill the need for a complete list of zellengleichen supergroups but also a list in Schönflies' notation which is both sufficient and preferable for spectroscopic studies. Since preparing the first draft of the text of this paper we have received a new list by Neubüser & Wondratschek (1970) which inverts the list of maximal subgroups to yield a list of minimal supergroups. Finally, it is perhaps worth mentioning that the determination of the 1191 'black and white' space groups involved studies of all the halving subgroups of the Fedorov space groups so that a table of 'subgroups of space groups' appeared in the monograph of Koptsik (1966). Although this in reality is only a list of halving klassengleichen and zellengleichen subgroups (of all indexes) it contains so many errors and omissions that we would need to write a separate paper to make it a useful source of information.

The Tables

Tables 1-7 contain a complete list of zellengleichen supergroups for each space group. The groups outside parentheses are minimal supergroups, those preceding the semicolon being doubling while those following it

Table 5 (cont.)

C_{4h}^3	$D_{4h}^3, D_{4h}^4(O_h^2), D_{4h}^7, D_{4h}^8$
C_{4h}^4	$D_{4h}^{11}, D_{4h}^{12}(O_h^4), D_{4h}^{15}, D_{4h}^{16}$
C_{4h}^5	$D_{4h}^{17}(O_h^5, O_h^8), D_{4h}^{18}(O_h^6)$
C_{4h}^6	$D_{4h}^{19}(O_h^7), D_{4h}^{20}(O_h^8, O_h^{10})$
C_{4v}^1	$D_{4h}^1(O_h^1), D_{4h}^7$
C_{4v}^2	D_{4h}^3, D_{4h}^5
C_{4v}^3	D_{4h}^{10}, D_{4h}^{16}
C_{4v}^4	$D_{4h}^{12}(O_h^4), D_{4h}^{14}$
C_{4v}^5	D_{4h}^2, D_{4h}^8
C_{4v}^6	$D_{4h}^4(O_h^2), D_{4h}^6$
C_{4v}^7	$D_{4h}^9(O_h^3), D_{4h}^{15}$
C_{4v}^8	D_{4h}^{11}, D_{4h}^{13}
C_{4v}^9	$D_{4h}^{17}(O_h^5, O_h^8)$
C_{4v}^{10}	$D_{4h}^{18}(O_h^6)$
C_{4v}^{11}	$D_{4h}^{19}(O_h^7)$
C_{4v}^{12}	$D_{4h}^{20}(O_h^8, O_h^{10})$
D_{2d}^1	$D_{4h}^1, D_{4h}^3, D_{4h}^{10}, D_{4h}^{12}, T_d^1(O_h^1, O_h^4)$
D_{2d}^2	$D_{4h}^2, D_{4h}^4, D_{4h}^9, D_{4h}^{11}, T_d^2(O_h^2, O_h^3)$
D_{2d}^3	$D_{4h}^5, D_{4h}^7, D_{4h}^{14}, D_{4h}^{16}$
D_{2d}^4	$D_{4h}^6, D_{4h}^8, D_{4h}^{13}, D_{4h}^{15}$
D_{2d}^5	$D_{4h}^1(O_h^1), D_{4h}^7, D_{4h}^9(C_3^3), D_{4h}^{15}$
D_{2d}^6	$D_{4h}^2, D_{4h}^8, D_{4h}^{10}, D_{4h}^{16}$
D_{2d}^7	$D_{4h}^3, D_{4h}^5, D_{4h}^{11}, D_{4h}^{13}$
D_{2d}^8	$D_{4h}^4(O_h^2), D_{4h}^6, D_{4h}^{12}(O_h^4), D_{4h}^{14}$
D_{2d}^9	$D_{4h}^{17}(O_h^5), D_{4h}^{19}, T_d^2(O_h^5, O_h^7)$
D_{2d}^{10}	$D_{4h}^{18}, D_{4h}^{20}(O_h^{10}); T_d^5(O_h^6, O_h^8)$
D_{2d}^{11}	$D_{4h}^{17}(O_h^5), D_{4h}^{18}(O_h^6); T_d^3(O_h^9)$
D_{2d}^{12}	$D_{4h}^{19}(O_h^7), D_{4h}^{20}(O_h^8); T_d^6(O_h^{10})$
D_4^1	$D_{4h}^1, D_{4h}^2, D_{4h}^3, D_{4h}^4; O^1(O_h^1, O_h^2)$
D_4^2	$D_{4h}^5, D_{4h}^6, D_{4h}^7, D_{4h}^8$
D_4^3	none
D_4^4	; O^7
D_4^5	$D_{4h}^9, D_{4h}^{10}, D_{4h}^{11}, D_{4h}^{12}; O^2(O_h^3, O_h^4)$
D_4^6	$D_{4h}^{13}, D_{4h}^{14}, D_{4h}^{15}, D_{4h}^{16}$
D_4^7	none
D_4^8	; O^6
D_4^9	$D_{4h}^{17}, D_{4h}^{18}; O^3(O_h^5, O_h^8), O^5(O_h^9)$
D_4^{10}	$D_{4h}^{19}, D_{4h}^{20}; O^4(O_h^7, O_h^8), O^8(O_h^{10})$
D_{4h}^1	; O_h^1
D_{4h}^{2-3}	none
D_{4h}^4	; O_h^2
D_{4h}^{5-8}	none
D_{4h}^9	; O_h^3
D_{4h}^{10-11}	none
D_{4h}^{12}	; O_h^4
D_{4h}^{13-16}	none
D_{4h}^{17}	; O_h^5, O_h^9
D_{4h}^{18}	; O_h^6
D_{4h}^{19}	; O_h^7
D_{4h}^{20}	; O_h^8, O_h^{10}

Table 6. Zellengleichen supergroups of hexagonal space groups

C_6^1	$C_{6h}^1(D_{6h}^1, D_{6h}^2), C_{6v}^1, C_{6v}^2, D_6^1$
C_6^2	D_6^2
C_6^3	D_6^3
C_6^4	D_6^4
C_6^5	D_6^5
C_6^6	$C_{6h}^2(D_{6h}^3, D_{6h}^4), C_{6v}^3, C_{6v}^4, D_6^6$
C_{3h}^1	$C_{6h}^1(D_{6h}^1, D_{6h}^2), C_{6h}^2(D_{6h}^3, D_{6h}^4), D_{3h}^1, D_{3h}^2, D_{3h}^3, D_{3h}^4$
C_{6h}^1	D_{6h}^1, D_{6h}^2
C_{6h}^2	D_{6h}^3, D_{6h}^4
C_{6v}^1	D_{6h}^1
C_{6v}^2	D_{6h}^2
C_{6v}^3	D_{6h}^3
C_{6v}^4	D_{6h}^4
D_{3h}^1	D_{6h}^1, D_{6h}^4
D_{3h}^2	D_{6h}^2, D_{6h}^3
D_{3h}^3	D_{6h}^1, D_{6h}^3
D_{3h}^4	D_{6h}^2, D_{6h}^4
D_6^1	D_{6h}^1, D_{6h}^2
D_6^{2-5}	none
D_6^6	D_{6h}^3, D_{6h}^4
D_{6h}^{1-4}	none

Table 7. Zellengleichen supergroups of cubic space groups

T^1	$T_d^1(O_h^1, O_h^4), T_d^4(O_h^2, O_h^3), T_h^1, T_h^2, O^1, O^2$
T^2	$T_d^2(O_h^5, O_h^8), T_d^5(O_h^6, O_h^9), T_h^3, T_h^4, O^3, O^4$
T^3	$T_d^3(O_h^9), T_h^5, O^5$
T^4	T_h^6, O^6, O^7
T^5	$T_d^6(O_h^{10}), T_h^7, O^8$
T_d^1	O_h^1, O_h^4
T_d^2	O_h^5, O_h^7
T_d^3	O_h^9
T_d^4	O_h^2, O_h^3
T_d^5	O_h^6, O_h^8
T_d^6	O_h^{10}
T_h^1	O_h^1, O_h^3
T_h^2	O_h^2, O_h^4
T_h^3	O_h^5, O_h^9
T_h^4	O_h^7, O_h^8
T_h^5	O_h^9
T_h^6	none
T_h^7	O_h^{10}
O^1	O_h^1, O_h^2
O^2	O_h^3, O_h^4
O^3	O_h^5, O_h^6
O^4	O_h^7, O_h^8
O^5	O_h^9
O^{6-7}	none
O^8	O_h^{10}
O_h^{1-10}	none

We are grateful to the United Kingdom Science Research Council for the award of a Research Studentship (to JEL).

References

- ASCHER, E. (1966). *Phys. Letters*, **20**, 352.
 ASCHER, E. (1967). *Chem. Phys. Letters*, **1**, 69.
 ASCHER, E. (1968). *Lattices of equi-translation subgroups of the space groups*. Internal report of the Battelle Institute Advanced Studies Centre, Geneva, 2nd ed.
 ASCHER, E., GRAMLICH, V. & WONDRATSCHEK, H. (1969). *Acta Cryst.* **B25**, 2154.
 FELSCH, V. & NEUBÜSER, J. (1963). *Mitteilung des Rheinisch-Westfälische Instituts für Instrumentelle Mathematik (Bonn)*, **2**, 39.
 HERMANN, C. (1929). *Z. Kristallogr.* **69**, 533.
 HILTON, H. (1903). *Mathematical Crystallography and the Theory of Groups of Movements*. Oxford Univ. Press.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Vol. I. Berlin: Borntraeger.
 KOPTSIK, V. A. (1966). *Shubnikov Groups*, Table 10. Moscow Univ. Press.
 LANDAU, L. D. (1937). *Phys. Z. Sowjet.* **11**, 26.
 LIFSHITZ, E. M. (1942). *J. Phys. Moscow*, **6**, 61.
 NEUBÜSER, J. & WONDRATSCHEK, H. (1966). *Krist. Tech.* **1**, 529.
 NEUBÜSER, J. & WONDRATSCHEK, H. (1969). *Maximal subgroups of the space-groups*. Internal report, 2nd typing. (This differs only in a very few minor misprints and improvements from the original 1965 edition. The whole work was prepared for publication in the next edition of Vol. I of *International Tables for X-ray Crystallography*.)
 NEUBÜSER, J. & WONDRATSCHEK, H. (1970). *Minimal supergroups of the space-groups*. Internal report.
 NIGGLI, P. (1919). *Geometrische Kristallographie des Diskontinuums*, Table 1. Leipzig: Borntraeger.

Acta Cryst. (1972). **A28**, 489

Klassengleichen Supergroup-Subgroup Relationships between the Space Groups

BY L. L. BOYLE AND J. E. LAWRENSON

University Chemical Laboratory, Canterbury, Kent, England

(Received 18 February 1972)

A list of physically significant klassengleichen subgroups and supergroups of the 230 space groups is presented with a discussion of the criteria governing the limitations on the allowed changes in volume of the unit cell.

In a previous paper (Boyle & Lawrenson, 1972) we have enumerated the zellengleichen supergroups of the 230 Fedorov space groups. By definition, no change in the volume of the unit cell was involved and although such relationships are extremely useful for many physical applications, klassengleichen changes are often necessary if radical simplifications of a crystal struc-

ture are to be effected. In a klassengleiche ascent in symmetry, the volume of the unit cell is reduced so that not only does the number of molecules per unit cell, Z , change, but also the sites occupied by the various molecules and ions comprising the crystal attain a higher point symmetry. By definition, a klassengleiche relationship can only hold between two space groups having the same crystal class (unit cell group) and therefore in Schönflies notation only the superscript in the space group symbol may change. The principles underlying these relationships were laid down by Hermann (1929) and again in a useful paper by Neubüser & Wondratschek (1966). The enumeration of the black-and-white space groups (Belov, Neronova &

Table 1. *Klassengleichen relationships between the triclinic space groups*

$$S_2 \begin{array}{c} 1 \\ 1 \end{array} \left| \begin{array}{c} 1 \\ z \end{array} \right.$$

Code: $z=2$.

Table 2. *Klassengleichen relationships between the monoclinic space groups*

C_2	1	2	3	C_{1h}	1	2	3	4	C_{2h}	1	2	3	4	5	6
1	z	.	e	1	z	.	e	.	1	z	.	e	.	.	.
2	z	z	e	2	z	z	e	e	2	z	z	e	.	.	.
3	v	.	z	3	v	.	z	.	3	v	.	z	.	.	.
				4	.	v	z	v	4	z	.	e	z	e	e
									5	v	z	e	z	z	e
									6	a	.	z	v	.	v

Code: $e=1, 2, 4, 8$; $z=2, 4, 8$; $v=4, 8$; $a=8$ with the restriction that $Z_{\max}=4$ for C_2 and C_{1h} groups and 8 for C_{2h} groups.