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THE CRYSTAL STRUCTURE OF EHRLEITE, A TETRAHEDRAL SHEET STRUCTURE

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ABSTRACT

The crystal structure of ehrleite, $Ca_2ZnBe(PO_4)_2(PO_3OH)\cdot 4H_2O$, triclinic, a 7.130(4), b 7.430(4), c 12.479(9) Å; α 94.31(5), β 102.07(4), γ 82.65(4)°, V 640.3(6) Å^3, space group $P\bar{1}$, has been solved by direct methods and refined by full-matrix least-squares to an R index of 9.3% using 2282 observed ($I > 2.5\sigma I$) reflections measured on a twinned crystal. The (BeO_4) and (ZnO_4) tetrahedra, each connected to four other tetrahedra, share corners with two- and three-connected $(P\varnothing_4)$ ($\varnothing$: unspecified ligand) tetrahedra to form a thick tetrahedral sheet parallel to (010). These sheets are linked by [7]- and [8]-co-ordinated Ca atoms, and by an extensive network of hydrogen-bonding. The chemical formula differs from that given in the original description of the mineral. Notable is the presence of an acid phosphate group that is involved in local positional disorder of the P cation; local bond-valence and long-range neutrality arguments suggest a $Zn^{2+} \rightleftharpoons 2H^+$ substitution in ehrleite.

Keywords: ehrleite, crystal structure, phosphate.

SOMMAIRE

On a déterminé la structure cristalline de l'ehrléite, $Ca_2ZnBe(PO_4)_2(PO_3OH)\cdot 4H_2O$, minéral triclinique, a 7.130(4), b 7.430(4), c 12.479(9) Å, α 94.31(5), β 102.07(4), γ 82.65(4)°, V 640.3(6) Å^3, groupe spatial $P\bar{1}$, par méthodes directes. L'affinement par moindres carrés à matrice entière, qui a porté sur un individu maclé et 2282 réflexions observées ($I > 2.5\sigma I$), a atteint un résidu R de 9.3%. Des tétraèdres (BeO_4) et (ZnO_4), chacun lié à quatre autres tétraèdres, partagent leurs sommets avec des tétraèdres $(P\varnothing_4)$ ($\varnothing$: groupement non spécifié) qui sont liés avec deux ou trois autres tétraèdres, ce qui donne un feuillet relativement épais de tétraèdres parallèle à (010). Ces feuillets sont liées par des atomes de calcium à coordinance 7 ou 8 et par un réseau important de liaisons hydrogène. La formule chimique diffère de celle qui a été donnée dans la description originelle de cette espèce. On a découvert un groupement de phosphate acide impliqué dans un désordre de position du cation P. Des considérations de la somme des valences des liaisons et de la neutralité électrostatique à grande échelle dans le cristal font penser qu'il y a une substitution de Zn^{2+} pour $2H^+$ dans l'ehrléite.

(Traduit par la Rédaction)

Mots-clés: ehrléite, structure cristalline, phosphate.

INTRODUCTION

Ehrleite is a hydrated phosphate of calcium, beryllium and zinc, recently found at the Tip Top mine, Black Hills, South Dakota, and described by Robinson *et al.* (1985). Two distinct associations were recorded: on a matrix of beryl and quartz, mitridatite, roscherite, hydroxyl-herderite, goyazite–crandallite and erhleite crystallized in that order; the other occurrence is on a matrix of beryl, botryoidal apatite, Mn-oxides, roscherite, parascholzite and ehrleite, which have formed in that order. As well as the intrinsic interest of relating the ehrleite structure to its position in the crystallization sequence, the formula of ehrleite, $Ca_4Be_3Zn_2(PO_4)_6\cdot 9H_2O$, reported by Robinson *et al.* (1985), suggests some unusual features. There are an odd number of Be atoms and (H_2O) groups; thus in the space group $P\bar{1}$, at least one of each species must occupy special positions. Be is generally tetrahedrally co-ordinated by oxygen atoms; if this is the case in ehrleite, neither Be nor (H_2O) can occupy a special position of point symmetry $\bar{1}$, suggesting a number of possibilities: (i) the space group of ehrleite is $P1$; (ii) the structure has symmetry $P1$ but has very considerable positional disorder; (iii) Be has an unusual co-ordination number; (iv) the given formula is incorrect. To resolve these points, and to characterize what promised to be an intriguing array of atoms, a structural study of ehrleite was undertaken.

EXPERIMENTAL

The material used was taken from the holotype specimen, NMNS#49289, deposited at the National Museum of Natural Sciences in Ottawa; this corresponds to the first paragenesis mentioned in the introduction. As with all ehrleite crystals examined (Robinson *et al.* 1985), the crystal used in this work is twinned by reflection on {001}. These are contact twins, but because of the rarity of the material and its brittle character, we made no attempt to break the crystal along the twin plane. It was obvious from precession photographs that there was significant overlap of reflections due to twinning; however, the overlap was not merohedral, and because ehrleite is

TABLE 1. EHRLEITE: CRYSTAL DATA AND REFINEMENT INFORMATION

a	7.130(4)Å	Crystal size (mm)	0.16x0.28x0.40
b	7.430(4)	Radiation	MoKα, Graphite monochromated
c	12.479(9)	Total unique |Fo|	2911
α	94.31(5)	No. of |Fo|, I>2.5σI	2648
β	102.07(4)	No. of |Fo| used	2282
γ	82.65(4)°	R (observed)	9.3%
V	640.3(6)Å³	wR (observed)	10.3%

Space Group $P\bar{1}$

Unit cell contents: $2[Ca_2ZnBe(PO_4)_2(PO_3OH).4H_2O]$

$R = \Sigma(|Fo|-|Fc|)/\Sigma|Fo|$

$wR = [\Sigma w(|Fo|-|Fc|)^2/\Sigma wFo^2]^{\frac{1}{2}}, w = 1$

triclinic, no simple relationship between single and overlapped reflections was apparent.

The crystal was mounted on a Nicolet $R3m$ automated four-circle diffractometer equipped with a Mo X-ray tube. Twenty-five reflections were measured on a random orientation photograph and aligned automatically. Some of the reflections gave problems because of double maxima due to partial overlap of reflections from different components of the twin; these were replaced by others until twenty-five satisfactory reflections were aligned. With the fairly relaxed constraint that only thirteen of the twenty-five reflections have to be satisfied, the correct cell was found, and all of the reflections were indexed. This cell and its corresponding orientation matrix corresponded to one of the twin components; reflections with (near) integral indices also (usually) belonged to the same twin component, and reflections having nonintegral indices were found to belong to the other twin component. Deletion of the latter reflections followed by least-squares refinement gave a much better cell, and identified two more reflections from the other component of the twin. Final least-squares refinement gave adequate precision; the resulting cell-parameters are given in Table 1, together with other information pertinent to data collection and final refinement.

Intensity data were collected according to the method of Hawthorne (1985). A total of 3214 reflections was measured over one asymmetric unit out to a maximum 2θ of 60°. Ten strong reflections uniformly distributed with regard to 2θ were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0 to 350°. These data were used to calculate an ellipsoidal absorption-correction; because the crystal is a twin, the absorption correction was not particularly accurate, and the merging R index was only 5.4% for the azimuthal data. One hundred and forty reflections were rejected for unequal backgrounds on each side of the peak; scan profiles showed that these are all partly overlapped reflections from different components of the twin. Standard data-reduction resulted in 2911 reflections, of which 2648 were considered as observed ($I > 2.5\sigma I$).

SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with coefficients of anomalous dispersion, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. R indices are of the form given in Table 1 and are expressed as percentages.

Inspection of the precession photographs showed that the majority (>70%) of the reflections were unaffected by overlap, and consequently the twinning was not considered during the first stages of the solution of the structure. The structure was solved by direct methods assuming the space group $P\bar{1}$. The phase set with the highest combined figure of merit gave a solution for one Zn, two Ca and three P atoms that converged to an R index of 38%. Successive difference-Fourier maps located the oxygen atoms and a Be atom, and full-matrix least-squares refinement converged to an R index of 18.9%. Inspection of the list of structure factors showed many reflections for which $|F_o| >> |F_c|$, presumably the result of overlap due to twinning. However, it was apparent that the structural model was also not correct, as the current formula, $Ca_4Be_2Zn_2(PO_4)_3 \cdot 9H_2O$, was not electrostatically neutral. It was necessary to discard overlapped reflections, but it was also necessary not to discard single reflections that did not agree because of current inadequacies of the structural model. Consequently, we proceeded by iteratively discarding a few structure factors with the largest positive ΔF ($= |F_o| - |F_c|$) values, followed by a cycle of least-squares refinement and calculation of a difference-Fourier map with a structural model in the space group $P1$. This process gradually reduced to a model with an R index of 9.4% for 2426 reflections; the space group was still $P1$, but there was no obvious noncentrosymmetric character to the structure, and atoms related by an apparent centre of symmetry tended to show high correlations of parameters. This is to be expected when a centrosymmetric structure is refined in a noncentrosymmetric space-group. Conversion to the space group $P\bar{1}$ gave the same R index. However, the one additional atomic position found during this sequence did not immediately seem to make stereochemical sense; there was one "atom" 1.80 Å from P(3), 1.56 Å from O(12) and 1.81 Å from OW(2) (OW = H_2O). The isotropic temperature-factor of P(3) was 0.016, significantly larger than those of P(1) and P(2) (= 0.0075), suggesting that the scattering at P(3) was slightly less than that appropriate for a fully occupied P site. This suggested that *either* P(3) *or* the anomalous atomic position was occupied, charge balance being most easily satisfied by partial occupancy of each site by P. This last site was designated P(4), and the occupancies of P(3) and P(4) were initially set such that their sum was unity; their temperature factors were fixed at the mean value of P(1) and P(2). Least-squares refinement of all variables, including the occupancies but not the temperature factors of *both* the P(3) and P(4) positions, resulted in convergence at an *R* index of 9.3%. The temperature factors of P(3) and P(4) were adjusted to be equal to the mean value for P(1) and P(2), and the full-matrix least-squares refinement was repeated. The joint occupancy of the P(3) and P(4) positions was 0.896(9) + 0.108(8) = 1.004(12); the unconstrained convergence to total joint occupancy of 1.0 P supports the disordered model. Careful inspection of the region in the difference-Fourier map failed to show the corresponding disordered oxygen atoms for the lower-occupancy configuration; this is perhaps not surprising in view of the problems with twinning and the small amount of scattering expected for one-tenth of an oxygen atom.

Final atomic positions are given in Table 2, selected interatomic distances and angles in Tables 4 and 5, and an empirical bond-valence analysis in Table 6. Observed and calculated structure-factors (Table 3) may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 2. ATOMIC PARAMETERS FOR EHRLEITE

	x	y	z	U(x10^4)
Ca(1)	0.2746(3)	0.0009(3)	0.5520(2)	100(3)
Ca(2)	0.0190(3)	0.9548(3)	0.2076(2)	147(5)
Zn	0.1424(2)	0.4630(2)	0.1820(1)	129(3)
P(1)	0.0542(4)	0.2810(3)	0.3790(2)	79(5)
P(2)	0.3587(4)	0.6943(3)	0.3773(2)	83(5)
P(3)^1	0.2454(4)	0.3698(4)	-0.0403(2)	81^3
P(4)^2	0.142(3)	0.366(3)	0.815(2)	81^3
Be	0.2675(18)	0.4992(17)	0.5492(11)	80(23)
O(1)	-0.0047(11)	0.0951(9)	0.3918(6)	112(14)
O(2)	0.1367(11)	0.2617(10)	0.2713(7)	124(15)
O(3)	0.2187(11)	0.3139(10)	0.4800(7)	145(15)
O(4)	-0.1094(11)	0.4355(10)	0.3723(6)	120(15)
O(5)	0.4184(11)	0.8860(10)	0.3927(7)	133(15)
O(6)	0.2643(11)	0.6708(10)	0.4751(7)	134(15)
O(7)	0.2098(11)	0.6833(10)	0.2705(7)	144(15)
O(8)	0.5264(11)	0.5440(10)	0.3687(6)	125(15)
O(9)	0.3212(12)	0.4261(11)	0.0807(7)	171(16)
O(10)	0.4326(12)	0.3277(10)	-0.0941(7)	155(16)
O(11)	0.1467(13)	0.2013(11)	-0.0552(7)	200(17)
O(12)	0.1224(12)	0.5277(10)	-0.0993(7)	146(15)
OW(1)	0.4563(12)	-0.1817(11)	0.6981(7)	164(16)
OW(2)	0.1986(11)	0.2079(10)	0.7054(7)	141(15)
OW(3)	-0.2512(13)	0.1624(12)	0.1374(8)	232(18)
OW(4)	0.2661(15)	0.9749(13)	0.1104(9)	293(21)

^{1}P(3) occupancy = 0.890(9); ^{2}P(4) occupancy = 0.107(8); ^{3}fixed during refinement.

DISCUSSION

Description of the structure

There are three unique P positions in ehrleite, one of which shows some positional disorder. Each of the P atoms is co-ordinated by four oxygen atoms in a tetrahedral arrangement showing a typical range of bond lengths and angles. The variation in P – O bond lengths correlates well with the local bond-valence requirements of the anions (Table 6). This is particularly notable for the P(3) tetrahedron, which is a (PO_3OH) acid phosphate group. The O(10) oxygen is an (OH) group, requiring less than the average P – O bond-valence of 1.25 v.u., and consequently the P(3) – O(10) bond is significantly longer than the other P – O bonds in the structure.

There is one unique Zn position in the structure, and the Zn atom is tetrahedrally co-ordinated by four oxygen atoms. There is not much dispersion in the Zn – O bond lengths (<0.02 Å), but the (ZnO_4) tetrahedron shows considerable angular distortion (Table 3). There is one unique Be position, again tetrahedrally co-ordinated by four oxygen atoms, with a typical range of bond distances and angles. The variation in Zn – O and Be – O distances can be rationalized in terms of the local anion bond-

TABLE 4. SELECTED BOND-LENGTHS (Å) IN EHRLEITE

P(1)-O(1)	1.523(8)	P(3)-O(9)	1.539(9)
P(1)-O(2)	1.565(9)	P(3)-O(10)	1.601(9)
P(1)-O(3)	1.559(8)	P(3)-O(11)	1.494(9)
P(1)-O(4)	1.522(7)	P(3)-O(12)	1.512(8)
<P(1)-O>	1.542	<P(3)-O>	1.537
P(2)-O(5)	1.526(8)	P(4)-O(12)	1.56(2)
P(2)-O(6)	1.542(10)	P(4)-P(3)	1.80(2)
P(2)-O(7)	1.525(8)		
P(2)-O(8)	1.543(8)		
<P(2)-O>	1.534		
Zn-O(2)	1.941(8)	Be-O(3)	1.607(14)
Zn-O(7)	1.959(8)	Be-O(4)b	1.648(16)
Zn-O(9)	1.956(9)	Be-O(6)	1.626(16)
Zn-O(12)a	1.948(8)	Be-O(8)c	1.616(14)
<Zn-O>	1.951	<Be-O>	1.624
Ca(1)-O(1)	2.577(7)	Ca(2)-O(1)f	2.481(8)
Ca(1)-O(1)d	2.386(9)	Ca(2)-O(2)f	2.544(8)
Ca(1)-O(3)	2.511(8)	Ca(2)-O(7)	2.371(7)
Ca(1)-O(5)e	2.471(9)	Ca(2)-O(11)a	2.332(8)
Ca(1)-O(5)c	2.393(8)	Ca(2)-OW(2)b	2.536(9)
Ca(1)-O(6)e	2.570(8)	Ca(2)-OW(3)f	2.365(9)
Ca(1)-OW(1)	2.403(8)	Ca(2)-OW(4)	2.363(12)
Ca(1)-OW(2)	2.469(8)		
<Ca(1)-O>	2.473	<Ca(2)-O>	2.427
OW(1)-O(2)	2.840(11)	OW(3)-O(11)	2.880(12)
OW(1)-O(8)	2.743(11)	OW(3)-O(12)	2.693(13)
OW(2)-O(4)	2.840(10)	OW(4)-O(10)	2.929(12)
OW(2)-O(5)?	3.198(11)	OW(4)-O(11)	2.691(13)
O(10)-O(9)	2.666(12)		

a: $\bar{x}$,1-y,$\bar{z}$; b: $\bar{x}$,1-y,1-z; c: 1-x,1-y,1-z; d: $\bar{x}$,$\bar{y}$,1-z; e: x,y-1,z; f: x,y+1,z.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN EHRLEITE

O(1)-O(2)	2.458(12)	O(1)-P(1)-O(2)	105.5(4)
O(1)-O(3)	2.460(11)	O(1)-P(1)-O(3)	105.9(4)
O(1)-O(4)	2.560(10)	O(1)-P(1)-O(4)	114.3(4)
O(2)-O(3)	2.558(11)	O(2)-P(1)-O(3)	109.9(5)
O(2)-O(4)	2.536(11)	O(2)-P(1)-O(4)	110.5(4)
O(3)-O(4)	2.535(10)	O(3)-P(1)-O(4)	110.6(4)
<O-O>P(1)	2.517	<O-P(1)-O>	109.5
O(5)-O(6)	2.447(12)	O(5)-P(2)-O(6)	105.8(5)
O(5)-O(7)	2.467(11)	O(5)-P(2)-O(7)	107.9(4)
O(5)-O(8)	2.575(10)	O(5)-P(2)-O(8)	113.9(4)
O(6)-O(7)	2.509(12)	O(6)-P(2)-O(7)	109.8(5)
O(6)-O(8)	2.558(12)	O(6)-P(2)-O(8)	112.0(4)
O(7)-O(8)	2.473(10)	O(7)-P(2)-O(8)	107.3(4)
<O-O>P(2)	2.505	<O-P(2)-O>	109.5
O(9)-O(10)	2.502(13)	O(9)-P(3)-O(10)	105.6(5)
O(9)-O(11)	2.537(11)	O(9)-P(3)-O(11)	113.5(5)
O(9)-O(12)	2.506(11)	O(9)-P(3)-O(12)	110.4(4)
O(10)-O(11)	2.499(13)	O(10)-P(3)-O(11)	107.6(5)
O(10)-O(12)	2.494(11)	9(10)-P(3)-O(12)	106.4(5)
O(11)-O(12)	2.505(12)	O(11)-P(3)-O(12)	112.8(5)
<O-O>P(3)	2.507	<O-P(3)-O>	109.4
O(3)-O(4)b	2.680(11)	O(3)-Be-O(4)b	110.9(9)
O(3)-O(6)	2.720(11)	O(3)-Be-O(6)	114.5(9)
O(3)-O(8)c	2.595(10)	O(3)-Be-O(8)c	107.3(8)
O(4)b-O(6)	2.608(13)	O(4)b-Be-O(6)	105.6(8)
O(4)b-O(8)c	2.609(11)	O(4)b-Be-O(8)c	106.2(8)
O(6)-O(8)c	2.685(10)	O(6)-Be-O(8)c	111.9(9)
<O-O>Be	2.650	<O-Be-O>	109.4
O(2)-O(7)	3.242(11)	O(2)-Zn-O(7)	112.5(3)
O(2)-O(9)	3.323(13)	O(2)-Zn-O(9)	117.0(3)
O(2)-O(12)a	2.927(10)	O(2)-Zn-O(12)a	97.7(3)
O(7)-O(9)	3.100(12)	O(7)-Zn-O(9)	104.7(4)
O(7)-O(12)a	3.310(11)	O(7)-Zn-9(12)a	115.8(3)
O(9)-O(12)a	3.194(12)	O(9)-Zn-O(12)a	109.7(3)
<O-O>Zn	3.183	<O-Zn-O>	109.6
O(1)-O(3)	2.460(11)	O(1)-Ca(1)-O(3)	57.8(2)
O(1)-OW(2)	3.944(12)	O(1)-Ca(1)-OW(2)	102.8(2)
O(1)-O(1)d	3.124(16)	O(1)-Ca(1)-O(1)d	78.0(3)
O(1)-O(5)e	3.207(1))	O(1)-Ca(1)-O(5)e	78.9(2)
O(1)-O(6)e	3.579(13)	O(1)-Ca(1)-O(6)e	88.1(2)
O(3)-OW(2)	3.014(12)	O(3)-Ca(1)-OW(2)	74.5(3)
O(3)-O(5)e	3.504(10)	O(3)-Ca(1)-O(5)e	89.5(3)
O(3)-O(5)c	3.014(10)	O(3)-Ca(1)-O(5)c	75.8(3)
OW(1)-OW(2)	3.228(10)	OW(1)-Ca(1)-OW(2)	83.0(3)
OW(1)-O(1)d	3.180(11)	OW(1)-Ca(1)-O(1)d	83.2(3)
OW(1)-O(5)e	3.830(12)	OW(1)-Ca(1)-O(5)e	103.6(3)
OW(1)-O(5)c	2.864(12)	OW(1)-Ca(1)-O(5)c	73.4(3)
OW(1)-O(6)e	3.023(11)	OW(1)-Ca(1)-O(6)e	74.9(3)
OW(2)-O(1)d	2.851(10)	OW(2)-Ca(1)-O(1)d	71.9(3)
OW(2)-O(5)c	3.197(12)	OW(2)-Ca(1)-O(5)c	82.2(3)
O(1)b-O(6)e	3.041(11)	O(1)b-Ca(1)-O(6)e	75.6(3)
O(5)e-O(5)c	3.147(11)	O(5)e-Ca(1)-O(5)c	80.6(3)
O(5)e-O(6)e	2.447(12)	O(5)e-Ca(1)-O(6)e	58.0(3)
<O-O>Ca(1)	3.147	<O-Ca(1)-O>	79.5
O(7)-OW(4)	3.170(14)	O(7)-Ca(2)-OW(4)	84.1(3)
O(7)-O(1)f	3.612(13)	O(7)-Ca(2)-O(1)f	96.2(3)
O(7)-O(11)a	3.368(11)	O(7)-Ca(2)-O(11)a	91.5(3)
O(7)-OW(2)b	2.991(11)	O(7)-Ca(2)-OW(2)b	75.1(3)
OW(4)-O(2)f	3.008(13)	OW(4)-Ca(2)-O(2)f	75.5(3)
OW(4)-O(11)a	3.295(14)	OW(4)-Ca(2)-O(11)a	89.1(3)
O(1)f-O(2)f	2.458(12)	O(1)f-Ca(2)-O(2)f	58.6(3)
O(1)f-OW(2)b	2.851(10)	O(1)f-Ca(2)-OW(2)b	69.3(3)
O(1)f-OW(3)f	3.331(11)	O(1)f-Ca(2)-OW(3)f	86.8(3)
O(2)f-OW(3)f	3.063(12)	O(2)f-Ca-OW(3)f	77.1(3)
O(11)a-OW(2)b	3.091(11)	O(11)a-Ca(2)-OW(2)b	78.7(3)
O(11)a-OW(3)f	2.879(10)	O(11)a-Ca(2)-OW(3)f	75.6(3)
OW(2)b-OW(3)f	3.434(12)	OW(2)b-Ca(2)-OW(3)f	88.9(3)
<O-O>Ca(2)	3.119	<O-Ca(2)-O>	80.5

valence requirements of the structure. There are two unique Ca positions, Ca(1) co-ordinated by eight atoms, six of oxygen and two (H_2O) groups, and Ca(2) co-ordinated by seven atoms, four of oxygen and three (H_2O) groups.

The structure of ehrleite is illustrated in Figure 1. The sheet-like nature of the structure is immediately apparent; the P, Be and Zn tetrahedra share corners to form a thick sheet parallel to (010). Sandwiched between these sheets and linking them are layers of [7]- and [8]-co-ordinated Ca atoms. Details of the sheet can be seen in Figure 2. The (BeO_4) and (ZnO_4) tetrahedra are 4-connected, that is they each link to four other tetrahedra, whereas the (PO_4) tetrahedra are not; P(1) and (P2) are 3-connected, both linking to two (BeO_4) tetrahedra and one (ZnO_4) tetrahedron, and P(3) is 2-connected, linking to two (ZnO_4) tetrahedra. This is the maximum connectivity allowed without having P – O – P linkages, a linkage that seems to be fairly unstable (with respect to hydrolysis?) in natural minerals.

The details of the intersheet linkage are best seen in Figure 3. The [8]-co-ordinated Ca(1) links to three oxygen atoms of each adjacent sheet, and the co-ordination polyhedron is completed by two (H_2O) groups. The [7]-co-ordinated Ca(2) links to two oxygen atoms of each adjacent sheet, and the co-ordination polyhedron is completed by three (H_2O) groups. Intersheet linkage is increased through hydrogen bonding from the (H_2O) groups to oxygen anions of the sheets. Although the hydrogen atoms were not located directly from the X-ray data, a sensible hydrogen-bond arrangement could be derived from local bond-valence requirements (Table 6) and the local geometry around each (OH) and (H_2O) group. In Table 6, bond valences of the hydrogen bonds were assigned such that the bond-valence sums around the donor anions are ideal (2 v.u. in all cases). The amount and strength of the hydrogen-bonding attest to its importance in the ehrleite structure; only four of the twelve oxygen anions in the sheet are not hydrogen-bond acceptors. The acid phosphate hydroxy group, O(10), is of particular interest, as it is bonded to P(3) and to no other (non-hydrogen) cation. As one would expect from local bond-valence considerations, the P(3) – O(10) distance of 1.60 Å is quite long for a P – O bond, with a bond-valence value of 1.06 v.u.; this would suggest that the hydrogen of the O(10) hydroxyl group would show no significant hydrogen-bonding. However, the O(10) oxygen also acts as a hydrogen-bond acceptor for the OW(4) group, and hence can also act a hydrogen-bond donor to O(9), which satisfies the local bond-valence requirements about O(9).

Disorder

One of the phosphorus atoms in the structure seems to show positional disorder over two distinct positions P(3) and P(4), with an occupancy ratio of about 9:1. Unfortunately, the corresponding oxygen

TABLE 6. BOND-VALENCE* TABLE FOR EHRLEITE

	P(1)	P(2)	P(3)	Be	Zn	Ca(1)	Ca(2)	OW(1)^1	OW(1)^2	OW(2)^1	OW(2)^2	OW(3)^1	OW(3)^2	OW(4)^1	OW(4)^2	H(10)	Σ
O(1)	1.310					0.198 0.300	0.243										2.051
O(2)	1.166				0.527		0.212		0.145								2.050
O(3)	1.185			0.535		0.228											1.948
O(4)	1.314			0.483						0.233							2.030
O(5)		1.299				0.248 0.295					(0.233)						2.075
O(6)		1.242		0.510		0.201											1.962
O(7)		1.303			0.498		0.310										2.111
O(8)		1.239		0.523				0.145									1.907
O(9)			1.253		0.501											0.215	1.969
O(10)			1.057												0.158	0.785	2.000
O(11)			1.423				0.339						0.157	0.158			2.077
O(12)			1.352		0.516							0.157					2.025
OW(1)						0.289		0.855	0.855								1.999
OW(2)						0.249	0.216			0.767	0.767						1.999
OW(3)							0.315					0.843	0.843				2.001.
OW(4)							0.316							0.842	0.842		2.000
Σ	4.925	5.083	5.085	2.051	2.042	2.008	1.951	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	

*calculated from the curves of Brown (1981); bond-valences are in v.u. (valence units).

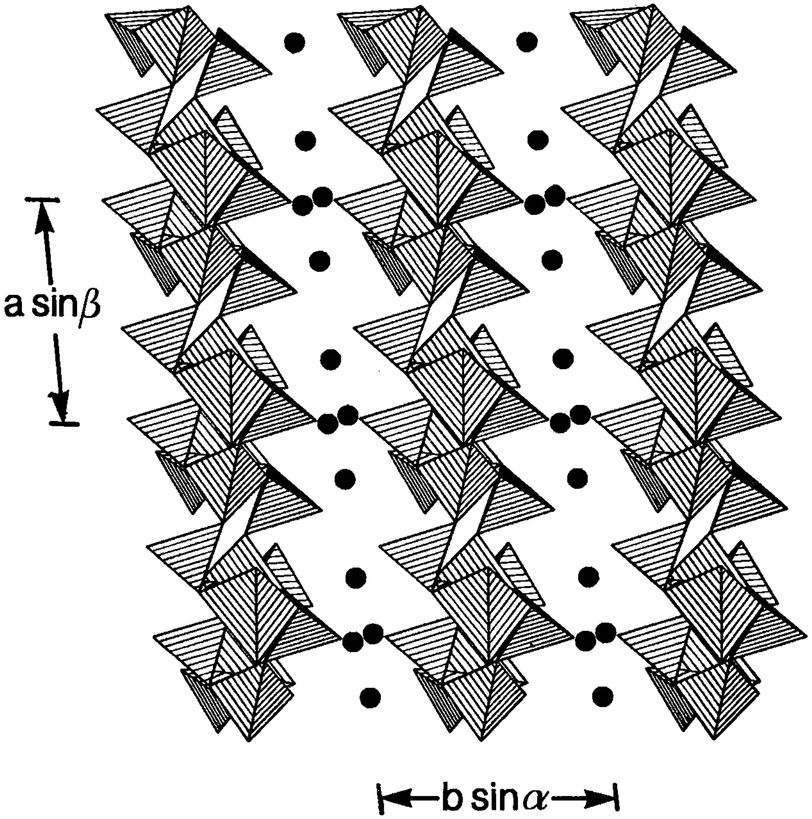

FIG. 1. The structure of ehrleite projected down Z; in this view, the different tetrahedra are not distinguished, and the Ca atoms are represented by filled circles.

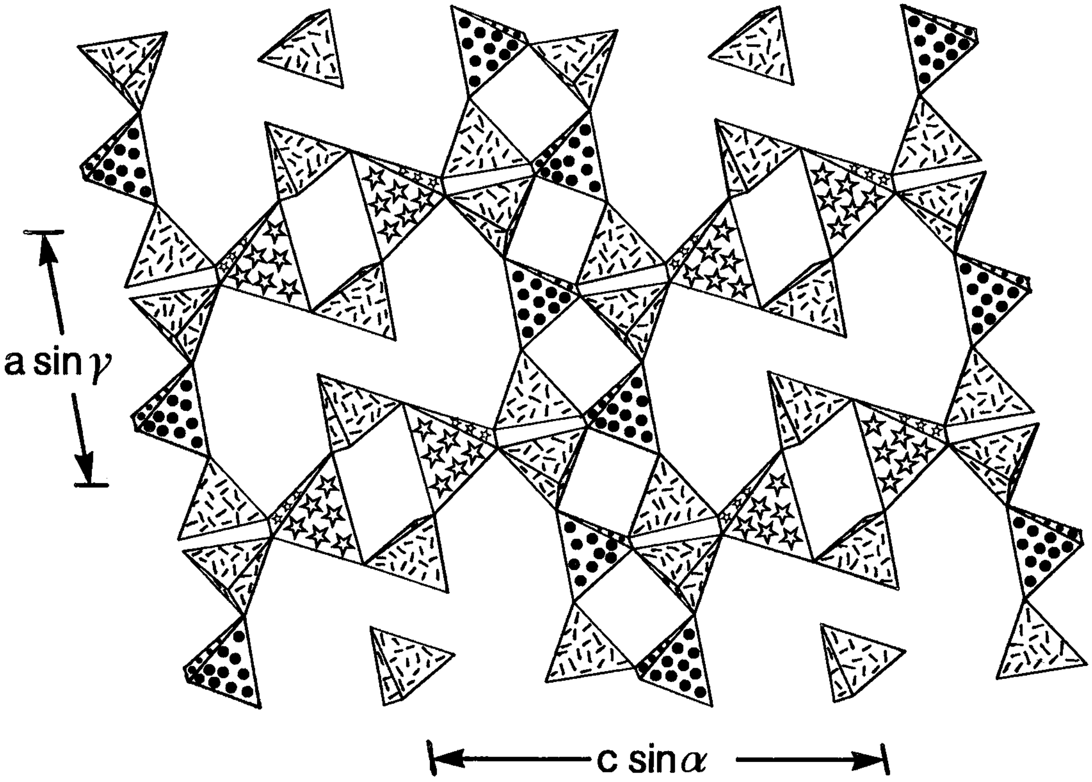

FIG. 2. The structure of erhleite viewed down Y, perpendicular to the plane of the tetrahedral sheet; P tetrahedra are dashed, Zn tetrahedra are shown by stars, and Be tetrahedra are indicated by large dots. Note that the Zn and Be tetrahedra are connected to four other tetrahedra, whereas the P tetrahedra are connected to only two or three other tetrahedra.

atoms about the P(4) position could not be seen because of the small amount of scattering expected from them, combined with the problems of working with a twinned crystal. However, inspection of the local geometry does suggest a possible reason for this disorder.

P(4) has a normal P - O bond separation of 1.56 Å from the O(12) oxygen, but much longer nonbonded separations (>2 Å) from the remaining oxygen atoms around the P(3) positions; in addition, P(4) - OW(2) is 1.81 Å. When the P(4) position is occupied by phosphorus, the P(3) position is vacant, and the O(10) oxygen is no longer bonded to a phosphorus atom. Conversely, there is a short separation between P(4) and OW(2), a distance of 1.81 Å. Thus it would seem reasonable to suggest that when P(4) is occupied, the O(10) anion is an (H_2O) group (now not bonded to a non-hydrogen cation) and relaxes away from the P(4) position, and the O(12) anion is an (OH) group, moving toward P(4) and becoming the acid part of its co-ordination polyhedron. The details of the other anions presumably bonded to P(4) are not clear; possibly O(11) moves toward P(4) when it is occupied. Certainly the P(4) - Zn separation of 2.26 Å is extremely short; the Zn position may be unoccupied when P(4) is occupied. The isotropic temperature-factor of Zn is significantly higher than those of the other tetrahedrally co-ordinated cations (Table 2), suggesting that only approximately 90% occupancy of this position is feasible. No additional electron-density was seen in the final difference-maps that could possibly be due to an additional partly occupied Zn position. Consequently, any vacancies at the Zn position would need to be compensated by introducing additional positive charge to the structure, presumably in the form of hydrogen atoms. This mechanism would then solve the local bond-valence imbalance around the O(9) anion when P(4) is occupied and Zn is empty; two hydrogen atoms bond to O(9), making it an (H_2O) group and compensating for the bond-valence loss from the unoccupied P(3) and Zn positions, and maintaining long-range electroneutrality owing to the vacancy at the Zn position.

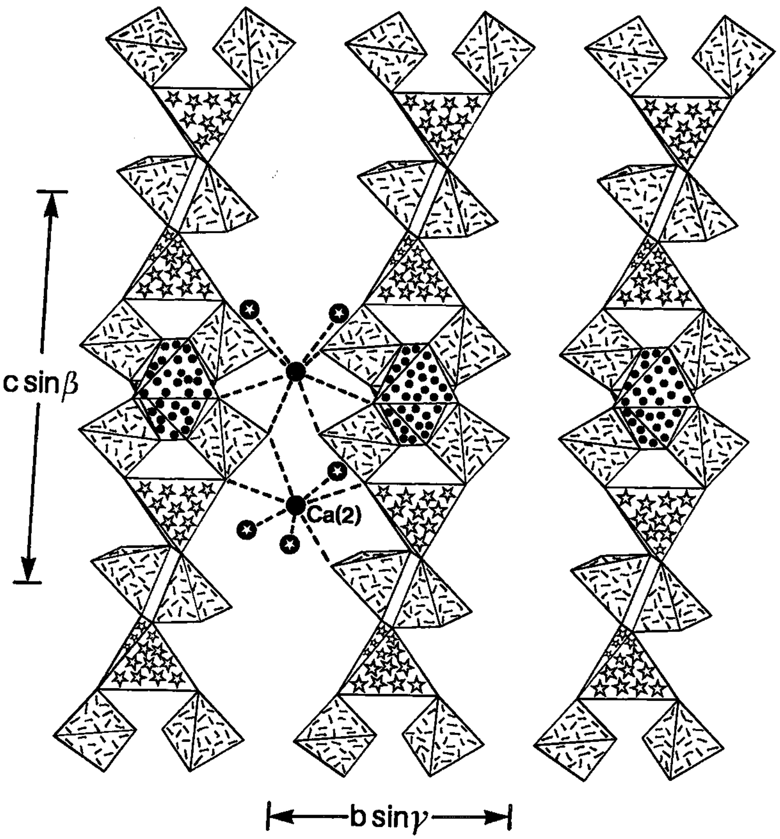

FIG. 3. The structure of ehrleite viewed down *X*; the legend is as in Figure 2, with Ca atoms shown as filled circles, and (H_2O) groups as starred circles. The sheets are linked by [7]- and [8]-co-ordinated Ca atoms; only one of each type is shown for clarity.

The chemical formula of ehrleite

Robinson *et al.* (1985) reported the formula of ehrleite as $Ca_4Be_3Zn_2(PO_4)_6{\bullet}9H_2O$, whereas the present results give a formula of $2[Ca_2ZnBe(PO_4)_2(PO_3OH)(H_2O)_4]$, ignoring the aspects of positional disorder in the structure. The latter is a more simple formula from a structural viewpoint, as it does not require the extensive positional disorder or very low symmetry that would be necessary for the original formula. However, the positional disorder of the acid phosphate group discussed above does suggest some compositional complications. The P(3) position is occupied by P only 90% of the time; when the P(4) position is occupied by P (10% of the time), then the associated Zn position is probably vacant, and an adjacent oxygen atom becomes an (H_2O) group. This would suggest the following modified formula: $2[Ca_2Zn_{1-x}BeH_{2x}(PO_4)_2(PO_3OH){\bullet}4H_2O]$. In this regard, it is noteworthy that the originally proposed formula had $9H_2O$, and Be in stoichiometric excess in Zn.

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