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A COMPARISON OF THE CRYSTAL STRUCTURES OF PSEUDOLAUEITE AND LAUEITE

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ABSTRACT

The pseudolaueite and laueite crystal structures have as a common feature infinite chains of corner-linked Fe-coordination octahedra. The way in which these chains are linked by the phosphate groups and Mn-coordination octahedra into three-dimensional frameworks are topologically distinct. The details of the distortions of the coordination octahedra can be accounted for by the extended electrostatic valence rule, provided one considers the contributions of the hydrogen atoms. It is proposed that pseudolaueite and laueite are not true polymorphs because laueite contains appreciable amounts of Mn^{3+} in the Mn-site.

INTRODUCTION

Strunz (1954, 1956) has described two new minerals from Hagendorf-Süd, Bavaria: laueite, $MnFe_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$ and pseudolaueite, $MnFe_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$ (or $7H_2O$). A third mineral with the same chemical composition is stewartite (Tennyson, 1956). Strunzite (Frondel, 1957), originally suspected to be another polymorph of laueite, actually has a lower water content (Correia Neves, 1960). All these minerals are alteration products of triphylite and are frequently associated with rockbridgeite and with each other.

The crystal structure of laueite was solved by Moore (1965) and by Plieth *et al.* (1965). The crystal structure of pseudolaueite was determined recently and will be reported in detail, together with the structures of the vauxite-group minerals, by Baur and Rama Rao (in preparation). The crystal data of the two minerals are listed in Table 1. The unit-cell parameters found by Baur and Rama Rao for pseudolaueite are close to those reported by Strunz (1956).

CRYSTAL STRUCTURE OF PSEUDOLAUEITE

Pseudolaueite from the type locality Hagendorf-Süd (Specimen #P239, University of Chicago Collection) was used for the structure determination. Three-dimensional X-ray data were collected on a precession camera using MoKα radiation. The structure was solved from a three-dimensional Patterson synthesis and refined by least-squares and Fourier method to $R=0.086$ for 1069 observed F_{hkl} assuming isotropic temperature factors. The positional parameters and the temperature factors are listed in Table 2. It is apparent from the crystal structure determination

TABLE 1. CRYSTAL DATA

	Pseudolaueite (Baur & Rama Rao)	Laueite (Strunz, 1954)
a	9.647 Å	5.28 Å
b	7.428 Å	10.66 Å
c	10.194 Å	7.14 Å
α	90°	107.92°
β	104.63°	110.98°
γ	90°	71.12°
V	706.8 Å^3	346.6 Å^3
Z	2	1
ρ (calc)	2.51g·cm^{-3}	2.56 g·cm^{-3}
ρ (meas)	2.463g·cm^{-3} (Strunz, 1956)	2.44–2.49g·cm^{-3}
Space group	$P2_1/a$	$P\bar{1}$

that the water content of pseudolaueite corresponds to $8H_2O$, thus removing the doubt Strunz (1956) had on this point.

The structure of pseudolaueite (see Fig. 1) is composed of infinite chains of corner-sharing coordination octahedra around the Fe-atoms. These chains extend parallel [010] and weave around the 2_1-axis. The composition of these chains is $[FeO_3(OH)(OH_2)]^{4-}{}_n$. They are linked by phosphate groups to form two-dimensional sheets of the composition $FePO_4(OH)(OH_2)]^{1-}$ parallel to (001). These sheets in turn are linked by the coordination octahedra around the Mn^{2+} atoms into a three-dimensional network of composition $MnFe_2{}^{3+}(PO_4)_2(OH)_2(OH_2)_6$. Oxygen atom O($w$9) is not coordinated to any of the cations but is instead hydro-

TABLE 2. PSEUDOLAUEITE, POSITIONAL AND THERMAL PARAMETERS. x, y, z IN FRACTIONS OF THE CELL EDGE, B IN Å^2

Atom	x	y	z	B
Mn	0.0000	0.0000	0.0000	1.3
Fe	.2466	.1294	.5015	0.6
P	.5117	.3753	.6823	0.8
O(p1)	.1607	.1001	.6585	1.0
O(p2)	.4368	.2138	.6033	1.0
O(p3)	.0322	.1554	.8357	1.2
O(p4)	.0734	.0495	.3592	1.2
O(h5)	.6774	.1205	.4805	1.0
O(w6)	.3400	.1676	.3321	2.2
O(w7)	.2461	.9636	.0818	2.2
O(w8)	.0169	.2330	.1276	1.7
O(w9)	.3702	.0573	.8817	1.8

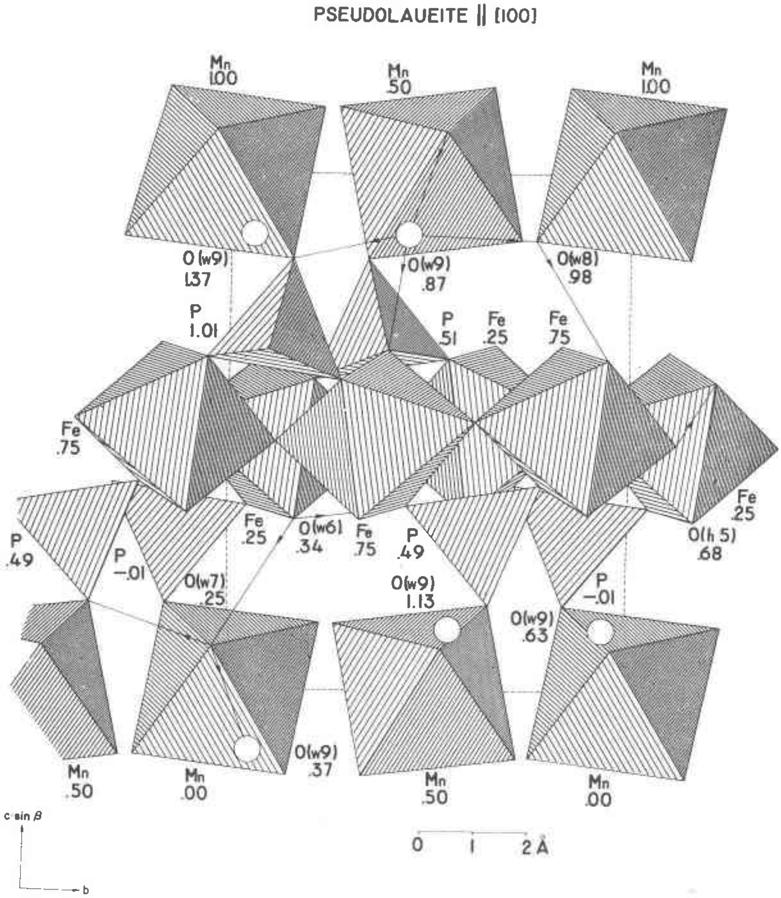


Fig. 1. Pseudolaueite, view parallel [100]. Polyhedral representation; water molecules not bonded to cations are shown as circles. Some of the hydrogen bonds are indicated by arrows pointing toward the acceptor atoms. The central atoms of the coordination polyhedra, the water molecules which are not bonded to cations and the donor atoms of hydrogen bonds are identified and their height is given in fractional coordinates.

gen bonded to the framework structure. The complete chemical formula is therefore $MnFe_2^{3+}(PO_4)_2(OH)_2(OH_2)_6 \cdot 2H_2O$.

It is easily possible to differentiate between the oxygen atoms belonging to OH groups and those which have to be identified as H_2O molecules by considering the distribution of electrostatic bond strengths and by making reasonable assumptions about the hydrogen bonding. Oxygen atom O(*h*5) cannot be a water molecule and therefore must be the hydroxyl oxygen atom because:

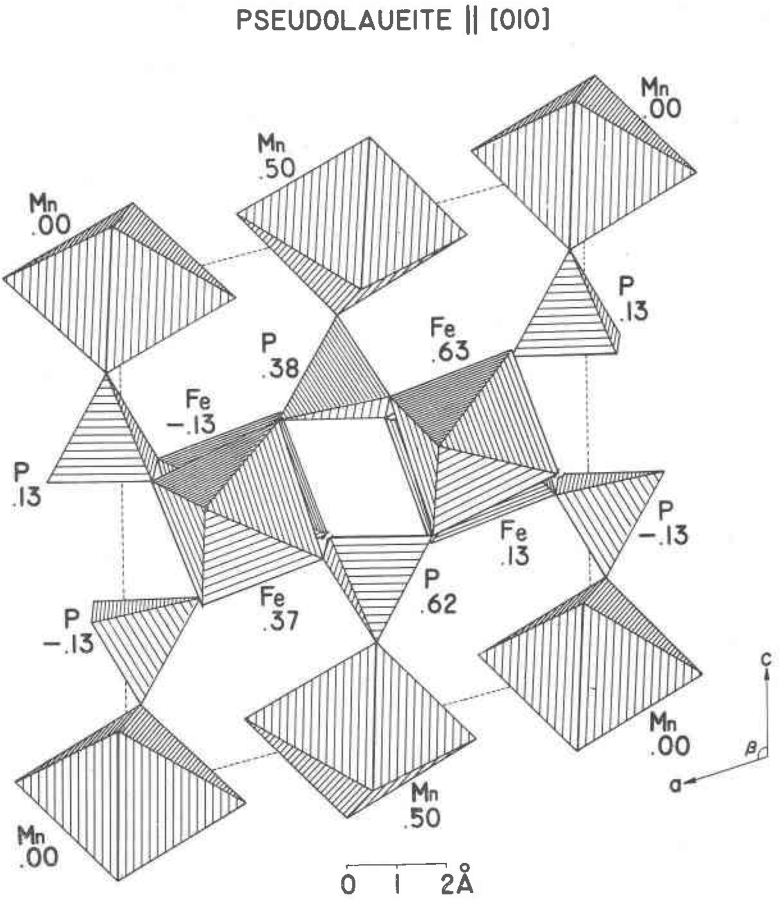


Fig. 2. Pseudolaueite, view parallel [010].

1. It is bonded to two Fe^{3+} atoms. The largest sum of electrostatic bond strengths (ζ) known to be received by a water molecule oxygen atom from metal cations is 0.67. This is in kieserite, $MgSO_4 \cdot H_2O$, where the water oxygen atom is coordinated to two Mg^{2+} (Baur, 1961). Atom O(*h*5) receives however a bond strength of 1.0 from the two Fe^{3+} atoms.
2. It has only one contact shorter than 3.1 Å to another oxygen atom outside of the octahedral coordination around Fe. This distance O(*h*5)→O(*p*2) of 2.98 Å is assumed to be a hydrogen bond. If O(*h*5) were a water molecule it should form two hydrogen bonds.

There are nine oxygen-oxygen distances from 2.65 Å to 3.10 Å in

Table 3. Bond Lengths and ζ-Values in Pseudolaueite and Laueite

The standard deviations for pseudolaueite are 0.01 Å or smaller, for laueite 0.02 Å or smaller. The values for laueite have been calculated using the parameters published by Moore (1965).

Pseudolaueite	distance	ζ	Laueite	distance	ζ
Fe-O(h5)	1.968 Å	1.83	Fe(1)-O(h5)	1.967 Å	1.83
Fe-O(p4)	2.006	2.08	Fe(1)-O(p4)	1.981	1.92
Fe-O(p1)	1.991	1.92	Fe(1)-O(p1)	2.001	1.92
Fe-O(h5)	1.987	1.83	Fe(2)-O(h5)	1.919	1.83
Fe-O(p2)	1.968	1.92	Fe(2)-O(p2)	1.964	1.92
Fe-O(w6)	2.159	2.17	Fe(2)-O(w6)	2.103	2.50
average	2.013		average	1.989	
Mn-O(w8)	2.146 Å	2.00	Mn-O(w8)	2.078 Å	2.00
Mn-O(p3)	2.121	1.92	Mn-O(p3)	2.083	1.92
Mn-O(w7)	2.325	2.17	Mn-O(w7)	2.188	2.00
average	2.197		average	2.116	
P-O(p1)	1.529 Å	1.92	P-O(p1)	1.522 Å	1.92
P-O(p2)	1.522	1.92	P-O(p2)	1.525	1.92
P-O(p3)	1.542	1.92	P-O(p3)	1.550	1.92
P-O(p4)	1.533	2.08	P-O(p4)	1.537	1.92
average	1.532		average	1.534	

length which can be interpreted as hydrogen bonds (Table 4). The two longest of them $O(w6) \rightarrow O(p4)$ and $O(w7) \rightarrow O(p3)$ are longer than hydrogen bonds usually are. The hydrogen bond angle geometry however is in both cases favorable ($O(w7)-O(w6)-O(p4) = 120°$ and $O(w9)-O(w7)-O(p3) = 89°$) and therefore it can be estimated that the distances H - - - O (acceptor) are about 2.1 to 2.2 Å, which means that they correspond to very weak hydrogen bonds.

CRYSTAL STRUCTURE OF LAUEITE

The structure of laueite (Moore, 1965) can be described as consisting of chains of the same bulk composition as in pseudolaueite. However, the chains in laueite consist of two different alternating motifs: one is $[Fe(1)O_4(OH)]^{6-}$, the other $[Fe(2)O_2(OH)(OH_2)_2]^{2-}$. The chains are linked by the phosphate groups into sheets parallel to (010). These sheets of composition $[FePO_4(OH)(OH_2)]^{1-}$ are connected by the coordination

TABLE 4. ASSUMED HYDROGEN BONDS IN PSEUDOLAUEITE AND LAUEITE

Pseudolaueite		Laueite	
O(h5)→O(p2)	2.983 Å	O(h5)→O(p2)	2.750 Å
O(w6)→O(p4)	3.041	O(w6)→O(p4)	2.614
O(w6)→O(w7)	2.908	O(w6)→O(w9)	2.620
O(w7)→O(w9)	2.704	O(w7)→O(w9)	2.825
O(w7)→O(p3)	3.101	O(w7)→O(w6)	3.136
O(w8)→O(w9)	2.655	O(w8)→O(p1)	2.684
O(w8)→O(p4)	2.660	O(w8)→O(p3)	2.730
O(w9)→O(p1)	2.654	O(w9)→O(p3)	2.774
O(w9)→O(p3)	2.755	O(w9)→O(w6)	3.089
average	2.83	average	2.80

octahedra around Mn^{2+} atoms and form a three-dimensional framework (Figs. 3 and 4) of composition $MnFe_2^{3+}(PO_4)_2(OH)_2(OH_2)_6$. The remaining water molecules are not coordinated to a cation so that the chemical formula is the same as for pseudolaueite: $MnFe_2^{3+}(PO_4)_2(OH)_2(OH_2)_6\cdot 2H_2O$.

Using the same reasoning as in the case of pseudolaueite one can

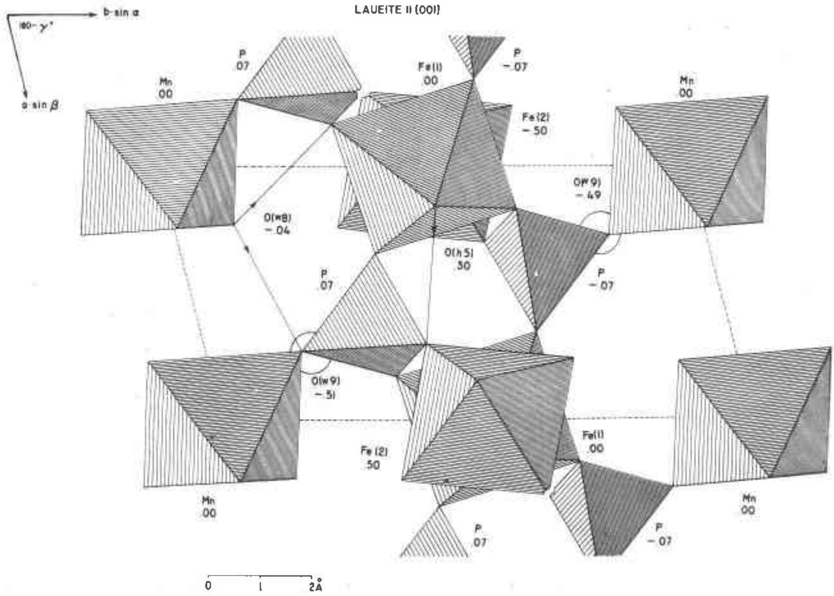


FIG. 3. Laueite, view parallel [001].

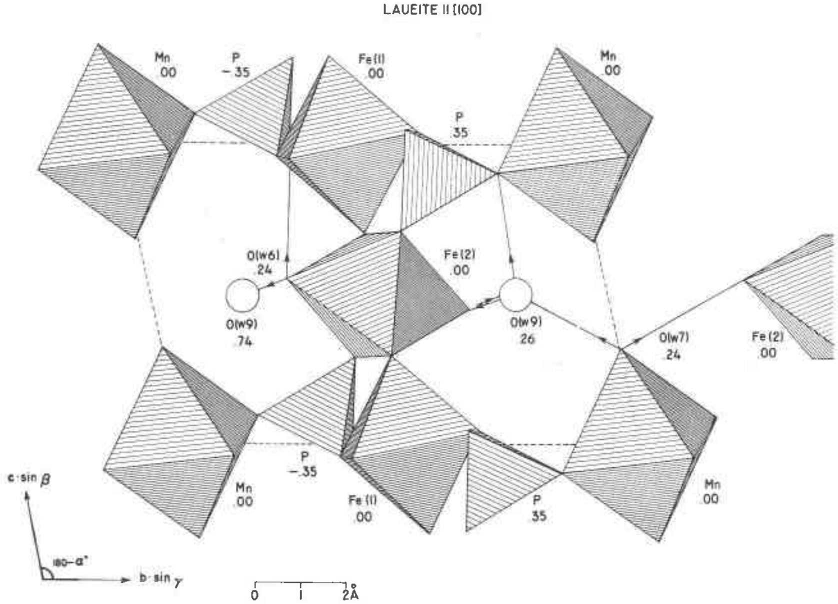


FIG. 4. Laueite, view parallel [100].

identify for laueite the oxygen atom linking the two Fe^{3+} coordination octahedra as the hydroxyl oxygen atom. All the remaining oxygen atoms, except those bonded to the P atom, must therefore belong to water molecules. There are nine oxygen-oxygen distances ranging from 2.61 Å to 3.14 Å in length which are assumed to be hydrogen bonds (Table 4). The two longest of these both involve O(*w*6) as acceptor atom. The angle O(*w*9)–O(*w*7)–O(*w*6) is 124°, thus making a reasonable hydrogen bonding arrangement for O(*w*7) possible although the distance O(*w*7)→O(*w*6) is 3.14 Å. The angle O(*p*3)–O(*w*9)–O(*w*6) is only 76°. This together with the distance O(*w*9)→O(*w*6) of 3.09 Å make it likely that the hydrogen bonding interaction between O(*w*9) and O(*w*6) is extremely weak.

For the purposes of this paper the oxygen atoms in laueite have been renamed in such a way that corresponding oxygen atoms in the two structures have the same numbers. The correspondence with Moore's (1965) numbering system is given in Table 5.

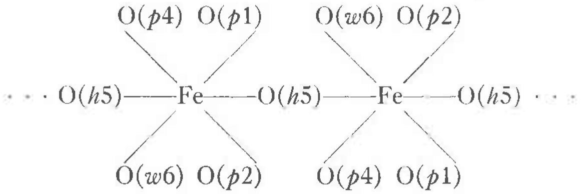
COMPARISON OF THE FRAMEWORK GEOMETRY

The chain of Fe coordination octahedra in pseudolaueite is made up of crystallographically equivalent atoms which are related by the 2_1 axis:

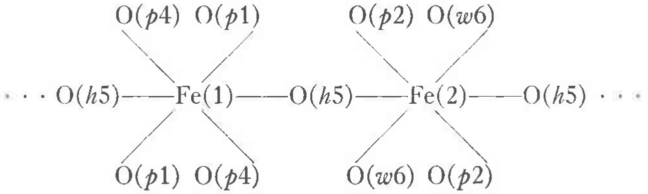
TABLE 5. ELECTROSTATIC BOND STRENGTHS IN PSEUDOLAUEITE AND LAUEITE

The last column gives Moore's (1965) numbering of the atoms in laueite.

	Pseudolaueite						Laueite							
	Mn	Fe	P	H(d)	H(a)	ζ	Mn	Fe(1)	Fe(2)	P	H(d)	H(a)	ζ	
O(p1)		0.5	1.25		0.17	1.92		0.5		1.25		0.17	1.92	O(4)
O(p2)		0.5	1.25		0.17	1.92			0.5	1.25		0.17	1.92	O(8)
O(p3)	0.33		1.25		2×0.17	1.92	0.33			1.25		2×0.17	1.92	O(6)
O(p4)		0.5	1.25		2×0.17	2.08		0.5		1.25		0.17	1.92	O(7)
O(h5)		2×0.5		0.83		1.83		0.5	0.5		0.83		1.83	O(3)
O(w6)		0.5		2×0.83		2.17			0.5		2×0.83	2×0.17	2.50	O(9)
O(w7)	0.33			2×0.83	0.17	2.17	0.33				2×0.83		2.00	O(2)
O(w8)	0.33			2×0.83		2.00	0.33				2×0.83		2.00	O(1)
O(w9)				2×0.83	2×0.17	2.00					2×0.83	2×0.17	2.00	O(5)



In laueite the chain consists of coordination octahedra around two crystallographically nonequivalent Fe-atoms situated in inversion centers:



Therefore the chains are linked by the phosphate groups in topologically different ways in both structures (compare Fig. 2 and 3) and one cannot view one as a slight distortion of the other.

The difference in arrangements can be illustrated by comparing the layer near zero height parallel (001) in laueite with the layer parallel (110) in pseudolaueite. In laueite the polyhedra around Mn, Fe(1), and P are arranged in an approximate checker-board fashion within the layer of composition $[\mathrm{MnFe}^{3+}(\mathrm{PO}_4)_2(\mathrm{OH})_2(\mathrm{OH}_2)_4]^{3-}$ (see Fig. 3). The structure can be thought of being composed of such layers, which are connected to each other by the Fe(2) coordination octahedra. In pseudolaueite layers of this same type cannot be identified. The checker-board arrangement is incomplete because each Fe-octahedron is surrounded by only three phosphate groups.

INTERATOMIC DISTANCES

Since both structures are frameworks of coordination polyhedra, the hydrogen bonding is relatively unimportant for the lattice energy of the crystal structures and therefore for their cohesion. The only atoms which are solely bonded by hydrogen bonds are the water oxygen atoms O(*w*9). All other water molecules and the hydroxyl groups form strong bonds with the cations and the hydrogen bonds are only of secondary importance. The actual hydrogen bonding distances will therefore be determined partly by the steric requirements of the framework. This may account for the large spread in hydrogen bonding distances in pseudolaueite and laueite: 2.61 to 3.14 Å (Table 4). In crystal structures which are held together solely by hydrogen bonds the hydrogen donor and acceptor interactions will largely determine the distances and therefore the spread will be smaller. In $MgSO_4 \cdot 7H_2O$ for example the hydrogen bond distances range from 2.70 Å to 2.98 Å (Baur, 1964).

Even though the hydrogen bonds cannot contribute substantially to the framework geometry of these crystal structures they still have to be taken into account in a consideration of the distortion of the coordination octahedra. As has been shown previously (Baur, 1961) many of the distortions of coordination polyhedra in ionic or partly ionic compounds can be accounted for by an extension of Pauling's (1960) electrostatic valence rule. In compounds containing hydrogen atoms their contribution cannot be neglected. The sums of electrostatic bond strengths presented in Table 5 are calculated assuming that each hydrogen bond contributes $\frac{1}{6}$ of one bond strength (column H(a)) to the acceptor atom. This was found to be a reasonable assumption in a number of salt hydrates studied (Baur, 1962). The remaining $\frac{5}{6}$ of the bond strength is counted towards the sum of the bond strengths of the donor atom of the hydrogen bond (column H(d)). The resulting ζ-values are listed in Table 3 together with the bond lengths. It can be seen that generally bonds involving oxygen atoms which are oversaturated (have a high ζ-value) are longer than the average bond length for this coordination polyhedron, while oxygen atoms which are undersaturated form shorter bonds to the cations. It seems to be a rule that hydroxyl oxygen atoms which are linking corners of two coordination octahedra around three valent cations form bonds which are shorter than the average. This rule can only be rationalized if one assumes, as is being done here, that the hydrogen atom contributes less than 1.0 in bond strength to the hydroxyl oxygen atom.

The only bond distance which apparently does not follow the extended electrostatic valence rule is Mn–O(*w*7) in laueite. Oxygen atom O(*w*7) is not oversaturated, but Mn–O(*w*7) is clearly longer than the average. This might be correlated with the fact that the average length of the hydrogen bonds formed by O(*w*7) is significantly longer than the average for all hydrogen bonds in laueite (or other hydrates). If Mn–O(*w*7) were any shorter the hydrogen bonding interactions of O(*w*7) would be even weaker. More likely however is the following different interpretation.

The average Fe-O and P-O distances in pseudolaueite and laueite agree well with each other and with values found in comparable crystal structures. However, there is a significant difference in the average Mn-O distances in the two compounds (Table 3). The value in pseudolaueite matches with average Mn-O distances determined in several well documented crystal structures: 2.201Å in $LiMnPO_4$ (Geller and Durand, 1960), 2.175 Å in $K_2Mn(SO_4)_2 \cdot 4H_2O$ (Strikanta *et al.*, 1968), 2.181 Å in

$Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Montgomery *et al.*, 1966) and 2.206 Å in $MnCl_2 \cdot 4H_2O$ (Zalkin *et al.*, 1964). The average value of these four determinations is 2.191 Å. The short average Mn-O distance and the particularly long Mn-O(*w*7) distance in the Mn-coordination octahedron in laueite can both be explained if one assumes that the Mn^{2+} ions are partly oxidized to Mn^{3+}. Since the structure determination of MnF_3 (Hepworth and Jack, 1957) it is known that Mn^{3+} exhibits the static Jahn-Teller distortion. From the structure determinations of α-Mn_2O_3 (Norrestam, 1967) and manganite, MnOOH (Dachs, 1963) we know the dimensions of the high-spin octahedral complex of oxygen atoms around a Mn^{3+} ion: two distances are about 2.26 Å, two are about 1.98 Å and the remaining two 1.89 Å. The four shorter Mn^{3+}-O distances form a square planar arrangement with a mean Mn^{3+}-O distance of 1.94 Å. The difference in bond lengths ascribed to the Jahn-Teller effect (Dunitz and Orgel, 1960) is $2.26-1.94=0.32$ Å. The average of all six Mn^{3+}-O distances in the distorted octahedron is 2.04 Å. Since the average Mn-O distance in laueite is 2.116 Å, which is exactly halfway between the values for Mn^{2+} and Mn^{3+}, one can assume that about half of the Mn-atoms are oxidized to Mn^{3+}. An independent estimate can be made by looking at the distortion in the Mn-octahedron: it is $2.19-2.08=0.11$ Å. This is a third of the distortion for a coordination around a Mn^{3+} ion and can be interpreted as meaning that one third of the Mn atoms are in the Mn^{3+} state. The conclusion is that a substantial part of the Mn-sites is occupied by Mn^{3+} ions. One should not place too much weight on the actual numerical values because it is known from the only chemical analysis published for laueite that lighter and smaller ions are present and complicate the picture: Strunz's (1956) analysis could be written as

$$(\overset{2+}{\mathrm{Mn}}_{0.78}\mathrm{Ca}_{0.02}\mathrm{Al}_{0.2})(\overset{3+}{\mathrm{Fe}}_{1.8}\overset{2+}{\mathrm{Fe}}_{0.1}\mathrm{Mg}_{0.07}\overset{2+}{\mathrm{Mn}}_{0.04})(\mathrm{PO}_4)_2(\mathrm{OH})_2(\mathrm{OH}_2)_6 \cdot 2\mathrm{H}_2\mathrm{O}.$$

This would explain the small size of the octahedron around the Mn-site, however it would not account for the distortion of the coordination octahedron. It is possible to explain the shape of the Mn-coordination in the laueite specimen which was used by Plieth *et al.* for the structure determination in terms of a complete oxidation to Mn^{3+}: the observed distances are Mn-O(*w*8) 1.85 Å, Mn-O(*p*3) 2.04 Å, Mn-O(*w*7) 2.18 Å, while the average is 2.02 Å. This raises the possibility that laueite and pseudolaueite are not really polymorphs but that instead laueite is a phase stable only when the Mn-site is partly populated by Mn^{3+} ions. Laueite should then be formulated as $(Mn^{2+},Mn^{3+})(Fe,M)_2(PO_4)_2(O,OH)_2$-$(OH,OH_2)_6 \cdot 2H_2O$ where M could be Al, Mg or Fe^{2+}. The charge balance could be maintained in several ways: by divalent cations in the Fe-sites, by replacement of OH by O, or by replacement of H_2O by OH.

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