

Concerning inorganic crystal structure types

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Abstract

All representatives of an inorganic crystal structure type can be found systematically in the new database SICS (Standardized Inorganic Crystal Structures). It is derived from the Inorganic Crystal Structure Database (ICSD) by selecting the best determination of each phase. In addition, each entry is given in a standardized description and complemented by searchable descriptors Δ , which give the difference between all structures of an isopointal set. Because of the large number of structures the full information on relationships present can only be found by means of the new database itself. Some examples are given here in printed form. The limitations and the possibilities of expansion of SICS in terms of the concept of 'structure types' are demonstrated.

1. Introduction

In inorganic crystal chemistry similarity of structures helps us to understand the conditions under which compounds of a certain composition form certain crystal structures. The similarity of crystal structures can be determined at different levels from the general similarity of three-dimensional 'maps' of whole structures or from part of them [e.g. *cyclo*-hexasilicates (*P6/mcc*) and *cyclo*-hexaphosphates (*P2₁/a*)] to the coincidence of symmetry, unit-cell dimensions and atomic positions. For the first of these levels new algorithms have been developed, as described in recent papers (Burzlaff & Malinovsky, 1997; Dzyabchenko, 1994).

For the last level the term 'structure type' has been used since the beginning of structural crystallography (Ewald & Hermann, 1931). In order to clarify the divergent use of this term a subcommittee on the nomenclature of inorganic structure types of the International Union of Crystallography, Commission on Crystallographic Nomenclature, has published some recommendations (Lima-de-Faria *et al.*, 1990). Following this report one has to distinguish between:

- (i) isopointal structures: structures with the same space group and Wyckoff sequence;
- (ii) configurational isotypic structures: isopointal structures with similar coordination of the constituents;
- (iii) crystal-chemically isotypic structures: configurational isotypic structures with similar physical/chemical characteristics of corresponding atoms and bonds.

Besides these generally valid definitions there exist some types of special relationships:

- (i) type \leftrightarrow antitype: important physical/chemical characteristics of the constituent atoms are interchanged;
- (ii) homeotype: similar coordination of the constituents without being isopointal;
- (iii) interstitial type: in derivatives, additional Wyckoff positions of the parent structures are (progressively) occupied;
- (iv) interstitial homeotype: in derivatives, additional Wyckoff positions of the parent structures are (progressively) occupied but derivative and parent structures cannot be traced back to isopointal structures;
- (v) polymorphic compound: a chemical composition existing with different configurations of the constituents;
- (vi) polytype: stacking of layers of (nearly) identical structures (a special case of polymorphic structures) (Guinier *et al.*, 1984).

The concept of isopointal (isopuntal) structures was first suggested by Lima-de-Faria (1968) and then introduced by Pearson (1972); the term *Wyckoff sequence* (*i.e.* Wyckoff letters and number of occupied sites) was first presented by Parthé (1987) and systematically used for the classification of structure types in the *TYPIX* handbook (Parthé *et al.*, 1993/1994) and the *TYPIX* database (*TYPIX*, 1995; Cenxual, 1995). In so far as these definitions give precise rules, they can be transformed to computer programs which allow automatic searching in appropriate databases for compounds which are related in a particular way. If the term 'similar' is used in these definitions, the programs can only work successfully if the similarity is defined by an algorithm.

It is the aim of a continuing project (Bergerhoff *et al.*, 1996) to develop such programs which can be used in conjunction with the ICSD (FIZ-Karlsruhe, 1997). In the following sections the idea underlying these programs is described and the experience gained in developing and using a database of Standardized Inorganic Crystal Structures (SICS) is reported.

2. Revision of the ICSD

For the successful application of such programs the database has to be revised and supplemented in three steps. The result of this is a new database, SICS, which is

connected to the ICSD by references *via* the collection numbers.

(i) In the first step of the revision all entries of the ICSD were standardized following Parthé & Gelato (1984) using their program *STRUCTURE TIDY* (Gelato & Parthé, 1987). The result is a unique choice of the unit cell, the origin and the space-group setting, a unique choice of the representative coordinate triplets and a unique ordering and numbering of the atoms. With this transformation, isopointal structures are, in principle, readily recognized.

(ii) In a second step, for each pair of isopointal structures a Δ value was calculated as a measure of similarity of isoconfigurational structures. Δ is the product of $\Delta(c)$ and $\Delta(d)$, where $\Delta(c)$ is the sum of the weighted mean differences of the atomic coordinates of structure (1) and (2),

$$\Delta(c) = \sum m[(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2} / \sum m, \quad (1)$$

(m is the multiplicity of the Wyckoff site) and $\Delta(d)$ is the relation between the axial ratios of structures (1) and (2),

$$\Delta(d) = [(b_1/a_1)(c_1/a_1)] / [(b_2/a_2)(c_2/a_2)], \quad (2)$$

where the numerator is greater than the denominator.

Multiplication of $\Delta(c)$ and $\Delta(d)$ (3) results in a combined indicator Δ which is zero in the case of complete coincidence. Experience leads to weighting $\Delta(c)$ with $2^{1/2}$,

$$\Delta = [2^{1/2}\Delta(c) + 1]\Delta(d) - 1. \quad (3)$$

For monoclinic and triclinic structures angles are neglected because experience shows that for non-similar structures Δ is high in any case.

Nevertheless, this procedure will not always lead to low Δ values between similar structures. In borderline cases (Parthé & Gelato, 1984, p. 175) the strong criteria for selecting and ordering parameters in the program *STRUCTURE TIDY* may lead to very different parameters of two standardized structures which are expected to be similar. Therefore, for each pair of isopointal structures, alternative sets of equivalent positions x, y, z , cell choices and settings were selected in such a way that Δ becomes a minimum.

Collecting all Δ for pairs of isopointal structures leads to a matrix, called the Δ matrix, of the set of isopointal structures characterized by the space group and the Wyckoff sequence. Fig. 1 shows such a matrix for the isopointal set (148) $R\bar{3} - f^3ba$.

(iii) Finally, in a third step, the contents of the ICSD were reduced to one representative of each phase only in SICS. This was carefully done by selecting the

	A1	A2	A3	A4	B1	B2	B3	B4	B5	B6	C1	D1	D2	D3	D4	E1	F1	F2	F3	F4	F5	G1	Sum
A1	—	0,02	0,02	0,02	0,17	0,17	0,19	0,17	0,16	0,16	0,22	0,31	0,31	0,34	0,36	0,36	0,63	0,63	0,64	0,65	0,65	1,18	7,34
A2	0,02	—	0,01	0,02	0,18	0,18	0,20	0,20	0,19	0,18	0,20	0,31	0,33	0,34	0,35	0,35	0,61	0,61	0,62	0,63	0,64	1,20	7,34
A3	0,02	0,01	—	0,02	0,18	0,18	0,19	0,18	0,17	0,17	0,20	0,32	0,33	0,35	0,37	0,35	0,61	0,62	0,63	0,63	0,64	1,20	7,34
A4	0,02	0,02	0,02	—	0,17	0,17	0,18	0,18	0,18	0,17	0,20	0,31	0,32	0,33	0,35	0,36	0,62	0,63	0,64	0,64	0,65	1,19	7,34
B1	0,17	0,18	0,18	0,17	—	0,03	0,02	0,02	0,02	0,01	0,24	0,25	0,27	0,28	0,29	0,45	0,75	0,78	0,73	0,74	0,75	1,02	7,34
B2	0,17	0,18	0,18	0,17	0,03	—	0,04	0,04	0,04	0,04	0,22	0,23	0,25	0,26	0,27	0,47	0,71	0,72	0,74	0,73	0,74	0,99	7,19
B3	0,19	0,20	0,19	0,18	0,02	0,04	—	0,00	0,01	0,02	0,26	0,26	0,28	0,28	0,30	0,46	0,77	0,79	0,73	0,75	0,76	1,00	7,47
B4	0,17	0,20	0,18	0,18	0,02	0,04	0,00	—	0,01	0,02	0,28	0,26	0,28	0,28	0,30	0,45	0,79	0,79	0,77	0,74	0,82	1,00	7,57
B5	0,16	0,19	0,17	0,18	0,02	0,04	0,01	0,01	—	0,01	0,25	0,26	0,28	0,29	0,30	0,45	0,78	0,79	0,76	0,81	0,82	1,01	7,57
B6	0,16	0,18	0,17	0,17	0,01	0,04	0,02	0,02	0,01	—	0,24	0,26	0,31	0,32	0,30	0,45	0,77	0,78	0,75	0,80	0,81	1,02	7,57
C1	0,22	0,20	0,20	0,20	0,24	0,22	0,26	0,28	0,25	0,24	—	0,31	0,33	0,34	0,35	0,29	0,50	0,51	0,52	0,53	0,53	1,33	7,84
D1	0,31	0,31	0,32	0,31	0,25	0,23	0,26	0,26	0,26	0,26	0,31	—	0,04	0,04	0,05	0,58	0,83	0,84	0,84	0,87	0,88	0,88	8,91
D2	0,31	0,33	0,33	0,32	0,27	0,25	0,28	0,28	0,28	0,31	0,33	0,04	—	0,01	0,02	0,60	0,87	0,88	0,88	0,89	0,91	0,77	9,14
D3	0,34	0,34	0,35	0,33	0,28	0,26	0,28	0,28	0,28	0,32	0,34	0,04	0,01	—	0,02	0,60	0,88	0,89	0,89	0,91	0,92	0,78	9,37
D4	0,36	0,35	0,37	0,35	0,29	0,27	0,30	0,30	0,30	0,30	0,35	0,05	0,02	0,02	—	0,62	0,90	0,91	0,92	0,93	0,94	0,76	9,61
E1	0,36	0,35	0,35	0,36	0,45	0,47	0,46	0,45	0,45	0,45	0,29	0,58	0,60	0,60	0,62	—	0,30	0,31	0,36	0,32	0,33	1,75	10,27
F1	0,63	0,61	0,61	0,62	0,75	0,71	0,77	0,79	0,78	0,77	0,50	0,83	0,87	0,88	0,90	0,30	—	0,02	0,06	0,02	0,02	2,11	13,51
F2	0,63	0,61	0,62	0,63	0,78	0,72	0,79	0,79	0,79	0,78	0,51	0,84	0,88	0,89	0,91	0,31	0,02	—	0,06	0,02	0,03	2,17	13,71
F3	0,64	0,62	0,63	0,64	0,73	0,74	0,73	0,77	0,76	0,75	0,52	0,84	0,88	0,89	0,92	0,36	0,06	0,06	—	0,08	0,08	2,12	13,81
F4	0,65	0,63	0,63	0,64	0,74	0,73	0,75	0,74	0,81	0,80	0,53	0,87	0,89	0,91	0,93	0,32	0,02	0,02	0,08	—	0,01	2,19	13,81
F5	0,65	0,64	0,64	0,65	0,75	0,74	0,76	0,82	0,82	0,81	0,53	0,88	0,91	0,92	0,94	0,33	0,02	0,03	0,08	0,01	—	2,20	14,11
G1	1,18	1,20	1,20	1,19	1,02	0,99	1,00	1,00	1,01	1,02	1,33	0,88	0,77	0,78	0,76	1,75	2,11	2,17	2,12	2,19	2,20	—	27,81
Sum	7,34	7,36	7,36	7,36	7,34	7,19	7,47	7,57	7,57	7,59	7,84	8,91	9,14	9,33	9,61	10,22	13,54	13,76	13,81	13,87	14,12	27,87	226,11

Formula	COL	Formula	COL	Formula	COL
A1 (Co (NH3)5 (H2O)) (Cr(CN)6)	47195	B5 (Zn (H2O)6) (SiF6)	34757	E1 Ge2 (H2 P O2)6	37318
A2 (Co (NH3)6) (Cr(CN)6)	806	B6 (Ni (H2O)6) (SiF6)	34758	F1 (Ca.65 Pr.35) (Pr6 Co) I12	63305
A3 (Cr (NH3)6) (Cr(CN)6)	61679	C1 Ce7 O12	4113	F2 Sc (Sc6 Co) I12	63303
A4 (Co (NH3)6) (Co(CN)6)	2560	D1 Ho3 Sc O6	23480	F3 Y (Y6 Fe) I12	63304
B1 (Ni (H2O)6) (GeF6)	63450	D2 Mn3 W O6	74952	F4 Sc (Sc6 B) Cl12	201975
B2 ((Cu.96 Zn.04) (H2O)6) (SiF6)	20631	D3 Ca3 U O6	35457	F5 Sc (Sc6 N) Cl12	201976
B3 (Co (D2O)6) (SiF6)	65778	D4 Mg3 Te O6	9089	G1 Cs (Er6 C) I12	300268
B4 (Co (H2O)6) (SiF6)	34759				

Fig. 1. Δ matrix of the isopointal set (148) $R\bar{3} - f^3ba$ (submatrices A, B, D and F are given in bold; COL = collection number in the ICSD and SICS; Sum = sum of matrix elements in rows and lines).

Table 1. *Examples of solid solutions, polymorphs and polytypes*

COL is the collection number in the ICSD and SICS; SGR-WS is the space group and Wyckoff sequence; Year is the year of publication; + before COL indicates additional entries in the ICSD.

COL	Formula	SGR-WS	Year
+62524	Mg ₂ (SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1987
100428	(Mg _{1.867} Fe _{0.133})(SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1979
+66181	(Mg _{1.8} Fe _{0.2})(SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1989
+66183	(Mg _{1.74} Fe _{0.26})(SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1989
66195	(Mg _{1.63} Fe _{0.37})(SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1989
39795	(Mg _{1.48} Fe _{0.52})(SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1993
66186	(Mg _{1.39} Fe _{0.61})(SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1989
9336	(Mg _{1.274} Fe _{0.716})(SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1973
69462	(Mg _{1.147} Fe _{0.853})(SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1990
+34815	(MgFe)(SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1968
+66192	(Mg _{0.26} Fe _{0.74})(SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1989
26375	Fe ₂ (SiO ₄)	(62) <i>Pnma</i> - <i>dc</i> ⁴ <i>a</i>	1981
+26153	ZnCl ₂	(14) <i>P2</i> ₁ / <i>c</i> - <i>e</i> ⁹	1961
+2459	ZnCl ₂	(33) <i>Pna2</i> ₁ - <i>a</i> ³	1978
+26154	ZnCl ₂	(122) <i>I42d</i> - <i>da</i>	1961
26152	ZnCl ₂	(137) <i>P4</i> ₂ / <i>nmc</i> - <i>db</i>	1961
24168	SiC	(160) <i>R3m</i> - <i>a</i> ¹⁰	1944
18136	SiC	(160) <i>R3m</i> - <i>a</i> ¹⁶	1965
24631	SiC	(160) <i>R3m</i> - <i>a</i> ¹⁸	1952
24632	SiC	(160) <i>R3m</i> - <i>a</i> ³⁴	1952
23887	SiC	(160) <i>R3m</i> - <i>a</i> ³⁸	1962
24633	SiC	(160) <i>R3m</i> - <i>a</i> ⁵⁰	1952
24634	SiC	(160) <i>R3m</i> - <i>a</i> ⁵⁶	1952
+24261	SiC	(186) <i>P6</i> ₃ <i>mc</i> - <i>b</i> ² <i>a</i> ²	1959
+15325	SiC	(186) <i>P6</i> ₃ <i>mc</i> - <i>b</i> ⁴ <i>a</i> ²	1967
24630	SiC	(186) <i>P6</i> ₃ <i>mc</i> - <i>b</i> ⁶ <i>a</i> ²	1952

determination of a structure which is the best in our opinion. It is usually the latest one, preferably with a low *R* value, measured at room temperature and normal pressure and determined by neutron diffraction if relevant. Before selecting the best determination, errors in the database which are known (including changes of space groups, *e.g.* Baur & Kassner, 1992; Parthé *et al.*, 1993) or detected during the process of comparison in step (ii) will be corrected as far as possible in the course of the project. Because of the subjectivity in selecting the best entry there is a cross-reference from the SICS entry to all corresponding entries in the ICSD. For further discussion, relevant entries also contain the entry number in *TYPIX* (Parthé *et al.*, 1993/1994; Parthé, 1996). In addition it is intended to add a structural formula describing the structural features of the phase in question (Lima-de-Faria *et al.*, 1990; Lima-de-Faria, 1994).

SICS is a reference tool which gives direct access to the most reliable and complete determination of a given phase, defined by the precise chemical composition, space group and Wyckoff sequence. It should be noted that in nonstoichiometric compounds each different chemical composition is treated as a special phase, as are certain chemical compositions described in different space groups or different Wyckoff sequences (Table 1).

SICS, the revised version of the ICSD, is now also a better basis for statistical investigations of interatomic distances (Bergerhoff & Brandenburg, 1999) or relationships between chemistry and symmetry because (i) multiple determinations are eliminated and (ii) many errors are corrected. Thus, statistics for the distribution of inorganic structures over the 230 space groups are more reliable than before. However, it should be noted that research follows certain fashions, *e.g.* the isopointal structures (123) *P4/mmm* - *ihg*²*fda* and (47) *Pmmm* - *tsrq*²*heba* are both very common in SICS because they are adopted by the high-temperature superconductors YBa₂Cu₃O_{6+x}.

SICS in its 1996/1 release contains 27 388 structures compared with the 41 477 entries in the corresponding release of the ICSD. In addition to the contents of the corresponding ICSD entry, a SICS entry stores all Δ values between it and all the other isopointal structures. One command leads to the Δ matrices which form the basis for the following discussion on the term 'structure type'.

The discussion will be presented from different points of view and illustrated by examples. However, it is impossible to show all existing relations in printed form. The database technique is the only way to access particular results given in the tremendous number of data accumulated by the scientific community.

3. Discussion of Δ matrices

Δ matrices of sets of isopointal structures can be displayed, supplemented by the chemical formulae of the entries and organized in such a way that sets of isoconfigurational structures are recognized (see §6).

There are three types of Δ matrix, although there can be transitions between the types. The possibility of differentiating between the types often depends on the number of members known in the isopointal set.

(i) Δ matrices with homogeneously low Δ values. All members of the set of isopointal structures form a structure type.

(ii) Δ matrices where lines and rows can be interchanged in such a way that ranges with homogeneously low Δ values allow splitting into submatrices. In principle, each submatrix forms its own structure type.

(iii) Δ matrices in which such submatrices overlap, indicating an increasingly distorted structure type.

It is obvious that the first type of Δ matrix is found among structures having no adjustable positional parameters and when $\Delta(d)$ is not far from one. As a result of the standardized description, such structure types are well defined by just the space group and Wyckoff sequence. However, there are several other sets of isopointal structures forming a homogeneous matrix of low Δ values in spite of having adjustable positional parameters. Typical examples of both kinds in SICS 1996/1 are listed in Table 2.

Table 2. Examples of sets of isopointal structures with homogeneously low Δ matrices

SGR-WS is the space group and Wyckoff sequence; APP is the number of adjustable positional parameters; ISO is the number of isopointal structures; Δ is the maximal Δ in the set.

Representative	SGR-WS	APP	ISO	Δ
Fluorite	(225) $Fm\bar{3}m - ca$	0	296	0
Rock salt	(225) $Fm\bar{3}m - ba$	0	350	0
Ideal perovskite	(221) $Pm\bar{3}m - dba$	0	187	0
Caesium chloride	(221) $Pm\bar{3}m - ba$	0	21	0
Sphalerite	(216) $F43m - ca$	0	53	0
Spinel	(227) $Fd\bar{3}m - ecb$	1	412	0.04
Wurtzite	(186) $P6_3mc - b^2$	1	28	0.03
Garnet	(230) $Ia\bar{3}d - hdca$	3	150	0.04
Hg ₃ S ₂ Cl ₂	(199) $I2_13 - ba^2$	3	6	0.05
Hexagonal perovskite	(194) $P6_3/mmc - khf^2ba$	4	41	0.06
Langbeinite	(198) $P2_13 - b^5a^4$	19	17	0.04

An example of the second type of Δ matrix is the set (148) $R\bar{3} - f^3ba$. Fig. 1 shows the complete Δ matrix. Submatrices are denoted A, B, C, D, E, F and G. Obtaining such submatrices with low Δ values by appropriate interchange of lines and rows is described in §6. Although there are octahedrally coordinated centres throughout like Co and Cr in submatrix A or Ni and Ge

Table 3. Examples of structure types and their antitypes

SGR-WS is the space group and Wyckoff sequence.

SGR-WS	Type	Antitype	Δ
(225) $Fm\bar{3}m - ecba$	K ₃ MoF ₆	Li ₆ NBr ₃	0.06
(225) $Fm\bar{3}m - eca$	Co(NH ₃) ₆ I ₂	(NH ₄) ₂ PtI ₆	0.01
(206) $Ia\bar{3} - eda$	Mn ₂ O ₃	Ca ₃ N ₂	0.02
(199) $I2_13 - ba^2$	Hg ₃ Te ₂ Br ₂	K ₂ Pb ₂ O ₃	0.02
(185) $P6_3cm - c^3ba$	Cu ₃ P	LaF ₃	0.02
(166) $R\bar{3}m - c^2a$	Th ₃ N ₄	Al ₄ C ₃	0.09
(166) $R\bar{3}m - c^3a$	In(CuAl)O ₄	Al ₄ C ₃	0.02
(166) $R\bar{3}m - cba$	NaCoO ₂	Ca ₂ NCl	0.01
(139) $I4/mmm - ge^3ba$	Sr ₃ V ₂ O ₇	Li ₇ O ₂ Br ₃	0.02
(139) $I4/mmm - e^2ca$	P ₂ OSr ₄	K ₂ NiF ₄	0.04
(139) $I4/mmm - e^2ca$	I ₂ ONa ₄	K ₂ NiF ₄	0.06
(128) $P4/mnc - hgea$	Tl ₄ CrI ₆	Tl ₂ SCL ₄	0.06
(62) $Pnma - dc^5$	RbBa(PO ₄)	[Zn(NH ₃) ₄]I ₂	0.06
(14) $P2_1/c - e^2a$	K ₂ Cd ₂ O ₃	Cd ₃ O ₂ Cl ₂	0.04

in submatrix B, Δ values reveal differences which are reflected by the chemical formulae. Compounds in submatrix F and the only compound in submatrix G, Cs(Er₆C)I₁₂, have the same formula type and octahedral cluster. However, the packing is different and leads to a different structure type for Cs(Er₆C)I₁₂ in the sense defined above. The fairly high Δ values between F3 and

	AA1	AA2	AA3	AA4	AA5	AA6	AA7	AA8	AA9	AB1	AB2	AB3	AB4	AB5	AB6	AB7	AC1	AC2	AC3	AD1	AD2	AE1	AE2	B1	C1	Sum
AA1	0,00	0,01	0,02	0,01	0,03	0,02	0,03	0,06	0,02	0,02	0,03	0,01	0,04	0,04	0,04	0,06	0,06	0,09	0,09	0,12	0,17	0,22	0,28	0,27	1,74	
AA2	0,00	0,01	0,02	0,01	0,03	0,02	0,03	0,07	0,02	0,02	0,03	0,01	0,04	0,04	0,04	0,06	0,06	0,09	0,10	0,12	0,17	0,23	0,28	0,27	1,77	
AA3	0,01	0,01	0,04	0,02	0,05	0,02	0,02	0,07	0,03	0,02	0,03	0,02	0,03	0,05	0,05	0,05	0,06	0,09	0,09	0,12	0,17	0,24	0,28	0,26	1,82	
AA4	0,02	0,02	0,04	0,02	0,02	0,03	0,05	0,05	0,02	0,03	0,04	0,02	0,04	0,04	0,05	0,06	0,07	0,10	0,10	0,13	0,16	0,21	0,26	0,28	1,85	
AA5	0,01	0,01	0,02	0,02	0,03	0,02	0,03	0,06	0,03	0,03	0,04	0,02	0,05	0,04	0,05	0,07	0,07	0,10	0,10	0,13	0,17	0,23	0,28	0,27	1,87	
AA6	0,03	0,03	0,05	0,02	0,03	0,04	0,06	0,06	0,03	0,03	0,04	0,03	0,05	0,04	0,04	0,07	0,07	0,10	0,10	0,13	0,15	0,20	0,27	0,29	1,96	
AA7	0,02	0,02	0,02	0,03	0,02	0,04	0,03	0,06	0,03	0,03	0,04	0,03	0,05	0,06	0,06	0,07	0,07	0,11	0,11	0,13	0,18	0,24	0,28	0,26	1,96	
AA8	0,03	0,03	0,02	0,05	0,03	0,06	0,03	0,08	0,04	0,04	0,04	0,04	0,05	0,06	0,07	0,07	0,08	0,11	0,11	0,14	0,19	0,25	0,30	0,24	2,14	
AA9	0,06	0,07	0,07	0,05	0,06	0,06	0,06	0,08	0,05	0,06	0,05	0,06	0,07	0,04	0,04	0,05	0,05	0,09	0,09	0,12	0,14	0,20	0,23	0,30	2,14	
AB1	0,02	0,02	0,03	0,02	0,03	0,03	0,03	0,04	0,05	0,01	0,01	0,01	0,02	0,02	0,03	0,04	0,04	0,08	0,08	0,10	0,14	0,20	0,26	0,29	1,60	
AB2	0,02	0,02	0,02	0,03	0,03	0,03	0,04	0,06	0,01	0,01	0,01	0,01	0,02	0,03	0,03	0,04	0,04	0,07	0,07	0,10	0,15	0,22	0,27	0,28	1,64	
AB3	0,03	0,03	0,03	0,04	0,04	0,04	0,04	0,05	0,01	0,01	0,02	0,01	0,02	0,03	0,03	0,03	0,03	0,06	0,07	0,09	0,14	0,21	0,26	0,29	1,64	
AB4	0,01	0,01	0,02	0,02	0,02	0,03	0,03	0,04	0,06	0,01	0,01	0,02	0,03	0,03	0,03	0,05	0,05	0,08	0,08	0,11	0,16	0,21	0,27	0,28	1,64	
AB5	0,04	0,04	0,03	0,04	0,05	0,05	0,05	0,07	0,02	0,02	0,01	0,03	0,04	0,04	0,03	0,04	0,06	0,08	0,08	0,09	0,16	0,22	0,27	0,29	1,79	
AB6	0,04	0,04	0,05	0,04	0,04	0,06	0,06	0,04	0,02	0,03	0,02	0,03	0,04	0,01	0,03	0,03	0,06	0,06	0,06	0,09	0,12	0,19	0,24	0,31	1,68	
AB7	0,04	0,04	0,05	0,05	0,05	0,04	0,06	0,07	0,04	0,03	0,03	0,03	0,03	0,04	0,01	0,03	0,03	0,06	0,06	0,09	0,12	0,19	0,24	0,31	1,73	
AC1	0,06	0,06	0,05	0,06	0,07	0,07	0,07	0,07	0,05	0,04	0,04	0,03	0,05	0,03	0,03	0,03	0,03	0,01	0,04	0,04	0,06	0,12	0,19	0,23	0,32	1,81
AC2	0,06	0,06	0,06	0,07	0,07	0,07	0,08	0,05	0,04	0,04	0,03	0,05	0,04	0,03	0,03	0,03	0,01	0,03	0,04	0,06	0,12	0,18	0,23	0,33	1,82	
AC3	0,09	0,09	0,09	0,10	0,10	0,10	0,11	0,11	0,09	0,08	0,07	0,06	0,08	0,06	0,06	0,06	0,04	0,03	0,02	0,03	0,10	0,16	0,21	0,36	2,32	
AD1	0,09	0,09	0,09	0,10	0,10	0,10	0,11	0,11	0,09	0,08	0,07	0,07	0,08	0,08	0,06	0,06	0,04	0,04	0,02	0,03	0,03	0,08	0,14	0,19	0,37	2,31
AD2	0,12	0,12	0,12	0,13	0,13	0,13	0,14	0,14	0,12	0,10	0,10	0,09	0,11	0,09	0,09	0,09	0,06	0,06	0,03	0,03	0,07	0,12	0,17	0,40	2,75	
AE1	0,17	0,17	0,17	0,16	0,17	0,15	0,18	0,19	0,14	0,14	0,15	0,14	0,16	0,16	0,12	0,12	0,12	0,12	0,10	0,08	0,07	0,06	0,18	0,44	3,67	
AE2	0,22	0,23	0,24	0,21	0,23	0,20	0,24	0,25	0,20	0,20	0,22	0,21	0,21	0,22	0,19	0,19	0,19	0,18	0,16	0,14	0,12	0,06	0,14	0,51	4,96	
B1	0,28	0,28	0,28	0,26	0,28	0,27	0,28	0,30	0,23	0,26	0,27	0,26	0,27	0,27	0,24	0,24	0,23	0,23	0,21	0,19	0,17	0,18	0,14	0,57	6,17	
C1	0,27	0,27	0,26	0,28	0,27	0,29	0,26	0,24	0,30	0,29	0,28	0,29	0,28	0,29	0,31	0,31	0,32	0,33	0,36	0,38	0,40	0,44	0,51	0,57	7,82	
Sum	1,74	1,77	1,82	1,85	1,87	1,96	1,96	2,14	2,14	1,60	1,64	1,64	1,65	1,79	1,68	1,73	1,81	1,82	2,32	2,31	2,75	3,67	4,96	6,17	7,82	

	Formula	COL	Formula	COL	Formula	COL		
AA1	MgTiO ₃	65794	AB1	MgGeO ₃	200415	AC2	MgSiO ₃	31176
AA2	CoTiO ₃	48107	AB2	MnTiO ₃	60006	AC3	CdGeO ₃	30971
AA3	MnFe ₅ Sb ₅ O ₃	24431	AB3	ZnGeO ₃	33722	AD1	LiAsO ₃	202862
AA4	NiMnO ₃	31853	AB4	FeTiO ₃	67046	AD2	NaSbO ₃	78011
AA5	NiTiO ₃	33854	AB5	CaSnO ₃	29204	AE1	CrSiTe ₃	71020
AA6	CoMnO ₃	31854	AB6	NaMnCl ₃	2552	AE2	(Cu ₅ Al ₅)PSe ₃	67892
AA7	ZnTiO ₃	22382	AB7	CuVO ₃	19046	B1	KSbO ₃	33546
AA8	MnSnO ₃	29203	AC1	MnGeO ₃	69591	C1	NH ₄ SnF ₃	1452
AA9								

other members of the submatrix F may indicate errors. Indeed, $z(Y)$ in $18f$ is wrong and will be corrected. Ce_7O_{12} (C) and $Ge_2(H_2PO_2)_6$ (E) are the only representatives of their structure types in the isopointal set (148) $R\bar{3} - f^3ba$.

For the third type of Δ matrix, the isopointal set (148) $R\bar{3} - fc^2$ is a typical example and is common for all structures of the formula type ABX_3 . There are two larger (AA1–AC2, AB1–AD1) and three smaller submatrices (AC1–AD2, AD1–AE1, AE1–AE2) which overlap (Fig. 2). Compared with Fig. 1, there is a smooth transition between these submatrices. Therefore the boundary between the structure types is open to discussion. In all structures the elements A and B are both six-coordinated by two groups of three equivalent distances $A-X$ or $B-X$. Up to AD2, the mean difference between these two groups of distances is only 8%, indicating a fairly regular octahedron which is characteristic for the ilmenite type ($FeTiO_3$). However, in $CrSiTe_3$ (AE1), $(Cu_{0.5}Al_{0.5})PSe_3$ (AE2), $KSbO_3$ (B1) and NH_4SnF_3 (C1) there are differences of 50, 65, 20, and 38%. Moreover, in $CrSiTe_3$ (AE1) the distance Si–Si is smaller than the distances Si–Te and in $(Cu_{0.5}Al_{0.5})PSe_3$ (AE2) the distance P–P is in between the two groups of P–Se distances. Therefore, these structures certainly form different structure types.

The examples show that the Δ values are only a first guide to the recognition of structure types. The number of structures belonging to a structure type depend on the Δ range selected and on the member selected to be the representative of the type. The limits on Δ for discussion of potential isoconfiguration depend on the situation. Comparing atomic distances or drawing the structures in question side by side in two windows and adjusted to equal dimensions, easily done using *DIAMOND* (Brandenburg, 1996), will often help to decide whether they are isoconfigurational (see Fig. 3). Sometimes increasing Δ values may be correlated with the distortion of the coordination of the constituent atoms by

calculating characteristic numbers for the distortion of the coordination polyhedra following, e.g., Balic Zunic & Makovicky (1996). Bear in mind that the origin of large Δ values can also be errors in the database. Comparing two structures in detail can often help to pinpoint the error (see §6).

4. Special structural relationships

In many isopointal sets and all types of Δ matrix we find examples of the type \leftrightarrow antitype relation as shown in Table 3. Such antitypes often reveal that coordination polyhedra around anionic nonmetals and their connections may be a characteristic feature of some structures (e.g. $TeHg_3$ pyramids in $Hg_3Te_2Br_3$ are connected to form three-dimensional networks like the PbO_3 pyramids in $K_2Pb_2O_3$) (Bergerhoff, 1964; Bergerhoff & Paeslack, 1968; Krivovichev *et al.*, 1997, 1998).

In some structure types vacant positions can be filled by additional atoms forming a new structure type. However, the Wyckoff positions of the first (parent type) form a subset of the Wyckoff positions of the second (interstitial type). The Δ matrices for such pairs are not calculated regularly because they are too numerous. Nevertheless, they can be calculated by the program *SIMILAR*, the retrieval program for SICS. Some examples are given in Table 4.

Some structures are characterized by a certain framework as their only essential structural element. Additional constituents may occupy different voids in different amounts. In the Wyckoff sequences of these non-isopointal structures one may find a common set of Wyckoff letters. Such sets describe what can be called a 'framework type'. Additional Wyckoff letters then give the places of interstitial atoms or molecules. Pyrochlores and zeolites form typical examples; one is discussed in §5.

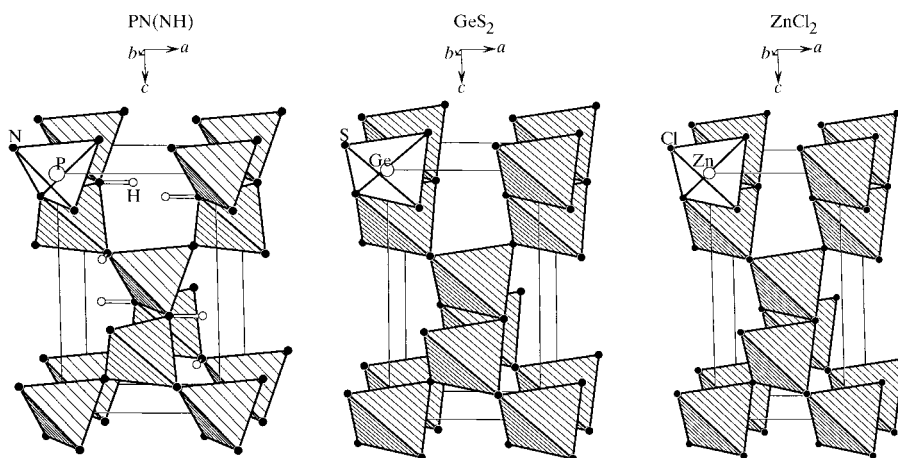


Fig. 3. Structures of $PN(NH)$, GeS_2 and $ZnCl_2$, three structures of the isopointal set (122) $I\bar{4}2d - da$.

Table 4. Examples of pairs of parent and interstitial types

WS is the Wyckoff sequence; voids of parent types are indicated by _ in WS; additional atoms in interstitial types are outside the square brackets.

Space group	WS	Parent type	WS	Interstitial type	Δ
(227) $Fd\bar{3}m$	e_cb	Fe(FeNi)O ₄	$edcb$	Ni _{0.1} [Fe _{0.9} (FeNi)O ₄]	0.01
(225) $Fm\bar{3}m$	ec_a	Rb ₂ TeBr ₆	$ecba$	Ni[Sr ₂ WO ₆]	0.001
(225) $Fm\bar{3}m$	e_ba	NaSbF ₆	$ecba$	Sr ₂ [NiWO ₆]	0.035
(216) $F4\bar{3}m$	ec_a	ZnSO ₄	$ecba$	Cs[LiMoO ₄]	0.002
(216) $F4\bar{3}m$	e_ba	BaSO ₄	$ecba$	Li[CsMoO ₄]	0.01
(194) $P6_3/mmc$	$_ca$	VS	dca	[TmCu]Si	0.001
(166) $R\bar{3}m$	c_a	MnBr ₂	cba	Na[LuS ₂]	0.04
(129) $P4/nmm$	$dc^2_$	WO ₃	dc^2a	Na _{0.1} [WO ₃]	0.008
(87) $I4/m$	hed_a	Rb ₂ TeBr ₆	$hedba$	Ni[Sr ₂ WO ₆]	0.02

Table 5. Δ values between FeCuS₂ (chalcopyrite) and the other members of the isopointal set (122) $\bar{I}4\bar{2}d - dba$

The headings are explained in the related text; + before COL indicates additional entries in the ICSD.

Δ	COL	A(4a)B(4b)X ₂ (8d)	c/a	$x(8d)$	ψ	CN(X/X)
—	2518	FeCuS ₂	1.97	0.2426	44.1	6+4+2=12
0.005	+68324	GeZnAs ₂	1.96	0.24533	44.4	4+2+4+2=12
0.005	+23706	GeZnP ₂	1.96	0.24184	44.0	4+2+4+2=12
0.006	+74456	GaCuTe ₂	1.98	0.2434	45.0	8+4=12
0.007	28735	CuAlTe ₂	1.98	0.250	45.0	8+4=12
0.010	28752	AgInTe ₂	1.96	0.250	45.0	8+4=12
0.010	28737	CuGaSe	1.96	0.250	45.0	8+4=12
0.010	+22182	SnCdAs ₂	1.96	0.238	43.6	2+4+4+2=12
0.012	28736	CuGaS ₂	1.96	0.250	45.0	8+4=12
0.013	+62626	LiInTe ₂	1.95	0.2441	44.3	4+2+4+2=12
0.013	28733	AlCuS ₂	1.96	0.23	42.6	2+4+4+2=12
0.014	74457	(Ga _{0.8} In _{0.2})CuTe ₂	1.99	0.265	46.7	2+4+4+2=12
0.015	28734	AlCuSe ₂	1.94	0.24	43.8	4+2+4+2=12
0.015	22183	SnCdP ₂	1.95	0.235	43.2	2+4+4+2=12
0.017	+22179	ZnSnP ₂	2	0.239	43.7	2+4+4+2=12
0.020	28743	CuTlSe ₂	1.99	0.23	42.6	2+4+4+2=12
0.022	+68323	SiZnAs ₂	1.94	0.23444	43.2	6+4+2=12
0.023	+68325	SnZnAs ₂	2	0.23235	42.9	2+4+4+2=12
0.025	74458	(Ga _{0.5} In _{0.5})CuTe ₂	2	0.2721	47.4	2+4+4+2=12
0.027	74459	(Ga _{0.2} In _{0.8})CuTe ₂	2	0.2745	47.7	2+4+4+2=12
0.028	+23680	SiZnP ₂	1.93	0.2309	42.7	2+4+4+2=12
0.029	63197	Cu _{0.938} InSe ₂	2.01	0.2281	42.4	2+4+4+2=12
0.030	63196	Cu _{0.923} InSe ₂	2.01	0.2268	42.2	2+4+4+2=12
0.031	28750	AgInS ₂	1.92	0.250	45.0	8+4=12
0.032	+73352	CuInTe ₂	2	0.222	41.6	2+4+4=10
0.032	63198	Cu _{0.944} InSe ₂	2.01	0.2231	41.7	2+4+4=10
0.033	63199	Cu _{0.945} InSe ₂	2.01	0.2226	41.7	2+4+4=10
0.033	63227	Cu _{0.947} InSe ₂	2.01	0.2227	41.7	2+4+4=10
0.033	28751	AgInSe ₂	1.92	0.250	45.0	8+4=12
0.033	+73351	CuInSe ₂	2.01	0.226	42.2	2+4+4+2=12
0.041	+71007	GaAgTe ₂	1.9	0.2403	43.9	4+2+4+2=12
0.047	28739	CuInS ₂	2	0.20	38.7	2+4=6
0.050	28746	AlAgTe ₂	1.88	0.24	43.8	4+2+4+2=12
0.053	28742	CuTlS ₂	2	0.19	37.2	2+4=6
0.061	+22185	GeCdAs ₂	1.89	0.22	41.3	2+4+4=10
0.070	+100467	GeCdP ₂	1.88	0.2161	40.8	2+4+4=10
0.091	28748	GaAgSe ₂	1.82	0.23	42.6	4+2+4=10
0.096	22187	SiCdAs ₂	1.85	0.202	38.9	2+4+4=10
0.101	28745	AlAgSe ₂	1.8	0.23	42.6	4+2+4=10
0.103	+23696	SiCdP ₂	1.84	0.2032	39.1	2+4=6
0.126	28744	AlAgS ₂	1.8	0.20	38.6	4+2=6
0.127	+23698	GaAgS ₂	1.79	0.20917	39.9	4+2=6
0.141	22189	SiMgP ₂	1.77	0.208	39.8	4+2=6
0.331	+66007	PLiN ₂	1.56	0.1699	34.2	4+2=6
0.346	34256	BLiO ₂	1.55	0.1574	32.2	4+2=6
0.471	23524	GeCa _{0.55} N ₂	1.41	0.164	33.3	4+2=6
0.666	4199	CoKO ₂	1.28	0.13	27.5	4+2=6

5. Discussion of space groups, Wyckoff sequences and number of members in isopointal sets

There are three interesting aspects of the systematic discussion of space groups and Wyckoff sequences:

- (i) relations between symmetry, chemical elements and their stoichiometry;
- (ii) structure types and their boundaries;
- (iii) error detection.

In *e.g.* space group (122) $I\bar{4}2d$ 29 different isopointal sets exist with the following numbers of members: *dba* 47 members; *eba* 15 members; e^3d^2cba , *da*: four members each; *eda* three members; e^9dc , e^7d^3a , e^6 , e^5d^2ba , e^3d^4a , e^2d^2 , e^2dc : two members each; e^5d^6 , ed^2ba , e^3d^3a , *eca*, $e^5d^2c^2ba$, e^6dc^2 , e^2d , e^6dc^7a , e^2d^2a , e^6d^2cba , e^3a , e^6d^4a , e^3d^3a , e^7 , e^4c , e^7b , e^4d^3a : one member each. Some Wyckoff sequences and thus symmetry elements are used frequently (*e.g.* *eba*), some others not at all (*e.g.* *dca*). This reflects the different distribution of chemical elements on certain Wyckoff sites and their combination in certain isopointal sets owing to crystallographic constraints (Brown, 1997). Some of the isopointal sets of space group (122) $I\bar{4}2d$ may be discussed in detail.

The most populated isopointal set (122) $I\bar{4}2d$ - *dba* has 47 members (Table 5). All structures belong to the formula type ABX_2 . They form a three-dimensional network consisting of slightly distorted AX_4 and BX_4 tetrahedra connected by all corners. From this point of view all belong to the same type, often called the chalcopyrite type (CuFeS_2). Table 5 is sorted on Δ calculated between the parent compound CuFeS_2 and the others. Table 5 also lists some other parameters which can be used to characterize the structures. The last members of the list show more or less strong deviations in the axial ratio *c/a* and the *x* coordinate of the site 8*d* which gives the twist angle ψ of the tetrahedra along the 4 axis. The last row in Table 5 shows the variation of the coordination of the *X* ions by the other *X*. The coordination number [CN(*X/X*)] is listed as the sum of the *X* atoms at equal distances inside a sphere the radius of which is

Table 6. The four structures of the isopointal set (122) $I\bar{4}2d$ - e^3d^2cba

Formula	Occupied Wyckoff positions		
	<i>b</i>	<i>dc</i>	e^3da
$\text{Co}_3(\text{AsO}_4)_2$	(Co) ₂	Co ₁₆	(AsO ₄) ₁₂
$\text{Mg}_3(\text{AsO}_4)_2$	(Mg) ₂	Co ₁₆	(MgO ₄) ₁₂
$\text{Fe}_{10.65}\text{Ge}_{5.33}\text{O}_{24}$	Ge ₄	Fe ₁₆	[(Fe _{0.17} Ge _{0.83})O ₄] ₈ (FeO ₄) ₄
$\text{NaMg}_4(\text{VO}_4)_3$	Na ₄	Mg ₁₆	(VO ₄) ₁₂

given by the shortest distance between two *X* atoms + 10%.

The 15 members of the isopointal set (122) $I\bar{4}2d$ - *eba* are all of the type AH_2BO_4 (*A* = Sr, K, Rb, Cs, NH₄; *B* = P, As, Ge) except $\text{Ag}(\text{GaSn})\text{Se}_4$ in which all sites are half occupied which therefore leads to a high Δ . The Δ matrix for the other compounds is homogeneous with $\Delta \leq 0.08$ except for $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{H}_2\text{AsO}_4$ and SrH_2GeO_4 . In view of the homogeneous formula type these exceptions indicate errors: in SrH_2GeO_4 there are four nearest O-atom neighbours at equal distances from Ge, but from the original data there are O ··· O distances of 1.4 Å which might be wrong (see Table 9) compared with the expected distance of 2.5 Å; the same improbable situation occurs in the two compounds $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{NH}_4\text{H}_2\text{AsO}_4$.

The isopointal set (122) $I\bar{4}2d$ - e^3d^2cba has four members belonging to three different formula types. However, for all six pairs $\Delta \leq 0.04$. Multiplying the formulae with the number of formula units in the unit cell and reorganizing them reveals the similarity of the structures (Table 6).

The isopointal set (122) $I\bar{4}2d$ - *da* has the four members GeS_2 , SiS_2 , ZnCl_2 and $\text{PN}(\text{NH})$. All form a framework of tetrahedra (Fig. 3). However, owing to the increasing distortion of these tetrahedra Δ increases in comparison with GeS_2 : 0.049 (SiS_2), 0.153 (ZnCl_2); 0.193 [$\text{PN}(\text{NH})$].

Seventeen isopointal sets are used only once for the description of structures and do not allow any direct

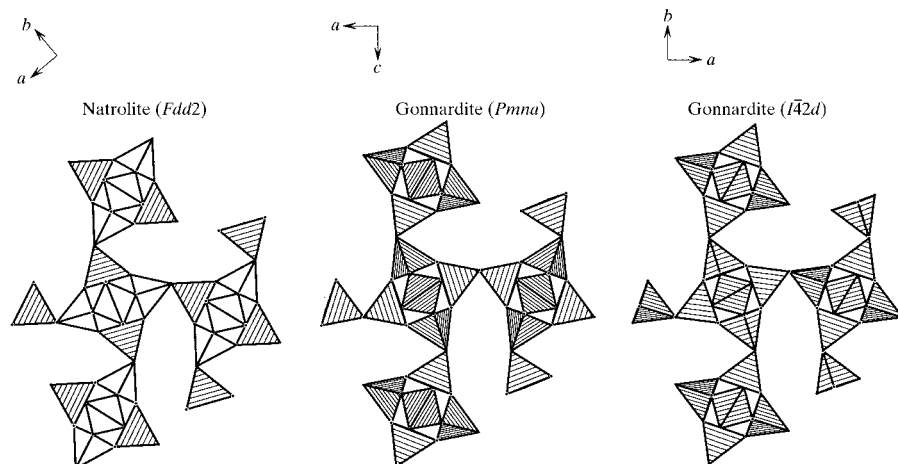


Fig. 4. (Si,Al)O₄ frameworks in the structures of natrolite (*Fdd2*) and gonnardites (*Pmna*, $I\bar{4}2d$). Natrolite: AlO₄ tetrahedra are shaded, SiO₄ tetrahedra are unshaded. Si and Al are on mixed sites in the gonnardites.

Table 7. Zeolites of type NAT

SGR-WS is the space group and Wyckoff sequence; COL is the collection number in the ICSD and SICS.

Mineral	SGR-WS	COL	Formula
Gonnardite	(122) $I\bar{4}2d - e^4 d^3 a$	29522	$\text{Na}_{6.53}\text{Ca}_{1.47}(\text{Al}_{9.40}\text{Si}_{10.6}\text{O}_{40})(\text{H}_2\text{O})_{11.94}$
Gonnardite	(122) $I\bar{4}2d - e^5 d^4 a$	71818	$(\text{Na}_{5.84}\text{Ca}_{1.6})(\text{Al}_9\text{Si}_{11}\text{O}_{40})(\text{H}_2\text{O})_{9.87}$
Gonnardite	(122) $I\bar{4}2d - e^6 d^4 a$	71821	$(\text{Na}_{5.84}\text{Ca}_{1.6})(\text{Al}_9\text{Si}_{11}\text{O}_{40})(\text{H}_2\text{O})_{14}$
Gonnardite	(122) $I\bar{4}2d - e^7 d^3 a$	71820	$(\text{Na}_{5.84}\text{Ca}_{1.6})(\text{Al}_9\text{Si}_{11}\text{O}_{40})(\text{H}_2\text{O})_{14.17}$
	(122) $I\bar{4}2d - e^3 da$		Common framework of (Si,Al)-O
[Natrolite	(122) $I\bar{4}2d - e^7 b$	67210	$\text{Na}_2[(\text{Al}_{1.92}\text{Si}_{3.08}\text{O}_{10})(\text{H}_2\text{O})_{1.96}]$
Gonnardite	(53) $Pnma - i^6 h^4 gfea$	20057	$\text{Na}_2\text{Ca}(\text{Al}_2\text{Si}_3\text{O}_{10})_2(\text{H}_2\text{O})_6$
Natrolite	(43) $Fdd2 - b^9 a$	69412	$\text{Li}_2(\text{Al}_2\text{Si}_3\text{O}_{10})(\text{H}_2\text{O})_2$
Natrolite	(43) $Fdd2 - b^9 a$	69411	$\text{Na}_2(\text{Al}_2\text{Si}_3\text{O}_{10})(\text{H}_2\text{O})_2$
Natrolite	(43) $Fdd2 - b^9 a$	69407	$\text{K}_2(\text{Al}_2\text{Si}_3\text{O}_{10})(\text{H}_2\text{O})_2$
Zeolite NAT	(43) $Fdd2 - b^9 a$	68687	$\text{Na}_{15.5}(\text{Ga}_{15.5}\text{Si}_{24.5}\text{O}_{80})(\text{H}_2\text{O})_{16}$
Mesolite	(43) $Fdd2 - b^9 a$	75199	$(\text{Na}_{5.22}\text{Ca}_{5.22})(\text{Al}_{16}\text{Si}_{24}\text{O}_{80})(\text{H}_2\text{O})_{11.31}$
Mesolite	(43) $Fdd2 - b^{10} a$	75200	$(\text{Na}_{4.96}\text{Ca}_{4.96})(\text{Al}_{16}\text{Si}_{24}\text{O}_{80})(\text{H}_2\text{O})_{23.36}$
Mesolite	(43) $Fdd2 - b^{28} a$	61242	$\text{NaCaAl}_2\text{Si}_3\text{O}_{10}(\text{H}_2\text{O})_{2.7}$
Scolecite	(9) $Cc - a^{19}$	30967	$\text{CaAl}_2\text{Si}_3\text{O}_{10}(\text{H}_2\text{O})_3$

comparison. Nevertheless, among these are several isopointal sets which describe the zeolite gonnardite (Table 7). A common isopointal set (122) $I\bar{4}2d - e^3 da$ could be given which describes the (Si,Al)-O framework. [The description of natrolite in (122) $I\bar{4}2d - e^7 b$ suggests an incorrectly determined structure.] However, in zeolite chemistry the term 'structure type' is related to the topology of the (Si,Al)-O framework (Meier *et al.*, 1996). Therefore, the zeolite type NAT of gonnardite, natrolite, scolecite, mesolite *etc.* also exists in other space groups (see Table 7). Looking at the *DIAMOND* graphical representations of the structures (Fig. 4) shows the large degree of similarity of the structures at least for the Si-Al-O framework.

The isopointal set (122) $I\bar{4}2d - eca$ describes CsH_2PO_4 . Bear in mind that the site *c* is 0,0,*z* and the site *b* in KH_2PO_4 [(122) $I\bar{4}2d - eba$] is $0,0,\frac{1}{2}$. Cs occupies *c* with $z = 0.4994$ and site occupation 0.5. Taking into consideration uncertainties in the measurements, CsH_2PO_4 could be shifted to (122) $I\bar{4}2d - eba$. Similar situations might exist for other isopointal sets, sometimes suggesting polymorphism which has to be checked in detail.

6. Using SICS

Crystal structure types in the ICSD and SICS are not characterized by names like 'rock salt' or 'rutile' because for many structure types there is no generally accepted naming scheme. Therefore in using SICS one starts with the retrieval program *SIMILAR* by selecting the chemical formula of the compound in question and listing the result (which may contain some polymorphs) in a table including the space group and Wyckoff sequence. Subsequently one can proceed in two ways:

(i) One marks the structure of interest and the command SEARCH ISOTYPIC STRUCTURES gives the number of members of the isopointal set within certain Δ ranges. Now one can display the list of structures in which only isoconfigurational structures are

expected. In general, with an expanding Δ range an increasing number of structures will be found. Nevertheless, the number of isoconfigurational structures also depends on the structure from which the search has been started. Examples of different results for such different starting points are marked by * in Table 8, which is a list of some examples of a search for isotypic structures.

(ii) One marks the structure of interest, enters the command SEARCH SYMMETRY INFORMATION and, with the cursor in the space-group field and subsequently in the Wyckoff-sequence field, the key F9 is used to bring symmetry into the menu. ENTER and DISPLAY now result in a list of *all* isopointal structures.

For further discussion, the whole Δ matrix of an isopointal set or part of it can be generated by the command COMPARE after marking the relevant entries. The matrix is usually sorted by increasing collection numbers (COL). It can be transferred to a spreadsheet program in which the sums of all matrix elements can be calculated in each line and each row. When lines and rows are now sorted for increasing sums, the type of matrix can be recognized (see §3). Sometimes this ordering can be further enhanced by interchanging lines and rows in such a way that all diagonal elements are kept zero.

To investigate the difference between single pairs of structures, one pair is marked and the command COMPARE now places the tables of coordinates side by side. If need be Δ is minimized by testing equivalent sets of coordinates (command FIT). The difference of single coordinate triplets is shown (command DIF) and can reveal the origin of deviations (as shown by \leftarrow in Table 9).

7. Limitations and expansions of SICS

The SICS project is still continuing. The elimination of errors in atomic coordinates and symmetry has not yet

Table 8. *Examples of the use of the command ISOTYPIC STRUCTURES*

ALL is the number of all members of the isopointal set; # indicates this range does not contain more members than the range before; * before formula indicates two different starting points for search in the same isopointal set.

Representative	Number of isopointal structures up to $\Delta =$									ALL	Isopointal set
	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09		
$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ (garnet)	94	147	147	147	147	147	147	147	149	152	(230) $Ia\bar{3}d - hdca$
Al_2MgO_4 (spinel)	304	403	408	410	410	411	#			412	(227) $Fd\bar{3}m - ecb$
NaSbF_6	5	6	7	8	#					9	(225) $Fm\bar{3}m - eba$
K_2PtCl_6	78	97	114	122	127	129	#			130	(225) $Fm\bar{3}m - eca$
Ba_2NiWO_6 (elpasolite)	58	147	194	196	196	196	197	#		198	(225) $Fm\bar{3}m - ecb a$
Mn_2O_3	5	11	34	#						35	(206) $Ia\bar{3} - eda$
RbGdO_2 (delafossite)	3	11	22	31	36	39	44	56	64	123	(166) $R\bar{3}m - cba$
Al_4C_3	1	3	5	6	9	11	16	16	17	50	(166) $R\bar{3}m - c^3a$
Mg_2SiO_4 (olivine)	57	83	96	108	116	125	130	134	138	140	(162) $P\bar{3}1m - dc^4a$
BiI_3	0	1	2	2	2	2	4	5	6	8	(148) $R\bar{3} - fc$
* CaCrF_6	0	0	3	4	5	6	11	19	43	43	(148) $R\bar{3} - fba$
* ZnPtF_6	0	2	2	3	4	6	8	13	15	43	(148) $R\bar{3} - fba$
ThSiO_4 (thorite)	2	40	52	55	58	58	59	#		64	(141) $I4_1/amd - hba$
Cs_3CoCl_5	0	2	3	4	8	8	11	12	14	19	(140) $I4/mcm - lhcb a$
TiO_2 (rutile)	7	16	24	32	38	41	47	48	49	54	(136) $P4_2/mnm - fa$
K_2PtCl_4	3	6	7	#						8	(123) $P4/mmm - jea$
* CuAlS_2 (chalcopryrite)	3	14	27	29	33	35	35	36	39	48	(122) $I\bar{4}2d - dba$
* AgAlS_2 (chalcopryrite)	0	1	5	6	6	7	8	9	10	48	(122) $I\bar{4}2d - dba$
K_2SO_4	1	1	6	11	16	23	26	33	38	85	(62) $Pnma - dc^5$
$\text{Ni}_2\text{Ga}(\text{BO}_3)_2$ (ludwigite)	6	11	13	14	15	15	15	15	17	18	(55) $Pbam - h^3g^5da$
KTiOPO_4	2	8	18	20	25	30	32	37	38	45	(33) $Pa2_1 - a^{16}$
* $\text{NaAlSi}_2\text{O}_6$ (clinopyroxene)	0	3	5	15	25	38	51	61	67	113	(15) $C2/c - f^4e^2$
* ZnSiO_3 (clinopyroxene)	0	0	0	1	2	6	16	27	41	113	(15) $C2/c - f^4e2$
K_2SnCl_6	0	1	2	2	4	4	5	#		29	(14) $P2_1/c - e^4a$

Table 9. *Example of comparison of two entries in SICS*

Compare 65534 (standardized) with 30320 (standardized):

INFO :		K(D ₂ PO ₄)				SrH ₂ GeO ₄			
SGR :		(122) $I\bar{4}2d - eba$				(122) $I\bar{4}2d - eba$			
CELL :		$a = 7.470, b = 7.470, c = 6.975 \text{ \AA}$				$a = 7.380, b = 7.380, c = 6.702 \text{ \AA}$			
		$\alpha = 90, \beta = 90, \gamma = 90^\circ$				$\alpha = 90, \beta = 90, \gamma = 90^\circ$			
		$c/a = 0.93, Z = 4$				$c/a = 0.91, Z = 4$			
WY	AT	x	y	z	AT	x	y	z	$\Delta(c)$
16e	O1:	0.148	0.080	0.126	O1:	0.090	0.160	0.160	0.104 ←
4b	K1:	0.000	0.000	0.500	Sr1:	0.000	0.000	0.500	0.000
4a	P1:	0.000	0.000	0.000	Ge1:	0.000	0.000	0.000	0.000

$$\Delta = 0.129$$

been completed. In triclinic and monoclinic crystal structures the standardization process may lead to very different unit cells in spite of existing relationships between crystal structures. The calculation of the lowest Δ value then demands the checking of all possible unit cells. At present this is not included in the program. Another problem exists in the comparison of structures in polar space groups.

Because a phase is defined in SICS by the precise chemical composition, space group and Wyckoff sequence (see §2) it may happen that some compounds apparently occur in too many polymorphs (e.g. SiO_2 occurs in 23 different isopointal sets). This needs further discussion.

In SICS 27 388 crystal structures are distributed over 7456 different Wyckoff sequences. 61% of them are occupied only once. That means 4548 structures (17%) cannot be compared with other structures. Moreover, in monoclinic and triclinic space groups the frequency of Wyckoff sequences with general positions occupied is much larger. Thus Δ matrices split more often into submatrices and more structure types exist with fewer representatives.

Future plans include designing a program which transforms crystal-structure descriptions from a space group to one of its maximal subgroups and then calculates Δ values between these new descriptions and the structures in these subgroups. Starting from an aristo-

type, structure trees of homeotypes (Bärnighausen, 1980; Baur, 1994) could be found automatically in this way.

SICS also makes possible the systematic investigation of the interdependence of structure, chemical composition and symmetry by the inspection of Δ matrices. This elucidates the term structure type and related terms like antitype, framework type, homeotype or polymorphism as well. Including all inorganic crystal structures – at least asymptotically – SICS is a database which can serve as a basis for all present and future investigations in inorganic crystal chemistry.

8. Final remarks

Examples given in §3–6 of this paper represent only some of the work we have done with SICS. If more Wyckoff sequences are investigated it can be expected that problems with the standardization procedure as well as failings in the calculation of the lowest Δ values will arise. The authors welcome any information on problems encountered by users. The availability of SICS is described at <http://www.rhrz.uni-bonn.de/~unc442/diamond.html>.

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