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Structure and twinning in spencerite

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SUMMARY. A refinement of the crystal structure of spencerite, $Zn_4(PO_4)_2(OH)_2\cdot 3H_2O$, was performed on a twin crystal from Salmo, British Columbia. Three-dimensional intensity data were collected by a Weissenberg apparatus. The *R* index was 0·098 for 335 independent observed reflections. The crystal structure previously determined is essentially confirmed. Co-ordination around Zn is both octahedral and tetrahedral. The atomic arrangement consists of complex sheets of co-ordination octahedra and tetrahedra around Zn and P atoms connected by layers of water molecules. The frequent occurrence of twinning in spencerite is explained from structural considerations.

SPENCERITE, a natural hydrated basic zinc phosphate with chemical formula $Zn_4(PO_4)_2(OH)_2\cdot 3H_2O$, was first found by Walker (1916) at the Hudson Bay mine, Salmo, British Columbia, where it occurs as polysynthetic aggregates with twin plane and composition surface {100}. The morphology suggests a monoclinic symmetry. In a recent investigation Niebsch (1966) determined the lattice parameters and the space group of the mineral (*P*2/*c*), and proposed an approximate structural model based on limited data.

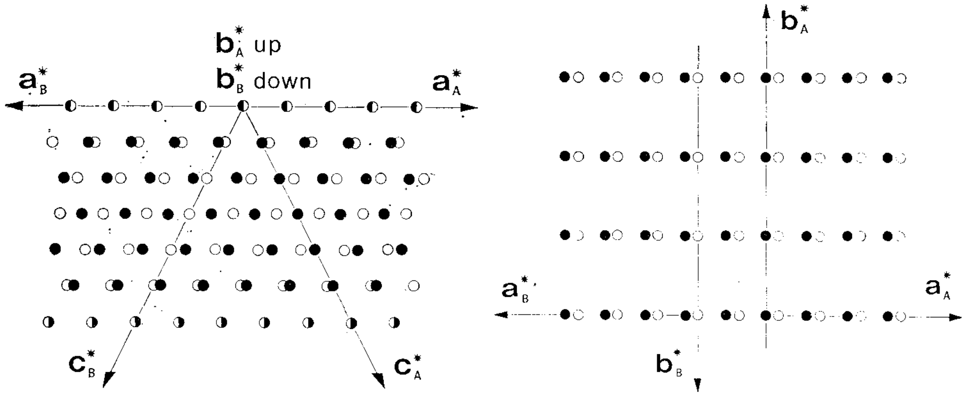
The purpose of our work is to refine the structure of spencerite using more data and to relate the structure and twinning in the mineral.

Experimental. The specimen of spencerite from Salmo, British Columbia, employed in the present study consists of a crystalline aggregate showing columnar texture. X-ray reflections collected by a powder-diffractometer were indexed up to $\sin\theta/\lambda = 0{\cdot}27$. Refinement of the lattice constants was then performed by a least-squares method. The results are *a* 10·448±0·003 Å, *b* 5·282±0·001 Å, *c* 11·208±0·003 Å, $\beta = 116^\circ\ 44'\pm 2'$, in good agreement with those proposed by Berry and reported in the A.S.T.M. card No. 13–195. The calculated density is 3·242 g.cm^{-3}; the observed value is 3·14 g.cm^{-3} (Palache *et al.*, 1951), and $Z = 2$.

A fragment with irregular shape was chosen for single crystal X-ray study and mounted with [001] as rotation axis. Diffraction effects from *hk*0 to *hk*6 were collected with Weissenberg equi-inclination technique employing Cu-*Kα* and Fe-*Kα* radiation.

The fragment proved to be twinned, since the appearance of the zero layer is normal while the upper layers have a double lattice character. Furthermore the orthorhombic pseudo-symmetry of the photographs proves that the twin plane is {100} and that the individuals of the twin have a nearly equal size. The superimposed *h*0*l* nets of the reciprocal lattices of individuals A and B are illustrated in fig. 1. $hk0_A$ and $\bar{h}\bar{k}0_B$ reflections superimpose and their intensities were reduced to an half in data reduction. The diffraction effects from *hk*1 to *hk*5 were easily indexed since no overlap occurs between reflections from the two individuals, as shown in fig. 2, where the *hk*2 layer of the reciprocal lattice of the twin is sketched. On Weissenberg photographs of the layer with $l = 6$, $hk6$ reflections from individual A are almost completely overlapped by $\overline{(h+5)}\,\bar{k}\,6$ reflections from individual B and therefore were not employed in the structural work.

The intensity data were measured with a microdensitometer and, after Lorentz-polarization correction, were approximately scaled by taking into account their exposure times. A total of 462 independent reflections were collected; of these 127 were too weak to be observed.



FIGS. 1 and 2: FIG. 1 (left). The superimposed a^*c^* nets of the twinned individuals. The closed circles belong to individual A; the open circles to individual B. FIG. 2 (right). The $hk2$ layer of the reciprocal lattice of the twin.

Structure refinement. A structure factor calculation using positional parameters by Niebsch and an over-all thermal factor $B = 1$ Å^2 showed that the proposed structure is correct. The discrepancy index R, defined as $\sum||F_0|-|F_c||/\sum|F_0|$, was 0·21 for all the observed reflections. A Fourier synthesis lowered R to 0·16. Refinement was then performed by means of a least-squares block-diagonal program written by Shiono for IBM 1130.

The weighting scheme was $w = 1$ for $|F_0|$ up to 4 times the minimum observable $|F_{\min}|$ and $w = (4|F_{\min}|/|F_0|)^2$ for higher values of F_0. Unobserved reflections were given $w = 0$. After four cycles, employing individual isotropic thermal parameters, the R index reached 0·098 and at this stage the refinement was stopped. The agreement between observed and calculated structure factors is quite acceptable considering the limitations in the data obtained from a twinned crystal: the intensities were not integrated in order to avoid overlaps of reflections on the photographs and were not corrected for absorption. A table of observed and calculated structure factors is deposited in the library of the Department of Mineralogy, British Museum (Natural History). The atomic scattering factors of Zn^{2+}, P, and O from the International Tables for X-ray Crystallography (1962) were used in calculations. Atomic coordinates, their standard deviations, and isotropic thermal parameters are listed in Table I together with the values from Niebsch.

TABLE I. *Fractional atomic co-ordinates with their standard deviations and isotropic thermal parameters. Comparison with the determination of Niebsch*

Present determination					Niebsch (1966)		
Atom	*x/a*	*y/b*	*z/c*	B(Å)^2	*x/a*	*y/b*	*z/c*
Zn(1)	0	0	0	1·75	0	0	0
Zn(2)	0	0·0226(13)	$\frac{1}{4}$	1·46	0	0·000	$\frac{1}{4}$
Zn(3)	0·2863(5)	0·7028(9)	0·4906(7)	1·29	0·285	0·704	0·490
P	0·1712(9)	0·5097(18)	0·1936(15)	0·16	0·171	0·500	0·190$_5$
O(1)	0·0775(22)	0·2680(46)	0·1566(31)	0·69	0·079$_5$	0·250	0·156$_5$
O(2)	0·0746(24)	0·7469(49)	0·1641(33)	1·00	0·079$_5$	0·750	0·156$_5$
O(3)	0·2805(25)	0·5027(50)	0·3375(36)	1·28	0·271	0·500	0·338
O(4)	0·2538(25)	0·5257(49)	0·1111(34)	0·89	0·269	0·500	0·114
OH	0·1691(28)	0·0027(54)	0·4414(38)	1·11	0·163	0·000	0·445$_5$
$H_2O(1)$	0·4967(24)	0·7873(52)	0·5873(30)	1·42	0·492	0·790	0·589$_5$
$H_2O(2)$	$\frac{1}{2}$	0·8153(71)	$\frac{1}{4}$	0·70	$\frac{1}{2}$	0·790	$\frac{1}{4}$

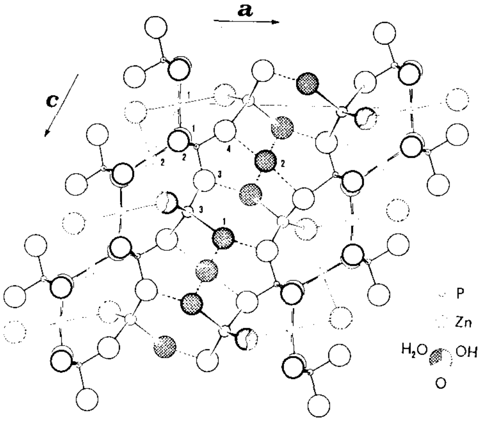


FIG. 3. View of the spencerite structure projected along the *b* axis.

Description and discussion of the structure

The structure of spencerite projected along the *b* axis is sketched in fig. 3. Bond lengths and bond angles are listed in Table II. The three Zn^{2+} ions in the asymmetric unit exhibit two different co-ordinations: those on special positions at inversion centres and on twofold axes have a distorted octahedral environment, while the other one, in a general position, is tetrahedral. The octahedra around Zn(1) and Zn(2) are formed by four oxygen atoms of four different PO_4 groups and by two hydroxyl groups with *trans*-configuration. The average Zn–O distances are 2·12 and 2·07 Å respectively. These values are in agreement with those reported in literature for Zn in sixfold co-ordination; a list of average $Zn^{[6]}$–O distances in recently determined crystal structures is reported by Ribar *et al.* (1970).

Zn(3) is co-ordinated by two oxygen atoms, an hydroxyl group and a water molecule; the mean Zn–O distance is 1·97 Å. This value is comparable with those found for tetrahedral zinc in other structures: in parahopeite (Chao, 1969) the average Zn$^{[4]}$–O distance is 1·953 Å; in Zn$_3$(BO$_3$)$_2$ (Baur and Tillmanns, 1970) it is 1·97 Å for three non-equivalent tetrahedral groups. Zn–O values observed for co-ordination numbers 6 and 4 respectively are significantly different, in agreement with the general observation that an increase of metal–ligand distance occurs with increasing co-ordination number.

TABLE II. *Interatomic distances and bond angles in spencerite*

(I) = x, y, z; (II) = $-x, 1-y, -z$; (III) = $x, -y, -\frac{1}{2}+z$; (IV) = $x, -1+y, z$;
(V) = $x, 1-y, \frac{1}{2}+z$; (VI) = $x, 1+y, z$; (VII) = $x, 2-y, -\frac{1}{2}+z$; (VIII) = $1-x, 1+y, \frac{1}{2}-z$;
(IX) = $x, y, \frac{1}{2}-z$; (X) = $-x, -1+y, \frac{1}{2}-z$; (XI) = $1-x, y, \frac{1}{2}-z$.

Zn(1)(I)	–O(1)(I)		2·11	±0·03 Å	×2
	–O(2)(II)		2·12	0·03	×2
	–OH(III)		2·14	0·03	×2
Zn(3)(I)	–O(3)(I)		1·99	±0·03 Å	
	–O(4)(V)		1·95	0·03	
	–OH(VI)		1·93	0·03	
	–H$_2$O(1)(I)		2·02	0·02	
H$_2$O(1)(VII)	–H$_2$O(2)(I)		2·77	±0·04 Å	
	–O(3)(VIII)		2·59	0·03	
O(1)(I) –	Zn(1)(I)	–O(2)(IV)	81·2°	±1·1°	
O(1)(I) –		–OH(III)	101·4°	1·1°	
O(2)(IV) –		–OH(III)	103·3°	1·1°	
O(1)(I)	–Zn(2)(I)	–O(2)(IV)	83·7°	±1·1°	
		–OH(IX)	81·5°	1·1°	
		–O(1)(IX)	101·5°	1·1°	
		–O(2)(X)	174·8°	1·1°	
		–OH(I)	102·2°	1·1°	
O(2)(IV)	–Zn(2)(I)	–O(2)(X)	91·2°	1·1°	
		–OH(I)	96·9°	1·2°	
		–OH(IX)	79·0°	1·1°	
OH(I)	–Zn(2)(I)	–OH(IX)	174·2°	1·2°	

Zn(2)(I)	–O(1)(I)		2·05	±0·03 Å	×2
	–O(2)(IV)		2·08	0·03	×2
	–OH(I)		2·08	0·03	×2
P(I)	–O(1)(I)		1·55	±0·02 Å	
	–O(2)(I)		1·55	0·03	
	–(O3)(I)		1·50	0·04	
	–(O4)(I)		1·52	0·03	
H$_2$O(2)(I)	–O(4)(I)		2·79	±0·03 Å	×2
O(3)(I)	–Zn(3)(I)	–O(4)(V)	108·7°	±1·2°	
		–OH(VI)	114·9°	1·4°	
		–H$_2$O(1)(I)	100·6°	1·1°	
O(4)(V)	–Zn(3)(I)	–OH(VI)	114·9°	1·3°	
		–H$_2$O(1)(I)	104·6°	1·2°	
OH(VI)	–Zn(3)(I)	–H$_2$O(1)(I)	111·8°	1·1°	
O(1)(I)	–P(I)	–O(2)(I)	109·7°	±1·3°	
		–O(3)(I)	110·6°	1·7°	
		–O(4)(I)	110·2°	1·7°	
O(2)(I)	–P(I)	–O(3)(I)	111·0°	1·8°	
		–O(4)(I)	108·5°	1·7°	
O(3)(I)	–P(I)	–O(4)(I)	106·8°	1·6°	
H$_2$O(2)(I)	–H$_2$O(1)(VII)	–O(3)(VIII)	119·4°	1·2°	
O(4)(I)	–H$_2$O(2)(I)	–O(4)(XI)	113·5°	1·5°	

Spencerite is an example of a mineral containing Zn in both octahedral and tetrahedral co-ordination: others are hydrozincite (Ghose, 1964), hopeite (Liebau, 1965), and parahopeite (Chao, 1969). However spencerite is the first mineral in which the octahedral to tetrahedral Zn ratio 1:1 has been observed, since in hydrozincite this ratio is 3:2 and in hopeite and parahopeite 1:2. Other synthetic compounds are known with the ratio 1:1, namely Zn$_2$Mo$_3$O$_8$ (McCarrol *et al.*, 1957) and Zn(OH)$_2$·ZnSO$_4$ (Iitaka *et al.*, 1962).

The PO_4 group has a regular shape with P–O values in the range 1·50–1·55 Å (mean value 1·53 Å).

The water molecule not bonded to the cations, $(H_2O)(2)$, forms two hydrogen bonds with O(4) at a distance of 2·79 Å and two with $H_2O(1)$ at 2·77 Å, the arrangement being nearly tetrahedral. The other water molecule $(H_2O)(1)$ in the asymmetric unit is linked to the tetrahedral zinc and forms two hydrogen bonds with $(H_2O)(2)$ and O(3) with distances of 2·77 and 2·59 Å. The hydroxyl group has been distinguished from the water molecules on the basis of a charge balance and possible hydrogen bonding. The scheme of charge balance, Table III, has been computed assuming that the charge of each hydrogen atom, when involved in hydrogen bonds, is distributed between the two oxygen atoms as $+\frac{3}{4}$ for the bonded and $+\frac{1}{4}$ for the unbonded atom; a 3·02 Å long contact between OH and O(4) has not been considered as a hydrogen-bond.

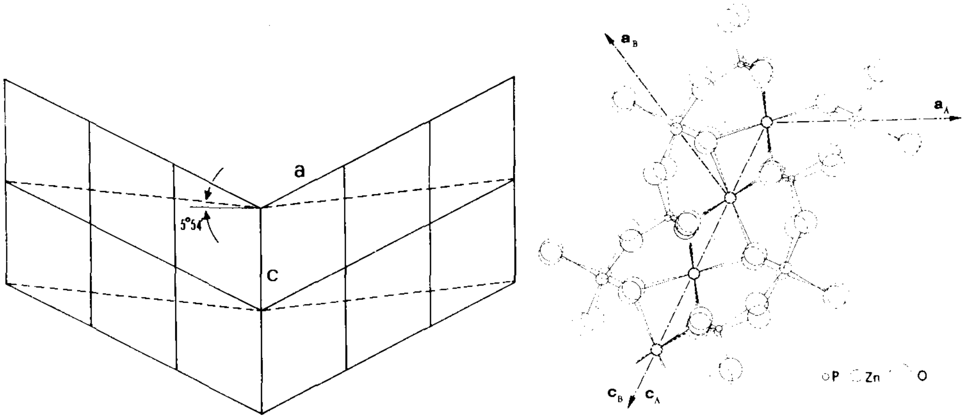
TABLE III. *Balance of electrostatic valences for oxygen atoms*

	Zn(1)	Zn(2)	Zn(3)	P	–H	–H...	...H–	Total
O(1)	$\frac{1}{3}$	$\frac{1}{3}$	—	$\frac{5}{4}$	—	—	—	$2-\frac{1}{12}$
O(2)	$\frac{1}{3}$	$\frac{1}{3}$	—	$\frac{5}{4}$	—	—	—	$2-\frac{1}{12}$
O(3)	—	—	$\frac{1}{2}$	$\frac{5}{4}$	—	—	$\frac{1}{4}$	2
O(4)	—	—	$\frac{1}{2}$	$\frac{5}{4}$	—	—	$\frac{1}{4}$	2
OH	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{2}$	—	1	—	—	$2+\frac{1}{6}$
$H_2O(1)$	—	—	$\frac{1}{2}$	—	—	$2\times\frac{3}{4}$	—	2
$H_2O(2)$	—	—	—	—	—	$2\times\frac{3}{4}$	$2\times\frac{1}{4}$	2

The atomic arrangement of spencerite consists of Zn octahedra sharing opposite faces in the *c* direction to form a chain to which Zn tetrahedra are linked by a vertex represented by an hydroxyl group. Neighbour chains are connected in the *b* direction by PO_4 groups forming a complex sheet parallel to the *bc* plane. Layers of water molecules are interposed between two of these adjacent sheets. The resulting system of hydrogen bonds builds up a three-dimensional framework. The structure explains the perfect {100} cleavage.

Twinning. From a geometrical point of view, the twinning of spencerite can be classified according to Friedel's (1926) notation as a twinning by pseudo-merohedry, with reflection plane (100), three-fold multiplicity, and an obliquity of 5° 54′. In fig. 4 the lattices of A and B individuals are sketched together with the pseudo-orthorhombic lattice of the twin.

Considering twinning with regard to structure, the discontinuity at the twin boundary must be bridged by a slice of the atomic arrangement that is common to the two individuals in order to minimize the boundary energy. This requirement is fulfilled in spencerite: the portion of structure shared by both crystals being represented by the sheet formed by Zn and P co-ordination octahedra and tetrahedra. Fig. 5 shows partial structures of the A individual (solid line) and of the B individual (dashed line) superposed at the boundary of the twin, after a shift of origin by $\frac{1}{4}c$. The overlapping is nearly perfect; this fact qualitatively explains the frequent occurrence of twinning from an energetical point of view. The pseudo-symmetry element that becomes the twin symmetry operator is then a glide plane (100) with translation component $\frac{1}{4}c$. According to the twinning theory of Holser (1958) the Zn and P sheet, in which the requisite symmetry for twinning pre-exists, represents the boundary slice of the twin.



FIGS. 4 and 5: FIG. 4 (left). Relationships between the monoclinic lattices of individuals A and B and the pseudo-orthorhombic lattice of the twin (dashed line). FIG. 5 (right). Atomic arrangement in individuals A (solid line) and B (dashed line) at the boundary of the twin.

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