

Order-disorder and polymorphism of the compound with the composition of scholzite, $\text{CaZn}_2[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$

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Abstract. The observed stacking disorder in scholzite can be explained by a stacking ambiguity of layers parallel to (100). This is due to equivalent surroundings of the calcium atoms on the boundary planes of two neighbouring layers in two possible relative positions to each other. Consequently, a series of possible polytypes of this compound was derived, among which the structure of parascholzite is a likely candidate, from which the space group and the lattice parameters could be found in agreement with these predictions. It was demonstrated that the OD structure does not consist of layers of one kind but of two kinds.

Introduction

In compounds possessing stacking disorder, it is desirable to retrieve the different possibilities for stacking of the two-dimensionally periodic layers. This is done in such a way that in any possible case the crystal chemical situation does not differ substantially from any other possibility, or that at least in each possible case there are no crystal chemical contradictions. This stacking ambiguity usually is due to special arrangements of the atoms on or in the vicinity of the boundary planes of the layers perpendicular to the stacking direction. It can also explain the existence of other modifications of this compound.

Streaks parallel to \mathbf{a}^* along the reciprocal lattice row lines of scholzite, $\text{CaZn}_2[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$, indicate a stacking disorder in the [100] direction of layers lying parallel to (100).

A fundamental building block was found in scholzite with the required properties for layer disorder. From this discovery it was possible to predict a series of polytypes for scholzite. One is the probable structure of the recently discovered mineral parascholzite [Sturman, Rouse and Dunn, 1981] or its enantiomorphic equivalent. I attempted to find an OD groupoid for an OD structure [Dornberger-Schiff, 1964] of either one kind or two kinds of layers. Since the scholzite structure is complex but has a substructure from which the entire structure can be derived by small distortions [Taxer, 1975] the idealized substructure with the cell constants $A = a_{\text{scholzite}}$, $B = b_{\text{scholzite}}/3$, $C = c_{\text{scholzite}}$ was selected for consideration. The lattice constants b and c of parascholzite are equal to B and C of the substructure of scholzite.

Each of the decompositions of the substructure of scholzite in this paper will have its own advantage.

Since in the following the full structure of scholzite is not of any interest the vectors \mathbf{a} , \mathbf{b} , \mathbf{c} denote the lattice vectors of the substructure of scholzite. x , y , z are the fractional coordinates of vector \mathbf{x} referring to this cell. In some Figures the axes are still denoted \mathbf{A} , \mathbf{B} , \mathbf{C} . According to our agreement they mean the same as \mathbf{a} , \mathbf{b} , \mathbf{c} , and correspondingly xyz mean the same as XYZ . But an index may change completely the meaning. — For those who never heard anything about OD structures a brief introduction will follow.

The OD theory takes care of the partial symmetry operations, motions which bring only a part of the crystal structure into coincidence with itself or with another part of the structure. [Dornberger-Schiff, 1964; Fichtner, 1980]. Therefore, it applies the theory of groupoids. The OD theory of equivalent layers is able to explain polytypism since an OD structure consists of an infinite number of layers one onto another where stacking disorder may occur when a stacking ambiguity exists. — At first a layer has to be defined. It is a building unit which is periodic in two dimensions parallel to the plane perpendicular to the stacking direction and which does not share any atom with an adjacent layer. Its width is denoted a_0 if $[100]$ is the stacking direction.

The partial symmetry operations are divided into two sets: one contains the λ symmetries which transform one layer into itself and which form one of the 80 layer groups. The other set contains the σ operations which are all transformations from a layer to an adjacent one. The groupoid symbols comprise in the first line the layer group and in the second the σ operations. The parentheses about certain symmetry symbols indicate that in that specified direction the periodicity needs not to exist. The OD theory requires the fulfilment of the vicinity conditions: if a layer pair $(L_q; L_{q+1})$ can be transformed into the layer pair $(L_p; L_{p+1})$ so that there is a coincidence of L_q or L_{q+1} with L_p or L_{p+1} , then $(L_p; L_{p+1})$ has to be geometrically equivalent to $(L_q; L_{q+1})$.

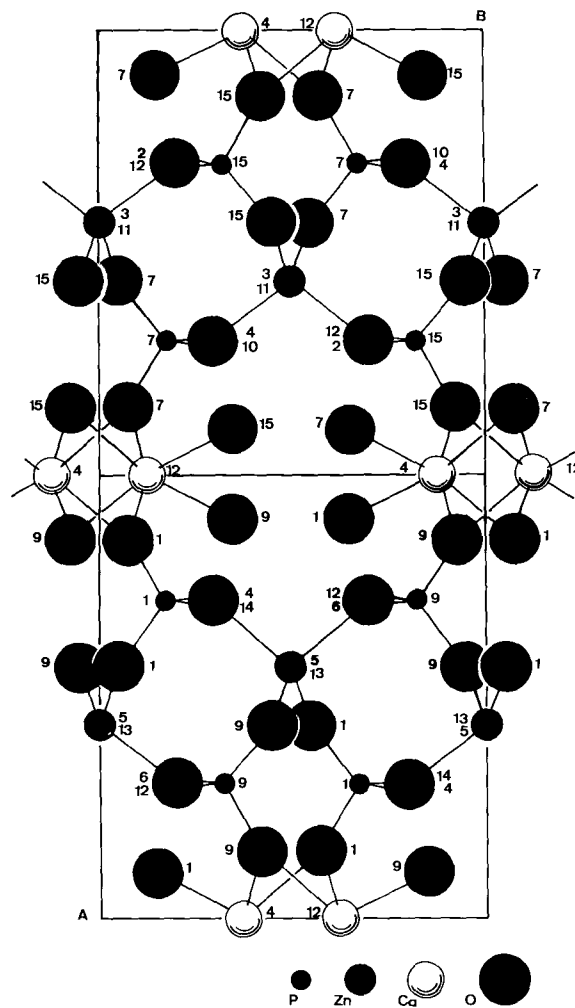


Fig. 1a. Projection of the idealized substructure of scholzite onto the (001) plane. The numbers indicate the idealized z coordinates in $\frac{1}{10}$ of c .

Usually it is the aim to find an OD structure of only one kind of layers since they are relatively simple compared with those consisting of more than one kind of layers.

The OD theory is the most powerful tool for handling stacking disorder. But its limits of application are defined by the groupoid theory. Hence, not each structure with stacking disorder can be an OD structure. Nevertheless, we should use the terms of it and try to find out that there is an OD structure or not.

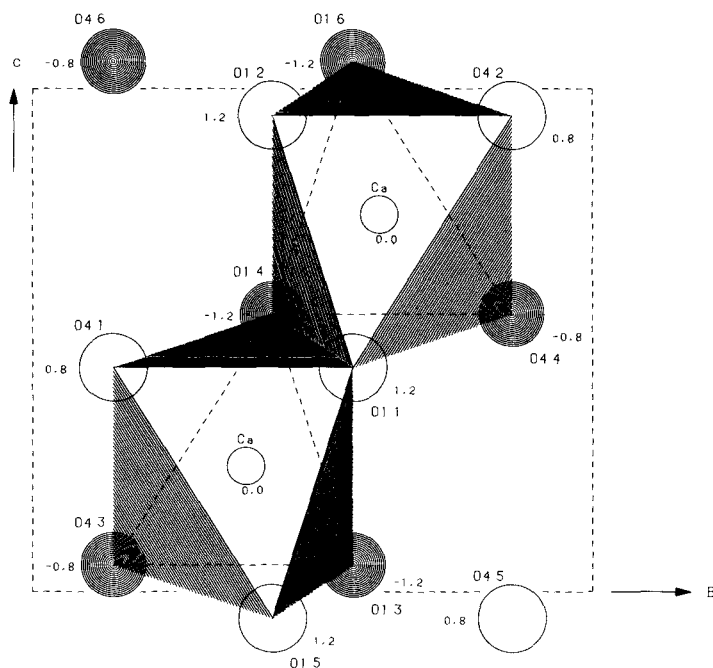


Fig. 1b

Fig. 1b, c. Illustration of the stacking ambiguity about the boundary plane in the idealized substructure of scholite by projections of the octahedral network onto (100). The numbers indicate the x coordinates in $\frac{1}{16}$ of a . In Figure 1b, c the oxygen atoms with positive x coordinates are located at identical positions, whereas in Figure 1c in comparison to Figure 1b the oxygen atoms with negative x coordinates (dark circles) are shifted to the alternate locations and correspondingly are the calcium atoms.

The stacking ambiguity

Let us consider the substructure of scholite in Figure 1a (Taxer, 1975) within one half of the subcell limited by $0 \leq x \leq \frac{1}{2}$, $0 \leq y \leq 1$, $0 \leq z \leq 1$. Decompose this partial structure into two components one containing only the calcium atoms, the second all the other atoms. The first component is designated F , the second A . Then it can be recognized (see Fig. 1) that the component A is symmetrical by translation $\frac{1}{2}, \frac{1}{2}, \frac{5}{8}$ to the other half of the cell being limited by $1 \geq x \geq \frac{1}{2}$, $0 \leq y \leq 1$, $0 \leq z \leq 1$. Hence the atoms of A are repeated at $\frac{1}{2} + x, \frac{1}{2} + y, \frac{5}{8} + z$. The layer built up by A and periodic in the directions \mathbf{b} and \mathbf{c} is also denoted A . The equivalent holds for F . Let us find all symmetrical equivalent layers of layer A , each a possible neighbor of A behind F by trying to use all space group and OD groupoid elements so that we obtain identical octahedral surroundings for the calcium atoms. To these possible symmetry elements belong the two translations $\frac{1}{2}, \frac{1}{2}, \varphi$

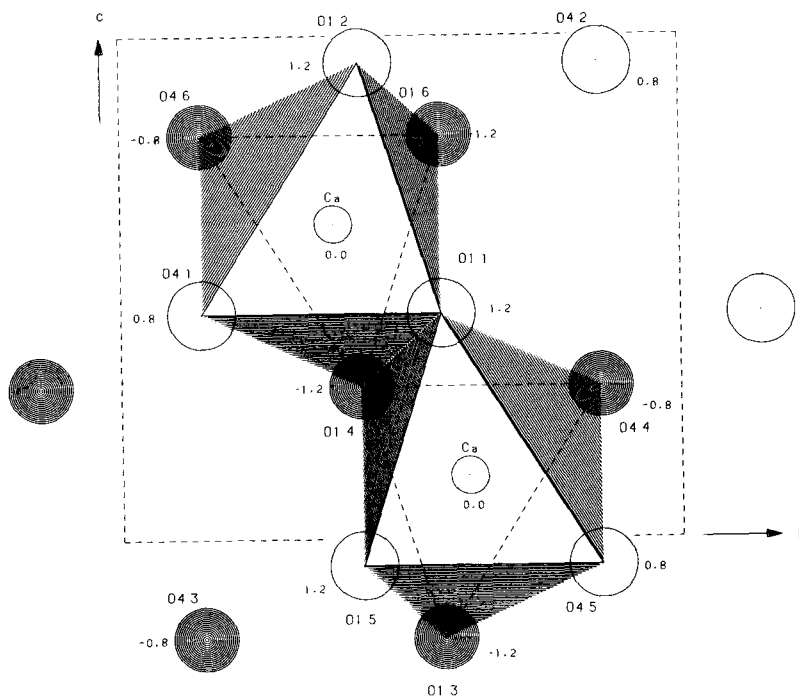


Fig. 1c

with $\varphi = \frac{3}{8}$ and $\varphi = \frac{5}{8}$ depending on which octahedral cavities were chosen by the calcium atoms. The corresponding translations for Γ are $\frac{1}{2}, \frac{1}{2}, \mu$ with $\mu = 0$ when $\varphi = \frac{5}{8}$ (as for instance in Fig. 1 a), and $\mu = \frac{3}{8}$ when $\varphi = \frac{3}{8}$. So for $\varphi = \frac{3}{8}$ the calcium atoms at x, y, z have to be repeated at $\frac{1}{2} + x, \frac{1}{2} + y, \frac{3}{8} + z$, and for $\varphi = \frac{5}{8}$ they are repeated at $\frac{1}{2} + x, \frac{1}{2} + y, z$.

With this background many phenomena of the stacking disorder in the compound with the composition of scholzite and parascholzite can be explained.

Figure 1b and 1c illustrate the stacking ambiguity at the boundary plane. Figure 1d shows the tetrahedral network behind the octahedral network in Figure 1b and 1c. The common atoms are the oxygens O1.

For convenience the layers with Γ and A are labelled in the following way: the layer containing the zeroth component of Γ , being Γ_0 , which follows the zeroth component of A , being A , is the zeroth layer. The first layer contains A_1 at lower x -coordinates than Γ_1 which lies at the boundary plane to the second layer. Also for convenience let us call the components $A_0, \Gamma_0, A_1, \Gamma_1, A_2, \Gamma_2, \dots$ "the layers $A_0, \Gamma_0, A_1, \Gamma_1, A_2, \Gamma_2, \dots$ ".

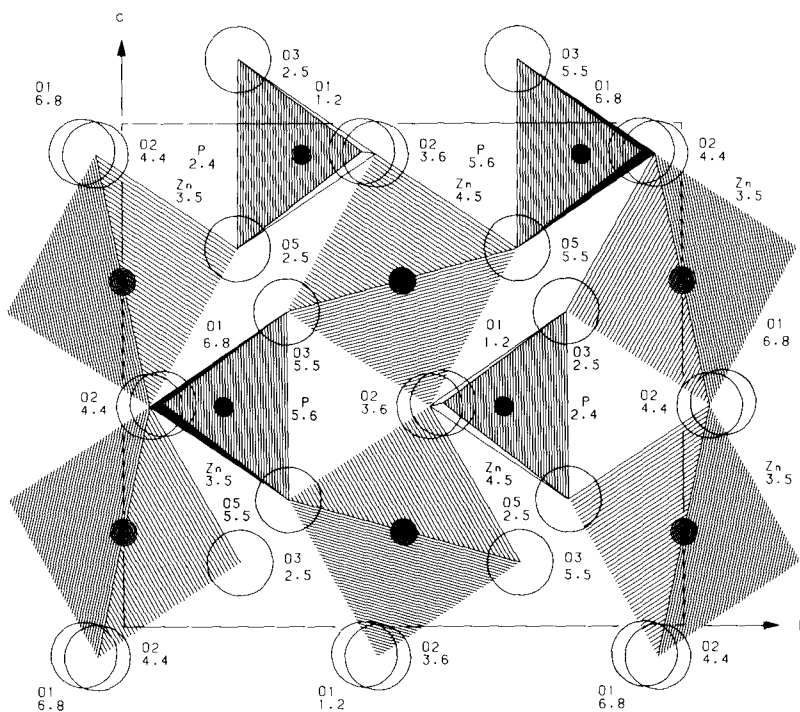


Fig. 1d. Projection of the tetrahedral network between two boundary planes in the idealized substructure of scholzite onto (100). It corresponds to A minus the water molecules (O4). The number indicate the x coordinates in $\frac{1}{16}$ of a .

Let us define some translation vectors:

$\mathbf{t}_{i,i+1}$ is the translation vector shifting layer A_i into the next layer A_{i+1} , so $\mathbf{t}_{i,i+1} = \frac{1}{2}, \frac{1}{2}, \varphi$ with $\varphi = \frac{3}{8}$ or $-\frac{3}{8}$. $\mathbf{t}_{i,j}$ is the translation which shifts A_i into its symmetrical equivalent in the j th layer, i.e. $\mathbf{t}_{i,j} = (j-i)/2, (j-i)/2, \xi/8$ with $\xi = 0, 1, \dots, 7$. $\mathbf{t}_i = \frac{1}{2}, \frac{1}{2}, \mu$ is the translation shifting the symmetrical equivalent of Γ_0 between the $(i-1)$ th and the i th layer of A_1 to its symmetrical equivalent between the i th and the $(i+1)$ th layer of A_0 . The relation

$$\mathbf{t}_i = \frac{1}{2} (\mathbf{t}_{i-1,i} + \mathbf{t}_{i,i+1})$$

follows from the dependence of μ on φ : $\mu = 0$ when $\varphi = \frac{3}{8}$ is followed by $\varphi = -\frac{3}{8}$ or vice versa, $\mu = \frac{3}{8}$ when $\varphi = \frac{3}{8}$ is followed by $\varphi = +\frac{3}{8}$, etc.

In this relation for \mathbf{t}_i the possible values of $\varphi = \frac{5}{8}$ and $\varphi = -\frac{5}{8}$ in both vectors, $\mathbf{t}_{i-1,i}$ and $\mathbf{t}_{i,i+1}$, should always be replaced by the equivalent values $\varphi = -\frac{3}{8}$ and $\varphi = \frac{3}{8}$ respectively, or, should always be substituted by the function $\frac{1}{8} \cdot \text{mod}(8 \cdot \varphi, 8) - \frac{1}{2} \cdot \text{mod}[\text{mod}(8 \cdot \varphi, 8), 3]$ which

transforms the set $\{\dots, \frac{5}{8}, \frac{3}{8}, \frac{3}{8}, \frac{5}{8}, \frac{11}{8}, \dots\}$ into the set $\{-\frac{3}{8}, +\frac{3}{8}\}$, so that the restriction is done automatically.

This relation helps to understand that the position of the layers Γ_i are determined by the stacking vectors between the layers A_i . So, for instance, the electron density distribution of the disordered crystal could be calculated by

$$\varrho(\mathbf{x}) = \varrho(A_0) [\delta(\mathbf{x}) + \delta(\mathbf{x} - \mathbf{t}_{0,1}) + \delta(\mathbf{x} - \mathbf{t}_{0,2}) + \dots] \\ + \varrho(\Gamma_0) \{\delta(\mathbf{x}) + \delta(\mathbf{x} - \mathbf{t}_1) + \delta[\mathbf{x} - (\mathbf{t}_1 + \mathbf{t}_2)] + \dots\},$$

where $\varrho(A_0)$ is the normalized two-dimensional periodic electron density distribution of the layer L_0 containing only A_0 , and $\varrho(\Gamma_0)$ is that of layer L_0 containing only Γ_0 , $\delta(\mathbf{x})$ is the three-dimensionally Dirac-function, and N is the number of layers each containing the components A and Γ . After substitution of the vectors \mathbf{t}_i using the relation for it derived above with all precautions and restrictions mentioned there the electron density distribution can be computed according to

$$\varrho(\mathbf{x}) = \varrho(A_0) \sum_{j=0}^N \delta(\mathbf{x} - \mathbf{t}_{0,j}) + \varrho(\Gamma_0) \sum_{j=0}^N \delta \left[\mathbf{x} - \frac{1}{2} (\mathbf{t}_{0,j} + \mathbf{t}_{1,j}) \right].$$

Derivation of a possible parascholzite structure

The subsequent application of the translation $\frac{1}{2}, \frac{1}{2}, \frac{3}{8}$ to the corresponding symmetrically equivalent positions of Γ and A yields the enantiomorphic equivalent of the idealized structure of parascholzite (see Fig. 2a). The monoclinic cell is C -centered. This can be understood by studying the Figure 2 series. The cell vectors $\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p$ of parascholzite and its enantiomorphic equivalent can be calculated by a linear combination of those of the subcell of scholzite:

$$(1) \quad \mathbf{a}_p = \mathbf{a} - \left(\frac{3}{4}\right)\mathbf{c} \\ \mathbf{b}_p = \mathbf{b} \\ \mathbf{c}_p = \mathbf{c} \\ \beta_p = 90^\circ + \tan^{-1} \left(\frac{3}{4} c/a\right)$$

respectively,

$$(2) \quad \mathbf{a}_{p'} = \mathbf{a} - \left(\frac{3}{4}\right)\mathbf{c} \\ \mathbf{b}_{p'} = \mathbf{b} \\ \mathbf{c}_{p'} = -\mathbf{c} \\ \beta_{p'} = 90^\circ + \tan^{-1} \left(\frac{3}{4} c/a\right)$$

if the conventional orientation of the axes is used. Table 1 shows the calculated values by Eq. (2) and comparison the measured values of Sturman, Rouse and Dunn (1981).

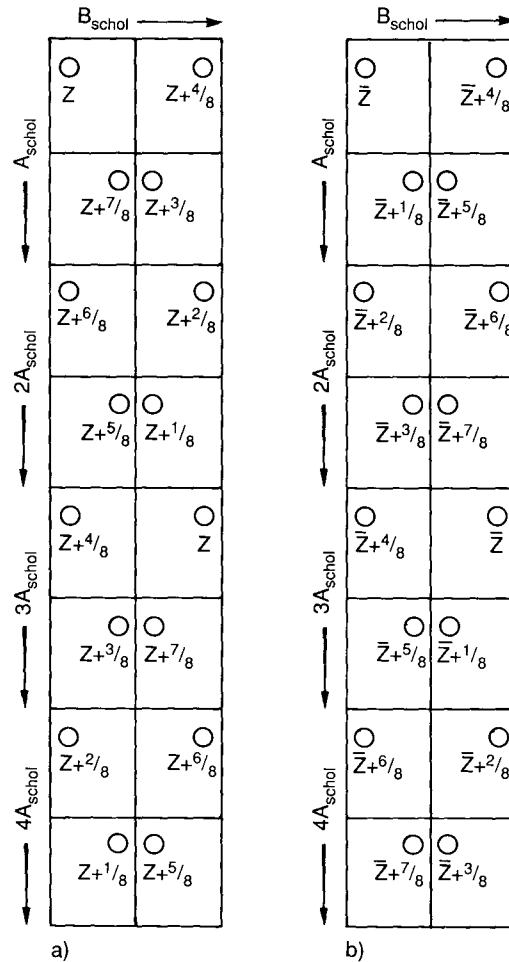


Fig. 2a. The derivation of the enantiomorphic equivalent of the parascholzite structure from the idealized substructure of scholzite.

Fig. 2b. The derivation of the parascholzite structure from the enantiomorphic equivalent of the idealized structure of scholzite. Reference was made to scholzite by using $-Z$ instead of $Z' = -Z$. A circle represents the asymmetric unit of parascholzite or its symmetrical equivalent if the space group Cc is assumed.

The idealized asymmetric unit of parascholzite is identical with that of the substructure of scholzite if parascholzite is assumed to have the space group $C2/c$. The component A has a symmetry center at $\frac{1}{4}, \frac{1}{4}, \frac{3}{16}$ referred to the coordinate system of the orthorhombic subcell of scholzite. Furthermore, there are mirrors at $z = \frac{7}{16}; \frac{15}{16}$, a twofold screw axis parallel to

Table 1. Derived values of the lattice constants of parascholzite from the substructure of scholzite.

Scholzite substructure (Taxer, 1975)	Parascholzite Relation to lattice constants of substructure of scholzite	Computed values	Hagendorf measured values, (Sturman, Rouse and Dunn, 1981)
$A = 17.149$ [Å]	$a_p = \sqrt{A^2 + \frac{9}{16}C^2}$	17.863 [Å]	17.864 [Å]
$B = 7.412$ [Å]	$b_p = B$	7.412 [Å]	7.422 [Å]
$C = 6.667$ [Å]	$c_p = C$	6.667 [Å]	6.674 [Å]
	$\beta_p = 90^\circ + \text{atan}\left(\frac{\frac{3}{4}C}{A}\right)$	106.25°	106.45°

Table 2. Derived atom coordinates of parascholzite from the idealized coordinates of the substructure of scholzite.

Atom	Scholzite, <i>Pbcn</i>			Parascholzite, <i>C 2/c</i>		
	<i>X</i>	<i>Y</i>	<i>Z</i>	x_p	y_p	z_p
Zn	$\frac{3}{11}$	$\frac{1}{2}$	$\frac{3}{16}$	$\frac{3}{11}$	$\frac{1}{2}$	0.017
P	$\frac{7}{20}$	$\frac{3}{16}$	$\frac{7}{16}$	$\frac{7}{20}$	$\frac{3}{16}$	0.825
Ca	0	$\frac{3}{8}$	$\frac{1}{4}$	0	$\frac{3}{8}$	0.75
O1	$\frac{7}{16}$	$\frac{1}{20}$	$\frac{7}{16}$	$\frac{7}{16}$	$\frac{1}{20}$	0.891
O2	$\frac{3}{16}$	$\frac{1}{20}$	$\frac{7}{16}$	$\frac{3}{16}$	$\frac{1}{20}$	0.703
O3	$\frac{3}{20}$	$\frac{4}{20}$	$\frac{2}{16}$	$\frac{3}{20}$	$\frac{4}{20}$	0.989
O4	$\frac{1}{20}$	$\frac{3}{20}$	$\frac{7}{16}$	$\frac{1}{20}$	$\frac{3}{20}$	0.6
O5	$\frac{7}{20}$	$\frac{6}{20}$	$\frac{4}{16}$	$\frac{7}{20}$	$\frac{6}{20}$	0.0125

[010] at $x, z = \frac{1}{4}, \frac{7}{16}$ and a twofold axis parallel to [100] at $y, z = 0, \frac{3}{16}$ in addition to those in the substructure of scholzite. So the layer group of this layer is $P\left(\frac{2}{b}\right)_{\frac{2_1}{c}} \frac{2_1}{m}$. So for deriving the initial atom coordinates for the asymmetric unit of parascholzite there is nothing else to do but to transform the orthorhombic coordinates of the idealized asymmetric unit of scholzite into those of the monoclinic axes. If parascholzite has no symmetry center, then *Cc* is the space group as shown in Figure 2b.

The initial coordinates of parascholzite are calculated by the following equations with the coordinates of the asymmetric unit the subcell of scholzite:

$$(3) \quad \begin{aligned} x_p &= x \\ y_p &= y \\ z_p &= \frac{3}{4}x + z. \end{aligned}$$

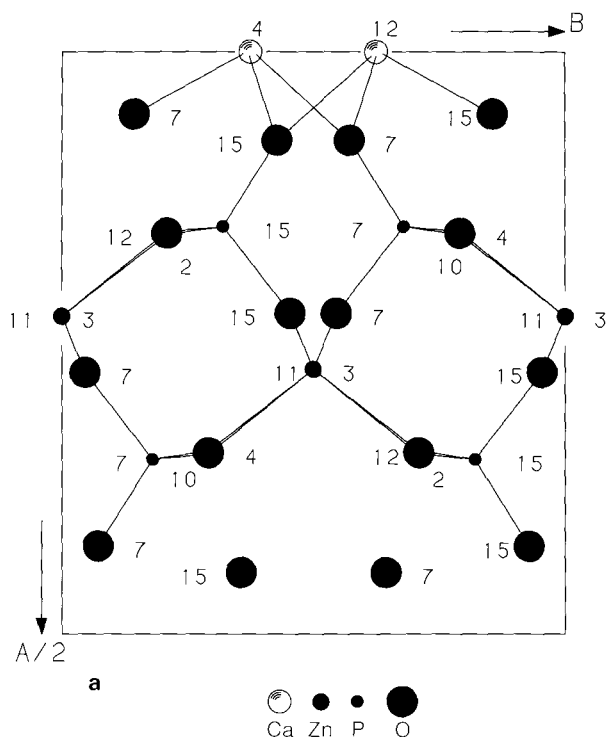


Fig. 3a

Fig. 3. Representation of the layer units T and U

(a) Projection of T onto (001)

(b) Projection of U onto (001).

The representation of the enantiomorphic equivalent of parascholzite with orthorhombic coordinates is drawn in Figure 2a. Bartl and Taxer (manuscript in preparation) have confirmed this structure by measurements of the X-ray diffraction intensities ($R = 0.035$ for structure factors of 1050 reflections).

Derivation of the possible polytypes of the scholzite compound

Let us consider another decomposition of the idealized substructure of scholzite into a set of equivalent layers which will be a powerful means of deriving all polytypes of this compound and for finding out whether this compound has an OD structure built up by a set of equivalent layers. The partial structure within the lower half-cell $0 \leq x \leq \frac{1}{2}$ will be designated by T , the other half-cell within the limits $\frac{1}{2} \leq x < 1$ will be designated by U' .

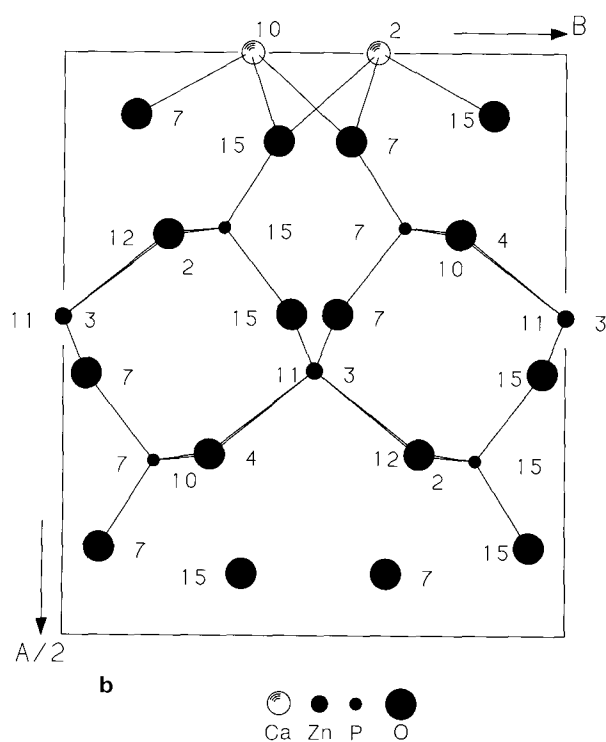


Fig. 3b

If U' is shifted by $-\frac{1}{2}, -\frac{1}{2}, -\frac{5}{8}$ above the lower half-cell all atoms coincide except the calcium atoms; $U' \delta[\mathbf{x} - (-\frac{1}{2}, -\frac{1}{2}, -\frac{5}{8})]$ is denoted U . T and U can be transformed into each other by a mirror perpendicular to (001) at $z = \frac{7}{16}, \frac{15}{16}$. From this transformation only the calcium atoms change their positions, A has the same position in both, T and U . So T is the enantiomorphic equivalent of U and vice versa. T is the union of F and A , so $T = F \cup A$ (see Fig. 3).

The application of the OD theory requires a definition of layers, L_i , $i = -\infty \dots, 0, \dots + \infty$, as building units with a set of atoms being unshared by the neighboring layer.

In this compound L is periodic in the directions \mathbf{b} and \mathbf{c} . Both layers, U and T , have the thickness $a_0 = a/2$. The plane group of both layers, U and T , is $P(1) c 1$. This determines the λ -symmetry of the layers. Let us first assume L_0 to be T .

By application of the translation $\frac{1}{2}, \frac{1}{2}, \frac{3}{8}$ we get an adjacent layer $L_1 = L_0 \delta[\mathbf{x} - (\frac{1}{2}, \frac{1}{2}, \frac{3}{8})]$. Another possibility of getting an adjacent layer L_1 is applying the n -glide plane parallel to (001) at $z = \frac{1}{4}, \frac{3}{4}$ upon $L_0 =$

Table 3. Possible U -type layers and T -type layers in L .

n	$U_n =$ $U \delta(x - 0,$ $0, n \frac{5}{8})$	z -coordinates of the calcium positions in 1/16th of c $(x, Y = 0, \frac{3}{8} \mid x, Y = 0, \frac{5}{8})$	$T_n =$ $T \delta(x - 0,$ $0, n \frac{3}{8})$	z -coordinates of the calcium atoms in T in 1/16th of c $(x, Y = 0, \frac{3}{8} \mid x, Y = 0, \frac{5}{8})$		
0	U_0	10	2	T_0	4	12
1	U_1	4	12	T_1	10	2
2	U_2	14	6	T_2	0	8
3	U_3	8	0	T_3	6	14
4	U_4	2	10	T_4	12	4
5	U_5	12	4	T_5	2	10
6	U_6	6	14	T_6	8	0
7	U_7	0	8	T_7	14	6

T , then $L_1 = U'$. So we can get for L_1 either a T -type layer or a U -type layer depending on the defined σ -symmetry. T -type layer of U -type layer means that only a translation is necessary to transform the considered layer into T or U , respectively. If L_0 is assumed to be U then the translation $\frac{1}{2}, \frac{1}{2}, \frac{5}{8}$ yields a U -type layer L ; the n -glide plane at $z = \frac{1}{8}, \frac{5}{8}$ would yield a T -type layer L . The sequence of the layers of type T parallel to the direction [100] each shifted by $\frac{1}{2}, \frac{1}{2}, \frac{3}{8}$ against the preceding one yields the very probable structure of parascholzite, the sequence of the layers of type U parallel to [100] shifted against the preceding one by $\frac{1}{2}, \frac{1}{2}, \frac{5}{8}$ yields the enantiomorphic equivalent of the parascholzite structure. The subsequent application of the reflection at the n -glide plane parallel to (001) on $L_0 = T$ yields the layer type sequence $-T-U-T-U-\dots$ in the [100] direction which is the idealized substructure of scholzite.

Let us denote $P_i = \delta[\mathbf{x} - (i/2, \text{mod}(i, 2)/2, 0)]$ with i being an integer indexing the i th layer and $U_m = \bar{U} \delta\{\mathbf{x} - [0, 0, \frac{1}{8} \text{mod}(m \cdot 5, 8)]\}$ and $T_m = T \delta\{\mathbf{x} - [0, 0, \frac{1}{8} \text{mod}(m \cdot 3, 8)]\}$ with $0 < m < 7$. Remember that we refer to the lattice constant $A = a$ and not to $a_0 = a/2$. Since the calcium atoms are situated on boundary positions and determine the layer of the set $U = \{U_m, m = 0, 1, \dots, 7\}$ or of the set $T = \{T_m, m = 0, 1, \dots, 7\}$, we have taken their z -coordinates in $\frac{1}{16}$ of c as characterization of U and T in Table 3.

Building up any layer sequence in the direction [100] we note from left to right the layers $-L_0 - L_1 \dots - L_i - L_{i+1} - \dots$ e.g. $-T_2 - T_3 - U_6 - U_7 -$ where again for shortness it has been assumed that each U_m or T_m with $m = 0, \dots, 7$ has been convoluted with P_i with i being the actual layer index. In Fig. 4 two examples are demonstrated. — Each U_m in layer L_i has to be followed by U_p with $p = \text{mod}(m + 1, 8)$ if the next layer shall be one of type U ; the corresponding holds for T . If T_n is followed by U_m , m has to be chosen so that in both, T_n and U_m , the calcium atoms have the same

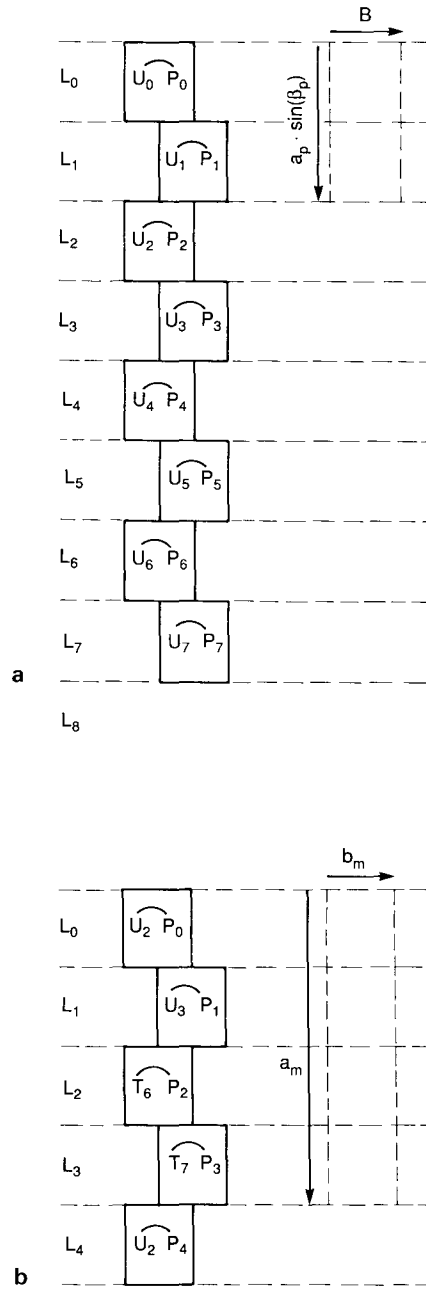


Fig. 4. Examples of derived polymorphs. (a) Schematic representation of parascholzite by U-type layers. (b) Schematic representation of $-U_2 - U_3 - T_6 - T_7 - \dots$.

Table 4. Some arrangements of *U*- and *T*-type layers being possible polytypes of the scholzite compounds or twins.

Label	Arrangement of layers of type <i>T</i> and <i>U</i> parallel [100] (all indices are to be taken as modulo 8, so $0 \leq n \leq 7$, μ is any positive integer, $n + \mu = \text{mod}(n + \mu, 8)$ all <i>U</i> and <i>T</i> have been folded by P_i , i is the layer index)	Space group (highest possible symmetry)	Lattice vector \mathbf{a}_m as a linear combination of \mathbf{a} , \mathbf{B} , \mathbf{c}
1	$-U_n - U_{n+1} -$	$C 2/c$	$\mathbf{a} - \frac{3}{4}\mathbf{c}$
2	$-T_n - T_{n+1} -$	$C 2/c$	$\mathbf{a} - \frac{3}{4}\mathbf{c}$
3	$-U_n - T_{q-n} -$	$Pbcn$	\mathbf{a}
4	$-U_n - U_{n+1} - \dots - U_{n+\mu+1} - U_{n+\mu} - T_{q-n-\mu} \dots - T_{q-n}$	$Pbcn$	$(\mu + 1)\mathbf{a}$
5	$-U_n - T_{q-n} - T_{10-n} - U_{n-1} - T_{10-n} T_{11-n}$	$C 2/c$	$3\mathbf{a} - \frac{1}{4}\mathbf{c}$
	$-T_n - U_{q-n} - U_{10-n} - T_{n-1} - U_{10-n} - U_{11-n}$	$C 2/c$	$3\mathbf{a} - \frac{3}{4}\mathbf{c}$
	$-U_n - T_{q-n} - \dots - T_{q-n+\mu} - U_{n-\mu} - T_{q-n+\mu} - \dots - T_{q-n+2\mu}$ μ is any positive odd integer example: $\mu = 3$ $-U_2 - T_7 - T_0 - T_1 - T_2 - U_1 - T_2 - T_3 - T_4 - T_5 -$	$C 2/c$	$(\mu + 2)\mathbf{a} - \frac{1}{8}\text{mod}(2\mu 5, 8)\mathbf{c}$ $5\mathbf{a} - \frac{3}{4}\mathbf{c}$
6	$-U_n - U_{n+1} - T_{8-n} - \dots - T_{8-n+\mu} - U_{n-\mu+1} - U_{n-\mu+2}$ $-T_{7-n+\mu} - \dots - T_{7-n+2\mu} -$ $2 \leq \mu$ (even) example: $\mu = 2$ $-U_1 - U_2 - T_7 - T_0 - T_1 - U_0 - U_1 - T_0 - T_1 - T_2 -$	Cc	$(\mu + 3)\mathbf{a} - \{1 - \frac{1}{8}\text{mod}[\text{mod}(10 - 2\mu, 8)5, 8]\} \cdot \mathbf{c}$ $5\mathbf{a} - \frac{1}{4}\mathbf{c}$
	7	$-U_n - U_{n+1} - T_{8-n} - \dots - T_{8-n+\mu} -$ with $\mu \geq 3$ (odd) example: $\mu = 3$ $-U_3 - U_4 - T_5 - T_6 - T_7 - T_0$	Pc
	and so on		

z-coordinates. For determining m with $m = 0, 1, \dots, 7$ it is convenient to use Table 3. Now we can fill up Table 4 by a series of certain periodic layer sequences which may be discussed as being or not being arrangements of maximal degree of order so representing probable resp. improbable polytypes of the compound. Their lattice constants b_m and c_m are equal to B and c of scholzite, a_m is characteristic for each of these hypothetical polymorphs. $a \cdot \sin\beta_m$ is equal to or a multiple of $A = a$ of scholzite. The use of this collection is to get an impression of what is likely to be a polymorph, a twin, nearly a parallel growth or an arrangement which tends to the state of disorder. The greater a_m the more improbable is the existence of crystallites or of domains consisting completely of the considered "polytype". The observations of Sturman, Rouse and Dunn (1981) concerning especially the syntaxial intergrowth of scholzite and parascholzite confirm these statements.

Order – disorder

The OD theory of OD structures of layers of one kind requires a set of equivalent layers and also a set of equivalent pairs of layers for assigning an OD groupoid to the considered compound. Since T and U are the enantiomorphic equivalents of each other, all layers in any layer sequence are equivalent to each other. But unfortunately this does not imply that all pairs of layers are equivalent to each other. Since there is no operation which could transform a pair $-U-U-$ into a pair $-U-T-$ or $-T-U-$ the second condition is not fulfilled in the general case, since, if one chooses to explain the streaks by stacking disorder, the U -type layers and T -type layers have to follow each other arbitrarily. Therefore, it was assumed that the scholzite compound has an OD structure consisting of two kinds of layers. To recognize this, the layers T and U have to be decomposed into two layers, respectively; one of them has the composition A and the other the composition Γ . Let us agree that the layers L_{2n} have the composition A and the layers L_{2n+1} have the composition Γ . Let us further assume that L_0 contains the subcomponent A of T or U . The σ -operations, which transform the layer L_0 into L_2 , may be either a translation $\frac{1}{2}, \frac{1}{2}, +\frac{3}{8}$ or a two-fold screw axis $2_r//[001]$, $r = +2 \cdot \frac{1}{8}$ at $xy = \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0$ etc., or a glide plane $n_{1,1} //(001)$ or a two-fold axis $2//[010]$ at $x = 0; \frac{1}{2}$ and $z = \frac{1}{4}; \frac{3}{4}$ or $\frac{5}{8}; \frac{1}{8}$ or a glide plane $c_r //(100)$, $r = \pm \frac{3}{8} \cdot 2$ at $x = 0; \frac{1}{2}$ etc. all referred to the orthorhombic coordinate system $\mathbf{a} = \mathbf{a}_{\text{scholzite}}$, $\mathbf{B} = \mathbf{b}_{\text{scholzite}}/3$, $\mathbf{c} = \mathbf{c}_{\text{scholzite}}$. Further, let L_1 contain the subcomponent Γ of U' . The following σ -operations for transforming L_1 into L_3 (i.e. the layer with the calcium atoms into the next "calcium layer") can be derived from the σ -operations $_{0,2}\sigma$ and $_{2,4}\sigma$. For instance, if $_{0,2}\sigma$ and $_{2,4}\sigma$ are twofold screw axes $2_r//[001]$, $r = \pm 2 \cdot \frac{1}{8}$ then $_{1,3}\sigma$ may be also a twofold screw axis

$2_s//[001]$ at $xy = \frac{3}{4}, \frac{1}{4}$ with $s = \frac{1}{2}(-1 + \frac{1}{2}r_{0,2} + \frac{1}{2}r_{2,4})$. If the translations are the σ -operations ${}_{0,2}\sigma$ and ${}_{2,4}\sigma$, then ${}_{1,3}\sigma = \frac{1}{2}({}_{0,2}\sigma + {}_{2,4}\sigma)$, etc. The following σ -operations¹ for transforming L_1 into L_3 are possible, but in general they are not present simultaneously:

$$\begin{aligned} &2_1//[010] \text{ at } x = \frac{3}{4}, z = 0 \text{ or } \frac{9}{16} \\ &2_1//[100] \text{ at } y = \frac{3}{4}, z = \frac{1}{2} \text{ or } \frac{13}{16} \\ &2_r//[001] \text{ at } xy = \frac{3}{4}, 0 \text{ and } \frac{3}{4}, \frac{1}{2}, \\ &\quad \text{with } r = 2 \cdot (\pm \frac{1}{8} \pm \frac{1}{8} - 1) \cdot \frac{1}{2} \\ &n_{1,1}//(001) \text{ at } z = \frac{1}{4}, \frac{3}{4} \text{ or } \frac{9}{16}, \frac{9}{16} \\ &n_{1,r}//(100) \text{ at } x = \frac{2}{4}, \quad r = -2 \cdot (\pm \frac{5}{8} \pm \frac{5}{8}) \cdot \frac{1}{2} \\ &\text{and the translations } \frac{1}{2}, \frac{1}{2}, r \text{ with } r = \pm \frac{3}{8} \text{ or } r = 0. \end{aligned}$$

If L_1 contains the subcomponent Γ of T there is a corresponding set of parameters and positions of these symmetry elements. To a compound with an OD structure consisting of two kinds of layers an Ehresmann groupoid can be assigned. Due to the different operations which may not exist simultaneously there are several possibilities of getting an Ehresmann groupoid; one only will be given as an example.

The Ehresmann groupoid consists of two groupoids, one for all layers L_{2n} with A or its symmetrical equivalents:

$$(1) \quad P \begin{pmatrix} 2 \\ b \end{pmatrix} \begin{matrix} 2 \\ c \\ m \end{matrix} \quad \text{with } r = \frac{1}{8} \cdot 2 \quad \text{and } s = \frac{3}{8} \cdot 2 \\ [(c_s) 1 2]$$

and the other for all layers L_{2n+1} containing Γ or its symmetrical equivalents:

$$(2) \quad P(1) \quad c \quad 1 \\ [(2_2) 2_1 2_r] \quad r = 0 \text{ or } \frac{1}{4} \text{ (referred to } a_0 = a/2 \text{ although all } L_{2n+1} \\ \text{have the thickness } 0 \text{ since each of them needs only} \\ \text{a plane, but not more than a thickness of less or} \\ \text{equal } \frac{1}{12} a \text{ so that the sum of the thicknesses of } L_{2n} \\ \text{and } L_{2n+1} \text{ is } a/2, \text{ and so references for } a_0 = a/2 \\ \text{make sense)}$$

Final remarks

Studying the idealized substructure of scholzite one realizes that both, a stacking ambiguity and the arrangement of the atoms in components of the substructure could admit symmetry elements which may not occur

¹ In chapter 2 "The stacking ambiguity" only one possibility of σ -operations was mentioned. There the layer T was decomposed into two *components* A and Γ . In this chapter it was decomposed into two different *layers*. Formally there is a great difference between these two decompositions.

simultaneously. Both properties allow a behaviour of good compatibility to changes in the environment (e.g. a replacement of an atom by another one.) — The method of finding the stacking disorder principle (stacking ambiguity) is not straight-forward, but the results are reliable due to the reconsideration and fulfilment of the crystal chemical requirements.

References

- Dornberger-Schiff, K.: Grundzüge einer Theorie der OD-Strukturen aus Schichten. Abh. Dtsch. Akad. Wiss., Kl. f. Chem. **3**. Berlin: Akademie Verlag 1964.
- Fichtner, K.: On groupoids in crystallography. MATCDY **9** (1980) 21–40 (match communications in mathematical chemistry. ISSN 0340-6253).
- Sturman, B. D., Rouse, R. C., Dunn, P. J.: Parascholzite, a new mineral from Hagendorf, Bavaria and its relationship to scholzite. Am. Mineral. **66** (1981) 843–851.
- Taxer, K.: Structural investigations on scholzite. Am. Mineral. **60** (1975) 1019–1022.