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Substructures and their application in crystal structure analysis

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Abstract. This paper presents various substructure definitions which are used mainly for crystal chemical discussions and for crystal structure analysis purposes. It is directed to the fact that a distinction has to be made between how the substructures should occur in nature, and those substructures which are specified for crystal structure determinations and accomodated to the set of measured structure factors employed in analyzing the structure. For the first case the *ideal substructure* or, if the substructure is disturbed, the *idealized substructures* are defined. The substructure definitions according to Buerger (1959) and Takéuchi (1972) specified for the second case are discussed. The underlying principles for the structure determination are pointed out, if a substructure is used.

Introduction

In past years the number of structure analyses increased in which an existing substructure was utilized as an aid for crystal structure determination. Several substructure definitions are in use. It is the intention of the following chapters to outline the properties of substructures occurring either as ideal substructures or as disturbed substructures, to define them, and to oppose them with two practical substructure definitions. One of these definitions is after Buerger (1959) and the other after Takéuchi (1972). These practical substructure definitions are accomodated to the measured structure factors. They are then discussed with respect to their generally different symmetry properties and to the general different Fourier transformations. In the last chapter an example demonstrates a series of the terms used in this paper. The mineral stannoidite was chosen as the example.

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The general character of substructures

The *ideal substructure* is defined as a structure component with a higher space group symmetry than that of the full structure or with a smaller unit cell being the *subcell* or, as in most cases, with both properties. The space group of the full structure is a subgroup of that of the substructure. According to this definition the ideal substructure is a set S consisting of g atoms S_i, $i = 1, \ldots, g$ in the entire cell being a subset of the superset G containing all atoms G_i, $i = 1, \ldots, p$ in the full structure, so that

$$S \subset G \text{ holds.} \tag{2.1}$$

All substructure atoms can be generated by the space group symmetry operations $R_j, j = 1, \ldots, n_s$ and the translation group T_s from the asymmetric unit S_a of the substructure. This group $R = \{T_s, (R_j, j = 1, \ldots, n_s)\}$ contains all symmetry operations of the full structure forming the group $D = \{T_g, (D_j, j = 1, \ldots, n_t)\}$ where T_g is the translation group of the full structure and D_j, $j = 1, \ldots, n_g$ are the space group symmetry elements of the full structure being a subgroup of R so that

$$D \subset R \text{ holds.} \tag{2.2}$$

The subunit vectors are designated by **A**, **B**, **C**, and the sublattice constants by A, B, C, a_s, β_s, γ_s. Since the unit vectors of the full structure are a linear combination of the subunit vectors **A**, **B**, **C** with integral coefficients, the transformation matrix $(U) = (s_{ij})$ with $i = 1, 2, 3$ and $j = 1, 2, 3$ for the transformation from the base **A**, **B**, **C** to the base **a**, **b**, **c** consists completely of integral numbers.

The number N of subcells in the entire cell is determined by $N = \det(U)$. Due to the subgroup-supergroup relation between the symmetries of the substructure and the entire structure, it is possible to choose a coordinate system for the entire structure lying parallel to that of the substructure so that

$$\begin{aligned} \mathbf{a}' &= N_1\ \mathbf{A} \\ \mathbf{b}' &= N_2\ \mathbf{B} \\ \mathbf{c}' &= N_3\ \mathbf{C}. \end{aligned} \tag{2.3}$$

The matrix $(\mathbf{X}) = (\xi_{ij})$, $(i = 1, 2, 3; j = 1, 2, 3)$ belongs to the transformation of **a**, **b**, **c** into **a**′, **b**′, **c**′ where the coefficients ξ_{ij} are integers possibly plus $^1/_2$, $^1/_3$, or $^2/_3$ if the original lattice is a nonprimitive one. Since $[\mathbf{a}', \mathbf{b}', \mathbf{c}'] = (X)(U)\{\mathbf{A}, \mathbf{B}, \mathbf{C}\}$ the numbers N_1, N_2, and N_3 are calculated according to

$$N_i = \sum_{j=1}^{3} \xi_{ij}\, s_{ji} \text{ with } i = 1, 2, 3. \tag{2.3a}$$

The number of subcells now can be obtained by

$$N' = N_1 \cdot N_2 \cdot N_3 \tag{2.4}$$

which has to be an integer.

In many cases the lowest cell primitivity gets lost for the sake of convenience so that the new cell is no longer a reduced one. *Henceforth it will be assumed that such a coordinate system for the entire structure has been chosen of which the axes will be denoted by* **a**, **b**, **c** *instead of* **a**′, **b**′, **c**′, *and the number of subcells within the entire cell by N instead of N′.*

The collection S of all substructure atoms lying within the entire cell can be comprised by the set relation

$$\begin{aligned}&S=\{S_i, i=1,\ldots,g \mid S_i(\mathbf{x})=[S_a(\mathbf{x})\cdot \overparen{R_j]\,\delta}\,(\mathbf{x}-n_1\,\mathbf{A}-n_2\,\mathbf{B}-n_3\,\mathbf{C})\\ &\text{for all}\, n_i=1,\ldots,N_i \text{ with } i=1,2,3 \text{ and } j=1,\ldots n_s\}\end{aligned} \tag{2.5}$$

where $\delta(\mathbf{x})$ is the three-dimensional Delta-Dirac-function.

In X-ray crystallography the atomic function of interest is the electron density distribution $\varrho(\mathbf{x})$ respectively $\varrho(\mathbf{X})$, where $\mathbf{x}$ and $\mathbf{X}$ mean $\mathbf{x}=x\mathbf{a}+y\mathbf{b}+z\mathbf{c}$ and $\mathbf{X}=X\mathbf{A}+Y\mathbf{B}+Z\mathbf{C}$ with x,y,z and X,Y,Z being the fractional coordinates of the atomic positions within the entire cell, respectively subcell. The electron density distribution of the substructure in the entire cell can be attained by forming the normalized sum S of all partial electron density distributions, so that analogously to (2.5) the following equation holds after having substituted S by $\varrho(\mathbf{x})$, S_i by $\varrho_i(\mathbf{x})$ etc.:

$$\begin{aligned}\varrho_S(\mathbf{x})&=S\,\{\varrho_{S_i}(\mathbf{x}),\ i=1,\ldots,g \mid \varrho_{S_i}(\mathbf{x})\\ &=[\varrho_{S_a}(\mathbf{x})\cdot \overparen{R_j)\,\delta}\,(\mathbf{x}-n_1\,\mathbf{A}-n_2\,\mathbf{B}-n_3\,\mathbf{C})\\ \text{for all } n_i&=1,\ldots,N_i \text{ with } i=1,2,3, \text{ and } j=1,\ldots n_s\}.\end{aligned} \tag{2.6}$$

In practical use one also speaks of a substructure when the high symmetrical arrangement of the atoms is disturbed by small deformations due to distortions, by substitution of some atoms by another kind of atoms, respectively groups of atoms or by a combination of both possibilities. The distortions cause small shifts of the atoms out of their ideal substructure positions. In the case of the substitution structures an atom A will be replaced after a subperiod or a special substructure symmetry operation by an atom B. If we supply correction functions by shifting the atoms in a distortion structure by a vector $\Delta\mathbf{x}$ to the ideal substructure position we define the set $S'(\mathbf{x})$ consisting of virtual atoms lying on the ideal substructure positions so that the following relation holds:

$$S'(\mathbf{x})=\{S'_i(\mathbf{x}),\ i=1,\ldots,g \mid S'_i(\mathbf{x})=\overparen{S_i(\mathbf{x})\,\delta}\,(\mathbf{x}-\Delta\mathbf{x})\}. \tag{2.7}$$

In a substitution structure the set S' is attained by multiplying the partial electron density distribution by an appropiate function $E(\mathbf{x})$ so that the following relation holds:

$$S'(\mathbf{x})=\{S'_i(\mathbf{x}),\ i=1,\ldots,g \mid S'_i(\mathbf{x})=S_i(\mathbf{x})\cdot E(\mathbf{x})\}. \tag{2.8}$$

If both disturbances are present both corrections have to be applied subsequently. For all three cases the following relations hold:

$$S' \not\subset G, \tag{2.9}$$

$$S \subset G. \tag{2.10}$$

All structures to which a set S' can be assigned are said to have an *idealized substructure* adjoined.

The ideal substructure comprises only a part of the atoms of the full structure, in disturbed substructures the number of the substructure atoms per entire cell is less or equal to the number of the atoms in the full structure.

For all substructures a complementary structure is defined by the following relation:

$$\text{substructure} + \text{complementary structure} = \text{full structure}. \tag{2.11}$$

An ideal substructure has an *ideal complementary structure*. In structures with disturbed substructures the set of those atoms which have nothing to do with the substructure is also called ideal complementary structure.

For the electron density distribution function $\varrho_s(\mathbf{x})$ of the substructure and $\varrho(\mathbf{x})$ of the full structure the following relations hold:

$$\varrho_s(\mathbf{x}) \leq \varrho(\mathbf{x}) \tag{2.11}$$

in each case with an ideal complementary structure (see below), and

$$\varrho_s(\mathbf{x}) < \varrho(\mathbf{x}) \tag{2.12}$$

in all cases generally without an ideal complementary structure (see below), and

$$\int^{\text{entire cell}} \varrho_s(\mathbf{x})\mathrm{d}\mathbf{x} < \int^{\text{entire cell}} \varrho(\mathbf{x})\mathrm{d}\mathbf{x} \tag{2.13}$$

in each case.

Most of what was stated here is in accordance with the general description of substructure given by Buerger (1959).

In crystal chemistry one would say that the ideal complementary structure consists of the additional atoms which have complicated the simpler structure (Buerger, 1947).

In contrast to the ideal complementary structure there is the *nonideal complementary structure*, the atoms of which belong neither only to the complementary structure nor only to the substructure.

In structures with disturbed substructures an ideal complementary structure need not exist so that in such a case each atom contributes a fraction of the electron density to the substructure and the rest to the complementary structure.

A full structure can have more than one substructure. It is possible that between these substructures superstructure-substructure relations exist. But they also can be independent upon each other as far as this can be allowed by the full structure.

The definitions of a 'practical substructure'

For practical applications, in which the presence of a substructure should be used, two apparently very similar but in fact basically very different definitions of a 'practicable substructure' are employed. The first one was introduced by Buerger (1959), the other by Takeuchi (1972) and others such as Fruen (1953). Since they are used in X-ray analysis one is interested mainly in the electron density distribution $\varrho(\mathbf{x})$.

Buerger's substructure definition is very close to the ideal substructure. The electron density distribution $\varrho_{\mathrm{BS}}(\mathbf{x})$ in Buerger's substructure is defined as comprising that part of the total electron density distribution which conforms to the subperiods and to the higher symmetry compared with that of the full structure or only to one of both. One can approximate it by finding the minimum function of a set of superposed electron density distribution functions $\varrho_p(\mathbf{x}), p = 1, \ldots, q$ computed from $\varrho(\mathbf{x})$ by letting the substructure symmetry operations and subperiods transform it times successively, where q is the number of the symmetry operations of the substructure not contained in the set of the full structure symmetry operations:

$$\varrho_{\mathrm{BS}}(\mathbf{x}) = M\ \{\varrho_p(\mathbf{x}), p = 1, \ldots, q| \tag{3.1}$$

$\varrho_p(\mathbf{x}) = [R_i \cdot \varrho(\mathbf{x})\delta(x - n_1 A - n_2 B - n_3 C)]$, $i = 1, \ldots, q'$ and $n_j = 1, \ldots, N_j$ with $j = 1, 2, 3$ and where q' is the number of the necessary space group operations including the identity operation so that $q' = n_s - n_t + 1$ and $q = n_s - n_t + N_1 + N_2 + N_3 - 2\}$.
n_s, n_t and N_j, $j = 1, 2, 3$ are defined in Chapter 2 where the choice of the coordinate system is also established. Redundant operations, e.g., the full structure space group operations, would not change the result. The complementary electron density distribution $\varrho_{\mathrm{BC}}(\mathbf{x})$ is defined by:

$$\varrho_{\mathrm{BC}}(\mathbf{x}) = \varrho(\mathbf{x}) - \varrho_{\mathrm{BS}}(\mathbf{x}). \tag{3.2}$$

In contrast to Buerger's substructure definition, Takéuchi's substructure is the N-fold superposition of the electron density distribution $\varrho(\mathbf{x})$ of the full structure with itself having been shifted N times along the vectors $n_1\mathbf{A} + n_2\mathbf{B} + n_3\mathbf{C}$ with $n_i = 1, \ldots, N_i$ where $i = 1, 2, 3$ and $N_1 \cdot N_2 \cdot N_3 = N$. This fulfills the condition $N = V_{\text{entire cell}}/V_{\text{subcell}}$ so that its electron density distribution can be written according to Taxer and Weick (1978) as a convolution product of the electron density distribution $\varrho(\mathbf{x})$ of the full structure and an appropiate point function in the following equation:

$$\begin{aligned}\varrho_{\mathrm{TS}}(\mathbf{x}) &= \frac{1}{N_1 \cdot N_2 \cdot N_3} \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \sum_{n_3=1}^{N_3} [\delta(\mathbf{x} - n_1\,\mathbf{A} - n_2\,\mathbf{B} - n_3\,\overset{\frown}{\mathbf{C})\ \varrho}\,(\mathbf{x})] \\ &= \langle \varrho(\mathbf{x}) \rangle_{\text{subcell}}.\end{aligned} \tag{3.3}$$

Here also one should be reminded of the choice of the coordinate system in Chapter 2.

So ϱ_{TS} is nothing else than the mean electron density distribution taken over all subcells superposed upon each other. The electron density distribution of the complementary structure, $\varrho_{\mathrm{TC}}(\mathbf{x})$, is to be calculated according to:

$$\varrho_{\mathrm{TC}}(\mathbf{x}) = \varrho(\mathbf{x}) - \varrho_{\mathrm{TS}}(\mathbf{x}). \tag{3.4}$$

From this equation, after substituting $\varrho_{\mathrm{TS}}(\mathbf{x})$ by (3.3), the following important relation can be derived:

$$\sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \sum_{n_3=1}^{N_3} \varrho_{\mathrm{TC}}(\mathbf{x} + n_1\mathbf{A} + n_2\mathbf{B} + n_3\mathbf{C}) = 0. \tag{3.5}$$

It should be recognized that the electron density distribution $\varrho_{\mathrm{TS}}(\mathbf{x})$ in Takéuchi's substructure has nothing to do with the electron density distribution in Buerger's substructure (Taxer and Weick, 1978). In contrast to Buerger's complementary structure, the function $\varrho_{\mathrm{TC}}(\mathbf{x})$ consists of negative and positive values, whereas $\varrho_{\mathrm{BC}}(\mathbf{x})$ is positive everywhere.

Takéuchi's substructure definition cannot be applied in contrast to Buerger's substructure definition if the ideal substructure is characterized only by higher symmetry and not by a smaller unit cell, i.e., $N = 1$.

A third practical substructure (Taxer and Weick, private communication, 1979) is defined by

$$\varrho_{\mathrm{HS}}(\mathbf{x}) = \frac{1}{q'}\left[\sum_{j=n_t+1}^{n_s} R_j\,\varrho_{\mathrm{TS}}(\mathbf{x})\right] \text{with } q' = n_s - n_t + 1. \tag{3.6}$$

The letter H refers to the higher symmetry in it than in $\varrho_{\mathrm{TS}}(\mathbf{x})$. It is mentioned here for completeness, but it is not dealt with in this paper.

The symmetry in the practical substructures

Buerger's substructure shows the higher space group symmetry of the ideal substructure as defined in chapter 2, while Takéuchi's substructure generally does not.

That the symmetry $\varrho_{\mathrm{TS}}(\mathbf{x})$ generally is not higher than that of the full structure is due to the fact that the atoms of both, the ideal and nonideal complementary structure, belong to Takéuchi's substructure. There they get a small weight since in the general case no atoms superpose after the superposition of the subcells, except the atoms of the ideal or disturbed substructure.

Since the space group of the full structure is a subgroup of that of the ideal substructure, the mean electron density distribution $\varrho_{\mathrm{TS}}(\mathbf{x})$ has at least the full structure symmetry and is never lower. The subcell parameters must fulfill all

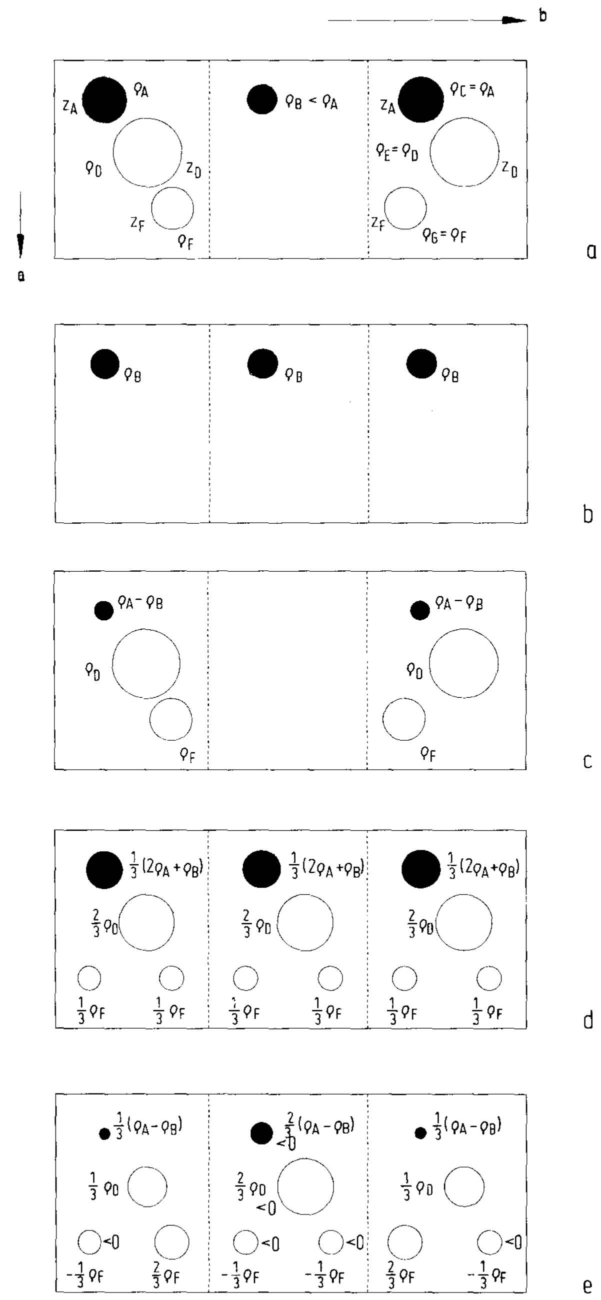
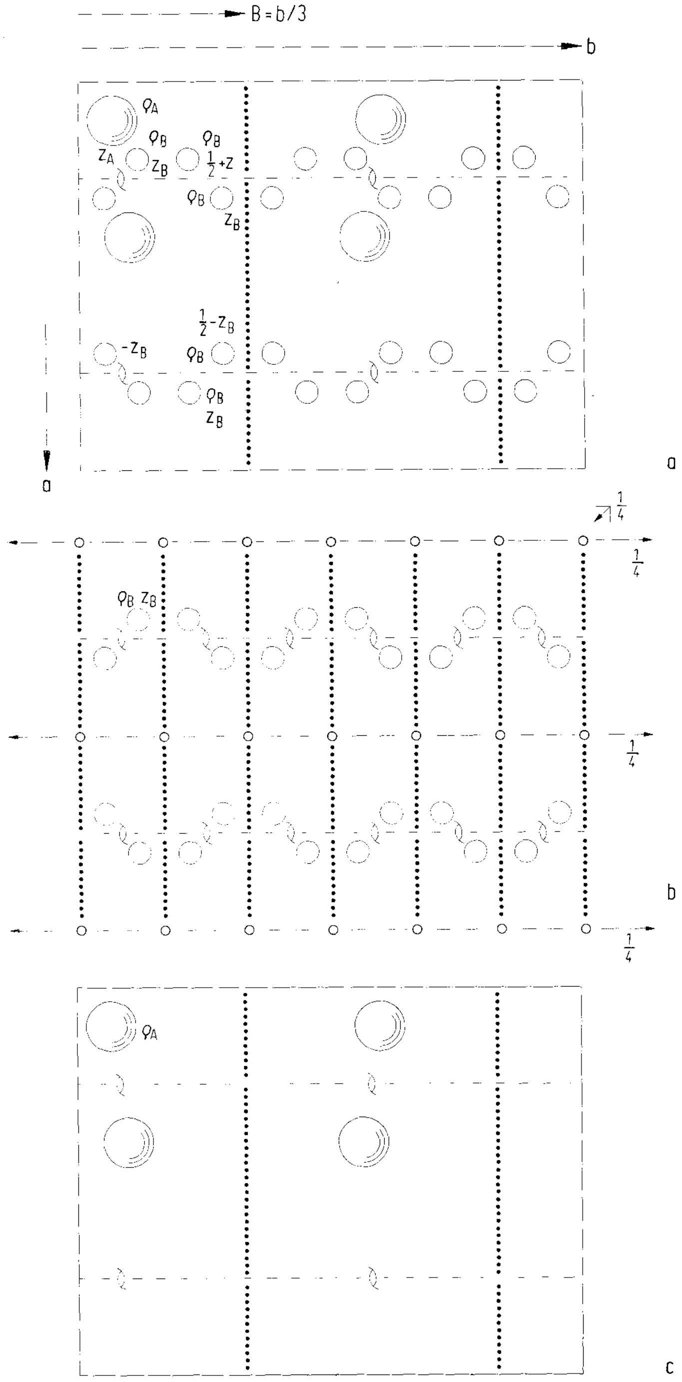


Fig. 1. a The projection of some structure with a substructure characterized by a smaller unit cell; **b** Buerger's substructure; **c** Buerger's complementary structure; **d** Takéuchi's substructure; **e** Takéuchi's complementary structure


B = b/3
b
ρA
ρB
ρB
zA
zB
1/2+z
ρB
zB
1/2-zB
-zB
ρB
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a
a
1/4
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ρB zB
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b
ρA
c

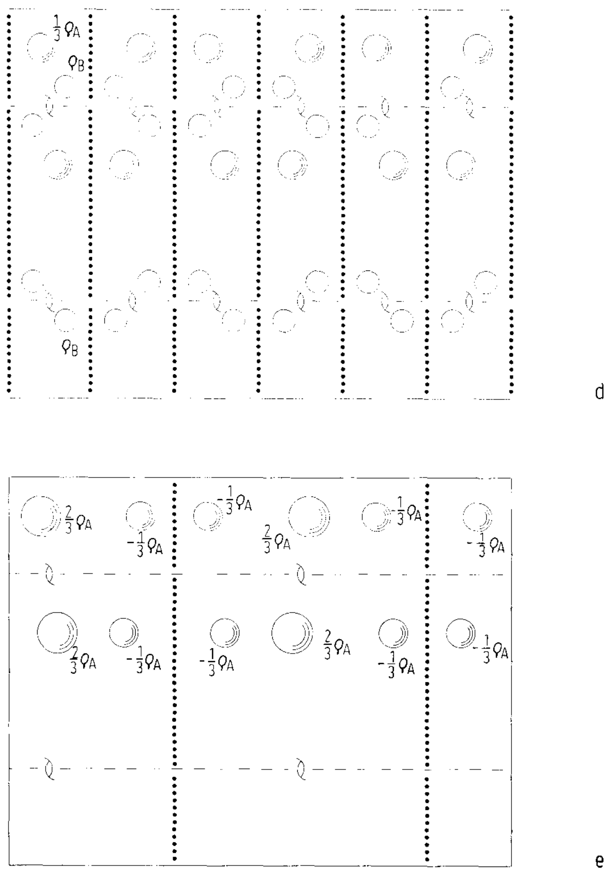
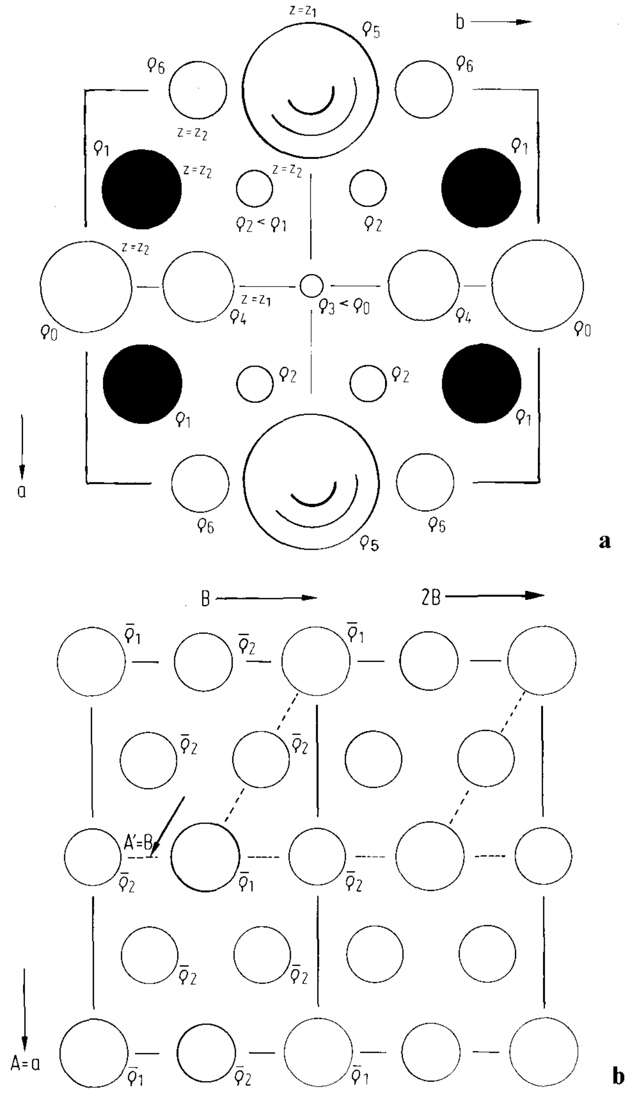


Fig. 2. Symmetry properties in the practical substructures and complementary structures. **a** Full structure, space group $Pbc2_1$; **b** Buerger's substructure, space group $Pbcn$ (the 2_1-axes$\|$**a** are not drawn); **c** Buerger's complementary structure, space group $Pbc2_1$; **d** Takéuchi's substructure, space group $Pbc2_1$; **e** Takéuchi's complementary structure, space group $Pbc2_1$. The anti-and-rational diminution-symmetries are not symbolized and can be recognized by looking to the weight, sign, and location of the atoms only

requirements of the space group of the idealized substructure, i.e. the correct Bravais lattice is an important condition for the occurrence of the higher symmetry. This can be seen from the fact that each atom in the full structure is located in one of the subcells which subdivide the entire cell. The symmetry elements of the full structure are located in one of the subcells. When we construct the mean electron density distribution $\varrho_{\mathrm{TS}}(\mathbf{x})$ the symmetry elements of the full structure are also propagated about the entire cell correspondingly to the atoms by the folding operations. Due to the prior condition that the set of full structure symmetry elements is a subset of the substructure symmetry elements the symmetry in $\varrho_{TS}(\mathbf{x})$ is not lower than in $\varrho(\mathbf{x})$.

The symmetry in $\varrho_{TS}(\mathbf{x})$ can in special cases be higher than that of the full structure. Figure 3 demonstrates an example where the symmetry of the full structure is orthorhombic and that of ϱ_{TS} is hexagonal. In this special case the ratio of the subcell parameteters hexagonal. In this special case the ratio of the subcell parameteters A and B must be $\sqrt{3}$, or $\frac{p}{q}\sqrt{3}$ with p, q integers.



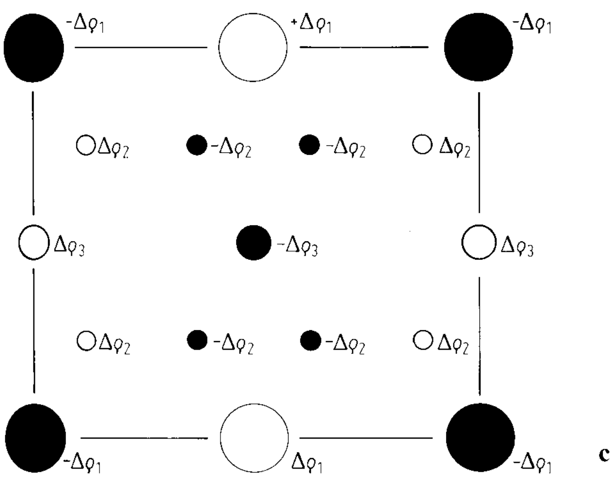


Fig. 3. A special case of substructure: the symmetry in Takéuchi's substructure is higher than in the full structure. **a** Full structure, $\varrho(\mathbf{x})$. The electron density about the atoms is symbolized by the length of the radius of the circles. The electron densities are: $\varrho_0 = 4\,[e^-/\text{Å}3]$, $\varrho_1 = 3.4\,[e^-/\text{Å}^3]$, $\varrho_2 = 1.6\,[e^-/\text{Å}^3]$, $\varrho_3 = 1\,[e^-/\text{Å}^3]$, $\varrho_4 = 3\,[e^-/\text{Å}^3]$, $\varrho_5 = 6\,[e^-/\text{Å}^3]$, and $\varrho_6 = 2.5\,[e^-/\text{Å}^3]$, so that $\varrho_0 + \varrho_3 = \varrho_1 + \varrho_2$, $\varrho_5 = 2\varrho_4$, and $\varrho_2 < \varrho_1$, and $\varrho_3 < \varrho_0$; **b** Takéuchi's substructure, ϱ_{TS}: $\bar{\varrho}_1 = \frac{1}{2}\varrho_5 = \varrho_4$, $\bar{\varrho}_2 = \frac{1}{2}(\varrho_0 + \varrho_3) = \frac{1}{2}(\varrho_1 + \varrho_2)$; **c** Takéuchi's complementary structure, ϱ_{TC}: $\Delta\varrho_1 = -\frac{1}{2}\varrho_5$, $\Delta\varrho_2 = \frac{1}{2}(\varrho_1 - \varrho_2)$, $\Delta\varrho_3 = \frac{1}{2}(\varrho_0 - \varrho_3)$

The tables prepared by Neubüser and Wondraschek (1969, 1970), contain all maximal subgroups and minimal supergroups to each space group.

The complementary structures always possess at least the full structure symmetry. In Takéuchi's complementary structure antisymmetry like transformations can be introduced. In fact this should be called 'anti- and diminution-symmetries' or 'anti-and-rational weight change-symmetries' since in addition to a sign change the motif will be multiplied by the rational fraction $1/(N-1)$, respectively $1/(N_i - 1)$ with $i = 1, 2, 3$ or by its inverse after the operation belonging to a space or translation group. No symbols have been invented so one has to study them in Figures 1e, 2e, and 3c by looking at the weight, sign, and position of the special 'atoms' which are 'equivalent' by these kinds of symmetries.

Figure 2 demonstrates the space group symmetry elements in $\varrho_{\mathrm{BS}}(\mathbf{x})$, $\varrho_{\mathrm{TS}}(\mathbf{x})$, $\varrho_{\mathrm{BC}}(\mathbf{x})$, and $\varrho_{\mathrm{TC}}(\mathbf{x})$.

It is always possible to construct a mean structure $\langle\varrho(\mathbf{x})\rangle_{\text{subcell}}$, with any integral value for N, respectively N_1, N_2, N_3, which makes sense mainly when a substructure can be recognized. In the theory of OD-structures by Dornberger-Schiff (1966) we find the 'superposition structure' which is another application of the mean structure. Its interpretation is different in each case of application. In our case the characteristic properties of the adjoined ideal substruture to which the higher symmetry and the existence of complementary structure belong form the secondary conditions by which a solution of the structure problem can be established.

The reciprocal space of the substructure and of the complementary structure

Since it is desired to have a separated set of measured data in the reciprocal space which can be easily handled for the determination of the substructure and the complementary structure, the definition of the practical substructure has been required. Each definition is a compromise in which the character of the ideal or idealized substructure can get lost for the sake of an easy interpretation of the measured structure factors.

The Fourier transformation of the electron density distribution of Buerger's substructure, $F_{\mathrm{BS}}(\mathbf{h}) = \mathfrak{F}[\varrho_{\mathrm{BS}}(\mathbf{x})]$, is zero everywhere except at those reciprocal lattice points $U_{\mathrm{BS}}(\mathbf{h})$ which belong to the reciprocal superlattice of the substructure and which do not belong to the set of locations where extinctions due to the substructure space group take place. The Fourier transformation of the complementary structure $F_{\mathrm{BC}}(\mathbf{h})$ is contained in both, the point set E_{BC} comprising the 'excess points'[1] (Buerger, 1959) and the points set U_{BS}, in short, in *all* nonextinguished reflections of the crystal, forming the set H. The set of Buerger's excess points comprise also the 'extinguished' reflections in the reciprocal lattice of the substructure. Therefore, it is not allowed to compute the Patterson synthesis of $\varrho_{\mathrm{BC}}(\mathbf{x})$ being equal to the function $\varrho_{\mathrm{BC}}(\mathbf{u}) \neq \overset{2}{\tilde{\varrho}}_{\mathrm{BC}}(\mathbf{x})$ with the intensities located at the excess points only, but with all intensities of the total reciprocal space. Of course, for this it would be necessary to correct all the intensities at U_{BS} in such a way as to get rid of the influence of the substructure. This is nearly impossible, at least the effort would be too large as compared with the result which can be obtained by simpler methods. In order to calculate the structure factors of the complementary structure, the right form factor curves are not available except for the atoms of the ideal complementary structure.

In the case of the practical substructure defined by Takéuchi (1972) the reciprocal space of the crystal can be decomposed into strictly separated sets of the reciprocal lattice points. The structure factors at the points in one of them have contributions only from the substructure, $\varrho_{\mathrm{TS}}(\mathbf{x})$; in the other set only from the complementary structure, $\varrho_{\mathrm{TC}}(\mathbf{x})$ (Taxer and Weick, 1978). The

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[1] The excess points E_{C} are defined as those points of the reciprocal lattice which do not belong to the set of points U_{S}, so that $E_{\mathrm{C}} = \bar{H}(U_{\mathrm{S}})$, which means that E_{C} is the complementary set of H related to U_{S}, where $H = \{\mathbf{h} \,|\, \mathbf{h} = h\mathbf{a}^* + k\,\mathbf{b}^* + l\mathbf{c}^*\}$, and, if $U_{\mathrm{S}} = U_{\mathrm{BS}}$, $U_{\mathrm{BS}} = \{\mathbf{H}_{\mathrm{S}} \,|\, \mathbf{H}_{\mathrm{S}} = H \cdot \mathbf{A}^* + k \cdot \mathbf{B}^* + L \cdot \mathbf{C}^*\} - \mathbf{H}_{\mathrm{S}}$ lying at substructure space group extinctions}. For forming $\bar{H}(U_{\mathrm{S}})$ a transformation of $\mathbf{H}_{\mathrm{S}}$ to $\mathbf{h}_{\mathrm{S}}$ has to be made, i.e., the base a^*, b^*, c^* should be used in both, U_{BS} and E_{BS}.

first comprises the 'strong reflections', U_{TS}, the second the 'weak reflections', E_{TC}, which also may be called 'excess points', namely *Takéuchi's excess points*. The weak reflections lie on reciprocal lattice sites which do not belong to the reciprocal superlattice of the substructure. The set of the strong reflections also includes *all* very weak reflections which are lying on the reciprocal superlattice of the substructure, None of these reflections may be considered as extinguished. Those points in this set which may be regarded as extinguished were already registered as that by the full structure. The extinctions due to the possible space group of the possible ideal or at least idealized substructure are not noticed at all.

The origin of the reciprocal space with its nonzero weight being either the structure factor or the intensity always belongs to the reciprocal superlattice of the substructure. The set of the intensities of the weak reflections can be calculated by the Fourier transformation of the folding square of the complementary structure only. The set of the structure factors are calculated by the Fourier transformation of the complementary structure alone (Taxer and Weick, 1978). It is therefore a fact that the electron density distributions of the practical substructure, $\varrho_{\mathrm{TS}}(\mathbf{x})$, and the complementary structure, $\varrho_{\mathrm{TC}}(\mathbf{x})$, scatter coherently, but they do not interfere.

And vice versa, the Patterson synthesis computed by the Fourier transformation of the weak intensities alone yields the convolution square of the complementary structure:

$$P_{\mathrm{TC}}(\mathbf{u}) = \frac{1}{v^2}\,\Sigma\,\Sigma\,\Sigma\; I(hkl)\cdot\cos 2\pi(h\mathbf{u} + k\mathbf{v} + l\mathbf{w})$$

with $\mathbf{u} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ and $hkl \in \{hkl\} \setminus \{HKL\} = H \setminus U_{\mathrm{TS}}$; (4.1)

$$\overset{2}{\varrho}_{\mathrm{TC}}(\mathbf{x}) = P_{\mathrm{TC}}(\mathbf{u}); \tag{4.1a}$$

v is the volume of the entire cell. $P_{\mathrm{TC}}(000)$ is always positive. In each Patterson synthesis $P_{\mathrm{TC}}(\mathbf{u})$ the following relations hold:

$$\sum_{n_1=1}^{N_1}\;\sum_{n_2=1}^{N_2}\;\sum_{n_3=1}^{N_3} P_{\mathrm{TC}}(n_1\mathbf{A} + n_2\mathbf{B} + n_3\mathbf{C}) = 0. \tag{4.2}$$

The amount of maxima and minima being due to vectors between 'atoms' in the complementary structure which are related to each other by space group symmetry operations *and* 'anti-and-diminution symmetry operations' is a multiple of the amount of the Harker vectors due to space group symmetry operations only. These form subsets of the superset of the unconventional Harker vectors. All conventional Harker vectors cause maxima in the Patterson function. The minima are due to vectors between the sets of space group symmetrical 'atoms' where one of the regarded sets consists of negative 'atoms' and the other of positive 'atoms' of the complementary function. For deformation structures sets of symmetrically equivalent 'dipols' are typical in the Patterson function; these dipols consist of a maximum in the close neighborhood of a minimum. Since ϱ_{TS} and the electron density of the idealized substructure need not be identical, the dipol vector needs not be equal to $\Delta\mathbf{x}$ in (2.7).

A substructure with only one genuine subperiod let us say **A**, conditions very simple relations. The weak and strong reflections lie on separated sheets in the reciprocal space. From the relation[2]

$$\sum_{n_1=1}^{N_1} P_{\mathrm{TC}}(n_1\mathbf{A}_1) = 0 \text{ follows that for } N_1 = 2 \text{ and } 3, \tag{4.3}$$

$$P_{\mathrm{TC}}(n_1\mathbf{A}_1) = \frac{-1}{N_1-1} P_{\mathrm{TC}}(000) \text{ for all } n_1 = 1, \dots, N_1-1. \tag{4.4}$$

In a substructure with three genuine subperiods a series of mean electron density distributions $\varrho_{\mathrm{TC}}(\mathbf{x})$ can be computed by the inverse Fourier transformation. It is possible to use deliberately **A** or **B** or **C** as $\mathbf{u}_1$ = subperiod 1 and to use one of the remaining ones as subperiod 2 and the other as subperiod 3, being denoted as $\mathbf{u}_2$ and $\mathbf{u}_3$, respectively. Perhaps a certain sequence may be suggested by the special problem. In any case in the whole there are seven different mean electron density distributions which are possible to be computed. These are:

$$\hat{\varrho}_i^{(1)} = \langle \varrho(\mathbf{x})\rangle_{\mathbf{u}_i} \text{ with } i = 1, 2, 3 \tag{4.5}$$

comprising three different ones,

$$\hat{\varrho}_{ij}^{(2)} = \langle\langle \varrho(\mathbf{x})\rangle_{\mathbf{u}_i}\rangle_{\mathbf{u}_j} \text{ with } i, j = 1, 2, 3 \text{ and } i < j, \tag{4.6}$$

comprising also three different ones,

$$\hat{\varrho}_k^{(3)} = \langle\langle\langle \varrho(\mathbf{x})\rangle_{\mathbf{u}_i}\rangle_{\mathbf{u}_j}\rangle_{\mathbf{u}_k} \text{ with } i \neq j \neq k \tag{4.7}$$

being all identical and, equal to $\varrho_{\mathrm{TC}}(\mathbf{x})$ of the regarded substructure. For their computation by a Fourier synthesis it is necessary to know which set of reflections may be used.

If we construct a substructure only by using $\mathbf{u}_1$ or $\mathbf{u}_2$ or $\mathbf{u}_3$, we subdivide the reciprocal space each time into two sets of reflections: the set of strong reflections $U11$, respectively $U22$, respectively $U33$, and the respective set of weak reflections, $E_{\mathrm{T}}^{(j)}$ (Uii) with $i = 1, 2, 3$ and $j = 1$.

The index j indicates the regarded number of genuine subperiods of the substructure. Regarding the substructure with all three subperiods, we can subdivide the entire reflection set H into a series of reflection subsets which refer to the various mean substructures and complementary structures (see Fig. 4).

---

[2] For deriving the relation (4.3) the electron density functions of the complementary structure in the subcells are denoted $\Delta\varrho_1(\mathbf{x})$, ..., $\Delta\varrho_{N_1}(\mathbf{x})$, respectively. The values of $P_{\mathrm{TC}}(n_j\mathbf{A}) \hat{=} Q_{\mathrm{TC}}(n_j\mathbf{A}) = \tilde{\varrho}_{\mathrm{TC}}(\mathbf{x})$ with $j = 1, \dots, N_1$ can be calculated by

$$P_{\mathrm{TC}}(n_j\mathbf{A}) = \sum_{j=1}^{N_1} \int_{\text{subcell}} \Delta\varrho_i(\mathbf{x}) \cdot \Delta\varrho(\mathbf{x})_{(i+j)\,\mathrm{modulo}\,N_1}\, \mathrm{d}v_{\mathbf{x}}.$$

Reconsidering (3.5) it can be seen immediately that the relations (4.3) and (4.4) hold. For deriving the relation (4.2) one has to continue in the same way

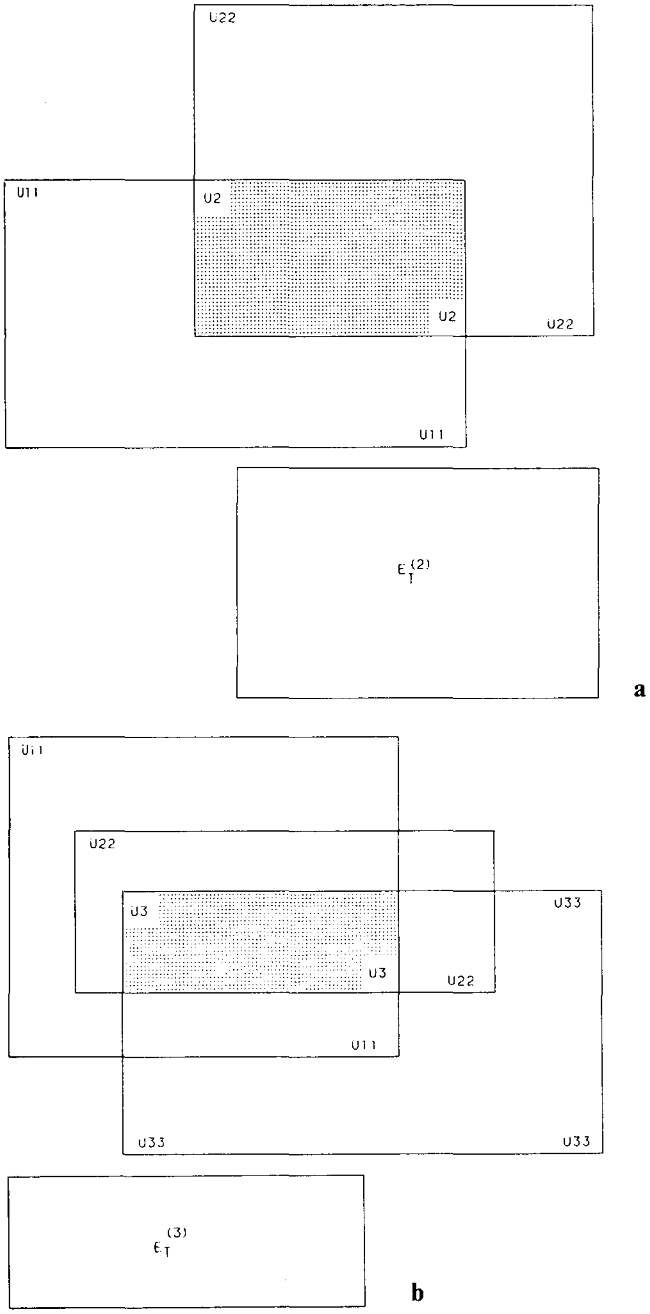

Fig. 4. Symbolic representation of the subsets of the reflection set at the presence of a substructure ϱ_{TS} with two or three subperiods; **a** ϱ_{TS} has two genuine subperiods; **b** ϱ_{TS} has three genuine subperiods. The main subsets like $U11$, $U22$, $U33$, $E_T^{(3)}$, and $U3$ are symbolized as rectangles. They are marked by their labels in diagonally opposite corners

$U3$ is the Fourier transformation of $\hat{\varrho}^{(3)}(\mathbf{x})$. It is the intersection of $U11$, $U22$, and $U33$:

$$U3 = U11 \cap U22 \cap U33. \tag{4.8}$$

It is not important whether Uii relates to **A**, **B**, or **C** as respective genuine subperiod. But a certain sequence, having once been chosen should be fixed.

The set $E_{\mathrm{G}}^{(3)}$ comprises all other reflections:

$$E_{\mathrm{G}}^{(3)} = H \setminus U3. \tag{4.9}$$

This set again can be decomposed into subsets which are the single intersection sets of $E_{\mathrm{M}}^{(3)}$ with the respective sets Uii, with $i = 1, 2, 3$

$$E_{\mathrm{M}}^{(3)}\,(Uii) = E_{\mathrm{G}} \cap Uii \tag{4.10}$$

and the subset which does not have any reflections in common with the sets Uii, with $i = 1, 2, 3$. It is demoted $E_{\mathrm{T}}^{(3)}$, so

$$E_{\mathrm{T}}^{(3)} = E_{\mathrm{G}}^{(3)} \setminus (U11 \cup U22 \cup U33). \tag{4.11}$$

The structure factors of $E_{\mathrm{G}}^{(3)}$ are calculated by $\mathfrak{F}[\hat{\varrho}^{(0)}(\mathbf{x}) - \hat{\varrho}^{(3)}(\mathbf{x})] \mathrel{\hat{=}} \mathfrak{F}[\varrho(\mathbf{x}) - \varrho_{\mathrm{TC}}(\mathbf{x})]$, so $E_{\mathrm{G}}^{(3)} = E_{\mathrm{TC}}$ simply. $\hat{\varrho}^{(0)}(\mathbf{x})$ is identical with $\varrho(\mathbf{x})$. Therefore,

$$F(E_{\mathrm{G}}^{(3)}) = \mathfrak{F}[\varrho(\mathbf{x}) - \hat{\varrho}^{(3)}(\mathbf{x})]. \tag{4.12}$$

The structure factors of $E_{\mathrm{M}}^{(3)}$ (Uii) are calculated by the Fourier transformation of $\hat{\varrho}^{(1)}(\mathbf{x}) - \hat{\varrho}^{(3)}(\mathbf{x})$, so

$$F[E_{\mathrm{M}}^{(3)}\,(Uii)] = \mathfrak{F}[\varrho_i^{(1)}(\mathbf{x}) - \varrho^{(3)}(\mathbf{x})] \text{ with } i = 1, 2 \text{ or } 3. \tag{4.13}$$

The subset $E_{\mathrm{T}}^{(3)}$ is related to the complementary structure $\varrho_{ij}^{(2)}(\mathbf{x}) - \varrho_k^{(3)}(\mathbf{x})$ with $i, j, k = 1, 2, 3$ and $i \neq j \neq k$, when the point weights are structure factors, by:

$$\mathfrak{F}^{-1}\, F\,(E_{\mathrm{T}}^{(3)}) = \varrho^{(2)}(\mathbf{x}) - \varrho^{(3)}(\mathbf{x}). \tag{4.14}$$

For the convolution square $P_{\mathrm{TC}}^{(2,3)}(\mathbf{u}) = \overbrace{\varrho^{(2)}(\mathbf{x}) - \varrho^{(3)}(\mathbf{x})}^{2}$ the following relation holds in addition to Eq. (4.2):

$$\sum_{n_i=1}^{N_i} P_{\mathrm{TC}}^{(2,3)}(n_i \mathbf{u}_i + n_j \mathbf{u}_j + n_k \mathbf{u}_k) = 0 \tag{4.15}$$

for all $i = 1, 2, 3$; $j = 1, 2, 3$; $k = 1, 2, 3$ and all $n_j = 1, \ldots, N_j$; $n_k = 1, \ldots, N_k$ and $i \neq j \neq k$.

This is due to the fact that all $\hat{\varrho}_{i,j}^{(2)}(\mathbf{x}) - \hat{\varrho}^{(3)}(\mathbf{x})$ with $i = 1, 2, 3$; $j = 1, 2, 3$ and $i < j$ are equal to each other and that the sum $\sum_{l=1}^{N_1} \Delta\varrho_{ijk} = 0$ in which $l = i$ or j or k with $l \leq i \leq N_1$, $l \leq j \leq N_2$, $l \leq k \leq N_3$. The indices i, j, k refer to the ith or jth or kth subcell in the direction **A** or **B** or **C**.

If we use the substructure with only two subperiods (see Fig. 4), although three possibly are present, the set $U2$ is given by

$$U2 = U11 \cap U22, \tag{4.16}$$

the set $E_{\mathrm{G}}^{(2)}$ by

$$E_{\mathrm{G}}^{(2)} = H \setminus U2, \tag{4.17}$$

the sets $E_{\mathrm{M}}^{(2)}$ by

$$E_{\mathrm{M}}^{(2)} = E_{\mathrm{G}}^{(2)} \cap Uii \text{ with } i = 1, 2 \tag{4.18}$$

and the set $E_{\mathrm{T}}^{(2)}$ by

$$E_{\mathrm{T}}^{(2)} = E_{\mathrm{G}}^{(2)} \setminus (U11 \cup U22). \tag{4.19}$$

For the subset $E_{\mathrm{T}}^{(2)}$ similarly the corresponding relations as for $E_{\mathrm{T}}^{(3)}$ can be derived, which holds for $E_{\mathrm{G}}^{(2)}$ and $E_{\mathrm{M}}^{(2)}$, too.

In general to all complementary electron density distributions $\tilde{\varrho}(\mathbf{x}) = \hat{\varrho}^{(k)}(\mathbf{x}) - \hat{\varrho}^{(l)}(\mathbf{x})$ with $k < l$ and $k = 0, 1, 2$ and $l = 1, 2, 3$ and in the most interesting cases $l = k + 1$, where $\hat{\varrho}^{(0)}(\mathbf{x})$ in this general notation refers to $\varrho(\mathbf{x})$ simply, a specific set of nonextinguished structure factors which are a subset of H corresponds in the reciprocal space. In order to select the right subset of H for the inverse Fourier transformation by computing the Fourier synthesis one has to check how far the following relations hold:

$$\sum_{n_i=1}^{N_j} \widehat{\tilde{\varrho}(\mathbf{x})\,\delta}(\mathbf{x} - n_i\,\mathbf{u}_j) = 0 \text{ for } j = 1, 2, 3. \tag{4.18}$$

Demonstration of the various terms at an example

The recently analyzed structure of stannoidite, $\mathrm{Cu_8Fe_2^{3+}(Fe^{2+}, Zn)Sn_2S_{12}}$, (Kudoh and Takéuchi, 1976) comprises a series of examples for the terms discussed in this paper. In Table 1 the structure parameters and the idealized coordinates are listed. Figure 5 shows a projection of the idealized structure onto (001). The structure parameters were refined with Cromer's approximation of the atomic form factors (Cromer and Waber, 1965; Cromer, 1965). In contrast to the usual expectation the R-value became lower than that of Kudoh and Takéuchi (1976).

Stannoidite has a series of substructures which are collated in Table 2. The multiple cell of stannoidite arose predominantly by substitution of various metal atoms in the ZnS structure and by a slight distortion.

The subcell of the most striking substructure is also orthorhombic with $A = a/2$, $B = b$, $C = c/3$. The probable space group is $A\,222$. Since $A \approx B \approx C$ holds a tetragonal substructure with the space group $I\bar{4}2m$ or even a cubic substructure with $F\bar{4}3m$, symmetry is worth consideration. But the deviations of A, B, and C from each other are already too large to carry out computations with atomic arrangements in these space groups in order to

Table 1. Structural parameters and idealized coordinates of stannoidite [$R = 5.3\%$ (isotropic), $R = 4.7\%$ (anisotropic)]

Atom	Occupancy	Equipoint	Coordinates			B [Å]^2	Idealized coordinates
			x	y	z		
M1	$0.783\,Zn^{2+}$ $+\,0.217\,Fe^{2+}$	$2a$ 222	0	0	0	1.53(12)	000
$M2$	Cu	$2b$ 222	$\frac{1}{2}$	0	0	2.16(15)	$\frac{1}{2}00$
$M3$	Cu	$2c$ 222	0	0	$\frac{1}{2}$	1.9(2)	$00\frac{1}{2}$
$M4$	Cu	$4f$ 2	0.2513(5)	0	$\frac{1}{2}$	1.42(9)	$\frac{1}{4}0\frac{1}{2}$
$M5$	Fe^{3+}	$4i$ 2	0	0	0.3305(4)	0.85(7)	$00\frac{1}{3}$
$M6$	Sn^{4+}	$4j$ 2	0	$\frac{1}{2}$	0.16907(15)	0.39(4)	$0\frac{1}{2}\frac{1}{6}$
$M7$	Cu	$8k$ 1	0.2466(3)	−0.006(3)	0.1689(3)	1.61(5)	$\frac{1}{4}0\frac{1}{6}$
$S1$	S	$8k$ 1	0.1318(15)	0.2443(15)	0.0808(7)	0.9(2)	$\frac{1}{8}\frac{1}{4}\frac{1}{12}$
$S2$	S	$8k$ 1	0.3833(11)	0.753(2)	0.0797(7)	1.2(2)	$\frac{3}{8}\frac{3}{4}\frac{1}{12}$
$S3$	S	$8k$ 1	0.130(2)	0.7495(15)	0.2524(8)	0.47(13)	$\frac{1}{8}\frac{3}{4}\frac{1}{4}$

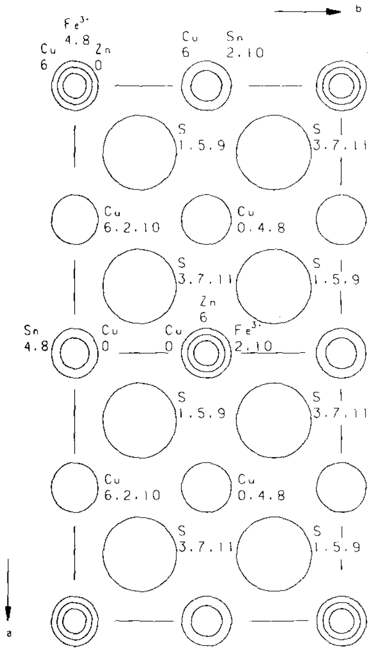

Fig. 5. Idealized structure of stannoidite with idealized *z*-coordinates in $\frac{1}{12}$ of *c*

reduce the number of free parameters in the full structure. In any case an idealization is required. The idealized substructure is shown in Figure 6. If one continues the idealization by transforming the copper atoms into iron atoms Fe^{3+}, the idealized substructure has the space group $F222$.

This substructure, denoted (*a*) in Table 2, can be 'decomposed' into two orthorhombic substructures having a subcell with $A = a/2$, $B = b$, $C = c$, and a space group $A222$ or a subcell with $A = a$, $B = b$, $C = c/3$, space group of the substructure $I222$. This is an example for the case that a set of substructure yielding parameters can be decomposed into two independent subsets. The characteristic substructure of all the mentioned substructures, denoted (*a*), (*b*), and (*c*) in Table 2, consists of the copper atoms M3 (see Table 2a).

Stannoidite has also an ideal substructure (see Table 2 and Fig. 7) with the subcell $A = a$, $B = b/2$, $C = c$, and with space group $B222$. It consists of the copper atoms $M2$ and $M3$ (see Table 1). All the other atoms and anything else belong to the complementary structure. If the eigensymmetry of the atoms $M2$ and $M3$ can be assumed to be *mmm* or higher, the space group is *Bmmm*.

For the substructure analysis the practical substructures which relate to the idealized substructures (*a*), (*b*), (*c*), and (*aii*) in Table 2 can be used.

Table 2a. Substructures in stannoidite

Substructure identification	Subcell	Probable space group of the substructure	Content atoms of the full structure participating (compare Table 1)	Kind of disturbance if any	Remarks
a	$A = a/2$, $B = b$, $C = c/3$	$A222$	$M1$, $M2$, $M4$, $M5$, $M6$, $M7$, $S1$, $S2$, $S3$	Predominantly substitution, light distortion	Idealization is necessary; compared with *ai*, *aii*, *a*1, and *a*2 it is here at a minimum
*a*1	$A = a/2$, $B = b$, $C = c/3$ $(A = B = C)$	$I\bar{4}2m$	$M1$, $M2$, $M4$, $M5$, $M6$, $M7$, $S1$, $S2$, $S3$	Predominantly substitution, light distortion	Only for topological considerations useful eg.,
*a*2	$A = a/2$, $B = b$, $C = c/3$ $(A = B = C)$	$F\bar{4}3m$	$M1$, $M2$, $M4$, $M5$, $M6$, $M7$, $S1$, $S2$, $S3$	Predominantly substitution, light distortion	for crystal chemistry
b	$A = a/2$, $B = b$, $C = c$	$A222$	$M1$, $M2$, $M4$, $M5$, $M6$, $M7$, $S1$, $S2$, $S3$	Predominantly substitution, light distortion	Only one subperiod is reconsidered
c	$A = a$, $B = b$, $C = c/3$	$I222$	$M1$, $M2$, $M4$, $M5$, $M6$, $M7$, $S1$, $S2$, $S3$	Predominantly substitution, light distortion	Only one subperiod is reconsidered
d	$A = a$, $B = b/2$, $C = c$	$B222$	$M2$, $M3$	No disturbance	Ideal substructure
*d*1	$A = a$, $B = b/2$, $C = c$	$Bmmm$	$M2$, $M3$	No disturbance	Ideal substructure
ai	$A = a/2$, $B = b$, $C = c/3$	$A222$	$M1$, $M2$, $M6$, $M5$ are to be considered as Fe^{3+}; light shifts of $M4$, $M5$, $M6$, and $M7$ to required places		Further idealization substructure (a)
aii	$A = a/2$, $B = b$, $C = c/3$	$F222$	Additionally $M2$ and $M7$ are to be considered as Fe^{3+}		Further idealization of substructure (a)
Similarly *bi*, *bii*, and *bii*, *cii* can be yielded					

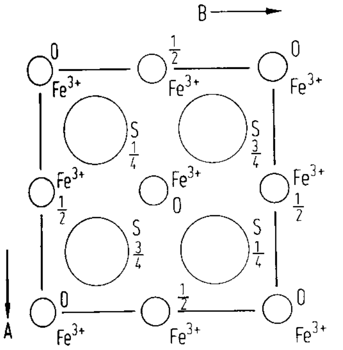

Fig. 6. Idealized substructure, ϱ_{BF}; $A = \frac{1}{2}a$, $B = b$, $C = \frac{1}{3}c$; $F222$

Table 2b. Complementary structures

Identification of corresponding substructure	Content	
	Ideal complementary structure (compare Table 1)	Nonideal complementary structure (compare Table 1)
a	$M2$	$M4$, $M5$, $M6$, $M7$, $S1$, $S2$, $S3$
b	$M2$	$M4$, $M5$, $M6$, $M7$, $S1$, $S2$, $S3$
c	$M2$	$M4$, $M5$, $M6$, $M7$, $S1$, $S2$, $S3$
d	$M1$, $M4$, $M5$, $M6$, $M7$, $S1$, $S2$, $S3$	none

Tables 3 and 4 contain the space group, cell, and structure parameters and other information about a series of them.

The set of the 'strong reflections' from which Takéuchi's subcell and substructure $TS1$ can be determined consists of all reflections hkl with $l = 3\,\mathrm{L}$ and $h = 2\,\mathrm{H}$ which could have been observed. Takéuchi's complementary structure $TC1$ can be determined from the set of the 'weak reflections' hkl with $h = 2\,\mathrm{H} + 1$ and $l = 3\,\mathrm{L} + 1$. The substructures $TS2$ and $TS3$ with one subperiod regarded as genuine condition strong and weak reflection sets. In $TS2$ the reflections hkl with $h = 2\,\mathrm{H}$, $k = \mathrm{K}$, $l = \mathrm{L}$, and in $TS3$ the reflections hkl with $h = \mathrm{H}$, $k = \mathrm{K}$, $l = 3\,\mathrm{L} \pm 1$ are the 'strong' ones, the remaining correspondingly the 'weak' ones.

The Fourier transformations of Buerger's substructures and complementary structures generate nonzero values at the identical reciprocal point sets as those of Takéuchi's substructure. So stannoidite cannot

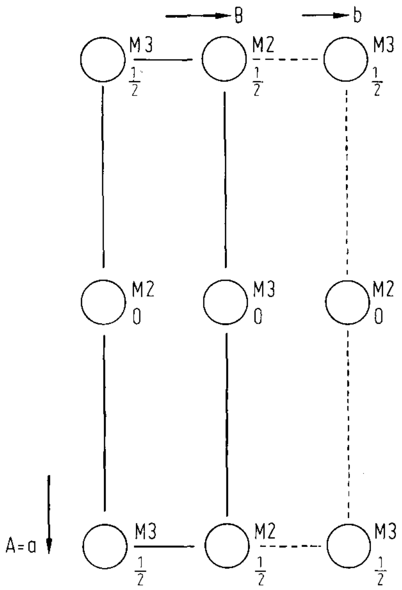

Fig. 7. Ideal substructure consisting of Cu-atoms only. $A = a$, $B = b/2$, $C = c$, $B222$, or $Bmmm$

demonstrate that the excess point sets of Buerger's and Takéuchi's substructures need not comprise the same points in the reciprocal space. $TS\,1$ have the space group $A\,222$; $TS\,2$ and $BS\,2$ refer to the idealized substructures (*b*) in Table 2; $TS\,3$ and $BS\,3$ correspond to (*c*) in Table 2. The space group for $TS\,2$ and $BS\,2$ is $A\,222$, while for $TS\,2$ and $BS\,3$ it is $I\,222$.

A great help for the determination of the substructures $TS\,1$, $TS\,2$ or $TS\,3$ is the analytical form of the scattering factors introduced by Cromer and Waber (1965). The convolution square of the substructures $TS1$, $TS2$, and $TS\,3$ can be obtained by calculating the Patterson synthesis with the intensities $I\,(hkl)$ with $h = 2\,\mathrm{H}$, $k = \mathrm{K}$, $l = 3\,\mathrm{L}$, respectively $h = 2\,\mathrm{H}$, $k = \mathrm{K}$, $l = \mathrm{L}$, respectively $h = \mathrm{H}$, $k = \mathrm{K}$, $l = 3\,\mathrm{L}$. Parallel to the interpretation of the Patterson synthesis the iterative Gaussian analysis after Hosemann and Schoknecht (1955) could be applied.

Since stannoidite has predominantly a substitution structure, it is possible to find more or less well fitting models of $TS\,1$, $TS\,2$, and $TS\,3$ using isotropic temperature factors and mean atomic scattering factors which can be resolved into a linear combination of the scattering curves of the metal atoms.

In Tables 3 and 4 the results of the substructure determinations with the coordinates and the isotropic temperature factors refined by least squares methods are listed. The anisotropic temperature factors were not added in Table 3, but the reliability factors of the refinements reconsidering them are given. For the computations all 422 published structure factors of the measured 429 ones (Kudoh and Takéuchi, 1976) were used.

Table 3. Refinement of the practical substructures in stannoidite

Practical substructure identification	Subcell and space group	'Atom'	'Occupancy'	Equipoint	Coordinates			Isotropic temperature factor B [Å]^2
					X	Y	Z	
TS 1	$A = a/2$,	$MS\,1$	$\frac{1}{2}(Cu^{1+} + Zn^{2+} + Fe^{3+} + Sn^{4+})$	$2a$ 222	0	0	0	0.84(3)
	$B = b$,	$MS\,2$	$\frac{1}{6}Cu^{1+}$	$2b$ 222	0	0	$\frac{1}{2}$	1.6(2)
	$C = c/3$,	$MS\,3$	Cu^{1+}	$2c$ 222	$\frac{1}{2}$	0	$\frac{1}{2}$	1.56(3)
	$A\,222$	S	S^{2-}	$4k$ 2	0.25396(4)	$\frac{1}{4}$	$\frac{1}{4}$	1.01(4)
TS 2	$A = a/2$,	$MS\,1$	$\frac{1}{2}(Zn^{2+} + Cu^{1+})$	$2a$ 222	0	0	0	0.2(2)
	$B = b$,	$MS\,2$	$\frac{1}{2}Cu^{1+}$	$2b$ 222	0	0	$\frac{1}{2}$	16(2)
	$C = c$,	$MS\,3$	$\frac{1}{2}(Fe^{3+} + Sn^{4+})$	$4e$ 2	0	0	0.3329(5)	0.86(9)
	$A\,222$	$MS\,4$	Cu^{1+}	$2c$ 222	$\frac{1}{2}$	0	$\frac{1}{2}$	0.1(10)
		$MS\,5$	Cu^{1+}	$4e$ 2	0	0	0.1662(10)	3.4(4)
		$S\,1$	S^{2-}	$8l$ 1	0.245(3)	0.245(3)	0.0849(8)	1.5(3)
		$S\,2$	S^{2-}	$4k$ 2	0.246(10)	$\frac{1}{4}$	$\frac{1}{4}$	0.6(4)
TS 3	$A = a$,	$MS\,1$	$\frac{1}{3}(Fe^{3+} + Zn^{2+})$	$2a$ 222	0	0	0	1.07(5)
	$B = b$,	$MS\,2$	$\frac{1}{3}Cu^{1+}$	$2c$ 222	0	0	$\frac{1}{2}$	1.9(2)
	$C = c/3$,	$MS\,3$	$\frac{1}{3}(2\,Sn^{4+} + Cu^{1+})$	$2b$ 222	0	$\frac{1}{2}$	$\frac{1}{2}$	0.69(3)
	$I\,222$	$MS\,4$	Cu^{1+}	$4f$ 2	0.2483(4)	0	$\frac{1}{2}$	1.57(4)
		S	S^{2-}	$8k$ 1	0.1270(2)	0.2485(15)	0.2477(6)	1.01(4)
TF	$A = a/2$, $B = b$,	$MS\,1$	$Cu^{1+} \hat{=} \frac{1}{12}(Zn^{2+} + 7\,Cu^{1+} + 2\,F3^{3+} + 2\,Sn^{+})$	$4a$ 222	0	0	0	0.92(5)
	$C = c/3$;	$MS\,2$	$\frac{1}{6}(Cu^{1+})$	$4b$ 222	0	0	$\frac{1}{2}$	4.6(4)
	$F\,222$	S	S^{2-}	$4c$ 222	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1.18(8)
BF	$A = a/2$,	MS	Fe^{3+}	$4a$ 222	0	0	0	0.97(6)
	$B = b$,	S	S^{2-}	$4c$ 222	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1.45(9)
	$C = c/3$;							
	$F\,222$							

In column 1 the letter T refers to a practical substructure after Takéuchi, and B refers to one after Buerger. The letter F refers to a face-centered lattice

Table 4. The reliability factors of the refinements of the practical substructures

Practical substructure (compare Table 3)	R isotropic %	R anisotropic %	Number of reflections; additional selection rule in respect to entire	Corresponding ideal substructure in Table 2
TS1	2.7	2.6	141 $h = 2\,\mathrm{H}$, $l = 3\,\mathrm{L}$	a
TS2	8.6	7.4	245 $h = 2\,\mathrm{H}$	b
TS3	4.2	3.8	224 $l = 3\,\mathrm{L}$	c
TF	4.3	4.1	87 $h = 2\,\mathrm{H}$, $k = \mathrm{K}$, $l = 3\,\mathrm{L}$ $H + \mathrm{K} = 2n$, $k + \mathrm{L} = 2n$, $H + L = 2n$	aii
BF	8.6	7.8	87 $h = 2\,\mathrm{H}$, $k = \mathrm{K}$, $l = 3\,\mathrm{L}$ $H + \mathrm{K} = 2n$, $k + \mathrm{L} = 2n$, $H + L = 2n$	aii

The complementary structures can be determined by the Patterson syntheses of the weak reflections hkl with $h \neq 2\,\mathrm{H}$ and $l \neq 3\,\mathrm{L}$.

The Patterson map has to be investigated at the sites where the maxima in the full Patterson synthesis would be located if the substructure would be the full structure. The application of the minimum function (Buerger, 1959) has been suggested by Takéuchi (1972).

Each atom in the full structure $\varrho_{\mathrm{A}}(xyz)$ generates five points with negative weight $-{}^{1}/_{6}$ and one point with positive weight ${}^{5}/_{6}$ in the complementary structure TC1. Similarly the complementary structures TC2 and TC3 can be derived from the full structure. So the electron density in TC1, TC2 respectively TC3 can be calculated by the following relations:

$$\begin{aligned}\varrho_{TC1}(\mathbf{x}) = {} & \tfrac{5}{6}\varrho\,(\mathbf{x}) - \tfrac{1}{6}\,\varrho\overparen{(\mathbf{x})\,[\delta}(\mathbf{x}-00\tfrac{1}{3}) + \delta(\mathbf{x}-00\tfrac{2}{3}) \\ & + \delta(\mathbf{x}-\tfrac{1}{2}00) + \varrho\,(\mathbf{x}-\tfrac{1}{2}0\tfrac{1}{3}) + \delta(\mathbf{x}-\tfrac{1}{3}0\tfrac{2}{3})], \qquad (5.1)\end{aligned}$$

$$\varrho_{TC2}(\mathbf{x}) = \tfrac{1}{2}\,\varrho\overparen{(\mathbf{x})\,[\delta}(\mathbf{x}) - \delta(\mathbf{x}-\tfrac{1}{2}00)], \qquad (5.2)$$

$$\varrho_{TC3}(\mathbf{x}) = \tfrac{1}{3}\,\varrho\overparen{(\mathbf{x})\,[2\,\delta}(\mathbf{x}) - \delta(\mathbf{x}-00\tfrac{1}{3}) - \delta(\mathbf{x}-00\tfrac{2}{3})]. \qquad (5.3)$$

What the complement structure looks like was derived from the full structure. This can be done generally as useful check of a structure, too. The reliability factors were computed to $R_{TC1} = 9.6\,\%$, $R_{TC2} = 9.4\,\%$, and $R_{TC3} = 10.3\,\%$ for 281 reflections, respectively 198 reflections, respectively 177 reflections. One has to pay attention when special positions after the anti-and-diminution translation had taken place get on less special positions. Buerger's substructure has been obtained by computing the minimum function as it was suggested in Eq. (3.1). Computation of the structure factors of Buerger's substructures was attempted, the one with space group $A\,222$ and the other with space group $F222$. This was done without trying to correct the observed structure factors as would be necessary to get an impression of the influence of the complement structure on the substructure. The result at the latter is contained in Table 3.

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