repulsion, which forces Li into the more distant octahedron such that in adjacent octahedra Li and Nb are located away from their common face.

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# Method of Crystal-Structure Similarity Searching

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### Abstract

An algorithm is presented which is used to recognize the similarity of crystal structures by matching a description of one structure against the equivalent descriptions of a second. Equivalent descriptions are considered since there are multiple possible ways of choosing the crystal axes and their origin, the asymmetric unit and atom numbering. Another idea used in the algorithm is to use positional and rotational parameters of the molecular fragments to describe the principal crystal structure. The two structures are considered to be similar if in such descriptions the corresponding cell parameters and the parameters of corresponding fragments differ from each other within the limits specified. As a result of such similarity searching, the type of structural similarity, including the transformation matrix of crystallographic axes and the atom correspondences, is determined. The algorithm has been put to practical use in the *CRYCOM* program. This program is compatible with the Cambridge Structural Database (CSD) through interaction with the *GEOM*78 program of CSD. The latter program is also used in




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*CRYCOM* for recognizing molecular fragments. The use of *CRYCOM* is illustrated in a few examples.

## 1. Introduction

In structural investigation, very frequently a problem arises when two or more crystal structures are to be compared with each other, in order to find similarity between them. Thus, a newly determined structure can be best described if one compares it with another similar structure which is already known. Recognition of similar crystal structures, such as identification of the structure types, is evidently present in structure classification work. Not only structures of different compounds can be the object of similarity searching. In polymorphism studies, the knowledge of geometrical relationships between the different structural forms of the same compound is often of principal importance. Finally, the comparison of a crystal structure with itself is also an important kind of problem because of the possibility of recognizing undescribed crystal symmetry, such as pseudosymmetry.

The only algorithm known so far to be aimed at recognizing and providing the best representation of similar inorganic structure data was that proposed by Parthé & Gelato (1984). Their principal idea to compare crystal structures will be discussed in parallel with our consideration.

Recently, Burzlaff & Rothammel (1992) formulated an approach to compare crystal structures in which the description of one structure is transformed by a correctly chosen mapping operation, to give an equivalent parameter set having numerical values close to that of the other structure. This idea is also used as a general principle throughout the present consideration. However, while introducing a set of average characteristics was of primary interest to Burzlaff & Rothammel (1992), in order to have a measure of the relationships between the structures, the way to construct the actual mapping operations is evidently not considered in their paper.

In contrast, the sole subject of the present paper is an algorithm used to find the transformation needed to bring the two structural descriptions into mutual correspondence, to provide the principal solution of the similarity problem. On the other hand, the questions concerning statistical treatment of similar descriptions are not considered here. From this note one can see that the Burzlaff & Rothammel (1992) paper and the present one deal mainly with two constituting parts of one problem.

## 2. Structure descriptions

The structure description is a set of data including a symbol of space group, six unit-cell parameters and a list of fractional atomic coordinates.

We assume that each atom is supplied with a name consisting of a chemical element symbol and a unique number – to distinguish atoms of same element. The atom-coordinate list contains the symmetry-independent atoms only. The order in which the atoms appear in the list (atom numbering) is essential for us, because different atomic sequences correspond to different equivalent descriptions.

## 3. Equivalent descriptions

The key problem is that any structure may be represented by multiple equivalent descriptions depending on the choice of the crystallographic reference system. This system includes the following three principal components: the crystal axes, including their origin; asymmetric unit; the atom-numbering scheme. Note that the choice of the first component defines both the unit-cell parameters and the coordinate list, while that of the latter two fixes the coordinate list only.

By changing the three components in every possible way and exploring all their combinations with each other, we are able to provide, in principle, the full list of equivalent descriptions of the structure.

## 4. Unique descriptions

The unique-description idea is the main idea explored by others to avoid ambiguity in representing crystal structure data. This assumes choosing the reference system in different structures in a standard way, so that the resulting structure parameters would fit certain inequality conditions depending on the crystal symmetry and lattice geometry. Parthé & Gelato (1984) derived a complete set of such conditions for all crystal symmetries and proposed to follow them in the representation of inorganic crystal structure data.

There are, however, two principal faults in their method precluding its use in full as a similarity-searching tool. First, as Parthé & Gelato (1984) recognize (giving a valid example), similar structures do not necessarily have similar unique descriptions: the unique description of one structure can be similar to a non-unique one of the other (while the two unique descriptions are not). Secondly, we would like to stress that the unique descriptions are not able to show us more than one correspondence variant between the two structures, while the other possible variants are left obscured. This is important in view of the possibility of using the similarity-searching algorithm for recognizing undescribed symmetry.

## 5. Similarity searching as a matching procedure

Let us define any two structural descriptions as similar if the deviations between their respective

parameters are within the preset limits. We can now build up our algorithm as a process to match a description of one structure against the equivalent descriptions of another, unless similar descriptions are found. There are three main questions to be answered with the help of such a procedure.

What are the similar descriptions?

What is the difference between them?

In what way are they similar?

The first question is used to decide if the structures are similar or not. The second is to determine the extent of structural dissimilarity (if any similarity exists). The last question concerns the transformation necessary to bring the original descriptions into the correspondence with each other.

## 6. Molecular-fragment descriptions

In most structures there may occur molecular fragments, the inner structure of which is insensitive to a particular crystal environment. Thus, it is possible to introduce a kind of structure description based on a few positional and rotational parameters which specify the arrangement of all fragments composing the crystal structure.

Let us assume that each independent fragment has orthogonal axes **u,v,w** to define its rotation within the crystal orthogonal axes **X,Y,Z** (attached to the crystal axes **a,b,c**) by a matrix $R$ (whose columns are the direction cosines of **u,v,w** in **X,Y,Z**). The fragment position is given by fractional coordinates $x,y,z$ that fix the fragment-axis origin in the **abc** system. (It may equally be represented in **XYZ** by corresponding orthogonal coordinates $X,Y,Z$.)

Several ways to relate the **abc** and **XYZ** systems with each other can be found in the literature. For generality, neither of them is specified here. We assume only that the correct relation is given by a matrix $A = A(a,b,c,\alpha,\beta,\gamma)$, the matrix elements of which are functions of the unit-cell parameters, representing the fractional $x,y,z$ to orthogonal $X,Y,Z$ coordinate transformation according to

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = A \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

Further note that to be able to handle asymmetric fragments of opposite chirality, we assume that the left-hand choice of fragment axes is permitted in addition to the conventional right-hand one.

Each independent fragment is assigned a unique name (consisting of a fragment-type specification and a sequential number), in order to distinguish the fragments of the same type from each other.

With such fragment descriptions introduced, some reformulation of the factors formulated previously to produce multiple descriptions is necessary. The new features are:

molecular fragments are now implied in place of atoms when referring to the asymmetric unit and numbering;

the fragment point symmetry appears as an additional factor to produce the equivalent fragment rotations.

Hirshfeld (1968) considered a similar problem of the interacting crystal and molecular symmetry when generating the equivalent molecular-crystal descriptions in the case of fixed unit-cell parameters. A more general approach to this problem, with the cell parameters being allowed to vary, was considered by us (Dzyabchenko, 1983). In this context, the present consideration concerns a more complicated symmetry case, accounting for the additonal effect caused by permutations of independent molecules.

Note that in the total algorithm, the introduction of molecular fragments can be regarded as simply an auxiliary step in order to reduce the number of structural parameters, at the expense of structure details having no actual influence on the similarity searching. As soon as the problem is solved in terms of fragments, it is easy to come back to atoms and find the atomic correspondences.

On the other hand, the molecular-fragment description can be very helpful in itself in understanding the principal features of the structures, such as crystal packing and molecular conformations.

## 7. Choosing the fragment symmetry

Typically, the fragment symmetry observed is not identical to that following from its chemical structure but is distorted to a certain extent by the crystal and chemical environment. In connection with this, the question can arise of which approximate symmetry should be taken into account in the case of a distorted fragment. We believe that, out of a number of possible symmetries, it is reasonable to choose, at least as a first approximation, the maximal one. A simple argument to do so is as follows. If the fragment symmetry is overestimated, it can only result in a few false variants of structural correspondence, in addition to the true ones (if any). The false solutions, however, can easily be recognized on progressing to single atoms. On the other hand, if the fragment symmetry was underestimated, one has a chance of missing the correct solution.

## 8. Structure-parameter deviations

For two descriptions representing structures (1) and (2), each having $N$ fragments within the asymmetric unit, we introduce the following set of $2N+6$ quanti-

ties defining the deviations between the respective structural parameters:

six unit-cell parameter differences (taken by absolute value)

$$|a_2-a_1|,\ |b_2-b_1|\ etc.,\ |\gamma_2-\gamma_1|,$$

to characterize similarity of the unit cells;

$N$ dimensionless fragment-origin distances

$$d=[(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2]^{1/2},$$

to characterize similarity of the fragment positions;

$N$ fragment turn angles $\Omega$, to characterize similarity of fragment rotations in the two structures. The turn angle is found as

$$\Omega=\arccos(w_{11}+w_{22}+w_{33}-1)/2,$$

where $w_{ii}$ are the three diagonal elements of a matrix $W$ to relate rotations $R_1$ and $R_2$ of the respective fragments according to

$$W=R_1^{-1}R_2. \qquad (8.1)$$

### 9. The fragment substructures and orbits

A structure motif formed by all symmetry-related fragments of type $Q$ will be called the substructure of fragment type $Q$, or substructure $Q$ for short. A motif formed by an $i$th independent fragment of type $Q$ and its symmetry partners will be called the $i$th crystallographic orbit of fragment type $Q$ (or orbit $Q_i$).

Each orbit is characterized, like ordinary structures, by the cell parameters and the set of parameters which define the fragment position and rotation.

Unlike the full structure, the factors which provide equivalent descriptions of a separate orbit are restricted to only (*a*) the cell axis transformations and origin shifts, and (*b*) the fragment symmetry, while the factor of asymmetric unit choice is implicitly present in (*a*), because the space group is a subgroup of the corresponding normalizer group.

Substructure $Q$ may be considered as superposition of all orbits of type $Q$. The full structure, in turn, may be considered as a superposition of the constituting substructures $A$, $B$, $C$ *etc.* With such a superpositional idea we can build up our full-structure algorithm as a sequence of independent substructure steps, each step matching the current substructures of the two structures against each other.

### 10. Affine normalizers

Affine normalizers play a key role in the generation of multiple structure descriptions. The affine normalizer $A(F)$ of a space group $F$ is the group of all affine transformations of the unit-cell vectors, leaving invariant the list of coordinate triplets (equivalent positions) of $F$ (Dzyabchenko, 1983). In other words, $A(F)$ lists all the affine transformations of the crystal axes without changing the description of $F$.

This definition differs from that used by others (Burzlaff & Zimmermann, 1980; Gubler, 1982; Koch & Fisher, 1987), who define $A(F)$ as the group of all affine mappings of $F$ onto itself. The two definitions exist because both passive and active points of view on the transformation itself are possible. One can see the advantage of the former for our purposes from the subsequent consideration.

Any affine normalizer can be represented by a set of $(S,\tau)$ operators consisting of matrices $S$ transforming the unit-cell vectors **a**, **b**, **c** according to

$$\begin{pmatrix}\mathbf{a}'\\ \mathbf{b}'\\ \mathbf{c}'\end{pmatrix}=\begin{pmatrix}s_{11}&s_{12}&s_{13}\\ s_{21}&s_{22}&s_{23}\\ s_{31}&s_{32}&s_{33}\end{pmatrix}\begin{pmatrix}\mathbf{a}\\ \mathbf{b}\\ \mathbf{c}\end{pmatrix},$$

and vectors $\tau$ characterizing the shift of the crystal origin.

The general rule for all affine normalizers is that the matrix $S$ elements are integers (not necessarily 0, 1 or $-1$ in case of monoclinic and triclinic space groups), with a condition on the $S$ determinant

$$\mathrm{Det}(S)=1\ \text{or}\ -1, \qquad (10.1)$$

preserving the cell volume.

As for $\tau$ vectors, their components can be altered according to the normalizer-group periodicity. The latter may be zero in the case of a polar space-group direction, or 1/2 in the case of non-polar directions (we do not mean here the normalizers derived from high-symmetry space groups, which are not treated directly in the present algorithm for reasons to be discussed later). The normalizer zero periodicity means that the corresponding component of $\tau$ can assume arbitrary real values.

Note that the matrix $S$ negative determinant means a change of chirality of the crystal axes. Although the left-hand choice of the crystal axes is rarely used in crystallography, it is necessary to allow such a choice for a while, in order to be able to compare crystal structures of opposite chirality. Indeed, the structure described in a left-hand axis set may equally be represented in the right-hand one, provided that the signs of one coordinate (or all three coordinates) of all the atoms are changed to their opposites. [Similar arguments for using the axes of changed chirality can also be found in the paper by Hirshfeld (1968).]

Lists of the affine normalizers have originally been published by Burzlaff & Zimmermann (1980) and Billiet, Burzlaff & Zimmermann (1982). They are

reviewed (together with the Euclidean normalizers and the automorphism groups – the predecessors of the affine normalizers) in the paper by Koch & Fischer (1987). The list of the affine normalizers is also available from our previous paper (Dzyabchenko, 1983*). It differs from the others with the choice of the *b* axis (instead of *c*) as the unique direction in the monoclinic space groups.

## 11. Reduced-symmetry descriptions

In order for the two structures to be compared with each other, they must obviously be described within the same space group, including the space-group setting, and have the same number of the corresponding fragment types. By corresponding fragment types we mean those identical or stereochemically equivalent in the two structures. (An interesting example of the stereochemical equivalence of molecules having markedly different chemical configurations can be found in §14.1).

At the same time, it is not so unusual that similarity occurs within structures having different exact symmetries. For example, as a result of a second-order polymorphous transformation, the crystal symmetry may change radically, while the structure itself may not.

Fortunately, it is always possible to replace the original structure description with one having a reduced symmetry group (up to *P*1), with the asymmetric unit extended at the expense of symmetry atoms.

(Strictly speaking, changing to trivial symmetry may be recommended even in the case of identically described symmetries in order to account for the presence of an undescribed symmetry and provide some extra equivalent descriptions prohibited by the exact symmetry).

## 12. Matching algorithm

Let us assume that a description of structure (1) (the reference description) is matched against each of the equivalent descriptions of structure (2). Any description of structure (1) may be chosen for this purpose. For example, one can find it suitable to choose the reference description according to the Parthé & Gelato (1984) standardization rules. [As have been noted above, this does not mean that the matched structure (2) description will necessarily fit the standardization rules also.]

The total algorithm includes the following principal steps:

(*a*) perform matching of unit cells,

(*b*) recognize all current-type fragments in the two structures,

(*c*) perform fragment matching,

(*d*) find substructure similarity,

(*e*) go to (*b*) for next fragment type.

### 12.1. *Matching of unit cells*

At this step the six independent metric matrix elements (metric coefficients) $g_{ij}$ of the unit cell of structure (1) are matched against the corresponding metric coefficients $g_{ij}'$ of the structure (2) trial-equivalent cell, according to the condition

$$|g_{ij}'(2) - g_{ij}(1)| < \Delta_{ij},$$

where $\Delta_{ij}$ are tolerance factors calculated from the unit-cell parameter tolerances specified in the input data. The trial-cell metric matrix, $G'$, is found as

$$G' = SGS',$$

where $S$ is the matrix part of an operator $(S,\tau)$ of the affine normalizer (see §10), $S'$ is the transposed $S$ matrix and

$$G = \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix},$$

the original cell metric matrix. Parameters $a'$, $b'$, $c'$, $\alpha'$, $\beta'$ and $\gamma'$ of the matched cell are readily obtained from $g_{ij}'$.

### 12.2. *Recognizing molecular fragments*

Recognition of molecular fragments in a three-dimensional atomic pattern is a very substantial step of the total algorithm. Fortunately, this problem has been well developed by others. Moreover, a suitable procedure specific to crystal state is available as an option of the *GEOM*78 program of the CSD (Allen *et al.*, 1979). We use it for our purposes with minor modifications (see §13 for some extra details).

### 12.3. *Fragment matching*

At this step each orbit of the current fragment type $Q$ of structure (1) is matched against the same type of orbit of structure (2). To be certain, let orbit $Q_i(1)$ be matched against $Q_j(2)$. In this process, the reference description of $Q_i(1)$ is compared with each of the equivalent descriptions of $Q_j(2)$. As has been stated in §9, the list of equivalent descriptions of a separate orbit is provided by the affine-normalizer and the fragment-symmetry operator lists. The former factor, however, after the unit-cell parameters

* The following changes should be made in Table 1 of this paper: (1) space group *Ccca* should be moved from the first line to the end of the third line, right after *Ibam*. (2) *Cmm*2, the only space group in the fourth line, should be moved to the line below, with the rest of the data in this line deleted completely.

are matched, is restricted by the fixed cell-parameter condition. The restricted operator list is given by the corresponding Cheshire group (Hirshfeld, 1968), a subgroup of the affine normalizer.

To derive a combined effect of the crystal axis transformation $S$ and the fragment-symmetry operation $M$ on the fragment turn angle, we use equation (10) from our earlier paper (Dzyabchenko, 1983) to express the current rotation $R_2'$ of the second structure fragment

$$R_2' = A'(S')^{-1} A^{-1} R_2 M. \qquad (12.1)$$

In this expression, $S'$ is matrix transposed to $S$; $A = A(a,b,c,\alpha,\beta,\gamma)$ is the fractional-to-Cartesian coordinate transformation matrix within original **a,b,c** axes; $A' = A(a',b',c',\alpha',\beta',\gamma')$ is the same as $A$ but referred to the transformed basis **a'**,**b'**,**c'**. The matrix elements of $A'$ are calculated by substituting the new cell parameters $a'$, $b'$, $c'$, $\alpha'$, $\beta'$, $\gamma'$ into the expressions of the matrix $A$ elements.

Replacing $R_2$ in (8.1) by the expression (12.1) for $R_2'$ we obtain the relative rotation matrix $W$ of the two fragments

$$W = R_1^{-1} A'(S')^{-1} A^{-1} R_2 M. \qquad (12.2)$$

In order to save computational time, prior to calculating the full matrix product (12.2), the sign of the determinant of $W$ is found first as the product of the six matrix determinant signs. In the case of det($W$) positive, $W$ itself is calculated and its trace is then checked further to be within the limit defined by the tolerance parameter for $\Omega$. Otherwise, the calculation of $W$ is cancelled and the routine proceeds to the next combination of $M$, $S$ and fragment orbit numbers $i$ and $j$.

The displacement vector **s** for the fragment-origin coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$ of the two structures is given by

$$\mathbf{s} = \mathbf{x}_2' - \mathbf{x}_1 = (S')^{-1}\mathbf{x}_2 - \boldsymbol{\tau} - \mathbf{x}_1,$$

where $\boldsymbol{\tau}$ is the translation part of the affine normalizer operator. Vector **s** is minimized by an absolute value by altering the components of $\boldsymbol{\tau}$ according to the normalizer periodicity. As a result, the characteristic distance $d$ is found as the length of the minimal **s**. $d$ is then checked to be within the limit specified for the fragment-origin displacement.

Note that no translation problem exists for fragment-origin matching in the case of space group $P1$, whose affine normalizer has vanishing periodicity in three dimensions, and, therefore, **s** can always be set to zero by an appropriate shift of the crystal origin.

### 12.4. *Substructure correspondence*

A collection of all fragment-to-fragment correspondences found for a given fragment type $Q$ still does not represent the correspondence of the two substructures as a whole. This is because the normalizer operators used to match the orbits were allowed to transform each orbit description independently of the other orbits. That was not absolutely correct, however, because the normalizer operators, by definition, act on the crystal axes, not the actual atoms, and hence they can only produce the changes in all the orbit descriptions *simultaneously*. In other words, the correspondences found are not, in general, consistent with each other.

On the other hand, unlike the normalizer, the space-group operators do allow the independent changes of the fragment-orbit descriptions. It was not necessary, however, to consider them explicitly before because they are part of the normalizer group and, therefore, are already present in the $(S,\boldsymbol{\tau})$ operator list.

The following conclusion can be made from these arguments. To derive a consistent set of fragment correspondences we should select from the available collection only those correspondences which have their $(S,\boldsymbol{\tau})$ operators equivalent to each other through a space-group operator as the multiplier (including trivial equality). This can also be formulated as the condition that each normalizer operator $(S,\boldsymbol{\tau})^{Qij}$ defining a $Q_i$ *versus* $Q_j$ fragment correspondence can be represented as the product of some operator $(S,\boldsymbol{\tau})^C$ common to all fragments and a space-group operator $(F,\mathbf{f})^{Qij}$ specific to the given fragment pair, *i.e.*

$$(S,\boldsymbol{\tau})^{Qij} = (S,\boldsymbol{\tau})^C * (F,\mathbf{f})^{Qij}. \qquad (12.3)$$

The set of fragment correspondences conforming to (12.3) gives us a solution of the correspondence problem for the current substructure $Q$, with $(S,\boldsymbol{\tau})^C$ representing the cell transformation and the crystal-origin shift, and $(F,\mathbf{f})^{Qij}$ giving independent motions necessary to obtain matching of the respective fragments. A procedure to find the solution of (12.3) is to match one of $(S,\boldsymbol{\tau})$ operators of the former collection [actually, any of them may be tried as the common factor $(S,\boldsymbol{\tau})^C$] against the others, using the space group as the matching factor.

Note that in the case of the undescribed symmetry present in the substructure, more than one variant of substructural correspondence are possible. These are represented by different $(S,\boldsymbol{\tau})^C$ operators that are not equivalent to each other through their products with the space-group operators.

### 12.5. *Full-structure similarity*

The full-structure searching process is performed as a sequence of the substructure steps described above, executed repeatedly and almost independently of each other. The only dependence between the

subsequent steps is that each step uses only those operators $(S,\tau)$ of the full affine-normalizer list that have been selected as $(S,\tau)^C$ in the preceding step. The operator $(S,\tau)^C$ found for the final substructure is that responsible for the full-structure correspondence.

Again, as stated above for separate substructures, more than one correspondence variant is also possible between the full structures in the case of undescribed symmetry being present.

We can now formulate the solution of the full-structure similarity searching problem as a set of *all* the different ways to bring the reference description of one structure to numerical agreement with an equivalent description of the second structure, each method characterized by: a normalizer operator giving the transformation matrix and the origin shift of the crystal axes; a reference table to name the corresponding fragments; space-group and fragment-symmetry operators for each pair of corresponding fragments; unit-cell and fragment-parameter deviations characterizing the extent of structural dissimilarity.

In completion, the atom–atom correspondences can be obtained. This is not too difficult a problem now because the atom matching is restricted to corresponding fragments already known. Finally, the new coordinate list of the second structure can be prepared.

## 13. Program *CRYCOM*

The present algorithm has been put to practical use in the *CRYCOM* (CRYstal COMparison) program. This program is made compatible with the Cambridge Structural Database (CSD) (Allen *et al.*, 1979) through the use of the *GEOM*78 program of geometric calculations. For this purpose, *GEOM*78 reads the FDAT structural data entries in CSD-formatted form from a subfile prepared preliminarily by the usual CSD means.

The second function of *GEOM*78 in *CRYCOM* is to recognize the user-defined molecular fragments in the atomic pattern generated from the coordinates. The information necessary to specify a fragment in the input data is the chemical connectivity, and, if necessary, a few geometric parameters to help the program to distinguish geometric isomers with the same connectivity pattern. Such a fragment description also includes some options to define the fragment orthogonal axes and origin, so that they could be assigned automatically in the same way for the same-type fragments.

The input information specific to *CRYCOM* itself is pretty short and includes the following items: symbol of the point-group symmetry of the fragment; the tolerances to restrict the structure-parameter deviations; some optional parameters to specify an operation mode or extra output.

In order to treat more than one fragment type one should prepare a batch of similar input data sets, each containing a fragment description and the necessary *CRYCOM* instructions. As the program begins, the first fragment-type data are entered and all calculations are performed for the corresponding-type substructures. In case of a substructural similarity, the program is run again for the next fragment type, *etc.*, unless the new fragment types are over. Such a step-by-step algorithm makes it possible to treat the structures composed of any number of fragment types – with no significant demand to the computer storage. This is not the case, however, with the number of same-type independent fragments, which increases the necessary computer storage and executing times quadratically.

The necessary affine-normalizer operators are generated in *CRYCOM* according to the space-group sequential number specified in the structural data. In the case of a non-standard space-group setting (recognized from the space-group symbol), the corresponding change to the standard setting is made automatically. Only triclinic, monoclinic and orthorhombic space groups are permitted in the input data to *CRYCOM*. The structures of higher symmetry are expected to be redescribed within a lower-symmetry group, a subgroup of the former space group (see §11).

The latter work can be performed as a preliminary step with another program, *DATREC*. This program provides the transformation of the original crystal structure data to an equivalent form according to the crystal-axis transformation matrix and origin shift specified. (The other function of this program is to generate the structural data records in the *FDAT* formatted form for the structures that are unavailable from CSD, such as those newly determined and inorganic ones.)

A typical sample of the output data from *CRYCOM* includes the following items: a nine-digit code of the matrix to transform crystal axes; the components of the crystal-origin shift vector; the matched description cell parameters of the second structure and their deviations from the corresponding first-structure ones; a list of the corresponding fragment pairs of the two structures and their deviation parameters: the fragment origin distance $d$ and the turn angle $\Omega$.

An extended printout contains more information on the matched fragments, including the Eulerian angles to describe fragment rotations and the operation of fragment symmetry needed to obtain the rotation matching.

The matched-description atomic coordinates of the second structure are generated as a result of an

Table 1. *Published crystal-structure data of* $Pu_3Co$, $Zr_3Co$, $PuBr_3$ *and* $PuCl_3$ (*left*) *and their relation to* $Pu_3Co$ (*right*)

$Pu_3Co$ [*Structure Reports* (SR) (1963). **28**, 17]
*Cmcm*, $a = 3.475$, $b = 10.976$, $c = 9.220$ Å (Reference data set)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Pu(1) | 0 | 0.0778 | $\frac{1}{4}$ |
| Pu(2) | 0 | 0.3678 | 0.0553 |
| Co | 0 | 0.7780 | $\frac{1}{4}$ |

$Zr_3Co$ [SR (1970). **35A**, 53]
*Cmcm*, $a = 3.27$, $b = 10.84$, $c = 8.95$ Å
Cell change: None
Origin shift: $\frac{1}{2}$, 0, $\frac{1}{2}$

| | $x$ | $y$ | $z$ | Atom of $Pu_3Co$* | Distance | Matching symmetry operation |
|---|---|---|---|---|---|---|
| Co | 0 | 0.740 | $\frac{1}{4}$ | Co | 0.02 | $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ |
| Zr(1) | 0 | 0.424 | $\frac{1}{4}$ | Pu(1) | 0.00 | $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ |
| Zr(2) | 0 | 0.135 | 0.05 | Pu(2) | 0.00 | $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ |

$PuBr_3$ [SR (1948). **11**, 282]
*Ccmm*, $a = 12.65$, $b = 4.10$, $c = 9.15$ Å
Cell change: $a' = b$, $b' = -a$, $c' = c$
Origin shift: None

| | $x$ | $y$ | $z$ | Atom of $Pu_3Co$ | Distance | Matching symmetry operation |
|---|---|---|---|---|---|---|
| Pu | 0.25 | 0 | $\frac{1}{4}$ | Co | 0.03 | $x, y, z$ |
| Br(1) | −0.07 | 0 | $\frac{1}{4}$ | Pu(1) | 0.01 | $x, y, z$ |
| Br(2) | 0.36 | 0 | −0.05 | Pu(2) | 0.01 | $x, \bar{y}, \bar{z}$ |

$TbCl_3$ [SR (1964). **29**, 274]
*Cmcm*, $a = 3.86$, $b = 11.71$, $c = 8.48$ Å
Cell change: None
Origin shift: $\frac{1}{2}$, 0, 0

| | $x$ | $y$ | $z$ | Atom of $Pu_3Co$ | Distance | Matching symmetry operation |
|---|---|---|---|---|---|---|
| Tb | 0 | 0.244 | $\frac{1}{4}$ | Co | 0.03 | $\frac{1}{2}+x, \frac{1}{2}+y, z$ |
| Cl(1) | 0 | 0.583 | $\frac{1}{4}$ | Pu(1) | 0.01 | $\frac{1}{2}+x, \frac{1}{2}+y, z$ |
| Cl(2) | 0 | 0.145 | 0.569 | Pu(2) | 0.02 | $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ |

* Atom to which the left-specified atom corresponds.

additional program run, with a structure-correspondence variant number specified in the input data. Optionally, one can obtain the resulting coordinate list permuted according to the recognized atomic correspondence.

## 14. Examples

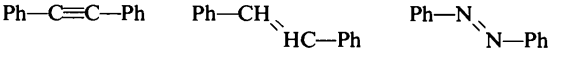
### 14.1. $Pu_3Co$, $Zr_3Co$, $PuBr_3$ *and* $TbCl_3$

The titled structures have been discussed by Parthé & Gelato (1983), who found that the standardized data of the latter two structures fail to exhibit their similarity with those of the former two. Namely, an additional shift of the crystal origin from the standard one was found necessary to bring the different data sets into correspondence.

We made the comparison of these structures on *CRYCOM*, with $Pu_3Co$ taken as the reference. In the input data the 'Any Atom' option was specified. This means that no information was given to *CRYCOM* to recognize the corresponding atom kinds by their chemical element labels.

As a result, we have found that this test problem is successfully solved with our algorithm. The correspondences found between the four structures are given in Table 1, where the published data are related to those of $Pu_3Co$ by indicating the crystal-axis transformation and origin shift, the names of corresponding atoms and associated distances, and the symmetry operations providing individual atom matching.

### 14.2. *Tolane, trans-stilbene and trans-azobenzene*




tolane *trans*-stillbene *trans*-azobenzene

Although the three molecules differ significantly with their configurations about the central fragments, their overall shapes and dimensions are remarkably similar (Fig. 1). Such a molecular similarity thus makes it possible to see the crystal similarity of the three structures.

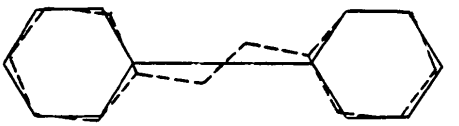


Fig. 1. *Trans*-stilbene (-azobenzene) molecule overlapped as well as possible with that of tolane.

Table 2. *Comparison of the tolane, trans-stilbene and trans-azobenzene crystal structure data from independent X-ray determinations*

| Compound | CSD refcode | Space group | Cell parameters (Å, °) a | b | c | β | Cell choice | Centres occupied Molecule 1 | Molecule 2 | Turn angle (°) Molecule 1 | Molecule 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (*a*) Published data (as retrieved from CSD) | | | | | | | | | | | |
| Tolane | DPHACT01 | $P2_1/a$ | 12.714 | 5.772 | 15.580 | 114.63 | II | 0, 0, 0 | 0, 0, $\frac{1}{2}$ | | |
| | DPHACT02 | $P2_1/a$ | 12.778 | 5.764 | 15.508 | 113.39 | I | $-\frac{1}{2}$, 0, 0 | 0, 0, $\frac{1}{2}$ | | |
| | DPHACT03 | $P2_1/c$ | 15.488 | 5.754 | 12.766 | 113.36 | I | 0, 0, 0 | $\frac{1}{2}$, $\frac{1}{2}$, 0 | | |
| *Trans*-stilbene | TSTILB01 | $P2_1/a$ | 12.382 | 5.720 | 15.936 | 114.15 | II | 0, 0, 0 | 0, 0, $\frac{1}{2}$ | | |
| | TSTILB03 | $P2_1/a$ | 12.287 | 5.660 | 15.478 | 112.03 | I | 0, 0, 0 | 0, $\frac{1}{2}$, $\frac{1}{2}$ | | |
| | TSTILB04 | $P2_1/c$ | 15.709 | 5.723 | 12.374 | 111.90 | I | $\frac{1}{2}$, 0, $\frac{1}{2}$ | 1, 0, 1 | | |
| *Trans*-azobenzene | AZOBEN01 | $P2_1/a$ | 12.144 | 5.756 | 15.396 | 114.08 | II | 0, 0, 0 | 0, 0, $\frac{1}{2}$ | | |
| | AZOBEN02 | $P2_1/c$ | 15.219 | 5.785 | 12.177 | 112.42 | I | $\frac{1}{2}$, 0, $\frac{1}{2}$ | 1, 0, 1 | | |
| (*b*) Transformed data after *CRYCOM* similarity search | | | | | | | | | | | |
| Tolane | DPHACT01 | $P2_1/c$ | 15.535 | 5.772 | 12.714 | 113.44 | I | 0, 0, 0 | $\frac{1}{2}$, $\frac{1}{2}$, 0 | 1.3 | 0.3 |
| | DPHACT02 | $P2_1/c$ | 15.508 | 5.764 | 12.778 | 113.39 | I | 0, 0, 0 | $\frac{1}{2}$, $\frac{1}{2}$, 0 | 0.2 | 0.3 |
| | DPHACT03 | $P2_1/c$ | 15.488 | 5.754 | 12.766 | 113.36 | I | 0, 0, 0 | $\frac{1}{2}$, $\frac{1}{2}$, 0 | 0 | 0 |
| *Trans*-stilbene | TSTILB01 | $P2_1/c$ | 15.678 | 5.720 | 12.382 | 111.96 | I | 0, 0, 0 | $\frac{1}{2}$, $\frac{1}{2}$, 0 | 2.9 | 4.2 |
| | TSTILB03 | $P2_1/c$ | 15.478 | 5.660 | 12.287 | 112.03 | I | 0, 0, 0 | $\frac{1}{2}$, $\frac{1}{2}$, 0 | 2.3 | 4.8 |
| | TSTILB04 | $P2_1/c$ | 15.709 | 5.723 | 12.374 | 111.90 | I | 0, 0, 0 | $\frac{1}{2}$, $\frac{1}{2}$, 0 | 3.0 | 4.1 |
| *Trans*-azobenzene | AZOBEN01 | $P2_1/c$ | 15.230 | 5.756 | 12.144 | 112.64 | I | 0, 0, 0 | $\frac{1}{2}$, $\frac{1}{2}$, 0 | 3.1 | 6.4 |
| | AZOBEN02 | $P2_1/c$ | 15.219 | 5.785 | 12.177 | 112.42 | I | 0, 0, 0 | $\frac{1}{2}$, $\frac{1}{2}$, 0 | 3.1 | 6.7 |

For each compound the crystal structures were published independently more than once. The available data, as retrieved from CSD, are present in the upper part of Table 2. A simple inspection of them does not allow someone to be certain of the isostructurality of the three compounds. Moreover, the structure identity of the same-compound determinations is also not evident. Indeed, as one can easily see, the structural data sets correspond to different settings and asymmetric unit choices. In this context, the different space-group settings ($P2_1/c$ and $P2_1/a$) are only a 'visible' aspect of the problem, while a hidden (and to some extent confusing) one is the occurrence of two different cell choices (denoted I and II in Table 1) with very close cell dimensions (see Fig. 2).

Another obstacle is that two independent molecules, each possessing an approximate molecular symmetry, are present (thus increasing furthermore the number of ways by which the atoms of the different structures should be compared with each other in order to find their correspondence).

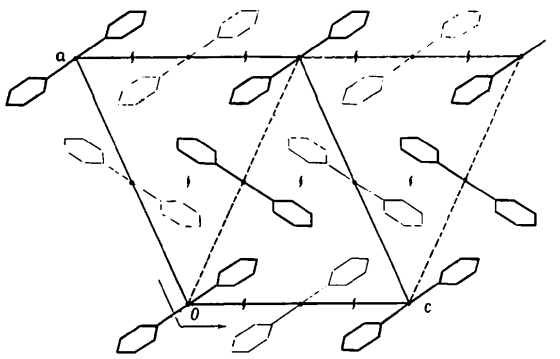



Fig. 2. Structure of tolane viewed along 010. The two cell choices (I and II) are shown by solid and broken lines, respectively.

The given situation was thus found by us quite suitable to demonstrate our method. Assuming DPHACT03 as the reference data, we used *CRYCOM* to search for alternative descriptions of the other structures (structure determinations) that would exhibit an agreement with DPHACT03.

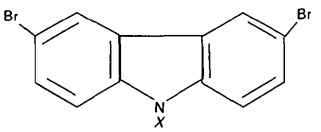
An averaged molecule with the same connectivity of non-H atoms (C/N-atom difference ignored) and an approximate *mmm* symmetry were specified in the input data for each of the three compounds. The three molecular axes were defined parallel to the longest molecular direction, normal to the molecular plane and as a vector product of the former two.

The *CRYCOM* results are given in Table 1(*b*). As one can see immediately, the new descriptions are now identical with respect to their space-group settings, unit-cell choices and representative molecules, while the respective unit-cell parameters are very close to each other. Again, the turn angles of the two independent molecules are also quite small, thus showing that the corresponding molecules in the different structures are rotated in the same way.

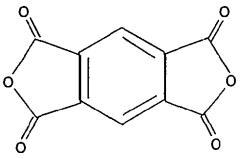
### 14.3. *The* (1:1.5) *molecular complexes of* 2,6-*dibromocarbazole* (*DBC*) *and N-methyl*-2,6-*dibromocarbazole* (*MeDBC*) *with pyromellitic dianhydride* (*PMDA*)

The structures of the titled compounds (DBC-PMDA and MeDBC-PMDA, respectively) (Table 3) have the same symmetry and are remarkably similar with regard to their unit-cell content. The latter includes one carbazole derivative molecule and one of the two independent PMDA molecules in general position while the second PMDA molecule at centre of symmetry (Bulgarovskaya, Zavodnik, Vozzhen-

nikov & Belsky, 1989; Dzyabchenko, Bulgarovskaya, Zavodnik & Stash, 1994). Geometric parameters of the two cells are also roughly similar. No evidence, however, had been available concerning atomic correspondence.




DBC ($X$ = H)
MeDBC ($X$ = Me)




In order to solve this similarity problem, the two structures were compared with each other using *CRYCOM*, with the DBC-PMDA data available matched against the equivalent descriptions of the MeDBC-PMDA structure. The fragments in the input data were described as the whole molecules, with the *mmm* molecular symmetry for PMDA and *mm*2 for DBC and MeDBC.

As a result of this calculation, the two structures were recognized to be similar. The reported and the matched-structure numerical data are presented in Table 3, while Fig. 3 illustrates this result graphically.

As one can see from Table 3, the matched description of MeDBC-PMDA has a different cell choice than that reported, with the $c$-axis length 20.692 Å greater than the former at 17.672 Å, the smallest possible value of this period. Moreover, the new $c$-axis length is not even the closest possible value after the smallest. Instead, a range of five other possible values between 17.672 and 20.692 Å occurs in the lattice.

The latter is important for the following reason. In the structure-standardization method (Parthé & Gelato, 1984), the unique cell is chosen based on the three shortest non-coplanar lattice translations, according to the Niggli reduced-cell main conditions (Niggli, 1928). The example given, however, presents a situation in which the unique structure descriptions are remarkably far from being able to help someone recognize the structural similarity.

### 14.4. *Polymorphous structures of barium (strontium) aluminate*

Barium aluminate, $BaAl_2O_4$, and its strontium isomorph, $SrAl_2O_4$, are observed in the monoclinic and two hexagonal forms (Table 4). While geometric relationships between the two hexagonal structures are trivial, this is not the case with the monoclinic and hexagonal ones.

Table 3. *Similarity of the crystal structures of* (1:1.5) *molecular complexes DBC-PMDA and MeDBC-PMDA*

(*a*) Crystal data: triclinic, $P\bar{1}$, $Z = 2$

| | DBC-PMDA | MeDBC-PMDA | |
|---|---|---|---|
| | Reported | Reported | Matched |
| $a$ | 7.305 | 7.634 | 7.634 |
| $b$ | 8.952 | 9.626 | 9.626 |
| $c$ | 18.558 | 17.672 | 20.692 |
| $\alpha$ | 99.00 | 76.56 | 107.16 |
| $\beta$ | 98.39 | 96.97 | 120.55 |
| $\gamma$ | 94.46 | 85.60 | 85.60 |

(*b*) Deviation parameters for molecules

| | DBC/ MeDBC | PMDA (in general position) | PMDA (at symmetry centre) |
|---|---|---|---|
| Distance (fractional units) | 0.06 | 0.08 | 0 |
| Turn angle (°) | 4.1 | 5.2 | 6.3 |

In order to test *CRYCOM* on this problem, the monoclinic and the $P6_322$ hexagonal structures were used for similarity searching. As a preliminary step to compare the two structures having quite different symmetry, changes to the $P1$ space-group frameworks were made using *DATREC* for the two sets of structural data, with all the symmetry atoms generated and included in the coordinate lists. In addition, the original cell of the hexagonal form was doubled along $b$ to bring the cell volume into correspondence with that of the monoclinic form (see Fig. 4). As a result, the two new sets of structural data, each containing four Ba, eight Al and 16 O atoms were generated.

As a main procedure, the $P1$ description of the monoclinic form was matched against the $P1$-2$b$ description of the hexagonal form as well as all equivalent forms of the latter within the $P1$ group.

While Ba and Al atoms were considered in this procedure as atoms, two alternative approaches have been tested to treat O atoms. In the first approach the O atoms were also treated as individual atoms, while in the second the $AlO_4^-$ tetrahedra, with an

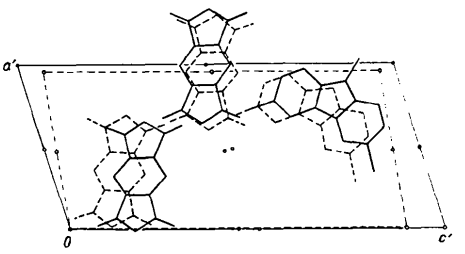



Fig. 3. A (010) view of the matched structure descriptions (symmetry molecules not shown) of DBC-PMDA (solid lines) and MeDMC-PMDA (broken lines).

Table 4. *Crystal data of the* $Ba(Sr)Al_2O_4$ *polymorphs*

| Crystal type | Space group | Z | Cation | Temperature (K) | Cell parameters (Å, °) a | b | c | β | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Hexagonal | $P6_322$ | 1 | Ba | 150 | 5.222 | | 8.766 | | (*a*) |
| | | | Sr | 680 | 5.147 | | 8.479 | | (*a*) |
| Hexagonal | $P6_3$ | 4 | Ba | 25 | 10.452 | | 8.799 | | (*b*) |
| | | | Sr | 25 | 10.470 | | 8.819 | | (*a*) |
| Monoclinic | $P2_1$ | 4 | Ba | −65 | 8.438 | 8.812 | 5.147 | 93.14 | (*a*) |
| | | | Sr | 25 | 8.447 | 8.816 | 5.163 | 93.42 | (*c*) |

References: (*a*) Ivanov, Bush & Zhurov (1989); (*b*) Hörkner & Müller-Buschbaum (1979); (*c*) Schulze & Müller-Buschbaum (1981).

idealized $\bar{4}3m$ symmetry, were introduced as molecular fragments instead of O atoms.

The *CRYCOM* search yielded a total of 24 variants of structural similarity between the two structures (see Table 6 for one of them), in accordance with the actual $P6_322$ symmetry of the hexagonal form (and the corresponding pseudosymmetry of the monoclinic form). Each of the variants assumes the cell change from 'double hexagonal' to that of orthogonal shape, and a correct shift of the crystal origin (see Fig. 4, right). The transformation matrix of each variant is characterized by a negative determinant reflecting opposite chirality of the two published atomic coordinate sets. One may judge the similarity of the two structures by looking at Fig. 5.

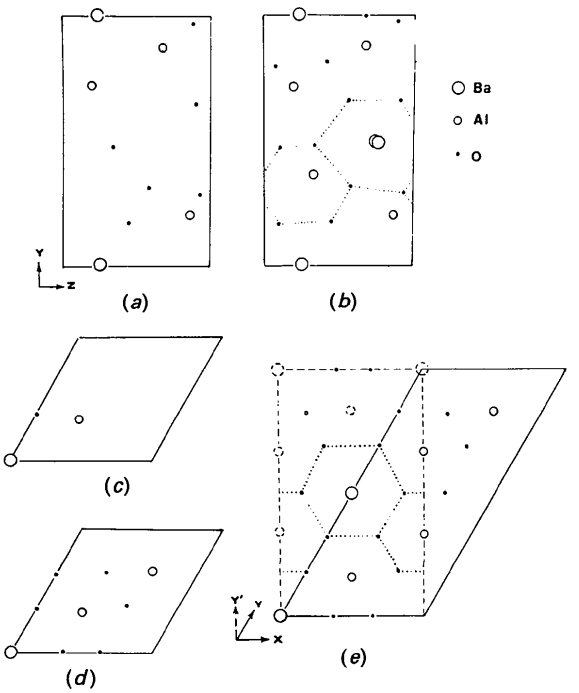



Fig. 4. Graphical structure descriptions of the two forms of barium aluminate. (*a*) Published $P2_1$ and (*b*) generated $P1$ descriptions of the monoclinic form. (*c*) Published, (*d*) $P1$ and (*e*) the double-cell $P1$ descriptions of the hexagonal form. Broken lines show an equivalent description matched to that one at the top part of the picture. (For better similarity recognition of the two pictures by eye the auxiliary lines are indicated by dots).

Table 5. *Atomic coordinates of the* $P6_322$ *hexagonal form of* $BaAl_2O_4$ *(Ivanov, Bush & Zhurov, 1989)*

| Atom | Wyckoff position | x | y | z |
|---|---|---|---|---|
| Ba | 2(*b*) | 0 | 0 | $\frac{1}{4}$ |
| Al | 4(*f*) | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.054 |
| O1 | 2(*c*) | $\frac{1}{3}$ | $\frac{2}{3}$ | $\frac{1}{4}$ |
| O2 | 6(*g*) | 0.360 | 0 | 0 |

Both the individual-atom and the tetrahedron approaches have been successful to solve the similarity problem of O atoms. The former approach, however, was found to require the computer capacity and execution time an order of magnitude as great as the second. Such a considerable difference can be explained by not only the different numbers of the participating fragments, but a better chance of recog-

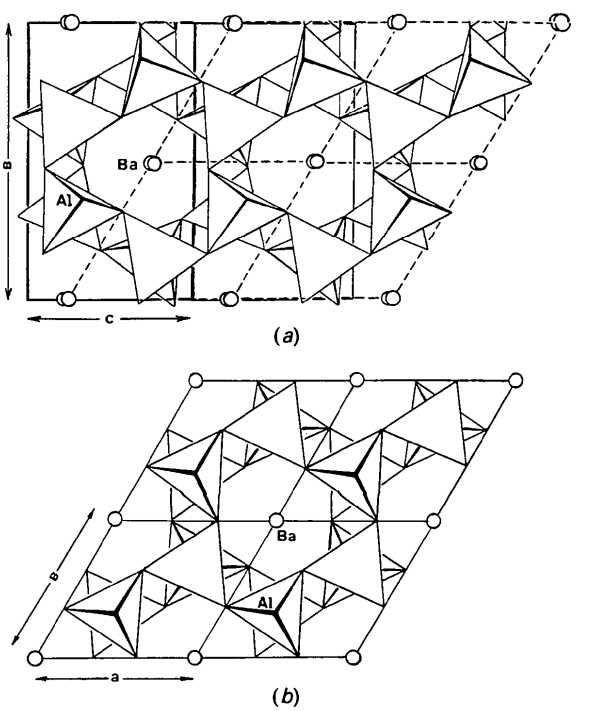



Fig. 5. The best view of the two forms of barium aluninate showing them to be similar. (*a*) (100) projection of the monoclinic structure. Broken lines indicate the pseudo-hexagonal lattice. (*b*) (001) projection of the hexagonal structure.

Table 6. *Relation between the monoclinic and the $P6_322$ hexagonal structures of* $BaAl_2O_4$

| *P*1 description of the monoclinic form | | | | Matched *P*1 description of the $P6_322$ hexagonal form (original coordinates from Table 5)<br>Cell change **a′ = c, b′ = −a−2b, c′ = −a**<br>Origin shift 0.2405, 0, 0.2507 | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Cell parameters (Å, °) | | | | | | | | | |
| *a* | *b* | *c* | *β* | *a* | *b* | *c* | *β* | | |
| 8.438 | 8.812 | 5.156 | 93.14 | 8.766 | 9.045 | 5.222 | 90.00 | | |
| Atomic coordinates | | | | | | | | Deviation parameters of $AlO_4^-$ tetrahedron: | |
| | *x* | *y* | *z** | | *x* | *y* | *z* | Distance | Turn angle (°) |
| Ba(1) | 0.4905 | 0.0000 | 0.2507 | Ba | 0.4905 | 0.0000 | 0.2507 | | |
| Ba(1′) | 0.5095 | 0.5000 | 0.7493 | Ba′ | 0.4905 | 0.5000 | 0.7507 | | |
| Ba(2) | 1.0292 | −0.0071 | 0.2020 | Ba(1) | 0.9905 | 0.0000 | 0.2507 | | |
| Ba(2′) | 0.9708 | 0.4929 | 0.7980 | Ba′(1) | 0.9905 | 0.5000 | 0.7507 | | |
| Al(1) | 0.1895 | 0.8314 | 0.7158 | Al(2) | 0.1865 | 0.8333 | 0.7507 | 0.03 | 17.6 |
| Al(1′) | 0.8105 | 0.3314 | 0.2842 | Al′(1) | 0.7945 | 0.3333 | 0.2507 | 0.04 | 13.9 |
| Al(2) | 0.7997 | 0.8394 | 0.7287 | Al(1) | 0.7945 | 0.8333 | 0.7507 | 0.02 | 25.3 |
| Al(2′) | 0.2003 | 0.3394 | 0.2713 | Al′(2) | 0.1865 | 0.3333 | 0.2507 | 0.02 | 23.0 |
| Al(3) | 0.7087 | 0.6685 | 0.2236 | Al(3) | 0.6865 | 0.6667 | 0.2507 | 0.04 | 20.2 |
| Al(3′) | 0.2913 | 0.1685 | 0.7764 | Al′ | 0.2945 | 0.1667 | 0.7507 | 0.04 | 16.0 |
| Al(4) | 0.6809 | 0.1707 | 0.7975 | Al′(3) | 0.6865 | 0.1667 | 0.7507 | 0.05 | 21.4 |
| Al(4′) | 0.3191 | 0.6707 | 0.2025 | Al | 0.2945 | 0.6667 | 0.2507 | 0.06 | 24.6 |

* From Schulze & Müller-Buschbaum (1981) for the strontium isomorph.

nizing similarity with the fragment rotations also taken into consideration.

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# The Optical Activity and Absolute Optical Chirality of $NaNH_4SO_4.2H_2O$


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### Abstract

The three independent tensor components of the gyration tensor of a crystal of the orthorhombic enantiomorphic compound $NaNH_4SO_4.2H_2O$, sodium ammonium sulfate dihydrate (SASD), are measured for the first time using the HAUP method. A full structure analysis ($R = 0.03$) has been per-