

ON QUANTITATIVE RELATIONS AMONG CRYSTALS STRUCTURES

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INTRODUCTION

The use of relations among crystal structures is very common in the process of crystal structure description: In many cases a new up to now unknown structure is discussed by comparison with a well known structure. This comparison is mostly expressed on a more or less linguistic level by sentences as 'particels A form a distorted cubic closed sphere packing' or 'half of the octahedral voids in this packing are occupied by particles B'.

Many classification concepts that try to arrange the known structures in a systematic way use the relations among the structures as a fundamental principle.

Differences in the estimation of relationships lead, however, to different or even contradictory schemes. For example the definition of families of structures in the textbook of H. M. Megaw (1973, p 282 ff) is restricted to 'one-to-one correspondence between all their atoms, and between all their interatomic bonds' (this is weakened later) and does not consider the symmetry relations. On the other hand it was shown by H. Bärnighausen (1975) that all the examples given in the textbook show in addition well defined relations with respect to symmetry. Quite another idea of structural families was developed by E. E. Hellner (1966). Starting from very simple point configurations (such as I, P or F latticesw) the decomposition of the basic configuration under the influence of subgroup relations leads to structural relations that are governed by symmetry and certain topological properties of the connection patterns. Thus not only structures with one-to-one correspondences between the atoms are related to each other. Many other concepts may be found in the literature. One reason for the differences in the estimation may arise from the fact that there is a lack of quantitative arguments.

A pair of crystal structures may be related with respect to different points of view:

i) They may be related to each other by correspondence or similarities between their translation lattices.

ii) They may be related by symmetry; e. g. they may have the same space group or one space group is a subgroup of the other or there is a common subgroup of importance for both of them.

iii) They may be related to each other by correspondence between their interatomic bonds or they may have the same or similar coordination schemes.

In this paper a procedure is proposed that allows not only to handle the different aspects of relationships in a valid and unique way but also a quantitative evaluation of the relationship. The procedure is based on the concept of mapping.

STRUCTURAL DESCRIPTORS

Before entering in a detailed discussion it is convenient to summarize the different possibilities for the description of a crystal structure:

i) A crystal structure may be described by the list of its *formal parameters*, i. e. the space group, the lattice parameters, the Wyckoff positions, and the atomic parameters if necessary. This description is complete and allows the construction of the structure (e. g. by the aid of a computer). The disadvantage of this procedure is evident; in most cases it does not give any idea to the reader about the arrangement of the atoms.

ii) To overcome this disadvantage it is very common to introduce a *local description* to illustrate the type of neighbourhoods for single atoms. This idea leads to the concept of coordination numbers and polyhedra. Strictly spoken only those neighbours are supposed to be coordinating that have shortest distances to the central atom. In many cases, however, it is difficult to decide whether a neighbour belongs to the coordination sphere of a certain atom or not. Different methods have been introduced to fix the coordination number, e. g. the principle of the largest gap (Brunner and Schwarzenbach, 1971). Since even this procedure leads to unsatisfying results in some cases, it may be supplemented by additional procedures as

the construction of Dirichlet-domains i.e. the domain of influence or by the discussion of equipotential faces etc.

iii) Since in most cases the description of local properties is not sufficient to fix the three dimensional structures *global descriptors* are added. These descriptors could be e. g. a Laves-symbol or a Laves-matrix (Laves, 1930), the use of the concept of n-connected nets (Wells, 1954-56), the reference to an aristotype (Megaw, 1973) etc. It should be emphasized, that it is very convenient to designate aristotypes by symmetry related symbols derived from the nomenclature of lattice complexes (Fischer, Burzlaff, Hellner, Donnay, 1973), as discussed below.

The combined use of local and global descriptors allows a illustrative representation of a crystal structure at least to a certain extent.

THE MAPPING PROCEDURE

A (derived) structure 2 is called to be related to a (basic) structure 1 if it can be mapped by a pair of matrices (A, S); A is a non singular 3 × 3 -matrix, S a column (1 × 3)-matrix. M = (A, S) is called the *mapping of the relationship*. The relationship is regarded to be complete only if the mapping takes into account the following three aspects:

i) *Mapping of the basis.*

If $B_b = (\underline{b}_{1b}, \underline{b}_{2b}, \underline{b}_{3b})$ represents the basis of the basic structure and $B_d = (\underline{b}_{1d}, \underline{b}_{2d}, \underline{b}_{3d})$ represents the basis of the derived structure the following relations should hold:

$$\text{If } \dot{B}_b = B_d \cdot A, \text{ then } B_b \approx c \cdot \dot{B}_b \text{ and } \dot{B}_d = B_b \cdot A^{-1}, \text{ then } \dot{B}_d \approx c \cdot B_d, \quad (1)$$

i. e. the image \dot{B}_b of B_d should be similar or very close to B_b and the image \dot{B}_d of B_b should be similar or very close to B_d ; c means a common scale factor. This relation can be expressed by the aid of the metrical tensor G. Making use of the equations

$$G = (g_{ik}) = (\underline{b}_i * \underline{b}_k) = B^t * B \quad (2)$$

the relations

$$\dot{G}_b = A^t \cdot G_d \cdot A \quad \text{and} \quad \dot{G}_d = (A^{-1})^t \cdot G_b \cdot A^{-1} \quad (3)$$

hold. For the metric tensors and their images the relations

$$G_b \approx c^2 \cdot \dot{G}_b \quad \text{and} \quad c^2 \cdot G_d \approx \dot{G}_d \quad (4)$$

are valid.

ii) Mapping of symmetry operations

A symmetry operation of the basic structure (R_b, T_b) can be mapped into an operation (\dot{R}_d, \dot{T}_d) described in the basis system of the derived structure:

$$(\dot{R}_d, \dot{T}_d) = (A, S) \cdot (R_b, T_b + L) \cdot (A, S)^{-1} \quad (5)$$

or in detail

$$\dot{R}_d = A \cdot R_b \cdot A^{-1} \quad (5a)$$

$$\dot{T}_d = A \cdot (T_b + L) + (E - \dot{R}_d) \cdot S \quad (5b)$$

The column matrix S contains the fractional components of the shift-vector from the origin of the derived unit cell to the origin of the basic unit cell described in the basis of the derived structure. L contains the (integral) components of those lattice points of the basic structure that lie inside the unit cell of the derived structure. E means the unit matrix.

Two different possibilities may occur:

a) The set $\{(R_d, T_d)\}$ is contained completely in the set $\{(\dot{R}_d, \dot{T}_d)\}$; that means the space group of the derived structure is a subgroup of the space group of the basic structure, the symmetry relationship is a 'Bärnighausen' relationship. This situation is called *symmetry relationship of type I*.

b) The set $\{(R_d, T_d)\}$ and the set $\{(\dot{R}_d, \dot{T}_d)\}$ have only a common subgroup. This situation is called *symmetry relationship of type II*.

iii) Mapping of atomic positions

The same mapping M used for the generation of the images of the ba-

sis and the symmetry operations must be used for the mapping of the atomic positions. The equation

$$\dot{X}_d = A \cdot (X_b + L) + S \tag{6}$$

produces images of all atoms of the basic structure, and the relationship can only be accepted if \dot{X}_d and X_d coincide or are very close together; X_d designates the atomic positions in the derived structure. Inverting the mapping direction images \dot{X}_b can be derived for all atoms of the derived structure with coordinates X_d :

$$\dot{X}_b = A^{-1} \cdot (X_d - S) - L \tag{7}$$

QUANTITATIVE EVALUATION OF A RELATIONSHIP

Following the different aspects of the concept of mapping four types of relations are distinguished, namely deviations between the lattices, local atomic displacements, mapping errors and symmetry relations of type I or II. For the first three types figures of merit will be introduced and used for the comparison of different pairs of structures; they can be combined to a total figure of misfit.

Deviations of the lattice

Since the determinant of the metric tensor equals the square of the volume of the unit cell it is reasonable to determine the scale factor in equation (4) (defined in (1)) such that the volume of the image unit cell of the basic structure equals to the volume of the unit cell of the derived structure. After this deviations and distortions can be discussed on the level of the metrical parameters. As linear deviations of the lengths of the basis vectors and / or distortions with respect to the angles between them may occur it is not convenient to compare the conventional metrical parameters. For the sake of homogeneity Delaunay parameters (1933) are introduced. The Delaunay base consists of the four vectors

$$\underline{b}_1, \underline{b}_2, \underline{b}_3, \underline{b}_4 \quad \text{with} \quad \underline{b}_4 = -\underline{b}_1 - \underline{b}_2 - \underline{b}_3, \tag{8}$$

the scalar products among them are called the Delaunay parameters $s_{12}, s_{13}, s_{14}, s_{23}, s_{24}, s_{34}$. They contain the same information as the elements of the metric tensor:

$$\begin{aligned}
 s_{12} &= g_{12}; & s_{14} &= -g_{11} - g_{12} - g_{13}; \\
 s_{13} &= g_{13}; & s_{24} &= -g_{12} - g_{22} - g_{23}; \\
 s_{23} &= g_{23}; & s_{34} &= -g_{13} - g_{23} - g_{33};
 \end{aligned}$$

Angular distortions and linear deviations will be taken into account simultaneously by the expression

$$f_{\text{dev}} = \frac{\sum |s_{ik}| - c^{-2} \cdot |\dot{s}_{ik}|}{\sum |s_{ik}|}, \quad (10)$$

the sum is taken over all Delaunay parameters of the derived structure, f_{dev} is called *figure of deviations*.

Local displacements

In general small deviations between the site of an atom of the derived structure and the related image of the basic structure will occur; these displacements might change from atom to atom, so they are local properties. They can be measured by the distance between the atom and its image:

$$d = |\underline{x}_d - \dot{\underline{x}}_d| \quad (11)$$

The effect of all local displacements will be taken into account by

$$f_{\text{dis}} = (\sum d_i) / (\sum d_{i\text{coor}}). \quad (12)$$

f_{dis} is called the *figure of displacement*. The sum includes all atoms in the unit cell of the derived structure; $d_{i\text{coor}}$ designates the shortest coordination distance for the i -th atom. Only the terms with $d_i \leq 0.5 \cdot d_{i\text{coor}}$ are included in the sum.

Mapping errors

Even in strongly related structures it may occur that the derived structure contains interstitial or cavity atoms compared with the basic structure. Of course the value of relationship should be lowered in these cases. For this purpose a *figure of failures* f_{fail} is introduced:

$$f_{\text{fail}} = \frac{\sum n_d + \sum \dot{n}_d}{N_d + \dot{N}_d}$$

N_d is the number of atoms in the unit cell of the derived structure, \dot{N}_d is the number of image atoms of the basic structure in the unit cell of the derived structure. The sums include all atoms in this cell; $n_d = 1$ if the value for the related d in equation (11) exceeds $d_{\text{coor}}/2$, $n_d = 0$ otherwise. The first sum takes care of missing atoms. Interstitial atoms are taken into account by the second sum; they are identified by reverse mapping.

The three evaluating figures may be combined in a way similar to obtaining a global figure of merit in direct methods procedures:

$$f_{\text{mis}} = 1 - (1 - f_{\text{dev}}) \cdot (1 - f_{\text{dis}}) \cdot (1 - f_{\text{fail}})$$

f_{mis} is called *figure of misfit*. All these figures range between 0 and 1; a relationship is stronger if these figures are closer to 0. Some applications will be discussed below.

ARISTOTYPES

Before discussing examples, it is necessary to examine more closely the term 'aristotype'. Two kinds of aristotypes may be distinguished:

i) In agreement with H. Megaw an aristotype may be defined as 'the simplest and most symmetrical member of any family'. The family consists of all structures that are related to the aristotype in the sense so defined. This definition is also in good agreement with the ideas of C. Hermann and P. P. Ewald (1931) concerning an ideal structure ('Idealfall'). In addition to maximal simplicity and highest symmetry geometrical parameters have to be fixed if they are free (e. g. axial ratios in non-cubic structures, etc.). To avoid confusion with actual structures aristotypes of this kind will be designated by symbols derived from the nomenclature of lattice complexes (1973) and supplementary geometrical parameters.

ii) It is not possible to define an aristotype as introduced above for all families of structures. E. g. the structures of halogens Cl_2 , Br_2 , I_2 form a family (A. F. Wells, 1975), however, there is no 'simplest and most symmetrical' representative. Consequently no ideal structure is described in the Strukturbericht (1937). In these cases it is proposed to fix the aristotype by the average of the standardized free parameters and to designate the aristotype by a trivial name, e. g. 'halogen' in our case above.

Table 1. List of structures and aristotypes.

structure	space group & origin	lattice parameters	coordinates			reference
			x	y	z	
'cP'	$P m \bar{3} m$ $m \bar{3} m$	a = 3.000	0	0	0	aristotype
'cF'	$F m \bar{3} m$ $m \bar{3} m$	a = 4.000	0	0	0	aristotype
'hE'	$P \frac{6_3}{m} m c$ $\bar{3} m$	a = 3.000 c = 4.899	1/3	2/3	1/4	aristotype
'halogen'	$A b m a$ 2/m	a = 8.936 b = 6.710 c = 4.577	0.1098	0	0.1388	aristotype
'cF; $\frac{111}{222}$ cF'	$F m \bar{3} m$ $m \bar{3} m$	a = 6.000	0	0	0	aristotype
'hE; P ₁₁₂ '	$P \frac{6_3}{m} m c$ $\bar{3} m$	a = 4.000 c = 6.532	0	0	0	aristotype
As	$R \bar{3} m$ $\bar{3} m$	a = 3.7598 c = 10.5475	0	0	0.2271	J. Appl. Cryst. 2, 30 (1969)
Se	$P 3_1 2 1$ $2_{[110]} \times 3_1$	a = 4.3662 c = 4.9536	0.2254	0	1/3	J. Appl. Phys. N. Y. 43, 1432 (1972)
Cl ₂	$A b m a$ 2/m	a = 8.26 b = 6.24 c = 4.48	0.1021	0	0.1222	SR 45A, 385 Acta Cryst. 18, 568 (1965)
Br ₂	$A b m a$ 2/m	a = 8.765 b = 6.752 c = 4.564	0.110	0	0.140	Acta Cryst. 12, 34 (1959)
I ₂	$A b m a$ 2/m	a = 9.784 b = 7.136 c = 4.686	0.1174	0	0.1543	Acta Cryst. 23, 90 (1967)
Ni As	$P \frac{6_3}{m} m c$ $\bar{3} m$	a = 3.169 c = 5.034	0	0	0	Can. J. Chem. 35, 1205 (1957)

Table 1. List of structures and aristotypes. (Continuation).

structure	space group & origin	lattice parameters	coordinates			reference
			x	y	z	
Mn P	$P \bar{1} n m$ $\bar{1}$ on 112_1	a = 5.917 b = 5.25 c = 3.17	0.1965 0.5686	0.0049 0.1878	1/4 1/4	Acta Chem. Scan. 16, 287 (1962)
Ti O ₂ Rutile	$P \frac{4_2}{m} n m$ m m m	a = 4.5845 c = 2.9533	0 0.3049	0 0.3049	0 0	Acta Cryst. B31, 1981 (1975)
Ti O ₂ Anatase	$I \frac{4_1}{a} m d$ 4 m 2	a = 3.7842 c = 9.5146	0 0	0 0	0 0.2081	Z. Krist. 136, 273 (1972)
Al ₂ O ₃ Corundum	$R \bar{3} c$ $\bar{3} m$	a = 4.574 c = 12.99	0 0.3064	0 0	0.3523 1/4	Acta Cryst. A38, 733 (1982)

EXAMPLES

The examples are selected in such a way that structures with strong and structures with poor relationships are included for comparison. Moreover it is assumed that they are well known to most crystallographers to give an impression about the validity of the procedure. The structural data for all structures used are presented in Table 1. The table contains the designation of the structure, the space group and information on the origin selected, the lattice parameters, the coordinates, and the reference. It starts with the description of seven aristotypes. The symbols 'cP' and 'cF' designate two cubic Bravais lattices; 'hE' designates the hexagonal close packing with the axial ratio $c/a = \sqrt{24/9} \approx 1.633$; 'halogen' means a structure that results from the averages of the parameters of the halogen structures Cl₂, Br₂, I₂. If voids in a basic arrangement (e. g. in 'cF' or 'hE', etc.) are occupied by additional atoms their distribution is indicated by the symbol following the semicolon; thus

$$\text{'cF; } \frac{1}{2} \frac{1}{2} \frac{1}{2} \text{' cF'}$$

designates a cubic close packing with occupation of all octahedral voids, 'hE; P₁₁₂' means a hexagonal close packing with occupation of all octahedral voids. The indices '112' indicate a transformation: the translation vec-

Table 2. Structural Relations.

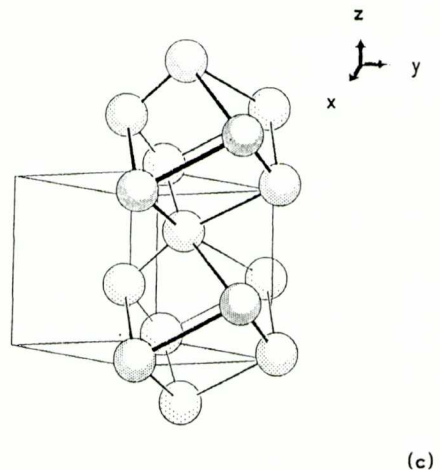
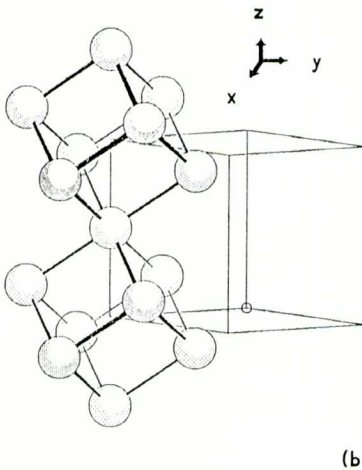
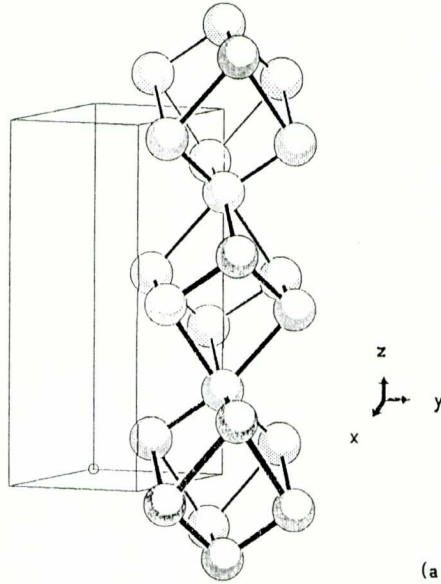
pairs of	transformation matrices				symmetry type, Index	figures of relation			
	A			S		f_{dev}	f_{dis}	f_{fail}	f_{mis}
As 'cP'	1/3	1/3	-2/3	0	(I)	0.154	0.074	0.000	0.216
	-1/3	2/3	-1/3	0					
	1/6	1/6	1/6	1/4	8				
Se 'cP'	2/3	-1/3	-1/3	-1/3	(I)	0.076	0.153	0.000	0.218
	1/3	1/3	-2/3	-1/3					
	1/3	1/3	1/3	0	24				
Ni As hE; P ₁₁₂	1	0	0	0	(I)	0.179	0.000	0.000	0.179
	0	1	0	0					
	0	0	1	0	1				
Mn P 'hE; P ₁₁₂ '	-1/2	-1/2	0	1/4	(I)	0.062	0.114	0.000	0.169
	0	0	1	1/2					
	1/2	1/2	0	1/4	6				
Al ₂ O ₃ 'hE; P ₁₁₂ '	1/3	-2/3	0	0	(I)	0.043	0.068	0.091	0.184
	2/3	-1/3	0	0					
	0	0	1/3	0	6				
Ti O ₂ Rutile 'hE; P ₁₁₂ '	-1/2	1/2	0	0	(II)	0.069	0.068	0.143	0.256
	0	0	1	1/2					
	1/2	1/2	0	0	6				
Ti O ₂ Anatase 'cF; $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ cF'	1	0	0	0	(I)	0.239	0.076	0.143	0.398
	0	1	0	0					
	0	0	1/2	0	12				
Cl ₂ Br ₂ I ₂ 'halogen'	1	0	0	0	(I)	0.043	0.037	0.000	0.079
	0	1	0	0		0.023	0.002	0.000	0.025
	0	0	1	0	1	0.047	0.040	0.000	0.085
'halogen' 'cF'	1/2	0	0	1/8	(I)	0.347	0.210	0.000	0.484
	0	1	0	0					
	0	0	1	1/4	24				

tors \underline{a}' , \underline{b}' , \underline{c}' of the P-lattice represented by the octahedral voids must be multiplied by the indices to match the translations of the structural unit cell, i.e. $1\underline{a}' = \underline{a}$, $1\underline{b}' = \underline{b}$, $2\underline{c}' = \underline{c}$.

The results of the quantitative evaluation of the relationships according to the procedure described above are given in Table 2. The first column contains the symbol of the structure and its aristotype. The next two columns give the mapping (A, S); the following column contains informations on the symmetry type and the index of the common subgroup. The last column contains the different figures of merit.

- (i) It is well known that the structures of the elements As and Se are strongly related to a cubic P-lattice (cf. figure 1). The quantitative analysis reveals that the deviations from 'cP' are of the same magnitude, but the relative importance of the lattice deviations and the local displacements of the atoms is widely different in the two structures.
- (ii) The next comparison concerns structures related to the NiAs-type (cf. figure 2 and figure 3). The detailed analysis shows that the deviations of the actual NiAs structure from the aristotype 'hE; P_{112} ' are significant because of the lattice deviations; the MnP structure has smaller overall deviations inspite of remarkably large local displacements (cf. figure 2a,b). Even the corundum structure shows a similar figure of misfit although only 2/3 of the octahedral voids are occupied as indicated by the figure of failures. Moreover the analysis shows that the description for rutile given by A. F. Wells (1975) is justified: the main part of the relatively large figure of misfit is due to the 1/2 occupation of the octahedral voids (cf. figure 2c).
- (iii) The second phase of TiO_2 , anatase, may be regarded to be related to the NaCl structure as already described by P. P. Ewald and C. Hermann (1931) (figure 4). In this case, however, the lattice deviations are substantial and lead together with the figure of failures to a large figure of misfit.
- (iv) The next example refers to three structures which without any doubt belong to the same aristotype, namely the structures of Cl_2 , Br_2 , I_2 . Consequently all figures of relation are close to zero. The combined figure of misfit, however, increases to 0.085 in the case of I_2 .
- (v) Although the halogen structure is clearly a layer structure it may be regarded as faintly related to a cubic close packing elongated along \underline{b} with tilted unit cells in direction of \underline{a} (cf. figure 5). The quantitative

evaluation results in a large figure of misfit mostly due a large figure of deviation stemming from the elongation in \underline{b} -direction. However, the Dirichlet domains support the relation: the rhombi paralell to \underline{b} are changed to hexagons as a consequence of the elongation in \underline{b} -direction, otherwise there are only small changes.



.. Projections of the structures of As (a), 'cP' (b), Se (c) in hexagonal setting.

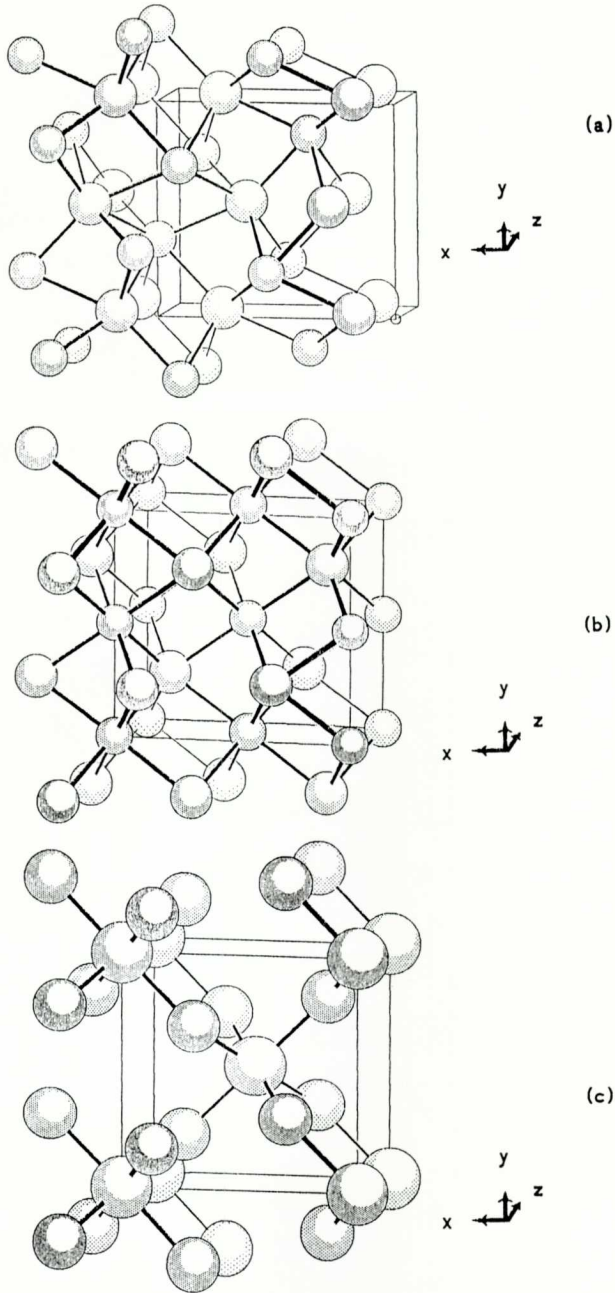
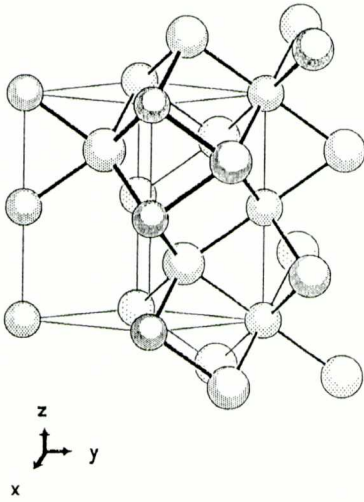
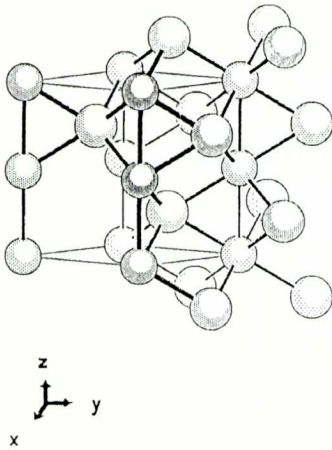


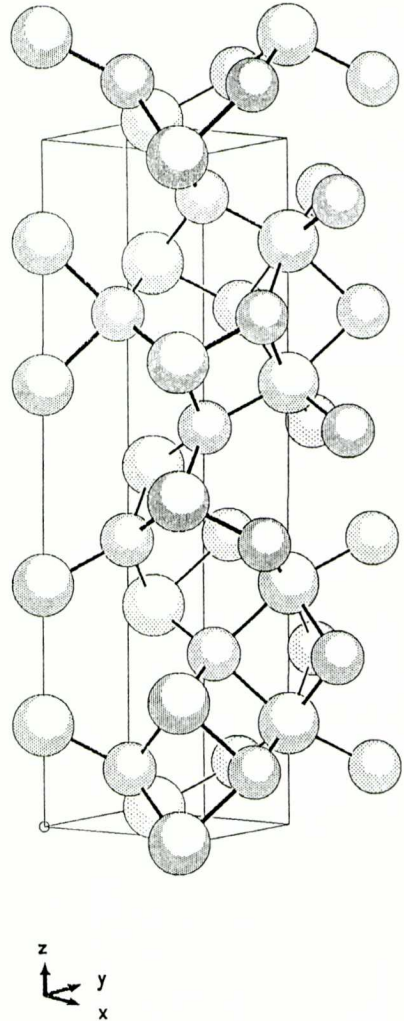
Fig. 2. Projections of the structures of MnP (a), 'hE; P_{112} ' in orthorhombic setting (b), TiO_2 rutile (c).



(a)



(b)



(c)

Fig. 3. Projections of the structures of 'hE; P_{112} ' (a) in hexagonal setting, NiAs (b) and Al_2O_3 corundum (c); for the sake of compatibility (c) shows only parts of the structure.

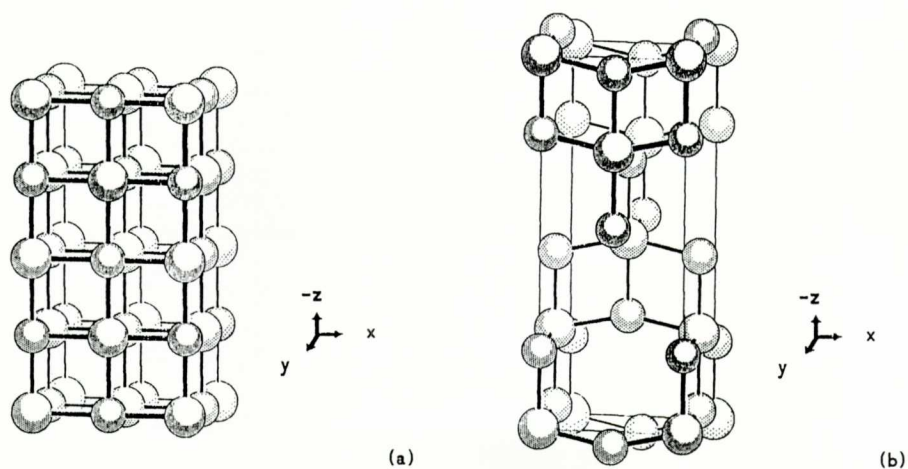


Fig. 4. Projections of the structures of 'cF'; $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ cF' (a) and Ti O₂ anatase (b).

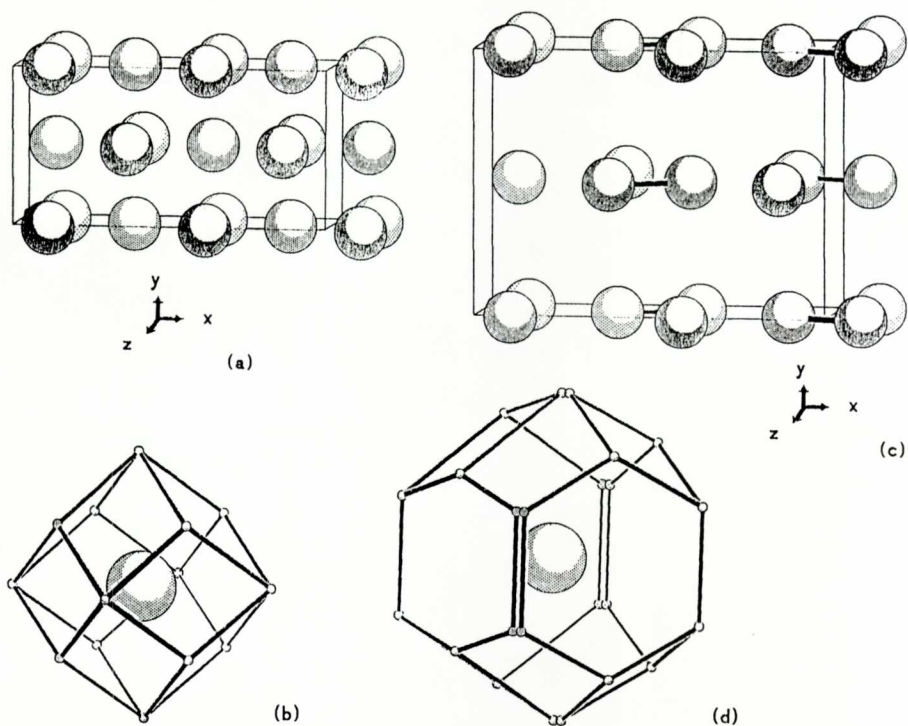


Fig. 5. Projections of the structure and Dirichlet domain for the cubic close packing 'cF' (a, b) and for the aristotype 'halogen' (c, d).

ABSTRACT

A procedure for the quantitative evaluation of structural relationships among crystal structures is introduced based on the concept of mappings represented by pairs of matrices (A, S). Lattice relationships, symmetry relationships, local atomic deviations and mapping failures are distinguished; for each type of relationship a figure of merit is constructed. The different figures are combined to a figure of misfit that might be used for the characterization of the structural relation. Some examples are discussed in detail.

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