

potential curves along [110] and $[\bar{1}\bar{1}0]$ and those along [100] and $[\bar{1}00]$ are both symmetric with respect to the Zn position, indicating no anisotropic anharmonic features. The curves of the former two potentials are slightly lower than those of the latter.

The potential curves interpret the residual electron densities observed in the difference Fourier map (Fig. 1). The positions of the positive peaks coincide with the smaller potential region, and those of the negative one with the larger potential.

In comparison with the neutron diffraction studies, the present experiment on the anharmonic thermal vibration of atoms in ZnX (X = S, Se, Te) encounters greater difficulty regarding the separation from the valence charge electron distribution mainly observed around the X atoms. However, it is confirmed by the difference Fourier synthesis that the difficulty is overcome by the refinement using the higher-order reflections. The cumulant expansion up to the fourth-rank tensors was adopted for the thermal parameters in the present anharmonic refinements.

The residual electron densities observed in the difference Fourier maps after the harmonic refinements indicate that ZnTe shows more notable anharmonicity than ZnS and ZnSe, and that the Zn atom in the three compounds shows a larger anharmonicity than X. These features are also disclosed by the OPP calculated from the anharmonic parameters.

The lattice-dynamical study by means of Raman spectroscopy elucidates that the compounds having the less ionic but probably more metallic bond character show a larger anharmonicity than the ionic compounds and that the bond distance of the former more

easily expands, as the interatomic forces are weakened.

References

- BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* **A30**, 129-147.
 BUSING, W. R. & LEVY, H. A. (1967). *Acta Cryst.* **22**, 457-464.
 COHEN, M. L. (1973). *Science*, **179**, 1189-1195.
 COOPER, M. J., ROUSE, K. & FUESS, H. (1973). *Acta Cryst.* **A29**, 49-56.
 COWLEY, R. A. (1963). *Adv. Phys.* **12**, 421-480.
 DICK, B. J. & OVERHAUSER, A. W. (1958). *Phys. Rev.* **112**, 90-103.
 FINGER, L. W. & PRINCE, E. (1975). *Natl. Bur. Stand. (US) Tech. Note No.* 854.
 JOHNSON, C. K. (1969). *Acta Cryst.* **A25**, 187-194.
 JOHNSON, C. K. & LEVY, H. A. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 311-336. Birmingham; Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 KELLERMANN, E. W. (1940). *Philos. Trans. R. Soc. London*, **238**, 513-548.
 KONTIO, A. & STEVENS, E. D. (1982). *Acta Cryst.* **A38**, 623-629.
 KUHS, W. F. (1983). *Acta Cryst.* **A39**, 148-158.
 KUSKOV, V. I., RUSAKOV, A. P. & MENTSER, A. N. (1972). *Sov. Phys. Solid State*, **14**, 1869-1870.
 LEE, B. H. (1970). *J. Appl. Phys.* **41**, 2984-2990.
 MCINTYRE, C. J., MOSS, G. & BARNEA, Z. (1980). *Acta Cryst.* **A36**, 482-490.
 MAIR, S. L. & WILKINS, S. W. (1976). *J. Phys. C*, **9**, 1145-1158.
 MERISALO, M. & KURITTU, J. (1978). *J. Appl. Cryst.* **11**, 179-182.
 MOSS, B., McMULLAN, R. K. & KOETZLE, T. F. (1980). *J. Chem. Phys.* **73**, 495-508.
 VEKILOV, YU. KH. & RUSAKOV, A. P. (1971). *Sov. Phys. Solid State*, **13**, 956-960.
 WILKINSON, G. R. (1973). *The Raman Effect*, Vol. II, edited by A. ANDERSON, pp. 811-987. New York: Academic Press.
 WILLIS, B. T. M. (1969). *Acta Cryst.* **A25**, 277-300.
 YAMANAKA, T. (1985). *Phys. Chem. Miner.* In preparation.
 YAMANAKA, T., TAKEUCHI, Y. & TOKONAMI, M. (1984). *Acta Cryst.* **B40**, 96-102.
 ZUCKER, U. H. & SCHULZ, H. (1982). *Acta Cryst.* **A38**, 563-568.

Acta Cryst. (1985). **B41**, 304-310

A Systematic Classification of Crystal Structures

BY LUDO K. FREVEL

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, USA

(Received 19 March 1984; accepted 7 May 1985)

Abstract

A concise scientific notation has been devised to classify the crystal structure of a stoichiometric compound expressed by the formula $\sum_E E_{\nu_E}$ where E represents the chemical symbol of element E and ν_E denotes the number of atoms of element E . Four items of information are coded in the composite notation: (a) the number of different elements, n_E , contained in the chemical formula; (b) the total number of atoms given by the chemical formula; (c) the applicable space group, S , expressed in the Hermann-

Mauguin notation; and (d) the number of formula 'molecules', z , per unit cell. The general form of any crystal structure is thus expressed as $n_E, \sum_E \nu_E S(z)$. For each crystal system its various crystal structures are catalogued in a hierarchical order so that the structure with the lowest values for $n_E, \sum \nu_E, z$ and the lowest space-group number is listed first. The crystal structure 1,1P1(1) heads the list of triclinic structures. A simple augmentation of the proposed notation makes it possible to classify also the non-stoichiometric defect structures.

Table 1. Comparison of the three dominant classifications of crystal structures

	Ewald-Hermann	Wyckoff	Pearson
Structure symbol	A1, A2, A3, ..., A20	a, c, b1, ..., g1	cF4, cI2, hP2, ..., oC4
Element	Cu, W, Mg, ..., α -U	Cu, α -Fe, Mg, ..., α -U	Cu, W, Mg, ..., α -U
Structure symbol	B1, B2, B3, ..., B37	RX a1, b1, c1, ..., d7	cF8, cP2, cF8, ..., tI16
Binary compound	NaCl, CsCl, ZnS, ..., TiSe (sphalerite)	NaCl, CsCl, ZnS, ..., TiSe	CINa, ClCs, SZn, ..., SeTI
Structure symbol	G1, G2	RMX ₃ , a1, a2	
Compound	CaCO ₃ , CaCO ₃ (calcite, aragonite)	NaNO ₃ , KNO ₃	
Structure symbol		X, g 28	
Compound	NaAl ₁ O ₄ (OH) ₂ (SeO ₄) ₄ · 12H ₂ O		

Introduction

Of the various comprehensive attempts to classify crystal structures, three compilations have proved especially useful to X-ray crystallographers: first, *Strukturbericht* (1931–1939) initiated by P. P. Ewald and C. Hermann in 1931 and continued after 1945 as *Structure Reports* (1951–1982) (Trotter, 1982); second, *Crystal Structures* (Wyckoff, 1963–1966); and third, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pearson, 1958, 1966). Various other attempts have been made to describe crystal structures in terms of their different subunits [see the extensive work and the comprehensive literature citation by Lima-de-Faria & Figueiredo (1976)]. The main concern of these efforts, however, has been the scientific *description* of complex inorganic structures, primarily the silicates. Of the above three major compendia, the first two list the crystal structure of a compound according to its chemical formula; the third classifies the structure of a metal on the basis of its Bravais lattice and the number of atoms in the conventional crystallographic unit cell for the standard space group and setting. A few specific examples in Table 1 contrast the three schemes of classification.

Strukturbericht symbols are convenient for the simpler structures (A1, A2, A3, B1, B2, B3); but the system of assigning letters *B*, *C* etc. to the structure type of a 1:1 binary compound, 1:2 binary compound, etc. has its obvious limitations for complicated compounds. Wyckoff's generalized chemical formulas such as RX , RX_2 , R_mX_n , $R_x(MX_3)_y$, etc. are superior to the arbitrary assignment of letters. However, to distinguish the structure of NaCl from that of CsCl the designations $RXa1$ and $RXb1$ are instituted, thereby introducing the same limitations as in the *Strukturbericht* classification. Pearson's scheme of listing the structures of crystalline metallic phases by a composite notation of the Bravais lattice (*aP*, anorthic primitive; *mp*, monoclinic primitive; *mC*, monoclinic *C*-centered; . . . ; *cP*, cubic primitive; *cI*, cubic body-centered; and *cF*, cubic face-centered) followed by the number of atoms in the accepted unit cell has a twofold advantage: first, of sorting the structures into six crystal systems; and, second, of

ordering the structures within a crystal system. Utilizing the small letters *a*, *m*, *o*, *t*, *h*, *c* mnemonic with the names of the six crystal systems is based on English and introduces an ambiguity in the accepted use of the letters *a*, *c*, and *m* in the space-group notation. Moreover, Pearson's classification symbols are not meant to be names for the structure types, since there may be an indefinite number of structures under a particular classification; e.g., for *cF8* there are three structure types; for *hP6*, 4 types; for *cF16*, 3 types; for *tP4*, 3 types; for *oP8*, 3 types; and for *mP12*, 2 types among 195 structures listed. Apparently, 'the problem of giving simple systematic names to crystal structure types is one that has received much thought, but it seems also to be a problem without any ready solution. The best that can be done is to name each structure type after a representative substance, as for example Cu_3Au , which has that structure' (Pearson, 1958).

Proposed solution to the classification of crystal structures

The twofold objective of the task at hand is to achieve a unique, concise, systematic *classification* of crystal structures (not a *description* of the various crystal structures), which classification will aid X-ray crystallographers firstly in finding a prototype structure for a new crystalline phase and secondly in predicting the more probable structures for a crystalline compound of known chemical formula. The first step in this endeavor is the creation of a compact scientific notation for a given crystal structure. For a notation to gain acceptance by the general scientific community, the notation should be simple, unique, machine-readable, open-ended, and useful. The particular notation decided upon was developed *a posteriori* as a by-product of the systematic classification of crystalline isomorphs. Four items of information are coded in the composite notation: (*a*) the number of different elements, n_E , contained in the chemical formula

$$\sum_E E_{\nu E} \quad (1)$$

where E represents the chemical symbol of element E and ν_E denotes the number of atoms of element E , (b) the total number of atoms, $\sum_E \nu_E$, given by the stoichiometric formula; (c) the appropriate space group, S , expressed in the Hermann-Mauguin notation; and (d) the number of formula 'molecules', z , per unit cell. The general form of any crystal structure is expressed as:

$$n_E \sum_E \nu_E S(z). \quad (2)$$

Two examples for each crystal system are given in Table 2 to illustrate the variation and the compactness of the new notation.

For any structure the product $z \sum_E \nu_E$ is equal to the total number of atoms in the unit cell. If $z\nu_E = 1$ for every element E in the stoichiometric formula, then expression (1) uniquely gives the appropriate chemical formula and assures the unique Wyckoff positional parameters. However, for $z\nu_E > 1$, the possibility exists that formula (1) may have to be multiplied by an integer μ to denote that at least one of the elements has more than one set of Wyckoff positional parameters. For example, TlSe has a structure based on the body-centered space group $I4/mcm$, where Tl atoms are of two sorts in positions fixed by symmetry:

$$\text{Tl}(1): (4a) \pm (00\frac{1}{4}); \pm (\frac{1}{2}, \frac{1}{2}, \frac{3}{4})$$

$$\text{Tl}(2): (4b) \pm (0\frac{1}{2}\frac{1}{4}); \pm (\frac{1}{2}, 1, \frac{3}{4}).$$

To convey this structural non-equivalence of the Tl atoms, the empirical formula TlSe is multiplied by $\mu = 2$. Accordingly the structure notation for TlTlSe₂ is

$$2,4I4/mcm(4).$$

In general the reduced number of formula 'molecules' per unit cell is given by

$$z_\mu = z/\mu, \quad (3)$$

where z/μ must be an integer.

Cataloguing the different crystal structures in a systematic manner entails setting some arbitrary rules. Rule (1): The different structures are segregated into the seven crystal systems: cubic, rhombohedral, hexagonal, tetragonal, orthorhombic, monoclinic, and triclinic. Rule (2): Within each crystal system, the structures are ordered so that the hierarchical conditions (4) and (5) are met for all ordinal values of $j \geq 1$ and $k \geq 2$.

$$1 = (n_E)_1 \leq (n_E)_j; \quad 1 = \left(\sum_E \nu_E \right)_1 \leq \left(\sum_E \nu_E \right)_j; \quad (4)$$

$$1 = z_1 \leq z_j; \quad S_1 \leq S_j$$

$$(n_E)_j \leq (n_E)_k; \quad \left(\sum_E \nu_E \right)_j \leq \left(\sum_E \nu_E \right)_k; \quad (5)$$

$$z_j \leq z_k; \quad S_j \leq S_k.$$

Table 2. Typical examples of the new notation of crystal structures

Crystalline phase	Crystal structure notation
Mn ₂ O ₃ , bixbyite	2,5Ia3(16)
KAl(SO ₄) ₂ · 12H ₂ O, alum	5,48Pa3(4)
CaCO ₃ , calcite	3,5R3c(2)
KAl ₃ (SO ₄) ₂ (OH) ₆ , alunite	5,26R3m(3)
Ca ₅ F(PO ₄) ₃ , fluorapatite	4,21P6 ₃ /m(2)
La ₂ (SO ₄) ₃ · 9H ₂ O	4,44P6 ₃ /m(2)
β-Sn (286 K < T < 505 K)	1,1I4/amd(4)
Na ₂ TiOSi ₄ O ₁₀ , narsarsukite	4,18I4/m(4)
Yb ₂ S ₄	2,7Pnam(4)
FePO ₄ · 2H ₂ O, strengite	4,12Pbca(8)
K ₂ Na ₂ Te ₂ O ₈ (OH) ₂ · 14H ₂ O	5,62I2/m(2)
[Pt(C ₂ H ₈ N ₂)(C ₇ H ₈ N ₄ O) ₂](PF ₆) [*]	7,67C2/c(4)
K ₂ Cr ₂ O ₇ (triclinic)	3,11P1(4)
CuZn ₂ (AsO ₄) ₂ , stranskiite	4,13P1(1)

* *cis*-Bis(7,9-dimethylhypoxanthine)(ethylenediamine)platinum(II) hexafluorophosphate.

The number of the space group S is the same as in *International Tables for X-ray Crystallography* (1965): namely, the triclinic space group $P1$ is number 1 and the cubic space group $Ia3d$ is number 230. In the rare cases when all four conditions in (5) become equalities, the two identical structure notations will be rendered unique by adding the respective chemical formulas. Then the structure for which its prototype phase has the smaller molecular volume, $(a \times b \cdot c)z^{-1}$, will precede the other structure. An abridged form of Table 3 illustrates the systematic ordering of the crystal structures of the elements.* For the eight cubic structure types, 82 elements are listed: 40 elements for structure $1,1Im3m(2)$; 32 for $1,1Fm3m(4)$; 4 for $1,1Fd3m(8)$; 2 for $1,1Pm3m(1)$; and 1 for each of the other four cubic structures. For the six rhombohedral structures, 13 elements are noted, with structure $1,1R\bar{3}m(2)$ showing 5 elements. The four hexagonal structures are dominated by $1,1P6_3/mmc(2)$ with 34 elements. For the eight tetragonal structures only 14 entries are listed with $1,1I4/mmm(2)$ having 5 elements. The orthorhombic system contains six structures with a total of 12 entries (10 elements). In the monoclinic system (7 structures, 5 elements) one encounters two allotropes of Se consisting of puckered eight-membered rings. The triclinic system is a null class for the elements. In Table 3, the descending order of the atomic number Z_E permits one to find readily the structure(s) of element E . Although the proposed structure notation is compact, for the sake of metallurgists it is expedient to abbreviate the three dominant metal structures to I structure or Mo structure, F structure or Cu structure, $P6_3$ structure or Mg structure in preference to b.c.c. structure, f.c.c.

* The entire Table 3 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42218 (18pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Classification of the crystal structures of the elements

For each structure type the representative elements are listed in ascending order of the respective atomic volume $V_E = (a \times b \cdot c)z^{-1}$. To avoid undue repetition the more recent literature values for the lattice constants have been arithmetically averaged. For individual citations see Wyckoff (1963-1966) and Landolt-Börnstein (1971). (Z_E is the atomic number, V_F the molecular volume.)

(I) Cubic structures					1,1 $P6_3/mmc$ (4)						
V_E (Å ³)	a (Å)	Element	Z_E	a_E (Å)	V_F (Å ³)	a (Å)	c (Å)	Element	Z_E	V_F (Å ³)	
1,1 $Pm\bar{3}m$ (1)					29-29	3-4690	11-240	α -Am(295 K)	57	37-42	
26-62	2-986	Sb(300 K, 70 kbar)	51	4-11 (He)	34-15	3-6579	11-790	α -Nd(300 K)	58	34-47	
37-43	3-345	α -Po(285 K)	84	3-5092	34-47	3-673	11-802	β -Ce(300 K)	59	34-56	
1,1 $Im\bar{3}m$ (2)					34-56	3-6725	11-8354	α -Pr(300 K)	60	34-15	
8-31	2-552	β - ⁹ Be(1530 K)	2	3-510	37-42	3-770	12-159	α -La(300 K)	95	29-29	
11-77	2-8663	α -Fe(300 K)	3	3-638	(IV) Tetragonal structures						
12-00	2-8845	Cr(295 K)	3	3-510	V_F (Å ³)	a (Å)	c (Å)	Element	Z_E	V_F (Å ³)	
...	1,1 $I4/mmm$ (2)						
115-74	6-14	¹³³ Cs(263 K)	94	3-638	22-54	3-995	2-825	HgII(77 K, high pressure)	49	26-14	
1,1 $Fm\bar{3}m$ (4)					
10-79	3-5082	⁶⁴ Ni(78 K)	2	4-240	26-14	3-2512	4-9467	In(300 K)	94	24-73	
10-80	3-5087	⁵⁸ Ni(78 K)	2	4-242	1,1 $P4_212$ (4)						
10-89	3-5187	⁵⁸ Ni(300 K)	3	4-40	20-31	4-897	3-388	β -Np	93		
10-94	3-5238	Ni(300 K)	10	4-4546	1,1 $I4_1/amd$ (4)						
11-13	3-5441	β -Co(290 K)	10	4-455	14-19	4-686	2-585	SiII(300 K, high pressure)	14		
...	
59-50	6-197	Xe(58 K)	95	4-894	27-05	5-8315	3-1814	β -Sn(300 K)	50		
1,1 $Fd\bar{3}m$ (8)					1,1 $P4_32_12$ (12)						
5-67	3-5670	C(diamond, 300 K)	6	6	20-45	5-93	6-98	GeIII(300 K, 125 kbar)	32		
20-02	5-43107	Si(300 K)	14	14	1,1 $P4_2/mnm$ (30)						
22-64	5-6575	Ge(300 K)	32	32	21-82	10-759	5-656	β -U	92		
34-16	6-4892	α -Sn(293 K)	50	50	1,1 $P4_2/nmm$ (50)						
1,1 $Ia\bar{3}$ (16)					7-82	8-80	5-05	B	5		
18-26	6-636	Si(300 C, 180 kbar)	14	14	1,2 $P4_2/mnm$ (2)						
1,1 $P4_132$ (20)					V_F (Å ³)						
12-59	6-3145	β - ⁵⁵ Mn(300 K)	25	25	40-00	3-957	5-109	N ₂ (21 K, 4000 kbar)	7		
1,1 $I\bar{4}3m$ (58)					1,2 $P4_2/ncm$ (8)						
12-21	8-9139	α - ⁵⁵ Mn(300 K)	25	25	V_F (Å ³)						
1,4 $I\bar{4}3m$ (58, r)					56-05	8-56	6-12	Cl ₂ (90 K)	17		
V_F (Å ³)					(V) Orthorhombic structures						
114-6	18-8	³¹ P ₄	15	15	V_E (Å ³)	a (Å)	b (Å)	c (Å)	Element	Z_E	
(II) Rhombohedral structures					1,1 $Amam$ (4)						
V_E (Å ³)	a (Å)	α (°)	Element	Z_E	20-75	4-9548	5-8695	2-8537	α -U(300 K)	92	
1,1 $R\bar{3}m$ (1)					1,1 $Pbnm$ (8)						
22-99	2-9863	70-743	Hg(5 K)	80	19-22	4-887	6-663	4-723	α -Np(295 K)	93	
23-36	3-005	70-533	Hg(227 K)	80	1,1 $Acam$ (8)						
36-61	3-359	98-217	β -Po(~350 K)	84	18-99	4-3763	10-478	3-3136	³¹ P(black)(295 K)	15	
1,1 $R\bar{3}m$ (2)					19-35	4-5156	7-6328	4-4904	Ga(42 K)	31	
14-49	3-524	57-25	³¹ P(300 K, ~70 kbar)	15	19-59	4-524	7-661	7-661	Ga(300 K)	31	
...	22-00	4-48	10-85	3-62	ϵ - ⁷⁵ As	33	
35-16	4-736	57-233	²⁰⁹ Bi(300 K)	83	1,1 $Fddd$ (8)						
1,1 $R\bar{3}m$ (3)					23-14	5-7682	10-162	3-1587	γ -Pu(510 K)	94	
32-50	8-92	23-3	Gd(300 K, high pressure)	64	1,2 $Bmab$ (4)						
33-11	8-996	23-217	Sm	62	V_F (Å ³)						
1,1 $R\bar{3}m$ (12)					57-73	6-24	8-26	4-48	Cl ₂ (115 K)	17	
7-28	5-057	58-06	α -B(300 K)	5	65-14	6-67	8-72	4-48	Br ₂ (80 K)	35	
1,1 $R\bar{3}m$ (108)					81-80	7-14	9-78	4-686	¹²⁷ I ₂ (110 K)	53	
7-59	10-12	65-47	B(300 K)	5	85-06	7-255	9-78	4-795	¹²⁷ I ₂ (300 K)	53	
1,6 $R\bar{3}$ (1)					1,8 $Fddd$ (16)						
V_F (Å ³)					V_F (Å ³)						
146-67	6-46	115-3	S ₆ (300 K)	16	205-68	12-866	24-486	10-446	α -S ₈ (300 K)	16	
(III) Hexagonal structures					(VI) Monoclinic structures						
V_E (Å ³)	a (Å)	c (Å)	Element	Z_E	V_E (Å ³)	a (Å)	b (Å)	c (Å)	β (°)	Element	Z_E
1,1 $P6_3/mmc$ (2)					1,1 $P2_1/m$ (16)						
8-11	2-286	3-5835	α - ⁹ Be(300 K)	1	20-01	11-968	4-823	6-183	101-80	α -Pu(290 K)	94
10-66	2-465	4-050	FeII(300 K, 150 kbar)	2	1,1 $I2/m$ (34)						
...	22-16	9-227	10-449	7-824	92-54	β -Pu(365 K)	94
57-08	4-32	7-064	β -Sr(520 K)	81	22-44	9-284	10-463	7-859	92-13	β -Pu(465 K)	94
1,1 $P3_121$ (3)					1,1 $P2/n$ (84)						
27-28	4-3656	4-9590	Se(300 K)	34	21-78	21-91	9-15	9-21	97-7	³¹ P(Hittorf)	15
33-98	4-4566	5-9268	Te(300 K)	52	1,2 $A2_1/m$ (4)						
1,1 $P6_3mc$ (4)					V_F (Å ³)						
8-80	2-4612	6-7079	C(graphite)	6	32-11	7-284	3-28	5-50	102-17	α - ¹⁹ F ₂ (23 K)	9

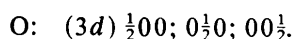
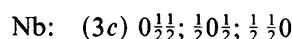
Table 3 (cont.)

1,8 <i>P</i> ₂ ₁ / <i>n</i> (4) α -Se ₈ <i>V_F</i> (Å ³)						
238-23	11-61	9-07	9-05	90-767	α -Se ₈ (300 K)	34
1,8 <i>P</i> ₂ ₁ / <i>a</i> (4) β -Se ₈ <i>V_F</i> (Å ³)						
241-00	12-85	8-07	9-31	93-133	β -Se ₈ (300 K)	34
1,8 <i>P</i> ₂ ₁ / <i>a</i> (6) <i>V_F</i> (Å ³)						
219-10	11-04	10-98	10-92	83-267	β -S ₈	16

structure, or h.c.p. structure. Thus one may speak of the $I \leftrightarrow F$ allotropism observed for Ca, Mn, Fe, Sr, La, Ce, Pr, Nd, and Yb; the $I \leftrightarrow P6_3$ allotropism for He, Li, Be, Na, Ti, Y, Zr, Ba, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, and Tl; and the $F \leftrightarrow P6_3$ allotropism for He, Li, Ne, Ar, Fe, Co, Sr, Yb, and Tl. It is interesting to note that the atomic volumes of the respective allotropes are nearly invariant if corrected to the same temperature and to a pressure of 1 kbar (1 kbar $\equiv 10^8$ Pa).

The notation developed above is based on perfect stoichiometry and on complete three-dimensional periodicity. However, even in the case of pure elements, there exists a randomness for multinuclidic elements such as Cu which is binuclidic. Thus, when examined by neutron diffraction, pure natural Cu is a substitutional solid solution, $^{63}\text{Cu}_{0.692}^{65}\text{Cu}_{0.308}$. An analogous situation obtains for X-ray diffraction in the case of the homogeneous binary solid solution $\text{Cu}_{1-x}\text{Ni}_x$, for which all the atomic positions in the F structure are occupied (however, with a random substitution of Ni atoms for Cu atoms within the bounds, $+0 \leq x \leq 1-0$). Incorporating this information in the proposed structure notation requires that n_E is not restricted to n_E elements (one does not count all the elements but only those for the pure unsubstituted prototype phase). This fact can be expressed by placing the negation sign of symbolic logic above n_E . Additionally the existence of a substitutional solid solution can be indicated by adding s after z . Thus the expanded notation of the modified 1,1*Fm*3*m*(4) structure is expressed as $\bar{1},1\bar{F}m3m(4,s)$ for $\text{Cu}_{1-x}\text{Ni}_x$. For a ternary substitutional solid solution, such as $\text{Au}_{1-x-y}\text{Ag}_x\text{Cu}_y$, the same notation would apply with the obvious boundary values on x and y ; i.e. $+0 \leq x+y \leq 1-0$ and $+0 \leq (x, y) \leq 1-0$. There is another randomness encountered among crystal structures; namely, free rotation or random orientation of a radical ion such as NH_4^+ , HS^- , CN^- , etc. To convey this information an r is placed after z . Accordingly, the structure notation for NH_4Cl ($233 < T < 456$ K) is $\bar{2},\bar{2}Pm3m(1,r)$. The proposed structure notation can also be augmented to encompass nonstoichiometric crystalline defect solids; e.g. interstitial solid solutions, vacancy compounds (subtractive solid solutions), and inclusion (insertion, intercalation) compounds. Interstitial solid solutions

(formed by transition metals and the non-metals H, B, C, and N) are nonstoichiometric phases in which the smaller atoms partially and randomly occupy interstitial tetrahedral or octahedral holes to varying extent depending on composition. For example, if the substitutional solid solution $\text{Fe}_{1-x}\text{Mn}_x$ is modified by the addition of small amounts of carbon to form the interstitial solid solution $\text{Fe}_{1-x}\text{Mn}_xC_\delta$, then the structure notation is modified to $\bar{1},1+\delta Fm3m(4,s,i)$ so that the addition of i signifies interstitial solid solution with δ restricted to $0 < \delta \ll 1$. Similarly for metal-deficient oxides such as $\text{Fe}_{1-\delta}\text{O}$, the augmented structure notation is $\bar{2},2-\delta Fm3m(4,\square)$ where \square denotes δ vacant sites among the Fe sites. However, the compound NbO should not be described as a defect NaCl arrangement. There are 3 NbO per unit cell with the following atomic positions in terms of space group $Pm3m$ (Wyckoff, 1963-1966):



Hence one is dealing with an ordered atomic arrangement (not a random defect structure) and the structure notation should be $\bar{2},2Pm3m(3)$. For inclusion compounds (which contain holes, tunnels, or gaps to accommodate atoms or molecules) nonstoichiometry arises from the variable concentration of trapped moieties as in the case of zeolites, clathrates, or intercalation compounds of graphite. To call attention to this structural feature in cubic $\text{NaAlSiO}_4 \cdot x\text{H}_2\text{O}$, its structure notation is expressed as $\bar{4},7+3xPm3m(12,\hat{i})$ where the suggestive symbol \hat{i} refers to inclusion compound.

Compounds with defect structures are listed with the corresponding stoichiometric crystal structures. Structures with \bar{n}_E in their structure notation are classified under the corresponding structures with positively specified n_E . Thus, homogeneous solid-solution phases like $\text{Cu}_{1-x}\text{Ni}_x$ are found under structure 1,1*Fm*3*m*(4). Likewise, NH_4Cl is included in the set of phases possessing the $\bar{2},2Pm3m(1)$ structure. Metal-deficient oxides like $\text{Co}_{1-\delta}\text{O}$ are treated as belonging to the $\bar{2},2Fm3m(4)$ structure. Moreover, structure $\bar{2},2Pm3m(1)$ precedes structure $\bar{2},2Fm3m(4)$ in accordance with the above specified rules. The phases FeFe_2O_4 , CoCo_2O_4 , FeFe_2S_4 , CoCo_2Se_4 , etc. have the common structure classified as $\bar{2},7Fd3m(8)$ and form a subclass of the general spinel group RM_2X_4 , the structure of which is classified as $\bar{3},7Fd3m(8)$. It is natural to subsume the subclass under $\bar{3},7Fd3m(8)$ as shown in Table 4.

The general hierarchy of crystal structures is cubic structures first, rhombohedral structures second, . . . , and triclinic structures seventh (Rule 1). Within each crystal system the structures are ordered according to Rule (2). If one designates the cubic crystal structures for the monoatomic elements as the ordered set

Table 4. Representatives of the spinel structure $3,7Fd3m(8)$

V_F (\AA^3)	a (\AA)	Phase
65.2	8.048	NiAl ₂ O ₄ (298 K)
—	—	—
73.8	8.390	CoFe ₂ O ₄ (inverse, partly disordered)
73.98	8.396	FeFe ₂ O ₄ (296 K); $\bar{3},7Fd3m(8)^*$
—	—	—
76.9	8.505	(Mg,Mn,Fe)Fe ₂ O ₄ ; $\bar{3},7Fd3m(8, s)^*$
—	—	—
119.1	9.84	FeFe ₂ S ₄ ; $\bar{3},7Fd3m(8)^*$
—	—	—
158.9	10.833	HgIn ₂ S ₄

* The negation symbol above 3 signifies that $\bar{3}$ is not restricted to 3; i.e. $\bar{3}$ may be 2 or greater than 3.

$\{1,1S_1(z)\}$ with $z = 1, 2, \dots$, then the cubic structures for compounds are listed in the following order:

$\{2,2S_1(z)\}, \{2,3S_1(z)\}, \dots, \{2,2+n_2S_1(z)\}$ for binary compounds with $n_2 = 1, 2, \dots$,

$\{N, NS_1(z)\}, \{N, N+1S_1(z)\}, \dots, \{N, N+n_N S_1(z)\}$

for N -ary compounds with $n_N = 1, 2, \dots$,

where S_1 refers to the cubic space groups: $P23$ (No. 195) to $Ia\bar{3}d$ (No. 230). For the rhombohedral structures the listing follows the same hierarchical order:

$\{1,1S_2(z)\}, \dots, \{1,1+n_1S_2(z)\}$ with $n_1 = 1, 2, \dots$

$\{2,2S_2(z)\}, \dots, \{2,2+n_2S_2(z)\}$ with $n_2 = 1, 2, \dots$

$\{N, NS_2(z)\}, \dots, \{N, N+n_N S_2(z)\}$ with $n_N = 1, 2, \dots$,

where S_2 refers to the trigonal space groups: $P3$ (No. 143) to $R\bar{3}/c$ (No. 167). The concluding set of structures pertains to the triclinic system, namely

$\{N, NS_7(z)\}, \dots, \{N, N+n_N S_7(z)\}$ with $n_N = 1, 2, \dots$,

where S_7 refers to the two triclinic space groups: $P1$

(No. 1) and $P\bar{1}$ (No. 2). If one is interested in listing the total number of structure notations for a particular set or subset, one has to be careful to select only those space groups compatible with $n_{E_i} \sum \nu_{E_i}$ and z . For example, for the subset $\{1,1S_1(1)\}$ only the space groups $P23$, $Pm3$, $P432$, $P\bar{4}3m$, and $Pm3m$ are applicable.

The unifying aspect of the proposed classification of crystal structures will not be appreciated until all the known structures have been classified in the format of Table 3. Although the classification separates from each other structures which are topologically

Table 5. Topologically equivalent structures

$3,5Pm3m(1)$		a (\AA)		Phase	T (K)
V_F (\AA^3)	50.65	3.70	—	DyMnO ₃	300
—	—	—	—	—	—
—	64.57	4.0118	—	BaTiO ₃	474
—	64.58	4.012	—	KNiF ₃	300
—	—	—	—	—	—
—	70.04	4.122	—	KFeF ₃	298
—	192.1	5.77	—	CsHgBr ₃	300
$3,5P6_3/mmc(6)$		a (\AA)		Phase	T (K)
V_F (\AA^3)	65.97	5.72	13.97	BaTiO ₃₋₆	300
—	66.70	5.735	14.05	BaTiO ₃	
—	67.53	5.74	14.2	BaTi _{1-x} Ir _x O ₃	$\bar{3},5P6_3/mmc(6,s)$
—	—	—	—	—	
—	83.99	6.213	15.074	CsMnF ₃	—
$3,5P4/nmn(1)$		a (\AA)		Phase	T (K)
V_F (\AA^3)	53.84	3.767	3.794	CeAlO ₃	300
—	—	—	—	—	—
—	64.27	3.9933	4.0303	β -PbTiO ₃	(298)
—	64.37	3.9947	4.0336	BaTiO ₃	293
—	—	—	—	—	—
—	73.42	4.274	4.019	KCrF ₃	—
$3,5Cm2m(2)$		a (\AA)		Phase	T (K)
V_F (\AA^3)	58.75	5.478	5.524	3.883	NaTaO ₃
—	64.26	5.669	5.682	3.990	BaTiO ₃
—	64.71	5.697	5.721	3.971	KNbO ₃

equivalent, but have different symmetries, one benefits from this separation by avoiding an over-emphasis on geometrical considerations of crystal structures and thus allowing for the classification according to lattice symmetries (e.g. magnetic lattices). To locate the various distortions of the cubic BaTiO₃ structure, one merely looks under the $3,5$ or $3,5\mu$ structures for $V_F = 65\mu(2)\text{\AA}^3$ and finds three additional polymorphs (see Table 5). It is very likely that future studies of BaTiO₃ will reveal other tetragonal polymorphs with $z = 4$ or 8 . Then a prediction of the probable lattice constants can be made from the unit cell of a prototype structure. Inasmuch as the published cubic substances constitute the largest class of determined structures, effort is being devoted to complete their systematic compilation first to be followed by the other crystal systems. The ultimate utility of the proposed classification will be realized with the publication of a comprehensive *Structure Directory*.

The author wishes to thank Professors W. H. Baur, J. Lima-de-Faria, F. Liebau and W. B. Pearson for their careful perusal of the original manuscript and for their constructive criticisms which aided significantly in clarifying the text.

References

- International Tables for X-ray Crystallography* (1965). Vol. I, 2nd ed. Birmingham; Kynoch Press.
Landolt-Börnstein (1971). *Numerical Data and Functional Relationships in Science and Technology*. New Series. Vol. 6. *Structure Data of Elements and Intermetallic Phases*. Berlin, New York: Springer-Verlag.

- LIMA-DE-FARIA, J. & FIGUEIREDO, M. O. (1976). *J. Solid State Chem.* **16**, 7–20.
- PEARSON, W. B. (1958). *A Handbook of Lattice Spacings and Structures of Metals and Alloys*. New York: Pergamon Press.
- PEARSON, W. B. (1966). *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, 2nd ed. New York: Pergamon Press.
- Structure Reports (1951–1982). Vols. 8–47. Utrecht: Oosthoek.
- Strukturbericht (1931–1939). Vols. 1–7. Leipzig: Akademische Verlagsgesellschaft. (Photolithoprint reproduction by Edwards Bros., Inc., Ann Arbor, Michigan.)
- TROTTER, J. (1982). Editor. *Structure Reports* Vol. 47A. *Metals and Inorganic Indexes*. Dordrecht/Boston: Reidel.
- WYCKOFF, R. W. G. (1963–1966). *Crystal Structures*, Vols. 1–5, 2nd ed. New York: Interscience.

Acta Cryst. (1985). **B41**, 310–319

The Energetics of Polytypic Structures: Further Applications of the ANNNI Model

BY ROSS J. ANGEL*

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, England

GEOFFREY D. PRICE†

Department of Geology, University College London, Gower Street, London WC1E 6BT, England

AND JULIA YEOMANS

Department of Theoretical Physics, University of Oxford, 1 Keble Road, Oxford OX1 3NP, England

(Received 21 February 1985; accepted 31 May 1985)

Abstract

The stability of long-period polytype stacking sequences can be shown to be dependent upon the energy contribution from interactions between the constituent modules (layers). Previous work has concentrated upon interactions between nearest and next-nearest (*i.e.* first and second) neighbour layers. It is shown that in some polytype systems, such as wollastonite, the equivalence of certain pairs of stacking sequences places constraints upon the allowed interactions between the modules. A mapping between these polytypic systems and a simple spin model, the Axial Next-Nearest-Neighbour Ising (ANNNI) model is developed in order to derive a theoretical phase diagram for these polytypes. The predictions of this phase diagram regarding the relative stability of polytype stacking sequences are shown to compare favourably with observations reported for natural mineral systems.

1. Introduction

Many crystal structures can be grouped into structural families based upon the stacking together of a number of structurally compatible modules. The classical polytypes are one type of such a family. As strictly defined, all modules (layers) are identical in chemical

composition and atomic positions, the various polytype structures differing only in the stacking sequence of the layers. However, Thompson (1981) has pointed out that, due to the stacking sequence itself, the layers in a particular polytype need not be crystallographically equivalent, so that the condition of strict structural and chemical equivalence might be relaxed in a practical definition of polytypism. Thompson therefore proposed that the term 'polytypism' should be used to describe the family of structural variants generated by changes in the stacking sequence of structurally compatible units, provided the overall chemistry remains unchanged. This definition of polytypism allows the internal structure of the modules to undergo small amounts of distortion so as to accommodate small stresses imposed on the module by the neighbouring modules in a stacking sequence.

The theories developed to explain the observed variety of stacking sequences in a given polytypic system may be grouped into two types. The kinetic theories suggest that growth mechanisms play a predominant role in generating polytypes, an early example being the spiral growth mechanism of Frank (1951). Although these may successfully explain the appearance of many polytype stacking sequences, they contribute nothing to our understanding of the relative stability of polytypically related structures, while the characterization of several reversible phase transformations between polytypes of SiC (Jepps & Page, 1983) suggests that polytypism is, at least partially, an equilibrium phenomenon. It was initially

* Current address: Department of Earth and Space Sciences, SUNY at Stony Brook, Stony Brook, New York, 11794, USA.

† To whom correspondence should be addressed.