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Structural Investigations on Scholzite

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Abstract

Scholzite, $Zn_2Ca[PO_4]_2 \cdot 2H_2O$, has a substructure with *Pbcn* symmetry, and subperiod $B = b/3$. Its actual structure (symmetry $Pbc2_1$) is a distortion of the substructure model with small shifts (mainly parallel to x) of the atomic positions in three adjacent subcells. The refinement of this distortion-structure model, which contains 45 atoms in the asymmetric unit, reduced the R value to 8.1 percent for 1924 observed reflections. The structure shows chains of ZnO_4 tetrahedra parallel to [001]. These chains are "Einereinfachketten," which are connected to other similar chains by isolated PO_4 tetrahedra. The calcium atoms are surrounded by distorted oxygen octahedra which are formed by one oxygen from each of four different PO_4 tetrahedra and two oxygens from two water molecules. The water molecules, in groups of four, occupy cages surrounded by two CaO_6 octahedra and four PO_4 tetrahedra.

Introduction

Scholzite, a secondary phosphate mineral, occurs at Reaphook Hill (Southern Australia) and in pegmatites at Hagendorf (Bavaria), Transbaikal near Zabajkali in Siberia (Timchenko and Siderenko, 1962), and in the pegmatite near Domazliče in Bohemia (Staňek, 1966). In its idealized formula, $Zn_2Ca[PO_4]_2 \cdot 2H_2O$, some of the zinc is replaced by minor manganese, magnesium, and very small amounts of iron. Strunz and Tennyson (1956) report an analysis of Hagendorf scholzite.

Space Groups and Unit Cells of the Structure and the Substructure

Professor Strunz kindly supplied Hagendorf material for a structural investigation. The observed diffraction pattern and the morphology show orthorhombic symmetry. The lattice constants were determined and refined to: $a = 17.149 \pm 0.003$ Å, $b = 22.236 \pm 0.002$ Å, $c = 6.667 \pm 0.001$ Å, $Z = 12$.

Most reflections with $k = 3n$ are very strong, whereas all reflections hkl with $k = 3n \pm 1$ are weak, indicating that scholzite has a substructure. The subcell has lattice constant $B = b/3$. If we consider only substructure reflections, the following extinction rule can be derived:

$$hK0,\ h + K = 2n \text{ present,}$$
$$0Kl,\quad K = 2n \text{ present,}$$
$$h0l,\quad l = 2n \text{ present.}$$

This is consistent with space group *Pbcn.*

In a structure with a substructure, the space group of the true structure is a subgroup of the space group of the substructure (Buerger, 1947). The orthorhombic subgroups of *Pbcn* are: $Pb2n$, $P2_122_1$, $P2_1cn$, and $Pbc2_1$. However, $Pb2n$ and $P2_1cn$ can immediately be discarded because superstructure reflections $hk0$, where $h + k = 2n + 1$, are clearly present. However, forbidden reflections for the other two space groups can also be observed, although they are extremely weak. We consider $Pbc2_1$ or $P2_122_1$ as more probable space groups for the entire structure of scholzite. Space group $Pbc2_1$ was confirmed by the subsequent refinement. The very weak forbidden reflections may be due to a lower-symmetry distribution of the hydrogen atoms or trace substituents.

Independently, Hill, Johnson, and Jones (1973) and Hill and Milnes (1974) determined scholzite's space group as $Pbc2_1$.

Intensity Measurements

Intensity data were collected with an automated single-crystal diffractometer (AED, Siemens) designed for an Eulerian-cradle geometry. Monochromatic Cu$K\alpha$ X radiation was employed. About 2750 reflections were measured in the asymmetric field of the Cu$K\alpha$ sphere. These intensities were corrected for

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background, Lorentz, polarization and absorption effects (μ = 161.1 cm^{-1}; the crystallite had the shape of an orthorhombic prism).

Substructure Determination

A Patterson synthesis using all reflections, another using only the superstructure reflections, and one using only the substructure reflections were calculated. By interpreting the Patterson synthesis of the substructure, a model was found whose parameters, based on film data, have been reported in Taxer (1970; see Fig. 1). The subcell model appears very reasonable, especially in light of the crystal chemistry. The interatomic distances and the bond angles compare well with the conventional values for the corresponding polyhedra. The structure model shows chains of ZnO_4 tetrahedra parallel to *c* which are connected to other similar chains by isolated PO_4 tetrahedra. The calcium atoms are surrounded by distorted oxygen octahedra which are formed by one oxygen from each of four different PO_4 tetrahedra and two oxygens from two water molecules. The ZnO_4 tetrahedra are arranged in "Einereinfachketten" (Liebau, 1956); these are chains of tetrahedra, all of which have the same orientation and whose bridge oxygen atoms lie on a line parallel to the chain direction. Such "Einereinfachketten" have only been found up to the present time in copper polygermanate, $(CuGeO_3)_x$ (Liebau, 1957; Kleber, 1969). The CaO_6 octahedra form zig-zag chains parallel to [001]. The water molecules, in groups of four, occupy cages surrounded by two CaO_6 octahedra and four PO_4 tetrahedra.

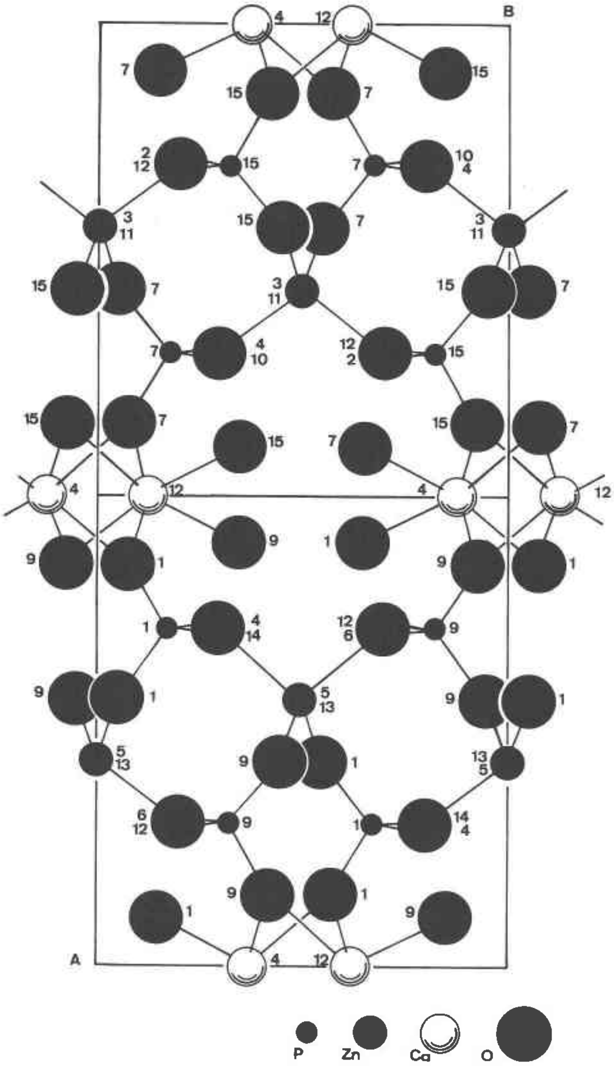

FIG. 1. Projection of the idealized substructure onto the (001) plane. The numbers indicate the idealized *z* coordinates in 1/16 of *c*.

Several cycles of refinement on the positional parameters and isotropic temperature factors reduced the discrepancy factor, $R = \Sigma \, ||F_{obs}| - |F_{calc}|| / \Sigma \, |F_{obs}|$, to 13.7 percent for about 700 structure factors.

Distribution of the Hydrogen Atoms of the Water Molecules

The hydrogen positions could not be determined from the diffraction data, but by means of crystal chemical criteria nine possible arrangements of the H positions in the substructure may be obtained. None of these fulfills the symmetry conditions of *Pbcn* except one which is very improbable since the crystal chemical requirements are not satisfied perfectly.

Determination of the Full Structure

Examination of the weak reflections with $k = 3n \pm 1$, of the type *hk*0, showed $h + k = 2n + 1$ present,

TABLE 1. Parameters (Fractional Coordinates and Temperature Factors) of the Atoms in the Asymmetric Unit of the Entire Structure of Scholzite*

Space Group $Pbc2_1$, R = 8.1 Percent

Atom	x	y	z	B(Å^2)
Ca(1)	0.0157(3)	0.1265(3)	0.254 (2)	0.69(6)
Ca(2)	-0.0067(3)	0.2065(3)	0.748 (2)	1.04(9)
Ca(3)	-0.0075(4)	0.8730(4)	0.758 (2)	2.25(11)
Zn(1)	0.2111(2)	0.0030(2)	0.1955(14)	0.46(5)
Zn(2)	-0.2299(2)	-0.0029(2)	0.3211(14)	0.35(5)
Zn(3)	0.2822(2)	0.1686(2)	0.1941(14)	0.81(6)

TABLE 1. Continued

Zn(4)	-0.2756(2)	0.1661(2)	0.3195(14)	0.72(7)
Zn(5)	0.2674(2)	0.8284(2)	0.1853(14)	0.68(6)
Zn(6)	-0.2108(2)	0.3302(2)	-0.1884(13)	0.71(5)
1st $(PO_4)^{3-}$tetrahedron				
P(1)	0.1525(4)	0.1108(4)	0.930 (2)	0.34(8)
O(1)	0.1551(10)	0.0784(8)	0.138 (3)	0.20(9)
O(2)	0.1568(11)	0.0653(9)	0.757 (4)	1.03(9)
O(3)	0.2279(13)	0.1519(12)	0.952 (5)	1.06(10)
O(4)	0.0782(10)	0.1483(9)	0.942 (4)	0.21(10)
2nd $(PO_4)^{3-}$tetrahedron				
P(2)	0.8523(4)	0.1034(3)	-0.444 (2)	0.16(8)
O(5)	-0.1546(12)	0.0644(12)	-0.246 (5)	2.3 (2)
O(6)	-0.1584(12)	0.0586(10)	0.381 (4)	1.02(11)
O(7)	0.7787(10)	0.1491(9)	-0.414 (5)	0.46(10)
O(8)	0.9297(10)	0.1356(9)	-0.437 (4)	0.95(10)
3rd $(PO_4)^{3-}$tetrahedron				
P(3)	0.1571(4)	0.2284(3)	0.442 (2)	0.17(10)
O(9)	0.1642(10)	0.2661(9)	0.631 (3)	0.48(9)
O(10)	0.1586(12)	0.2644(10)	0.257 (4)	0.76(10)
O(11)	0.2283(10)	0.1854(9)	0.468 (3)	0.14(9)
O(12)	0.0814(9)	0.1918(7)	0.475(3)	0.14(9)
4th $(PO_4)^{3-}$tetrahedron				
P(4)	0.8567(4)	0.2254(3)	0.070 (2)	0.13(8)
O(13)	-0.1532(10)	0.2600(10)	0.257 (3)	1.37(10)
O(14)	-0.1462(10)	0.2649(11)	-0.118 (4)	0.49(12)
O(15)	-0.2169(11)	0.1801(9)	0.076 (4)	0.17(9)
O(16)	-0.065 (13)	0.1925(12)	0.072 (5)	1.03(11)
5th $(PO_4)^{3-}$tetrahedron				
P(5)	0.1421(5)	0.8939(4)	0.435 (2)	0.67(8)
O(17)	0.1532(11)	0.9237(1)	0.637 (3)	0.49(9)
O(18)	0.1447(11)	0.9351(9)	0.260 (3)	0.19(9)
O(19)	0.2109(11)	0.8489(9)	0.438 (4)	0.59(9)
O(20)	0.0684(11)	0.8558(10)	0.454 (4)	0.35(10)
6th $(PO_4)^{3-}$tetrahedron				
P(6)	-0.1577(4)	0.8916(2)	0.056 (2)	0.13(9)
O(21)	-0.1581(10)	0.9361(11)	-0.115 (4)	1.69(12)
O(22)	-0.1658(11)	0.9253(13)	0.262 (5)	0.14(8)
O(23)	-0.0841(9)	0.8543(11)	-0.924 (4)	1.36(10)
O(24)	-0.2314(10)	0.8485(12)	-0.925 (5)	0.14(10)
Oxygen atoms of the water molecules				
O(25)	0.0497(13)	0.0459(12)	0.471 (5)	1.35(9)
O(26)	0.9453(11)	0.0533(9)	0.092 (4)	0.95(10)
O(27)	0.058 (2)	0.2857(14)	0.964 (5)	2.37(8)
O(28)	0.9593(2)	0.2906(14)	-0.456 (6)	1.98(10)
O(29)	0.0355(14)	0.9524(12)	0.965(12)	1.66(9)
O(30)	-0.055 (13)	0.9508(11)	-0.424 (11)	1.02(9)

* *All atoms are lying on the general position; the standard deviations are in parentheses.*

whereas $h + k = 2n$ are extremely weak. This means that the *n*-glide plane || (001) of the substructure does not exist in the entire structure. The distribution of the maxima *and* the minima of the Patterson synthesis of the complementary structure, calculated with only the weak reflections, ($k = 3K + 1$), suggests a distortion structure model in which the atomic positions are shifted slightly from those of the substructure model. Assuming $Pbc2_1$ to be the most probable space group of scholzite, I derived a model of the structure by calculating structure amplitudes and partial electron-density difference Fourier syntheses successively. The length and the directions of the shifts were obtained by refining only the space parameters.

All occupancies were assumed to be 1. After refinement of the isotropic temperature factors, the discrepancy factor, *R*, became 8.1 percent for 1924 "observed" reflections—they were separated from the non-observed ones, which could be measured neither visually nor with a photometer—from a total of 2750 measured structure factors. The weak reflections, $k = 3K \pm 1$, alone agree well with the structure model. The *R* value for 1300 superstructure reflections alone is 10.1 percent. The refined parameters are listed in Table 1. The temperature factors of the oxygens of the water molecules are relatively high, but this agrees with their relatively loose contacts. The interatomic distances and the bond angles lie within the range of the values which are found in other structures. The arrangement of the atoms in the entire structure is approximately the same as that in the substructure (see Fig. 2). The essential characteristics of the entire structure, compared with the sub-

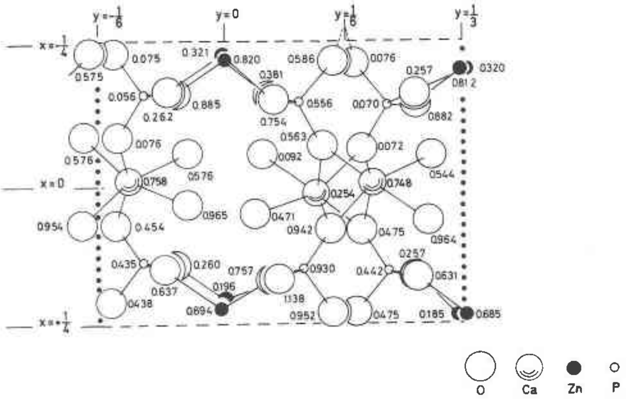

FIG. 2. The asymmetric unit of scholzite, space group $Pbc2_1$. The origin was shifted to facilitate a comparison with the substructure.

structure, are small shifts of the x coordinates of the corresponding atoms in the three adjacent subcells.

The attempt to derive a structure with the space group $P2_122_1$ resulted in a model yielding an R value of about 16 percent. The model contains 48 atoms in the asymmetric unit. The temperature factors are relatively high on the average, and in some cases unreasonably high. This result suggests that the space group of scholzite is $Pbc2_1$.

Acknowledgments

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