

A Procedure for the Classification of Non-Organic Crystal Structures.

I. Theoretical Background

HANS BURZLAFF^a AND YURI MALINOVSKY^b

^a*Lehrstuhl für Kristallographie, Institut für Angewandte Physik der Universität Erlangen-Nürnberg, Bismarckstrasse 10, D-91054 Erlangen, Germany,* and ^b*Institute of Crystallography of the Russian Academy of Sciences, Leninsky Prospekt 59, 117333 Moscow, Russia*

(Received 13 June 1996; accepted 6 November 1996)

In memoriam of Professor Boris K. Vainshtein†

Abstract

After a discussion of the historical background and of the properties of structural descriptors, the concept of mappings is applied to establish and quantify geometrical relationships among crystal structures. Mappings that lead to relationships are called *similarity operators*. Thus, all structures belonging to the same structure type can be collected, *e.g.* from the data of a data bank, by suitable similarity operators. Moreover, different structure types may be grouped into structure families using the same technique. A procedure is described to complete a similarity operator for a pair of structures if a relationship is present. A practical example is presented; further applications will be given in a separate paper.

1. Introduction

Since the amount of investigated and well known crystal structures is increasing rapidly (*cf.* the number of entries per year to the data bases), it is one of the most urgent problems of crystallography to find a suitable classification scheme to control the huge amount of data. In the present situation, it is difficult to find a relative of a given crystal structure or even to find out whether the structure under consideration belongs to an already known structure type. To make optimal use of the knowledge on crystal structures, *e.g.* for the development of new materials, a classification scheme is needed that collects related structures in the same group or class.

2. Historical background

The importance of the problem was recognized with the first edition of *Strukturbericht* by Ewald & Hermann (1931). They based their classification scheme (no. 1) (*cf.* pp. 7 *ff.*) on:

- (i) the lattice symmetry and the equivalence of the Wyckoff positions occupied in the structures;
- (ii) the type of chemical formula.

Structures that coincided with respect to these two properties were regarded as belonging to the same structure type.

This definition of a structure type, however, was not accepted by the crystallographic community since such different structures as CO₂ and FeS₂ pyrite belong to the same type. The later editions of *Structure Reports* did not use this classification scheme but restricted the arrangement of structures according to the chemical composition; despite this change, many old symbols for structure types are still in use as trivial names, *e.g.* Al5 type *etc.*

A new approach (no. 2) to the classification problem was applied by Pearson (1967). He introduced the Pearson symbol for classification, which consists of the Bravais-lattice symbol and the number of atoms within the unit cell. Of course, this symbol is not unique for a structure type but it allows at least a separation of crystal structures to simplify the recognition of closely related ones. A broader discussion referring to the term 'structure type' can be found in his textbook on crystal chemistry and physics of metals and alloys (Pearson, 1972): '... substances only have the same structure type when the atoms occupy the same site sets in the same space group and the atoms on a given site set have the same coordination'. Similar ideas and formulations can be found in other textbooks and papers.

Another attack (no. 3) on the problem was started by Parthé and co-workers in a series of publications. They sharpened the definition of a structure type: 'Two structures are called (configurationally) isotypic if they have the same space group, the same number of atoms in the unit cell on the same Wyckoff sites with the same or similar positional coordinates (*xyz*) and the same or similar values of the unit-cell axial ratios (*c/a, a/b, b/c*) and cell angles (α, β, γ)' (Parthé, 1990).

It is evident that approaches 2 and 3 are stricter than approach 1; both of them demand similarity with

† Deceased 28 October 1996.

respect to the coordination (provided by the similarity of coordinates in approach 3). However, they are too strict with respect to the Wyckoff positions because in approach 1 equivalent positions are tolerated as they should be, *e.g.* in the structural descriptions for ZnS, sphalerite,

$$(i) \quad \text{Zn in } 4(a) \ 000, \quad \text{S in } 4(c) \ \frac{1}{4} \ \frac{1}{4} \ \frac{1}{4}$$

and

$$(ii) \quad \text{Zn in } 4(b) \ \frac{1}{2} \ \frac{1}{2} \ \frac{1}{2} \quad \text{S in } 4(d) \ \frac{3}{4} \ \frac{3}{4} \ \frac{3}{4}$$

are equivalent in space group $\overline{F}43m$. They differ, however, with respect to the Wyckoff positions. Approach 3 tries to take care of this difficulty by standardization. Parthé & Gelato (1984, 1985) and Gelato & Parthé (1987) proposed a standardization procedure to resolve the ambiguities. It must be pointed out, however, that this procedure will give reasons for additional difficulties although it is very helpful in many cases.

Recently, Burzlaff & Rothammel (1992) and Malinovsky, Burzlaff & Rothammel (1993) investigated the conditions for geometrical relationships from a more comprehensive point of view using the concept of mappings. Before a discussion of the properties of mappings, it is convenient to summarize the terms that are used to describe a crystal structure.

3. Structural descriptors

A crystal structure is described uniquely by the set of its analytical descriptors:

(i) The basis B of the lattice; B is a 1×3 matrix that consists of three vectors:

$$B = (\mathbf{b}_1 \mathbf{b}_2 \mathbf{b}_3).$$

B determines the metric tensor G and thus the unit cell:

$$G = B'B = \begin{pmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \\ \mathbf{b}_3 \end{pmatrix} (\mathbf{b}_1 \mathbf{b}_2 \mathbf{b}_3) \\ = \begin{pmatrix} \mathbf{b}_1 \cdot \mathbf{b}_1 & \mathbf{b}_1 \cdot \mathbf{b}_2 & \mathbf{b}_1 \cdot \mathbf{b}_3 \\ \mathbf{b}_2 \cdot \mathbf{b}_1 & \mathbf{b}_2 \cdot \mathbf{b}_2 & \mathbf{b}_2 \cdot \mathbf{b}_3 \\ \mathbf{b}_3 \cdot \mathbf{b}_1 & \mathbf{b}_3 \cdot \mathbf{b}_2 & \mathbf{b}_3 \cdot \mathbf{b}_3 \end{pmatrix} = (g_{ik}). \quad (1)$$

(ii) The space group Γ given by the set of symmetry operators using the basis of the lattice:

$$\Gamma = \{(R_m; T_m)\}, \quad (2)$$

m is the order of the related point group $\{R_m\}$; this set can be restricted to the list of generators of the space group. Note that the space-group symbol normally does not fix the origin, the set of operators or generators, however, does.

(iii) For each of the N atoms in the asymmetric unit, a 3×1 matrix X_i must be given; X_i contains the coordinates. Since each atom in this list is connected

with a Wyckoff position, it is useful to give the Wyckoff letter in addition and the site symmetry. The X_i may be combined to a coordinate matrix

$$C = (X_i) = \begin{pmatrix} x_1 & x_2 & \dots & x_i & \dots & x_N \\ y_1 & y_2 & \dots & y_i & \dots & y_N \\ z_1 & z_2 & \dots & z_i & \dots & z_N \end{pmatrix}. \quad (3)$$

Beside the analytical descriptors, some geometrical descriptors are in use; two of them are of special importance:

(i) The *local* descriptors containing information on the neighbourhood of an atom, *i.e.* the coordination number and the coordination polyhedron. Although this descriptor may not be unique depending on the view of the user, it can be sufficiently fixed by rules or by computational procedures [*e.g.* by the method of the largest gap in a series of distances (Brunner & Schwarzenbach, 1971)]. Another approach is the use of the Dirichlet (1850) domain [or Voronoi (1907) domain or Wigner-Seitz (1933) cell] of the atom, the coordination number may be regarded as limited by the number of its faces. For labeling the coordination polyhedra, the modified symbolism of Donnay, Hellner & Niggli (1964) could be suitable.

(ii) The *global* descriptors containing information on the type of network or connection pattern of the structure. Several systems are in use strongly depending on the field of application. Since in this paper global descriptors are restricted to very general types like 'isolated groups', 'chains', 'layers', 'rings' *etc.*, no recommendations for a special system will be given.

4. Comparing crystal structures

Crystal structures may be regarded as infinite geometrical objects with special properties. They consist of a translational repetition of a finite volume, *e.g.* the unit cell, that contains a finite number of atoms, the distribution of which is governed by the discrete but infinite set of symmetry elements, *i.e.* the symmetry of a space group. Thus, the comparison of two crystal structures must take care of:

(i) the relationship among the sets of symmetry elements in geometrical or symmetry operators in an algebraic sense;

(ii) the relationship among the unit cells;

(iii) the relationship among the atomic positions.

The interdependence of these three properties does not allow the application of well known least-squares procedures as they are used for best rigid-body molecular fits (*e.g.* Ferro & Hermans, 1977, and citations therein) or the determination of the distortion of coordination polyhedra (Dollase, 1974) because shifts will occur in the general case that lead to different locations for related symmetry elements. Thus, a general mathematical procedure was looked for that is

more suitable for the treatment of relationships among symmetry operators, unit cells and atomic coordinates simultaneously using the basis of the crystal lattice; an adequate tool is the concept of affine mappings.

5. Mappings and images

Mappings may be represented by pairs of matrices $(M; V)$, M being a 3×3 , V a 3×1 matrix. It is convenient to use different notations, the pair notation, the block-matrix notation and the 4×4 matrix notation introduced by Bieberbach (1910); in the latter case, M and V are combined into a 3×4 matrix and extended by an additional fourth line (0001) to the 4×4 matrix \overline{M} :

$$(M; V) = \begin{pmatrix} M & V \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} m_1^1 & m_2^1 & m_3^1 & v^1 \\ m_1^2 & m_2^2 & m_3^2 & v^2 \\ m_1^3 & m_2^3 & m_3^3 & v^3 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \overline{M}. \tag{4}$$

Mappings may be inverted; assume

$$(\tilde{M}; \tilde{V}) = (M; V)^{-1},$$

then

$$\begin{pmatrix} M & V \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \tilde{M} & \tilde{V} \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} M\tilde{M} & M\tilde{V} + V \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} E & 0 \\ 0 & 1 \end{pmatrix}, \tag{5}$$

i.e.

$$\tilde{M} = M^{-1} \quad \text{and} \quad \tilde{V} = -M^{-1}V.$$

Mappings may be applied to the analytical descriptors of a crystal structure providing each descriptor with an image. If we adapt the notation of a descriptor to the extended notation of the mapping, the images can be represented easily by products of matrices. The adaptation is indicated by a ‘bar’ as follows.

(i) B is adapted by extending the matrix B by the \mathbf{o} vector:

$$\overline{B} = (\mathbf{b}_1 \mathbf{b}_2 \mathbf{b}_3 \mathbf{o}), \tag{6}$$

normally, \mathbf{o} equals the zero vector; it describes the shift of origin if the image of B is constructed.

(ii) $(R; T)$ is extended like $(M; V)$:

$$(R; T) \sim \begin{pmatrix} R & T \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} r_1^1 & r_2^1 & r_3^1 & t^1 \\ r_1^2 & r_2^2 & r_3^2 & t^2 \\ r_1^3 & r_2^3 & r_3^3 & t^3 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \overline{R}. \tag{7}$$

(iii) X is extended by a ‘1’ in an additional row:

$$\overline{X} = \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix}. \tag{8}$$

Images will be designated by a tilde ‘ \sim ’ above the label of a matrix. Since all analytical descriptors are related to the same basis, the three types of images are not independent of each other. If the image of a coordinate matrix is defined by

$$\tilde{\overline{X}} = \overline{M\overline{X}} \quad \text{or} \quad \tilde{X} = MX + V, \tag{9}$$

then

$$\tilde{\overline{B}} = \overline{BM}^{-1} \quad \text{or} \quad \tilde{B} = BM^{-1} \quad \text{and} \quad \tilde{\mathbf{o}} = \mathbf{o} - BM^{-1}V, \tag{10}$$

since

$$\overline{B\overline{X}} = \tilde{\overline{B}}\tilde{\overline{X}} = \overline{BM\overline{X}},$$

thus

$$\overline{N} = \tilde{\overline{B}}\overline{M}.$$

If the influence of a symmetry operation is designated by

$$\overline{Y} = \overline{R\overline{X}},$$

thus

$$\tilde{\overline{Y}} = \tilde{\overline{R}}\tilde{\overline{X}} = \overline{MR\overline{X}} = \tilde{\overline{R}}\overline{M\overline{X}},$$

then

$$\begin{aligned} \overline{MR} &= \tilde{\overline{R}}\overline{M} \quad \text{or} \quad \tilde{\overline{R}} = \overline{MRM}^{-1} \quad \text{or} \quad \tilde{R} = \overline{MRM}^{-1} \\ \text{and} \quad \tilde{T} &= (E - \tilde{R})V + N(T + L). \end{aligned} \tag{11}$$

$\{L\}$ covers the set of lattice-point coordinates to indicate the possible changes of T . Similarly, because of (10),

$$\tilde{G} = (M^{-1})^t G M^{-1}. \tag{12}$$

All images are simply products or sums of products of matrices under the assumption that M can be inverted.

It must be stressed that geometrical descriptors do not change under coordinate transformation, they are invariant with respect to mappings.

6. Similarity operators

The concept of mappings has been applied to different crystallographic problems in the past. In all cases, the images of analytical descriptors (all or some) are compared with corresponding analytical descriptors.

(a) Bertaut & Billiet (1978, 1979) gave a systematic derivation of all equivalent subgroups of a given space group using this concept. In this case, the images of the lattice basis of the space group must in addition be equal to the bases of the subgroups.

(b) Burzlaff & Zimmermann (1980) derived the affine normalizers of space groups by looking for those sets of mappings that lead to sets of images of the space-group operators identical with the space group:

$$\{\bar{M}\} \text{ such that } \{\bar{R}\} = \{(\bar{M}\bar{R}\bar{M}^{-1})\} = \{\bar{R}\}. \quad (13)$$

This set of mappings is always a supergroup of the space group, *i.e.* the normalizer group.

(c) Bertaut (1983) treated the displacive phase transition of hexagonal MnAs to orthorhombic MnAs with the aid of mappings. In this case, the images of the basis B and the coordinate matrix C of the hexagonal phase should be close, *i.e.* 'similar', to the related descriptors of the orthorhombic phase. Because of this property, Bertaut introduced the expression 'similarity operator' for such a mapping and finished his paper with the remark that 'similarity operators might be important for exploring structural relationships'.

(d) Schmahl & Liebau (1985) used similarity operators to evaluate probable paths of atoms in the phase-transition process and for the comparison of crystal structures. In particular, the thesis of Schmahl (1986) contains different considerations how to find the correct operator in the case of structures related by phase transitions, and a profound discussion on several properties of similarity operators may be found there. A paper by Schmahl (1990) deals with lattice similarities.*

A general structural relationship may be regarded – at least to a certain extent – as a generalized phase transition, the change of the analytical descriptors could be thought to result from 'chemical' forces instead of the variation of temperature or pressure, *e.g.* in the case of isomorphic replacements. Thus, we want to adopt the definition of Bertaut (1983).

A mapping of the analytical descriptors of a crystal structure that leads to a partial or complete similarity between the resulting images and the descriptors of a second crystal structure is called a similarity operator, the labels of such a mapping are changed from ($M: V$) to ($S: O$).

Since similarity operators work on all three types of analytical descriptors simultaneously, there are strong restrictions for the components.

(a) The image of the basis of structure (1) that should be similar to the basis of structure (2) follows (10), thus

$$B(2) \sim \bar{B}(1) = B(1)S^{-1} \quad \text{or} \quad \bar{B}(2)S = B(1). \quad (14)$$

The image of $B(1)$ defines a subgroup of the lattice (1) including the trivial one, *i.e.* the lattice itself. Thus, the components of S^{-1} must be coordinates of lattice points.

(b) According to (11), the image of the translation part of a symmetry operator is defined by

$$\begin{aligned} \bar{T} &= (E - \bar{R})O + S[T + L(1)] \\ \text{or} \quad (E - \bar{R})O &= \bar{T} - S[T + L(1)], \end{aligned} \quad (15)$$

i.e. the components of O are strongly restricted under the presence of symmetry operators; in fact, they are rational numbers as occur in the coordinates of special Wyckoff positions without degrees of freedom.

(c) If we look at a quartet of atoms in structure (1) not lying in a plane, we may collect the columns of their coordinates $\bar{X}_1, \bar{X}_2, \bar{X}_3, \bar{X}_4$ into a 4×4 matrix $\bar{Q}(1)$; their images are defined by the matrix product $\bar{Q}(2) = \bar{S}\bar{Q}(1)$. If there is a relationship to structure (2), there should be a quartet of coordinates $\bar{Q}(2)$ that is similar to the image of $\bar{Q}(1)$: $\bar{Q}(2) \sim \bar{Q}(1) = \bar{S}\bar{Q}(1)$. If we replace the image of $\bar{Q}(1)$ by $\bar{Q}(2)$, then a new matrix \bar{S} is introduced for which the following equations hold:

$$\bar{Q}(2) = \bar{S}\bar{Q}(1) \quad \text{or} \quad \bar{S} = \bar{Q}(2)\bar{Q}(1)^{-1} \sim \bar{S}. \quad (16)$$

If the deviations between \bar{S} and \bar{S} are small, the restrictions for the components of S and O discussed above can be used to adjust \bar{S} to \bar{S} ; however, all suitable quartets $\bar{Q}(2)$ have to be tested. The number of quartets in structure (2) may be very large, since also different arrangements within a quartet will lead to different results; it is restricted, however, by the following conditions:

(α) $\bar{Q}(1)$ and $\bar{Q}(2)$ should contain only atoms that correspond to each other with respect to their geometrical local and global descriptors;

(β) the quartets may be set up from symmetrically equivalent positions using the same sequence of operations or from the coordinates of atoms belonging to the same coordination polyhedron.

7. Quantification of structural relationships

Following the considerations above, we need a quantitative measure for the degree of similarity between two structures (1) and (2) on the basis of the analytical descriptors. Thus, we define functions for the three different types of descriptors derived from the comparison between the image of descriptor (1) and the related descriptor (2).

(i) From (10), the image of basis B_1 is defined by $B_1S^{-1} = (\mathbf{b}_1\mathbf{b}_2\mathbf{b}_3)S^{-1}$. The metrical properties of a lattice can be described by

$$\begin{array}{lll} b_1b_2b_3 & g_{ik} = \mathbf{b}_i\mathbf{b}_k \cos \beta_{ik} & d_{ik} = \text{abs}(\mathbf{b}_i + \mathbf{b}_k) \\ \beta_{23}\beta_{31}\beta_{12} & \text{or} & \text{or} \quad f_{ik} = \text{abs}(\mathbf{b}_i - \mathbf{b}_k) \\ \text{(metrical} & \text{(metric tensor} & \text{(length of face} \\ \text{parameters)} & \text{elements)} & \text{diagonals of the cell).} \end{array}$$

All three descriptions are equivalent (Malinovsky, Burzlaff & Rothammel, 1993). We use the last

* The present authors apologize that they missed the papers related to examples 1, 3 and 4 in their earlier publications.

representation to define the lattice deviation function 'dev':

$$\text{dev} = 1 - (1 - D_{12})(1 - D_{23})(1 - D_{32}),$$

$$D_{ik} = [|\tilde{\mathbf{d}}_{ik}(1) - \mathbf{d}_{ik}(2)| + |\tilde{\mathbf{f}}_{ik}(1) - \tilde{\mathbf{f}}_{ik}(2)|] / [\mathbf{d}_{ik}(2) + \mathbf{f}_{ik}(2)]. \quad (17)$$

The images of $\mathbf{d}_{ik}(1)$ and $\mathbf{f}_{ik}(1)$ must be rescaled such that the volume of the image of the unit cell of (1) equals the volume of the unit cell of (2); the scale factor *sc* is fixed by the condition

$$sc = \{\det[G(2)] / \det[\tilde{G}(1)]\}^{1/6} = [V(2) / \tilde{V}(1)]^{1/3}.$$

(ii) From (11), the image of a symmetry operation $(\tilde{R}_1; \tilde{T}_1)$ is $(\tilde{R}_1; \tilde{T}_1)$ with $\tilde{R}_1 = SRS^{-1}$ and $\tilde{T}_1 = (E - \tilde{R}_1)O + S(T + L_1)$, the index 1 designates structure (1). Two cases must be distinguished:

(I) $\{(R_2; T_2)\}$ is a subgroup of $\{(\tilde{R}_1; \tilde{T}_1)\}$; the Bärnighausen (1975) relation.

(II) $\{(R_2; T_2)\}$ and $\{(\tilde{R}_1; \tilde{T}_1)\}$ have only a common subgroup; the NiAs-rutile relation.

(iii) From (9), the image of a coordinate matrix *X* for an atom in structure (1) is given by $\tilde{X}_1 = S(X_1 + L_1) + O$; if the structures are similar, all (or nearly all) images should have close neighbours in structure (2) with matrices X_2 . Their displacement is measured by the distance between the points described by \tilde{X}_1 and X_2 , both of course related to the coordinate system of structure (2), $\Delta d_{12} = |B_2(\tilde{X}_1 - X_2)|$; Δd_{12} is compared with *dc*, the shortest distance occurring in the coordination polyhedron of the atom. For each X_{2i} and \tilde{X}_{1i} , failure indicators n_{2i} and \tilde{n}_{1i} are set to 1 if $2\Delta d_{12i} > dc_i$, and set to 0 otherwise.

Two functions are calculated.

(α) The displacement function 'dis':

$$\text{dis} = \frac{\sum_{i=1}^{\tilde{N}_1} (1 - \tilde{n}_{1i}) \Delta d_{12i} + \sum_{k=1}^{N_2} (1 - n_{2k}) \Delta d_{12k}}{\sum_{i=1}^{\tilde{N}_1} (1 - \tilde{n}_{1i}) dc_{1i} + \sum_{k=1}^{N_2} (1 - n_{2k}) dc_{2k}}. \quad (18)$$

(β) the failure function 'fail':

$$\text{fail} = \frac{\sum_{i=1}^{\tilde{N}_1} \tilde{n}_{1i} + \sum_{k=1}^{N_2} n_{2k}}{\tilde{N}_1 + N_2}. \quad (19)$$

The three functions may be combined to a figure of misfit 'mis':

$$\text{mis} = 1.0 - (1.0 - \text{dev})(1.0 - \text{dis})(1.0 - \text{fail}). \quad (20)$$

mis is close to zero if the relationship is a strong one.

It is evident that this investigation of relationships is a procedure to recognize whether two structures belong to the same structure type in the sense of Pearson's definition. At the same time, this procedure recognizes two structures to be configurationally isotopic in the

sense of Parthé if the figure of misfit is sufficiently small, without any need of standardization.

The interpretation of the calculated entities is not so straightforward as, for example, for a rigid-body comparison; the postulate concerning the images of the symmetry operators means that the symmetry elements of the derived structure can be located at exactly the same positions as the related elements of the basic structure provided that there are no lattice distortions. The function *dev* measures the deviations between the unit cells in the geometrical sense, *dis*, however, does not measure differences between distances but only the influence of the different coordinates. The basic assumption is that the separation of the different properties leads to a sufficiently good approximation. The calculations will be demonstrated using the relationship between PbS and NaSb₂ in Appendix A.

8. Structure types, structure families, aristotypes and roots

The two definitions of Pearson (1972) and Parthé (1990) may be combined to a new rule:

Rule no. 1: Two structures are called (configurationally) isotopic if they have the same space group and if they can be mapped to each other by a similarity operator with a sufficiently small figure of misfit. Some investigations show that a convenient value might be *mis* < 0.1.

The result of the investigations of the structures of Lovozerite type shows clearly that the concept of similarity operators not only collects those crystal structures that belong to the same structure type but also different structure types can be bundled into structure families if suitable similarity operators lead to small figures of misfit but mostly not as small as those within a structure type, *i.e.* if they are related to each other in a geometrical sense. Moreover, it should be emphasized that not only relationships of symmetry type I will be regarded but also those of symmetry type II can be included. Thus, another rule can be established:

Rule no. 2: Two structure types belong to the same family if they can be mapped to each other by a similarity operator with a sufficiently small figure of misfit. Preliminary investigations show that a convenient value might be *mis* < 0.2. The space groups of structure types belonging to the same family may follow a group-subgroup relation or may have only a common subgroup.

A structure family should be represented by its most important structure type. Since the members of a family differ with respect to their space groups, the outstanding representative should be characterized by a symmetry property. A suitable criterion could be the symmetry density *SD*, *i.e.* the number of symmetry operators per unit cell, *NG*, given by the multiplicity of the general

position, has to be multiplied by the determinant of the mapping matrix S .

$$SD = NG \det(S). \quad (21)$$

This definition leads to the next rule:

Rule no. 3: The structure type with the highest symmetry density SD that occurs in a structure family is regarded as its representative; it is called *aristotype*, in agreement with the definition of Megaw (1973).

It may happen that several aristotypes of different structure families show a clear but not too strong relationship to another aristotype. In this case, the outstanding aristotype is called a *root* of the different structure families. Root structure types and their derivatives may differ with respect to their geometrical descriptors.

It is evident that the application of the rules above results in a classification system for crystal structures that is based on geometrical relationships since the application works in a hierarchical sequence.

9. Comments

(a) In previous papers by the present authors, another method for finding the correct similarity operator was proposed for the case of those structures that belong to the same structure type. It was supposed that the matrices ($S; O$) should only run over all operations of the affine normalizer (see above) to take care of the different settings and of different choices of asymmetric units or representatives since all these structures have the same space group; the shift of origins should be determined by the shift between related symmetry elements. It turned out, however, that this method is not satisfactory for all space groups: three amendments have to be done.

(i) In hemimorphic space groups – *i.e.* the origin is not fixed by symmetry – a similar procedure has to be applied as is used in least-squares refinements to minimize the sum of distances (or squares of distances) between the images and the atoms.

(ii) In the monoclinic and triclinic cases, the normalizer operations do not include those transformations that take care of face diagonals as possible basis vectors; these transformations have to be investigated separately. For the same reason, there are strong objections against standardization procedures. Examples can be found showing that structures of the same type are distributed onto different standardized classes because the vectors $\mathbf{a} + \mathbf{c}$ and \mathbf{a} or \mathbf{c} are of similar length, *e.g.* in the monoclinic system.

(iii) In paramorphic space groups (*i.e.* space groups belonging to point groups $m\bar{3}$, $6/m$, $4/m$, 23 , 6 , $\bar{6}$, 4 , $\bar{4}$), additional mappings have to be considered; thus, the normalizer procedure is replaced by the Q -matrix method.

(b) There is a difficulty in selecting or determining the representative of a structure type in the case that there are free parameters. From the statistical point of view, the set of representatives of a structure type is a random test that contains information on the ideal structure type. At the moment, there is no procedure to evaluate the ideal parameters of a structure type on the basis of the known set of representatives; thus, it is proposed that the average parameters of the set be used as the actual type parameters. Under this assumption, the ideal parameters will be improved if the set of representatives is enlarged.

The method will be fully demonstrated in a separate paper but an example is given in Appendix A.

The authors thank the Deutsche Forschungsgemeinschaft for support.

APPENDIX A

Relationships between PbS and NaSbS_2

The structural data are taken from the ICSD base edition 1995, collection codes 38293 and 2481, respectively; all coordination polyhedra are octahedra $6o$, although the distortions stemming from different chemistry are significant (*cf.* Table 1). As the basic structure, PbS is chosen. The $Q1$ matrix is set up twice, first using the centre of the octahedron for Pb and the corners at the face (111) with coordinates (0.5, 0.0, 0.0), (0.0, 0.5, 0.0), (0.0, 0.0, 0.5), for S and then the quartet inverted at the centre. Strong chemical distortions lead to rather different approximated similarity operators that will be improved significantly if they are merged (*cf.* Table 2). The inverse computed with the average shows clearly in the first three columns coordinates of lattice points of structure (1), namely $(1\bar{1}0)$, $(\bar{1}\bar{1}0)$ and $(\frac{1}{2}\frac{1}{2}\bar{1})$; the mapping of the origin of structure (2) with site symmetry $\bar{1}$ ends in a good approximation close to a centre of symmetry in structure (1) at $(\frac{3}{4}\frac{1}{2}\frac{1}{4})$; the inverse of the adapted matrix S^{-1} is the correct similarity operator S . A computer program could easily use more sophisticated averaging procedures.

Table 3 contains the quantification results of the relationship: The unit-cell deviation is rather small with $\text{dev} = 0.030$, the local displacement of the atoms is significant with $\text{dis} = 0.093$; however, there are no failures ($\text{fail} = 0$), the misfit $\text{mis} = 0.121$ is of medium size.

It should be noted that the application to the octahedron of Na leads to the same results, the different shift of origin is compensated by the difference in the y coordinates for Na and Sb. Even the use of the octahedron for S will result in the same evaluation, indicating that the anti-structure problem is also covered. The choice of which atoms should be mapped to each other is free for the user (or a computer program); there is no need for an additional labelling of

Table 1. Structural data

dc = shortest coordination distance (Å), cp = coordination polyhedron (6o = octahedron). Structure (1): PbS, cubic, space group $Fm\bar{3}m$, $a = 5.934 \text{ \AA}$, collection code 38293, $V = 208.95 \text{ \AA}^3$; coordinates: Pb in 4(a) ($m\bar{3}m$) 000; $dc_{Pb} = 2.97$; $cp_{Pb} = 6o$; S in 4(b) ($m\bar{3}m$) $\frac{1}{2}00$; $dc_S = 2.97$; $cp_S = 6o$; metric tensor g_{ij} 35.2,0,0/0,35.2,0/0,0,35.2. Structure (2): NaSbS₂, monoclinic, space group $C2/c$, $a = 8.23$, $b = 8.25$, $c = 6.48 \text{ \AA}$, $\beta = 124.3^\circ$, collection code 2481, $V = 383.66 \text{ \AA}^3$; coordinates: Na in 4(e) (.2.) 0,0.134,0.25; $dc_{Na} = 2.91$; $cp_{Na} = 6o$; Sb in 4(e) (.2.) 0,0.603,0.25; $dc_{Sb} = 2.43$; $cp_{Sb} = 6o$; S in 8(f) (1) 0.220,0.412,0.240; $dc_S = 2.43$; $cp_S = 6o$; metric tensor g_{ij} 67.7,0,-31.7/0,68.0,0/-31.7,0,46.8.

$$\begin{matrix}
 Q1(a) & Q1^{-1}(a) & Q1(b) & Q1^{-1}(a) \\
 \begin{pmatrix} 0.0 & 0.5 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.5 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.5 \\ 1 & 1 & 1 & 1 \end{pmatrix} & \begin{pmatrix} -2 & -2 & -2 & 1 \\ 2 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix} & \begin{pmatrix} 0.0 & -0.5 & 0.0 & 0.0 \\ 0.0 & 0.0 & -0.5 & 0.0 \\ 0.0 & 0.0 & 0.0 & -0.5 \\ 1 & 1 & 1 & 1 \end{pmatrix} & \begin{pmatrix} 2 & 2 & 2 & 1 \\ -2 & 0 & 0 & 0 \\ 0 & -2 & 0 & 0 \\ 0 & 0 & -2 & 0 \end{pmatrix}
 \end{matrix}$$

Coordination polyhedron for Sb at (0.000,0.603,0.250) 6o

	Operation	Coordinates	Distance	Angle (°)				
				1	2	3	4	5
1	x y z	0.220 0.412 0.240	2.43					
2	-x y $\frac{1}{2}-z$	-0.220 0.412 0.260	2.43	99				
S3 3	-x 1-y -z	-0.220 0.588 -0.240	2.77	86	91			
4	x 1-y $\frac{1}{2}+z$	0.220 0.588 0.740	2.77	91	86	175		
5	$x-\frac{1}{2}$ $\frac{1}{2}+y$ z	-0.280 0.912 0.240	3.41	172	89	92	92	
6	$\frac{1}{2}-x$ $\frac{1}{2}+y$ $\frac{1}{2}-z$	0.280 0.912 0.260	3.41	89	172	92	92	83

Table 2. Evaluation of the similarity operator

$$\begin{aligned}
 \tilde{S}(a) &= \begin{pmatrix} 0.000 & 0.220 & -0.220 & -0.220 \\ 0.603 & 0.412 & 0.412 & 0.588 \\ 0.250 & 0.240 & 0.260 & -0.240 \\ 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} -2 & -2 & -2 & 1 \\ 2 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix} = \begin{pmatrix} 0.440 & -0.440 & -0.440 & 0.000 \\ -0.382 & -0.382 & -0.030 & 0.603 \\ -0.020 & 0.020 & -0.980 & 0.250 \\ 0 & 0 & 0 & 1 \end{pmatrix} \\
 \tilde{S}(b) &= \begin{pmatrix} 0.000 & -0.280 & 0.280 & 0.220 \\ 0.603 & 0.912 & 0.912 & 0.588 \\ 0.250 & 0.240 & 0.260 & 0.740 \\ 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 2 & 2 & 2 & 1 \\ -2 & 0 & 0 & 0 \\ 0 & -2 & 0 & 0 \\ 0 & 0 & -2 & 0 \end{pmatrix} = \begin{pmatrix} 0.560 & -0.560 & -0.440 & 0.000 \\ -0.618 & -0.618 & 0.030 & 0.603 \\ 0.020 & -0.020 & -0.980 & 0.250 \\ 0 & 0 & 0 & 1 \end{pmatrix} \\
 \tilde{S} = \frac{1}{2}[\tilde{S}(a) + \tilde{S}(b)] &= \begin{pmatrix} 0.500 & -0.500 & -0.440 & 0.000 \\ -0.500 & -0.500 & 0.000 & 0.603 \\ 0.000 & 0.000 & -0.980 & 0.250 \\ 1 & 1 & 1 & 1 \end{pmatrix}; \quad \tilde{S}^{-1} = \begin{pmatrix} 1.00 & -1.00 & -0.45 & 0.715 \\ -1.00 & -1.00 & 0.45 & 0.491 \\ 0.00 & 0.00 & -1.02 & 0.255 \\ 0 & 0 & 0 & 1 \end{pmatrix} \\
 \rightarrow S^{-1} &= \begin{pmatrix} 1 & -1 & -\frac{1}{2} & \frac{3}{4} \\ -1 & -1 & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & -1 & \frac{1}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix}; \quad S = \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 0 \\ -\frac{1}{2} & -\frac{1}{2} & 0 & \frac{5}{8} \\ 0 & 0 & -1 & \frac{1}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix}
 \end{aligned}$$

Table 3. Evaluation of mis

(i) Unit-cell deviation dev, scale factor sc = $(383.66/417.9)^{1/3} = 0.9719$, data for (2) derived from (1)

[110] :	11.65	11.53	$D_{12} = (0.12 + 0.12)/(11.65 + 11.65) = 0.0103$
[011] :	10.71	10.79	$D_{23} = (0.08 + 0.08)/(10.71 + 10.71) = 0.0075$
[101] :	7.15	7.06	$D_{13} = (0.08 + 0.18)/(7.15 + 13.34) = 0.0127$
[101] :	13.34	13.52	dev = $1.0 - 0.9897 \times 0.9925 \times 0.9873 = 0.0302$

(ii) Displacement dis and failures fail

	$X_i(2)$	$Im[X_i(1)]$	ΔX_i	Δd_i	dc_i	fail
Sb	0.000 0.603 0.250	0.000 0.625 0.250	0.000 -0.022 0.000	0.18	2.43	0
Na	0.000 0.134 0.250	0.000 0.125 0.250	0.000 0.009 0.000	0.07	2.91	0
S	0.220 0.412 0.240	0.250 0.375 0.250	-0.030 0.037 -0.010	0.39	2.43	0

dis = $2(0.18 + 0.07 + 0.78)/(2.43 + 2.91 + 4.86 + 11.88) = 2.06/22.08 = 0.0933$
 fail = 0

(iii) Figure of misfit mis

$$\text{mis} = 1.0 - 0.9698 \times 0.9067 \times 1.0 = 0.1207$$

corresponding atoms since the mapping process is unique for a fixed similarity operator.

References

- Bärnighausen, H. (1975). *Acta Cryst.* **A31**, S3.
 Bertaut, E. F. (1983). *Z. Kristallogr.* **164**, 95–108.
 Bertaut, E. F. & Billiet, Y. (1978). *C. R. Acad. Sci. Ser. A*, **287**, 989–991.
 Bertaut, E. F. & Billiet, Y. (1979). *Acta Cryst.* **A35**, 733–745.
 Bieberbach, L. (1910). *Math. An.* **70**, 297–336.
 Brunner, G. & Schwarzenbach, D. (1971). *Z. Kristallogr.* **133**, 127–133.
 Burzlaff, H. & Rothammel, W. (1992). *Acta Cryst.* **A48**, 483–490.
 Burzlaff, H. & Zimmermann, H. (1980). *Z. Kristallogr.* **153**, 151–179.
 Dirichlet, P. G. L. (1850). *Crelles J.* **40**, 209–227.
 Dollase, W. A. (1974). *Acta Cryst.* **A30**, 513–517.
 Donnay, J. D. H., Hellner, E. & Niggli, A. (1964). *Z. Kristallogr.* **120**, 364–374.
 Ewald, P. P. & Hermann, C. (1931). *Strukturbericht*, **1**, pp. 7–12.
 Ferro, D. R. & Hermans, J. (1977). *Acta Cryst.* **A33**, 345–347.
 Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 169–183.
 Malinovsky, Y., Burzlaff, H. & Rothamel, W. (1993). *Acta Cryst.* **B49**, 158.
 Megaw, H. D. (1973). *Crystal Structures: a Working Approach*, p. 283. Philadelphia/London/Toronto: W. B. Saunders.
 Parthé, E. (1990). *Elements of Inorganic Structural Chemistry*. Leipzig: Pöge Druck.
 Parthé, E. & Gelato, L. M. (1984). *Acta Cryst.* **A40**, 169–183.
 Parthé, E. & Gelato, L. M. (1985). *Acta Cryst.* **A41**, 142–151.
 Pearson, W. B. (1967). *Handbook of Lattice Spacings and Structures of Metals*, p. 2. Oxford: Pergamon Press.
 Pearson, W. B. (1972). *The Crystal Chemistry and Physics of Metals and Alloys*, p. 16. New York/London/Sidney/Toronto: Wiley Interscience.
 Schmahl, W. M. (1986). Thesis, University of Kiel, Germany.
 Schmahl, W. M. (1990). *Z. Kristallogr.* **191**, 23–28.
 Schmahl, W. M. & Liebau, F. (1985). *Z. Kristallogr.* **170**, 1164–1165.
 Voronoi, G. (1907). *Crelles J.* **133**, 97–178.
 Wigner, E. & Seitz, F. (1933). *Phys. Rev.* **43**, 804–810.