The crystal structures of kidwellite and 'laubmannite', two complex fibrous iron phosphates

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ABSTRACT

The previously unknown, complex crystal structures of two fibrous ferric iron phosphate minerals have been solved using single-crystal X-ray diffraction data. The structure of a slightly arsenatian kidwellite has been refined in space group $P2/c$ (a = 20.117(4), b = 5.185(1), c = 13.978(3) Å, β = 107.07(3)°, V = 1393.8(5) Å^3, Z = 2) to $R1$ = 5.21%; a revision of both space group symmetry and chemical formula is proposed. The idealized formula is $Na(Fe^{3+},M)_{9+x}(OH)_{11}(H_2O)_3(PO_4)_6$, where M = Fe^{3+}, Cu^{2+} or other metal cation, and $x \approx 0.3$. The structure of a slightly arsenatian 'laubmannite' (as defined by Moore, 1970) has been refined in space group $Pbcm$ (a = 5.172(1), b = 13.999(3), c = 31.083(6) Å, V = 2250.5(8) Å^3, Z = 4) to $R1$ = 3.14%. The revised, idealized formula is $(Fe^{3+},Fe^{2+},M)_{8+x}(OH,H_2O)_9(H_2O)_2(PO_4)_5$, where M = Fe^{3+}, Cu^{2+} or other metal cation, and $x \approx 0.1$. The framework structures of both minerals are similar. Dominant building units are dimers composed of face- and edge-sharing FeO_6 octahedra. Whereas kidwellite contains an additional trimer built of three corner-sharing FeO_6 octahedra, 'laubmannite' instead contains a dimer built of two corner-sharing FeO_6 octahedra. Kidwellite contains only trivalent iron, while one of the Fe sites in 'laubmannite' is occupied by a mixture of Fe^{3+} and Fe^{2+} in a 1:1 ratio. In both structures, the FeO_6-based building units are linked via corners to PO_4 tetrahedra; the M sites are located in narrow channels and have very low occupancies (~2 to 7%) and strongly distorted [6]- or [5+1]-coordinations. Close structural relations between kidwellite and 'laubmannite', and other fibrous iron phosphates explain observations of epitaxial intergrowths of them.

Introduction

Kidwellite and 'laubmannite' are two fibrous ferric iron phosphates which occur as late-stage or secondary minerals in a variety of environments, and are often associated with other iron phosphates such as dufrénite, rockbridgeite, beraunite, chalcosiderite, cacoxenite and strengite. The present work reports the previously unknown crystal structures of both minerals (based on single-crystal X-ray intensity data), and discusses their revised formulae, crystal-chemical characteristics and the occurrence of epitaxial intergrowths.

A preliminary account of the results of a structure determination of a different 'laubmannite' crystal has already been given (Kolitsch, 2001; $R1$ = 6.55%); the present results confirm and improve the earlier data. The present work is part of efforts to unravel the crystal chemistry of several complex and poorly characterized fibrous iron phosphates. In a previous study (Kolitsch, 1999), it was shown by X-ray powder diffraction and transmission electron microscopy that meurigite, $KFe_7^{3+}(PO_4)_5(OH)_7 \cdot 8H_2O$ (Birch *et al.*, 1996) is identical to the earlier described phosphofibrite, $KCuFe_{15}^{3+}(PO_4)_{12}(OH)_{12} \cdot 12H_2O$ (Walenta and Dunn, 1984). Unfortunately, no crystals of meurigite/phosphofibrite suitable for a single-crystal determination of their atomic arrangement have been found yet.

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Previous work

Kidwellite

Kidwellite was originally described by Moore and Ito (1978) from novaculite deposits in Arkansas, as well as from several other worldwide localities. A preliminary study of the species had used the designation 'Mineral A' (Moore, 1970). The mineral forms pale greenish, greenish yellow, greenish white or bright yellow radiating aggregates of small acicular to fibrous crystals. From single-crystal studies, Moore and Ito (1978) deduced space group $A2/m$, Am or $A2$, and the unit-cell parameters $a = 20.61(7)$, $b = 5.15(1)$, $c = 13.75(6)$ Å, $\beta = 112.64(15)°$, $V = 1347$ Å^3. The acicular crystals are elongated along [010]. Chemical analyses gave the simplified formula $NaFe_9^{3+}(OH)_{10}(PO_4)_6 \cdot 5H_2O$ (Moore and Ito, 1978).

Moore (1970) suggested that the crystal structure of kidwellite contains "h-clusters", a designation he had coined for clusters composed of three face-sharing $(Fe^{2+},Fe^{3+})O_6$ octahedra. The existence of 'h-clusters' was also inferred by Moore (1970) for the crystal structure of 'laubmannite' (see below).

Further studies of kidwellite are scarce, although occurrences of the mineral are numerous (e.g. Anthony *et al.*, 2000). On studying an impurity-free sample from a French locality using X-ray powder diffraction, Walenta and Binder (1980) noted a reflection at $d = 5.13$ Å ($I/I_{100} = 0.3$) which is not included in the powder data listed by Moore and Ito (1978), but is present in the earlier data given by Moore (1970), with $I/I_{100} = 0.5$. Walenta and Binder (1980) pointed out that this reflection can be indexed as 010, although this would contradict the A-centred monoclinic cell reported by Moore and Ito (1978). Infrared spectra for kidwellite from Cornwall were reported by Braithwaite and Corke (1980) who observed a sharp absorption at 3570 cm^{-1} and broad bands at 3300 and 3170 cm^{-1} (O$-$H stretching vibrations), as well as a broad band at 1635 cm^{-1} (H$_2$O bending mode). The features of the P$-$O vibrational bands indicated distorted PO$_4$ groups (Braithwaite and Corke, 1980). A poorly resolved infrared (IR) spectrum of a kidwellite sample from Germany was given by Dietrich (1978b).

An electron microprobe analysis of kidwellite sprays from the Broken Hill deposit, NSW, Australia, yielded the formula $(Na_{0.9}Ca_{0.05})_{\Sigma 0.95}(Fe_{8.1}^{3+}Al_{0.6}Zn_{0.2}Cu_{0.03})_{\Sigma 8.93}$ $[(PO_4)_{5.4}(AsO_4)_{0.6}]_{\Sigma 6.00}(OH)_{9.4} \cdot 7.1H_2O$ (Birch, 1990), based on the assumption that all Fe is trivalent and with OH calculated from charge-balance (H$_2$O content by difference). A sample from the Clara mine, Black Forest, Germany, was also found to contain considerable amounts of As, and additionally very minor Cu and Cl(?). Semiquantitative SEM-EDS analyses of a kidwellite from the Lausitz region, Germany, indicated that up to ~25% of the Fe may be substituted by Al (Witzke and Giesler, 1997).

Laubmannite

The fibrous ferric iron phosphate laubmannite has a more complicated history than kidwellite. It was described as a new mineral species by Frondel (1949) from Buckeye Mountain, near Shady, Polk County, Arkansas, USA, where it occurs as thick, brownish to brownish green, colour-banded crusts with a parallel-fibrous structure upon 'limonite'. A wet-chemical analysis of laubmannite from the type locality by Hallowell in 1948, cited by Frondel (1949), gave (wt.%) CaO 1.14, FeO 2.07, MnO 2.40, Fe$_2$O$_3$ 57.88, Al$_2$O$_3$ 0.05, P$_2$O$_5$ 25.95, H$_2$O$^-$ 0.44, H$_2$O$^+$ 10.06, sum 100.00. However, Frondel (1949) considered the $Fe^{2+}:Fe^{3+}$ ratio doubtful and assumed laubmannite to be isostructural with andrewsite on the basis of their similar X-ray powder diffraction patterns. Frondel (1949) proposed the formula $(Fe^{2+},Mn^{2+},Ca)_3Fe_6^{3+}$ $(PO_4)_4(OH)_{12}$ for laubmannite. Andrewsite, however, was later discredited as a mixture of hentschelite and rockbridgeite, with minor chalcosiderite (Dunn, 1990).

A reinvestigation of 'laubmannite' was conducted by Moore (1970), using material from the type locality and from the Leveäniemi mine, Svappavaara mining district, Norbotten province, Sweden. By powder and single-crystal X-ray diffraction (XRD) film methods, he showed that his 'laubmannite' is orthorhombic, with $a = 13.95$, $b = 30.77$, $c = 5.16$ Å, $V = 2214.9$ Å^3, and probable space group $Pbma$ (a non-standard setting of space group $Pbcm$). Moore (1970) describes the Arkansas material as "radial discoidal aggregates of fibers, rich yellowish-green in color." The X-ray powder pattern redetermined by Moore (1970) was very different from that of Frondel (1949). Therefore, Moore (1970) concluded that Frondel's X-ray sample probably consisted of a mixture of major dufrénite and minor amounts of other phosphates. However, Moore (1970) also noted that the original

chemical analysis would conform to the suggested formula of laubmannite but not to that of dufrénite. He concluded that the previous studies were not made on the very same material and that the mineral investigated by him was a distinct, unnamed species. From crystal-chemical and topological considerations he inferred that 'laubmannite' was, together with dufrénite, rockbridgeite, kidwellite (designated 'Mineral A' at that time), a member of a group of iron phosphates all of which contain clusters composed of three face-sharing $(Fe^{2+},Fe^{3+})O_6$ octahedra ('h-clusters'). Moore (1970) also mentioned the theoretical deduction of an unpublished preliminary model of the crystal structure.

Subsequently, a re-examination of the type specimen of laubmannite (Frondel, 1949) by Dunn (1990) demonstrated that this specimen consists of a variable mixture of dufrénite, kidwellite and beraunite. Consequently, Dunn (1990) formally discredited laubmannite, although he also concluded that the 'laubmannite' mineral characterized by Moore (1970) is a unique but unnamed species. The mineral described by Moore (1970) was later identified from only a small number of other occurrences. It has been reported from Indian Mountain, Cherokee Co., Alabama, USA (Barwood, 1974), the Rotläufchen mine, Waldgirmes near Wetzlar, Germany (Dietrich, 1978a,b, 1982), the Clara mine, Central Black Forest, Germany (Walenta, 1981) and Auerbach, Oberpfalz, Germany (Geipel, 1982; see also Stanjek, 1983). The occurrence at the Leveäniemi Mine, Svappavaara, Sweden mentioned by Moore (1970) was later confirmed (Bjällerud, 1989). An occurrence in New Mexico was mentioned by Gibbs (1991), but the sample was subsequently found to be beraunite (Northrop, 1996). A poorly resolved infrared spectrum of a 'laubmannite' from Germany was given by Dietrich (1978b). No other new data were reported except for some semiquantitative chemical compositions (Kolitsch, 2001; see Experimental section).

Oriented intergrowths

Epitaxial intergrowths of kidwellite and 'laubmannite' with either each other or with other iron phosphates were observed by several authors. For instance, Moore (1970) describes 'laubmannite' intergrown with dufrénite at the crystal tips of the latter. Dietrich (1978b) observed that kidwellite needles from the Rotläufchen mine were grown on the (011) faces of hydrothermally altered rockbridgeite, with the ~5.1 Å axes of both minerals being parallel. The same observation was also made for tiny 'laubmannite' needles grown epitaxially on rockbridgeite, and for oriented overgrowths of dufrénite on rockbridgeite (Dietrich, 1978a,b). From Namibia, fibrous kidwellite in oriented overgrowths on older rockbridgeite was described by Keller (1985), albeit without giving details. Walenta (1981, 1992) observed that 'laubmannite' from the Clara mine is partly replaced by beraunite in such a manner that the ~5.1 Å axis (c axis of Moore, 1970) of 'laubmannite' is parallel to the b axis (~5.1 Å) of beraunite. Equivalent oriented intergrowths of kidwellite on laubmannite have been observed (Walenta, 1990, 1992). Dufrénite crystals which, at their tips, grade into kidwellite were described by Walenta (1995). Fibrous kidwellite grading into 'laubmannite' was observed by Walenta and Theye (2001).

Experimental

Kidwellite

The kidwellite sample used for the present study is from the Clara baryte and fluorite mine, Black Forest, Germany. Tufts of pale olive-greenish acicular crystals up to ~0.5 mm long and ~0.01 mm in diameter cover 'limonite' on a matrix of quartz and minor baryte. Semiquantitative chemical analyses of the kidwellite by conventional energy-dispersive X-ray spectrometry in a scanning electron microscope (SEM-EDS) on several carbon-coated crystals showed the presence of major Fe and P, and very minor Al, Cu and As. The analytical results are similar to those obtained by Walenta (1990) on a kidwellite sample from the same locality.

Preliminary investigations of several acicular crystals were done with a Nonius KappaCCD single-crystal diffractometer which was equipped with a 300 µm diameter capillary-optics collimator to provide increased resolution. All crystals showed a primitive monoclinic unit cell, and the most suitable crystal was selected for an intensity data collection (for details see Table 1). The data were processed with the Nonius program suite DENZO-SMN and corrected for Lorentz, polarization, background and absorption effects. Observed extinctions and intensity statistics strongly suggested space group $P2/c$. The crystal structure was solved in space group $P2/c$ by direct

TABLE 1. Crystal data, data-collection information and refinement details for kidwellite and 'laubmannite' (Moore, 1970) from the Clara mine, Black Forest, Germany.

	Kidwellite	Laubmannite (sample LAUB2)
Crystal data		
Formula (idealized)	$Na(Fe^{3+},M)_{9+x}(OH)_{11}(H_2O)_3(PO_4)_6$	$(Fe^{3+},Fe^{2+},M)_{8+x}(OH,H_2O)_9(H_2O)_2(PO_4)_5$
Space group	$P2/c$ (no. 13)	$Pbcm$ (no. 57)
a, b, c (Å)	20.117(4), 5.185(1), 13.978(3)	5.172(1), 13.999(3), 31.083(6)
$\beta(°)$	107.07(3)	–
V (Å^3), Z	1393.8(5), 2	2250.5(8), 4
μ (mm^{-1}), ρ_{calc} (g cm^{-3})	5.86, 3.289	6.00, 3.372
Absorption correction	multi-scan (Otwinowsky and Minor, 1997)	multi-scan (Otwinowsky and Minor, 1997)
Crystal dimensions (mm)	$0.01 \times 0.01 \times 0.15$	$0.05 \times 0.07 \times 0.18$
Data collection and refinement		
Diffractometer	Nonius Kappa CCD system	Nonius Kappa CCD system
T (K); λ (Mo-$K\alpha$) (Å)	293; 0.71073	293; 0.71073
Detector distance (mm)	34	44
Rotation axis; width (°)	φ, ω; 1.0	φ, ω; 0.8
Total no. of frames	544	716
Collect. time/degree (s)	460	300
$2\theta_{max}$ (°)	52.78	55.00
h, k, l ranges	$-25 \rightarrow 24$, $-6 \rightarrow 6$, $-17 \rightarrow 17$	$-6 \rightarrow 6$, $-17 \rightarrow 18$, $-39 \rightarrow 40$
Total refl.s measured	5265	4773
Unique reflections	2850 (R_{int} = 4.55%)	2627 (R_{int} = 1.46%)
$R1(F)$, w$R2(F^2)$*	5.21%, 13.92%	3.14%, 9.09%
'Observed' reflections	1982 [$F_o > 4\sigma(F_o)$]	2239 [$F_o > 4\sigma(F_o)$]
No. of refined parameters	264	233
Extinct. coefficient	0.0004(4)	–
GoF	1.079	1.136
$(\Delta/\sigma)_{max}$	0.0001	0.001
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	-1.01, 1.12	-0.84, 0.83

Unit-cell parameters of kidwellite and 'laubmannite' were refined from 3090 and 3000 reflections, respectively. Scattering factors for neutral atoms were employed in the refinement.
* w = $1/[\sigma^2(F_o^2) + (0.07P)^2 + 5.4P]$; $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$ (kidwellite)
w = $1/[\sigma^2(F_o^2) + (0.048P)^2 + 7.2P]$; $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$ ('laubmannite')

methods (SHELXS-97, Sheldrick, 1997*a*), and the positions of all Na, Fe, P and O atoms were quickly located using subsequent difference-Fourier maps. A full-matrix, anisotropic least-squares refinement on F^2 (SHELXL-97, Sheldrick 1997*b*; see Table 1) showed that all three detected P sites were partly occupied by As, but to a different degree. From the Fourier difference maps, it was also apparent that there were three additional cation sites with very low occupancies and strongly distorted 'octahedral' coordinations. These sites were modelled as Cu atoms, and a final refinement step converged at $R1 = 5.21\%$ (Table 1). No H atoms could be located. The maximum peaks in the final difference-Fourier map were 1.12 and -1.01 e/Å^3. The refined positional and displacement parameters are given in Tables 2 and 3, and selected bond lengths and suggested hydrogen bonds in Table 4. A bond-valence analysis is given in Table 5. A list of observed and calculated structure factors (Table 6) has been deposited with the Principal Editor of *Mineralogical Magazine* and is available upon request.

'Laubmannite'

Two 'laubmannite' samples (as defined by Moore, 1970) were used for the present study, LAUB1 and LAUB2, both being from the Clara baryte and

TABLE 2. Fractional atomic coordinates and isotropic displacement parameters (in Å^2) for kidwellite.

Atom	x	y	z	U_{eq}/U_{iso}	Occupancy
Fe(1)	−0.31930(5)	−0.2542(2)	0.19789(8)	0.0080(3)	
Fe(2)	−0.17514(5)	−0.2401(2)	0.18336(8)	0.0088(3)	
Fe(3)	−0.43127(6)	−0.0041(2)	0.96833(8)	0.0151(3)	
Fe(4)	−0.19236(6)	−0.0145(2)	0.92828(8)	0.0131(3)	
Fe(5)	0.0	0.0	0.0	0.0145(4)	
P(1)	−0.27367(8)	0.2432(3)	0.07103(12)	0.0088(4)	$P_{0.857(3)}As_{0.143(3)}$
P(2)	−0.10006(9)	−0.7385(3)	0.29965(13)	0.0095(5)	$P_{0.936(3)}As_{0.064(3)}$
P(3)	−0.35088(10)	−0.2392(4)	0.81893(13)	0.0090(5)	$P_{0.969(3)}As_{0.031(3)}$
Na	0.0	0.1807(14)	0.75	0.0496(17)	
M(1)	0.0	0.5	0.0	0.018(7)	0.074(6)*
M(2)	−0.4316(8)	0.509(3)	0.9672(11)	0.020**	0.067(2)*
M(3)	−0.1943(7)	0.515(3)	0.9266(10)	0.016(5)	0.074(4)*
O(1)	−0.3506(3)	0.2407(10)	0.0091(4)	0.0150(12)	
O(2)	−0.2218(3)	0.2528(9)	0.0089(4)	0.0116(11)	
O(3)	−0.2589(3)	−0.0084(10)	0.1372(4)	0.0114(11)	
O(4)	−0.2575(3)	−0.5138(10)	0.1425(4)	0.0107(11)	
O(5)	−0.1000(3)	−0.4805(11)	0.2456(4)	0.0178(13)	
O(6)	0.0290(3)	0.2277(11)	0.1213(4)	0.0228(14)	
O(7)	−0.1591(3)	−0.2668(10)	0.8489(4)	0.0129(11)	
O(8)	−0.1104(3)	0.0381(11)	0.2227(4)	0.0223(14)	
O(9)	−0.2813(3)	−0.1897(11)	0.8954(4)	0.0226(14)	
O(10)	−0.3550(3)	−0.4954(10)	0.2708(4)	0.0204(13)	
O(11)	−0.4098(3)	−0.2232(10)	0.8678(4)	0.0142(12)	
O(12)	−0.3642(3)	0.0368(10)	0.2340(4)	0.0179(13)	
Oh(13)	−0.3916(3)	−0.2733(10)	0.0697(4)	0.0111(11)	
Oh(14)	−0.1624(3)	−0.2658(10)	0.0485(4)	0.0112(11)	
Oh(15)	−0.2189(3)	−0.2410(9)	0.3053(4)	0.0107(11)	
Oh(16)	−0.4729(3)	0.1709(12)	0.0667(4)	0.0218(14)	
Ow(17)	−0.4767(3)	0.2842(11)	0.8614(4)	0.0250(14)	
Oh(18)	−0.0955(3)	0.1400(12)	0.9762(4)	0.0210(13)	
Ow(19)	0.0278(3)	0.2856(11)	0.9185(4)	0.0236(14)	$(OH_{0.5}H_2O_{0.5})$***

Oxygens of hydroxyl groups are designated as Oh, those of water molecules as Ow.
* Occupancy factors refined based on assumption that M sites are occupied by Cu (see text).
** fixed. *** see text

fluorite mine, Black Forest, Germany. Several 'laubmannite' samples from other reported localities (Leveäniemi mine, Svappavaara mining district, Sweden; several occurrences in Polk Co., Arkansas, USA) were also investigated, but only very thin fibrous crystals were found, unsuitable for single-crystal data collections. In some cases the samples also turned out to be other misidentified phosphates (e.g. fibrous dufrénite or rockbridgeite). A crystal from sample LAUB1 was used for the original solution of the structure, a preliminary report of which was given in Kolitsch (2001); a crystal from LAUB2, which had a better crystal quality, was used for an improved refinement of the structure. Sample descriptions and data collections will be described for both samples, although only the (improved) results from LAUB2 will be listed in the Tables.

On the thumbnail-sized sample LAUB1, 'laubmannite' forms dark greenish to greenish brown, flat-lying radiating sprays of indistinct prismatic crystals up to ~0.5 mm in length. The sprays are associated with tiny, pale greenish chalcosiderite crystals and with very pale greenish, fibrous sprays of another Fe-phosphate (probably kidwellite). Sample LAUB2 consisted of several small broken hemispheres (diameter ~0.5 mm) with a radiating internal structure. The

TABLE 3. Anisotropic displacement parameters for kidwellite.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.0079(5)	0.0075(6)	0.0094(5)	0.0000(5)	0.0037(4)	−0.0004(5)
Fe(2)	0.0087(5)	0.0094(6)	0.0091(5)	0.0012(5)	0.0039(4)	0.0010(5)
Fe(3)	0.0151(6)	0.0154(6)	0.0150(6)	−0.0006(5)	0.0050(5)	0.0016(5)
Fe(4)	0.0125(6)	0.0140(6)	0.0136(6)	−0.0008(5)	0.0048(5)	0.0007(5)
Fe(5)	0.0124(8)	0.0155(9)	0.0153(8)	−0.0018(7)	0.0035(7)	−0.0010(7)
P(1)	0.0091(8)	0.0087(8)	0.0096(8)	−0.0001(7)	0.0043(6)	−0.0002(7)
P(2)	0.0096(9)	0.0094(9)	0.0097(9)	0.0010(7)	0.0033(7)	0.0005(8)
P(3)	0.0081(9)	0.0105(10)	0.0094(9)	−0.0012(8)	0.0043(7)	−0.0016(8)
Na	0.033(3)	0.088(5)	0.029(3)	0.0	0.012(3)	0.0
O(1)	0.014(3)	0.014(3)	0.016(3)	0.001(2)	0.005(2)	−0.001(3)
O(2)	0.011(3)	0.011(3)	0.014(3)	0.000(2)	0.005(2)	0.003(2)
O(3)	0.010(3)	0.010(3)	0.015(3)	0.007(2)	0.006(2)	0.004(2)
O(4)	0.007(3)	0.011(3)	0.015(3)	0.000(2)	0.004(2)	0.003(2)
O(5)	0.011(3)	0.022(3)	0.022(3)	0.011(3)	0.008(2)	0.004(3)
O(6)	0.014(3)	0.033(4)	0.020(3)	−0.012(3)	0.002(3)	−0.001(3)
O(7)	0.011(3)	0.014(3)	0.014(3)	−0.005(2)	0.005(2)	0.001(2)
O(8)	0.020(3)	0.023(3)	0.029(3)	−0.011(3)	0.014(3)	−0.007(3)
O(9)	0.011(3)	0.029(4)	0.025(3)	−0.002(3)	0.000(3)	−0.008(3)
O(10)	0.019(3)	0.016(3)	0.030(3)	0.008(3)	0.014(3)	0.002(3)
O(11)	0.013(3)	0.021(3)	0.011(3)	−0.004(2)	0.007(2)	0.002(2)
O(12)	0.018(3)	0.014(3)	0.021(3)	−0.009(2)	0.007(3)	0.002(2)
Oh(13)	0.010(3)	0.014(3)	0.006(3)	0.001(2)	−0.002(2)	−0.001(2)
Oh(14)	0.011(3)	0.012(3)	0.010(3)	0.002(2)	0.003(2)	0.000(2)
Oh(15)	0.016(3)	0.010(3)	0.006(2)	0.000(2)	0.003(2)	0.001(2)
Oh(16)	0.017(3)	0.028(4)	0.026(3)	0.002(3)	0.014(3)	−0.001(3)
Ow(17)	0.024(3)	0.026(4)	0.022(3)	0.010(3)	0.001(3)	0.000(3)
Oh(18)	0.014(3)	0.017(3)	0.030(4)	0.001(3)	0.004(3)	0.003(3)
Ow(19)	0.024(3)	0.031(4)	0.021(3)	0.009(3)	0.015(3)	0.006(3)

central, dark greenish zone of these hemispheres graded into a narrow, greenish to yellow-brown, altered outer zone, followed by a very narrow, brown, completely oxidized zone.

Semiquantitative chemical analyses of both 'laubmannite' samples and the associated phosphates were done by SEM-EDS on carbon-coated grains. LAUB1 contains major Fe, P and trace amounts of Cu and Mn. The associated kidwellite(?) contains trace amounts of Cu, whereas the spectrum of chalcosiderite did not show any impurity elements. The dark greenish part of LAUB2 contains major Fe, P and very small amounts of As, Cu and Al. The altered outer zone has practically the same composition, whereas the outermost oxidized zone contains only Fe and traces of P. Optical properties of LAUB1 were investigated in polarized light. Cleavage fragments showed a lath-like shape, straight extinction and negative elongation. Strong, bluish green to greenish brown pleochroic colours are observed, which can be attributed to Fe^{2+}-Fe^{3+} charge transfer colouration (Moore, 1970). Optical properties of LAUB2 were not studied.

Preliminary investigations of several crystal fragments from LAUB1 with a Nonius KappaCCD single-crystal diffractometer revealed a primitive orthorhombic unit-cell with parameters very close to those determined by Moore (1970). All fragments were elongated parallel to the short 5.16 Å axis, in agreement with Moore (1970). Most fragments showed, however, imperfect quality and were unsuitable for data collection. Eventually, a tiny elongate tabular cleavage fragment with suitable, albeit imperfect quality could be found. LAUB2 immediately provided a dark greenish cleavage fragment of good crystal quality. Orientation studies showed that the cleavage is perpendicular to the ~14 Å axis.

Both fragments were mounted on a Nonius KappaCCD diffractometer equipped with a 300 µm diameter capillary-optics collimator to

TABLE 4. Selected bond distances (Å) for the coordination polyhedra in kidwellite.

Fe(1)−O(10)	1.883(5)	Fe(2)−O(8)	1.914(6)
−O(12)	1.901(5)	−O(5)	1.955(5)
−Oh(13)	1.950(5)	−Oh(14)	1.980(5)
−O(3)	2.105(5)	−O(3)	2.015(5)
−O(4)	2.127(5)	−O(4)	2.128(5)
−Oh(15)	2.134(5)	−Oh(15)	2.137(5)
<Fe(1)−O>	2.017	<Fe(2)−O>	2.022
Fe(3)−O(11)	1.951(5)	Fe(4)−O(9)	1.937(6)
−Oh(13)	1.983(5)	−O(7)	1.956(5)
−O(1)	2.007(5)	−O(2)	1.983(5)
−Oh(16)	2.023(6)	−Oh(18)	2.029(6)
−Oh(16)	2.037(6)	−Oh(14)	2.071(5)
−Ow(17)	2.122(6)	−Oh(15)	2.111(5)
<Fe(3)−O>	2.021	<Fe(4)−O>	2.015
Fe(5)−Oh(18) ×2	1.989(6)	Na−Ow(19) ×2	2.320(6)
−O(6) ×2	2.008(5)	−O(8) ×2	2.422(7)
−Ow(19) ×2	2.044(6)	−O(5) ×2	2.529(7)
<Fe(5)−O>	2.014	<Na−O>	2.424
P(1)−O(1)	1.535(6)	P(2)−O(5)	1.536(6)
−O(2)	1.542(5)	−O(6)	1.538(6)
−O(3)	1.576(5)	−O(7)	1.539(5)
−O(4)	1.581(5)	−O(8)	1.553(6)
<P(1)−O>	1.559	<P(2)−O>	1.542
P(3)−O(9)	1.513(6)	M(1)−Ow(19) ×2	1.795(6)
−O(10)	1.524(6)	−O(6) ×2	2.152(6)
−O(11)	1.534(5)	−Oh(18) ×2	2.629(6)
−O(12)	1.548(5)	<M(1)−O>	2.192
<P(3)−O>	1.530		
M(2)−Oh(13)	1.817(16)	M(3)−O(7)	1.848(14)
−Ow(17)	1.892(16)	−O(2)	1.960(14)
−O(1)	2.091(16)	−Oh(14)	1.992(14)
−O(11)	2.101(16)	−Oh(15)	2.154(14)
−Oh(16)	2.478(16)	−O(9)	2.270(15)
−Oh(16)	2.524(16)	−Oh(18)	2.719(14)
<M(2)−O>	2.151	<M(3)−O>	2.157
Tentative hydrogen bonds			
Oh(13)···O(1)	2.856(7)	Ow(17)···O(10)	3.259(8)
Oh(14)···Ow(19)	2.610(8)	Oh(18)···Ow(19)	3.423(8)
Oh(15)	–	Ow(19)···Oh(14)	2.610(8)
Oh(16)···O(12)	2.782(8)		

provide increased resolution. Details of the intensity data collection of LAUB2 are given in Table 1. The data were processed with the Nonius program suite DENZO-SMN and corrected for Lorentz, polarization, background and absorption effects. For both LAUB1 and LAUB2, observed extinctions were in accordance with space groups $Pbcm$ and $Pbc2_1$, and intensity statistics gave very strong indications of the presence of a symmetry centre. The crystal structure was solved from the LAUB1 dataset by direct methods in space group $Pbcm$ (SHELXS-97, Sheldrick, 1997a) and the positions of all Fe, P and O atoms were found almost immediately. A full-matrix least-squares

TABLE 5. Bond-valence analysis for kidwellite.

	Fe(1)	Fe(2)	Fe(3)	Fe(4)	Fe(5)	P(1)	P(2)	P(3)	Na	Sum*
O(1)			0.512			1.298				1.81
O(2)				0.542		1.274				1.82
O(3)	0.393	0.501				1.163				2.06
O(4)	0.370	0.369				1.146				1.89
O(5)		0.589					1.242		0.139 ×2	1.97
O(6)					0.510 ×2		1.235			1.75
O(7)				0.587			1.232			1.82
O(8)		0.658					1.186		0.186 ×2	2.03
O(9)					0.618			1.300		1.92
O(10)	0.715							1.262		1.98
O(11)			0.595					1.228		1.82
O(12)	0.681							1.182		1.86
Oh(13)	0.597		0.546							1.14
Oh(14)		0.550		0.430						0.98
Oh(15)	0.363	0.360		0.386						1.11
Oh(16)			0.490							0.96
			0.472							
Ow(17)			0.375							0.38
Oh(18)				0.482	0.537 ×2					1.02
Ow(19)					0.463 ×2				0.245 ×2	0.71**
Sum*	3.12	3.03	2.99	3.05	3.02	4.88	4.90	4.97	1.14	

Bond-valence parameters used are from Brese and O'Keeffe (1991).
* Sum values involving bonds to P(1), P(2) and P(3) are based on the refined occupancies (P:As ratios) of these sites (see Table 2). Because of the very low occupancy and uncertain nature of the $M(1)$, $M(2)$ and $M(3)$ sites, their bond-valence contributions have not been taken into account; however, their important influence is discussed in the text.
** Occupancy of Ow(19) site is probably close to $(OH_{0.5}H_2O_{0.5})$ (see text).

refinement on F^2 in space group *Pbcm* (SHELXL-97, Sheldrick 1997*b*; see Table 1), involving anisotropic displacement parameters for all atoms, rapidly converged to $R1$ ~7%. At this point, the Fourier difference map revealed one small but distinct, above-background peak representing a site [5+1]-coordinated by O atoms at distances between ~1.9 and ~2.6 Å. This site, designated $M(1)$, was therefore assumed to be partially occupied by Cu and was modelled accordingly, while fixing its isotropic displacement parameter to a reasonable value; site occupancy refinements gave an occupancy factor of ~3%. The positions of H atoms could not be located. The refinement of LAUB1 converged to the final agreement factor $R1$ = 6.55%. This comparatively high residual is due to the poor counting statistics and the imperfect nature of the crystal fragment measured. A structure refinement using the LAUB2 dataset confirmed the presence of the $M(1)$ site, and led to the detection of a second, similar site, designated $M(2)$. The refinement converged at $R1$ = 3.14% (Table 1). Positions of four H atoms could be located. By contrast with LAUB1, the refinement of LAUB2 demonstrated the presence of minor As on two P sites, in agreement with the chemical analyses. The maximum peaks in the final difference-Fourier map were (LAUB1) 1.74 and -0.93 e/Å^3, and (LAUB2) 0.83 and -0.84 e/Å^3, respectively. The character of the strongest positive peaks is discussed below.

The final atomic positions and displacement parameters of LAUB2 are given in Tables 7 and 8. Selected bond lengths and calculated bond valences are listed in Table 9, including suggested

TABLE 7. Fractional atomic coordinates and isotropic displacement parameters for 'laubmannite' (Moore, 1970).

Atom	x	y	z	U_{eq}/U_{iso}	Occupancy
Fe(1)	−0.74484(9)	0.87846(4)	0.611299(17)	0.00747(14)	
Fe(2)	−0.75356(10)	0.95118(4)	0.699478(18)	0.01148(15)	
Fe(3)	−0.00434(11)	0.56070(4)	0.542350(18)	0.01121(15)	
Fe(4)	−0.00790(10)	0.70285(4)	0.689659(17)	0.00993(15)	
M(1)	0.516(4)	0.7015(16)	0.6889(7)	0.02**	0.0245(16)*
M(2)	−0.488(6)	0.561(2)	0.5416(10)	0.02**	0.0180(16)*
P(1)	0.24076(14)	0.52365(6)	0.63956(2)	0.0066(2)	$P_{0.874(3)}As_{0.126(3)}$
P(2)	−0.23810(16)	0.74415(7)	0.59199(3)	0.00513(19)	$P_{1.00}$
P(3)	−0.2554(2)	0.86207(9)	0.75	0.0065(3)	$P_{0.952(3)}As_{0.048(3)}$
O(1)	0.2364(5)	0.5553(2)	0.59225(9)	0.0122(6)	
O(2)	0.2535(5)	0.60714(19)	0.67209(9)	0.0112(5)	
O(3)	−0.4843(5)	0.95979(18)	0.64813(8)	0.0096(5)	
O(4)	−0.9926(5)	0.96279(18)	0.64946(8)	0.0099(5)	
O(5)	−0.5061(5)	0.7886(2)	0.58904(10)	0.0171(6)	
O(6)	−0.1905(6)	0.6973(2)	0.63559(9)	0.0164(6)	
O(7)	−1.0379(5)	0.8232(2)	0.58340(9)	0.0158(6)	
O(8)	−0.2213(5)	0.66974(19)	0.55583(9)	0.0135(6)	
O(9)	−0.2568(5)	0.80081(19)	0.70931(9)	0.0131(6)	
O(10)	−0.0135(7)	0.9291(3)	0.75	0.0154(8)	
O(11)	−0.5044(7)	0.9259(3)	0.75	0.0131(8)	
Oh(12)	−0.2748(5)	0.4753(2)	0.56640(9)	0.0138(6)	
Oh(13)	0.2459(5)	0.81073(19)	0.67283(9)	0.0101(5)	
Oh(14)	−0.2634(5)	0.5946(2)	0.70882(9)	0.0125(6)	
Oh(15)	0.1705(6)	0.4452(2)	0.51631(9)	0.0171(6)	
Ow(16)	0.2873(6)	0.6475(2)	0.51433(10)	0.0224(7)	
Oh(17)	0.1355(7)	0.6964(3)	0.75	0.0123(8)	
H(1)	−0.415(7)	0.508(4)	0.5742(18)	0.040(16)	
H(2)	0.411(5)	0.797(5)	0.676(2)	0.07(2)	
H(3)	−0.413(7)	0.607(5)	0.6968(18)	0.051(19)	
H(4)	0.128(14)	0.399(4)	0.5351(18)	0.07(2)	

Oxygens of hydroxyl groups are designated as Oh, those of water molecules as Ow.
* Both M(1) and M(2) sites were refined as Cu (see text); their U_{iso} values have been fixed.
** fixed

hydrogen bonds. A bond-valence analysis is presented in Table 10. A list of observed and calculated structure factors (Table 11) has been deposited with the Principal Editor of *Mineralogical Magazine* and is available upon request.

Description and discussion of the structures

Kidwellite

The structure solution demonstrates that kidwellite crystallizes in space group $P2/c$, and that the previously reported space group ($A2/m$, Am or $A2$; Moore and Ito, 1978) is incorrect. The space group revision may explain the statement of Moore and Ito (1978) that "Although the *b*- and *c*-axes could be established with confidence, selection of the *a*-axis presented serious problems". The observation of the presence of a medium-strong (010) reflection, violating A centering, in the X-ray powder diffraction pattern of kidwellite (Moore, 1970; Walenta and Binder, 1980) is confirmed, and validated by a calculated powder pattern ($I/I_{100} = 0.97$). The structure model obtained was used by Kia Wallwork and Allan Pring (pers. comm.) to perform a Rietveld refinement of synchrotron powder diffraction data collected on a kidwellite sample from Australia. This sample is nearly pure (it contains only trace amounts of Al, but no Cu or

TABLE 8. Anisotropic displacement parameters for 'laubmannite' (Moore, 1970).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.0062(3)	0.0065(3)	0.0097(3)	0.00004(19)	−0.00009(19)	0.00087(18)
Fe(2)	0.0112(3)	0.0129(3)	0.0103(3)	−0.0008(2)	−0.0008(2)	0.0000(2)
Fe(3)	0.0107(3)	0.0100(3)	0.0130(3)	0.0003(2)	0.0012(2)	0.0006(2)
Fe(4)	0.0101(3)	0.0095(3)	0.0102(3)	−0.0010(2)	−0.0007(2)	0.0022(2)
P(1)	0.0051(4)	0.0059(4)	0.0088(4)	−0.0004(3)	0.0000(3)	0.0005(3)
P(2)	0.0051(4)	0.0039(4)	0.0064(4)	−0.0010(3)	−0.0005(3)	0.0011(3)
P(3)	0.0044(6)	0.0046(6)	0.0105(6)	0.0	0.0	0.0005(4)
O(1)	0.0107(13)	0.0155(14)	0.0104(13)	0.0002(11)	−0.0025(10)	−0.0012(10)
O(2)	0.0119(13)	0.0076(13)	0.0141(13)	−0.0041(11)	−0.0003(10)	0.0025(10)
O(3)	0.0103(12)	0.0050(12)	0.0135(12)	0.0015(10)	−0.0017(10)	−0.0034(10)
O(4)	0.0077(12)	0.0097(13)	0.0122(12)	−0.0005(10)	−0.0008(10)	0.0040(10)
O(5)	0.0103(13)	0.0180(15)	0.0231(15)	−0.0078(12)	−0.0010(12)	0.0048(11)
O(6)	0.0222(14)	0.0166(15)	0.0105(13)	0.0044(11)	−0.0052(11)	−0.0018(12)
O(7)	0.0144(13)	0.0158(14)	0.0173(14)	0.0023(11)	−0.0028(11)	−0.0067(11)
O(8)	0.0190(14)	0.0086(13)	0.0129(13)	−0.0047(11)	−0.0015(11)	0.0058(11)
O(9)	0.0149(13)	0.0111(14)	0.0131(13)	−0.0031(11)	−0.0001(11)	0.0054(11)
O(10)	0.0127(18)	0.0074(19)	0.026(2)	0.0	0.0	−0.0021(15)
O(11)	0.0109(17)	0.0102(19)	0.0183(19)	0.0	0.0	0.0019(15)
Oh(12)	0.0126(13)	0.0144(14)	0.0144(13)	0.0036(11)	0.0033(11)	0.0018(11)
Oh(13)	0.0063(12)	0.0096(13)	0.0144(13)	0.0039(10)	−0.0002(10)	0.0002(10)
Oh(14)	0.0133(13)	0.0118(14)	0.0124(13)	0.0002(11)	0.0010(11)	−0.0017(11)
Oh(15)	0.0209(15)	0.0162(15)	0.0143(14)	−0.0026(12)	0.0024(12)	−0.0021(12)
Ow(16)	0.0203(15)	0.0239(18)	0.0229(16)	0.0086(13)	−0.0030(12)	−0.0100(13)
Oh(17)	0.0092(17)	0.020(2)	0.0079(17)	0.000	0.000 0.000	0.0022(15)

As, or other impurity elements) and has refined unit-cell parameters, $a = 20.022$, $b = 5.166$, $c = 13.983$ Å, $\beta = 106.867°$, $V = 1383.97$ Å^3, which are slightly smaller than those of the slightly arsenatian sample studied here, the volume of which is 0.7% larger. The structure model determined here is confirmed in detail by the Rietveld refinement ($R_{wp} = 2.6\%$), although none of the metal−oxygen distances in the Australian sample could be refined without severe restraints.

Kidwellite has a complex framework structure which shows some close relations to that of 'laubmannite' (see below). Unlike the structure proposed by Moore (1970), kidwellite does not contain any 'h-cluster' (trimers of three face-sharing (Fe^{2+},Fe^{3+})O_6 octahedra). The structure contains (Table 2) five Fe atoms, one Na atom, three P atoms, 19 O atoms, about 19 H atoms (none of which were detectable during the refinement), and three additional, cation sites with very low occupancies (see below). The Fe atoms are all [6]-coordinated by O atoms to form somewhat distorted FeO_6 octahedra. These octahedra have very similar average Fe−O bond lengths which range from 2.014 to 2.022 Å, and

bond-valence calculations demonstrate that all Fe sites host trivalent Fe (Table 5). The very minor Al contents detected by SEM-EDS seem to be homogeneously distributed among all five Fe sites.

The P atom in each of the three PO_4 tetrahedra is partially substituted by As atoms. In the P(1)O_4 group the P:As ratio is ~86:14, whereas in the P(2)O_4 and P(3)O_4 groups, the ratios are distinctly larger, 94:6 and 97:3, respectively (Table 2). Average P−O bond lengths for P(1), P(2) and P(3) are 1.559, 1.542 and 1.530 Å (Table 4), respectively, and are consistent with the refined P:As ratios.

Dominant elements of the kidwellite structure comprise three different, FeO_6-based polyhedral clusters (Fig. 1): one dimer composed of two face-sharing Fe(1)O_6 and Fe(2)O_6 octahedra, another built of two edge-sharing Fe(3)O_6 octahedra and one trimer built of three corner-sharing FeO_6 octahedra (Fe(4)O_6-Fe(5)O_6-Fe(4)O_6). These dimers and trimer are corner-linked to neighbouring, symmetry-related units, and to PO_4 tetrahedra. The resulting three-dimensional framework hosts narrow channels

TABLE 9. Selected bond distances (Å) for the coordination polyhedra in 'laubmannite' (Moore, 1970).

Fe(1)−O(5)	1.897(3)	P(1)−O(1)	1.536(3)
−O(7)	1.911(3)	−O(2)	1.547(3)
−O(12)	1.947(3)	−O(3)	1.567(3)
−O(3)	2.102(3)	−O(4)	1.570(3)
−O(4)	2.109(3)	<P(1)−O>	1.555
−O(13)	2.132(4)		
<Fe(1)−O>	2.016	P(2)−O(5)	1.521(3)
		−O(6)	1.524(3)
Fe(2)−O(4)	1.993(3)	−O(8)	1.534(3)
−O(14)	2.029(3)	−O(7)	1.539(3)
−O(11)	2.063(3)	<P(2)−O>	1.53
−O(10)	2.091(3)		
−O(3)	2.123(3)	P(3)−O(9) ×2	1.528(3)
−O(13)	2.132(4)	−O(10)	1.565(4)
<Fe(2)−O>	2.072	−O(11)	1.568(4)
		<P(3)−O>	1.547
Fe(3)−O(8)	1.942(3)		
−O(12)	1.987(3)	M(1)−O(9)	1.89(3)
−O(1)	1.990(3)	−O(14)	1.99(3)
−O(15)	2.014(3)	−O(2)	2.00(3)
−O(15)	2.021(3)	−O(13)	2.13(3)
−O(16)	2.121(3)	−O(6)	2.23(3)
<Fe(3)−O>	2.013	−O(17)	2.76(3)
		<M(1)−O>	2.17
Fe(4)−O(6)	1.931(3)		
−O(9)	1.977(3)	M(2)−O(12)	1.80(3)
−O(2)	1.980(3)	−O(16)	1.88(3)
−O(17)	2.0190(17)	−O(8)	2.11(3)
−O(13)	2.066(4)	−O(1)	2.13(3)
−O(14)	2.096(3)	−O(15)	2.44(3)
<Fe(4)−O>	2.012	−O(15)	2.52(3)
		<M(2)−O>	2.15
Possible hydrogen bonds*			
Oh(12)−H(1)**	0.90(2)	Oh(12)···O(1)	2.88(4)
Oh(13)−H(2)**	0.88(2)	Oh(13)···O(9)	2.81(4)
Oh(14)−H(3)**	0.88(2)	Oh(14)···O(2)	2.75(4)
Oh(15)−H(4)**	0.89(2)	Oh(15)···O(7)	2.78(4)
		Oh(12)−H(1)···O(1)	168(1)
		Oh(13)−H(2)···O(9)	153(1)
		Oh(14)−H(3)···O(2)	168(1)
		Oh(15)−H(4)···O(7)	167(1)

* H atoms belonging to Ow(16) and Oh(17) were not detectable, but possible hydrogen bonds are: Ow(16)···O(8) = 2.87 Å, and Oh(17)···O(14) = 2.82 Å.
** Restrained to distance of 0.90(2) Å

which run parallel to the principal axes (Fig. 1). The Na atom is located in the largest channel and shows a [6]-coordination sphere, in which the six O ligands form a slightly distorted (flattened) octahedron (Fig. 1), with an average Na−O bond length of 2.424 Å (Table 4) and a calculated bond-valence sum of 1.14 valence units (v.u.)

(Table 5). The anisotropic displacement parameters of the Na atom demonstrates some positional disorder parallel to the 5.19 Å axis (Table 3). Occupancy refinements of the Na site indicated the weak possibility of a partially occupied site. However, the strong correlation between site occupancy and displacement para-

TABLE 10. Bond-valence analysis for 'laubmannite' (Moore, 1970).

	Fe(1)	Fe(2)	Fe(3)	Fe(4)	P(1)	P(2)	P(3)	Sum*
O(1)			0.536		1.282			1.82
O(2)				0.550	1.244			1.79
O(3)	0.396	0.362			1.178			1.94
O(4)	0.388	0.514			1.169			2.07
O(5)	0.689					1.251		1.94
O(6)				0.628		1.241		1.87
O(7)	0.663					1.192		1.86
O(8)			0.610			1.208		1.82
O(9)				0.555			1.269 ×2	1.82
O(10)		0.395 ×2					1.148	1.94
O(11)		0.426 ×2					1.139	1.99
Oh(12)	0.602		0.540					1.14
Oh(13)	0.365	0.353		0.436				1.15
Oh(14)		0.467		0.402				0.87
Oh(15)			0.502					
			0.493					1.00
Ow(16)			0.376					0.38
Oh(17)				0.495 ×2				0.99
Sum*	3.10	2.52	3.06	3.07	4.87	4.89	4.83	

Bond-valence parameters used are from Brese and O'Keeffe (1991).
* Sum values involving bonds to P(1) and P(3) are based on the refined occupancies (P:As ratios) of these sites (see Table 6), and sum values involving bonds to Fe(2) are based on an assumed $Fe^{2+}:Fe^{3+}$ ratio of 1:1 on this site (see text; using only the parameters for either Fe^{3+} or Fe^{2+}, one would obtain bond-valence sums of 2.60 and 2.43 v.u., respectively.) Because of the very low occupancy and uncertain nature of the two M sites, their bond-valence contributions have not been taken into acccount; however, their important influence is discussed in the text. Contributions of H atoms are not listed.

meters precluded any definite statement, and the occupancy has, therefore, been kept at 100%. The wet-chemical analysis of type kidwellite (Moore and Ito, 1978) yielded Na contents which would indicate an occupancy of $\sim Na_{0.71}$ for the Na site. However, the formula of the kidwellite from Broken Hill analysed by electron microprobe (Birch, 1990) corresponds to an occupancy of $(Na_{0.9}Ca_{0.05})_{\Sigma 0.95}$ for the Na site.

Three further cation sites, $M(1)$, $M(2)$ and $M(3)$, with very low occupancies and strongly distorted 'octahedral' coordinations with $M-O$ bond lengths between 1.795(6) and 2.719(14) Å (Table 4) are located in the channels of the framework (Fig. 2). On the basis of the geometries of these sites, refinement behaviour of their isotropic displacement factors during trial refinements and the fact that chemical analyses has shown Cu as an impurity in the crystals, it was assumed that Cu occupies, at least partly, these sites. Refined occupancies are basically identical: $\sim 7\%$ for $M(1)$, $\sim 7\%$ for $M(2)$ and $\sim 7\%$ for $M(3)$

(Table 2). The assignment of Cu to these sites is hypothetical, and other candidates could be Fe, trace amounts of Mn, as well as Na atoms or H_2O molecules. The Rietveld refinement, mentioned already, of a Cu-free kidwellite sample by Kia Wallwork and Allan Pring (pers. comm.) also indicated very low occupancies of the M sites. Therefore, Cu does not seem to be essential for the kidwellite structure.

The three M sites in the crystal studied here have some fairly close contacts to several Fe sites: $M(1)-Fe(5) = 2.5925(5)$ ($\times 2$), $M(2)-Fe(3) = 2.526(16)$ and $2.660(16)$, and $M(3)-Fe(4) = 2.442(13)$ and $2.744(13)$ Å. Thus, repulsion forces preclude the possibility of high occupancies, and the neighbouring Fe sites might be locally vacant, if the respective M site is occupied. An analysis of the bond-valence contributions of the three M sites demonstrates that all those O atoms which are slightly underbonded (e.g. O(1), O(2), O(6) and O(7); Table 5) receive small bond-valence contribu-
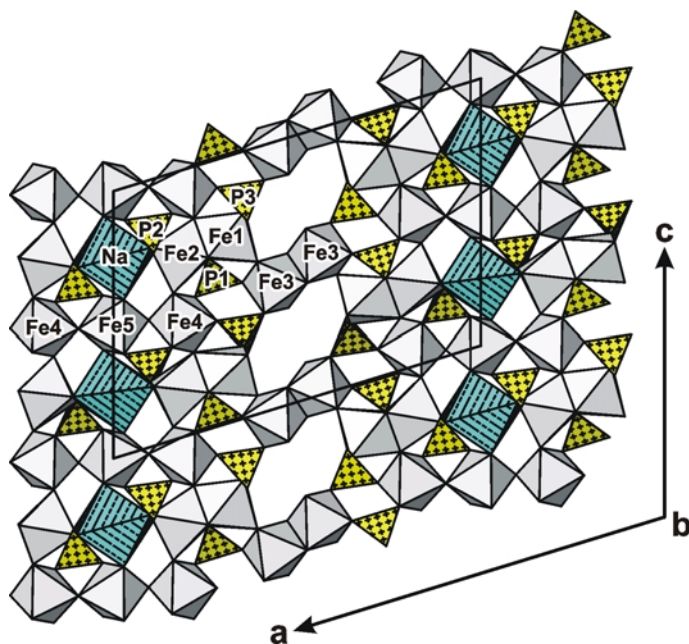
FIG. 1. The crystal structure of kidwellite projected along [010], i.e. the short ~5.1 Å axis. The FeO_6-based building units (face-sharing dimer, edge-sharing dimer and corner-sharing trimer) are easily recognized in this view. The NaO_6 octahedron (blue) is striped, and PO_4 tetrahedra (yellow) are marked with crosses. The partially occupied sites $M(1)$, $M(2)$ and $M(3)$ have been omitted for clarity. All drawings were done using *ATOMS* (Shape Software, 1999).

tions from the three M sites (Table 4). By contrast, the O atoms which are more or less saturated (e.g. O(3), O(5), O(8); Table 5), do not receive any of these bond-valence contributions. Thus, the three M sites provide a weak reinforcement of the atomic arrangement (cf. Fig. 2).

Derivation of the accurate chemical formula of kidwellite posed some problems. From the bond-valence calculations (Table 5) it is clear that O(1) to O(12) all represent O^{2-} anions, and that Oh(13) to Oh(16), and Oh(18) represent OH^- groups. Ow(17) (0.38 v.u.) clearly forms part of a water molecule bonded to Fe(3) only, but Ow(19) (0.71 v.u.), which is bonded to Fe(5) and Na, might represent a mixture of H_2O and OH^-. The condition of electroneutrality shows that the three partially M sites are necessary for an accurate definition of a charge-balanced structure. If Ow(19) is assumed to represent only H_2O, then one obtains the detailed structural formula $NaFe_9^{3+}M_{5x}(OH)_{10}(H_2O)_4(PO_4)_6$, where M = Fe^{3+}, Cu^{2+} or other metal cation, and $x \approx 0.07$. One formula unit then has ~29 positive charges (28.72 if M = only Cu^{2+}, or 29.08 if M = only

Fe^{3+}) and 28 negative charges. If, on the other hand, Ow(19) is assumed to have the occupancy $(OH_{0.5}H_2O_{0.5})$, the combined charge of all three M sites is close to the value necessary for compensating the then 29 negative charges. This would correspond to the structural formula $NaFe_9^{3+}M_{5x}(OH)_{10}(OH_{0.5}H_2O_{0.5})_2(H_2O)_2(PO_4)_6$. If Ow(19) is assumed to represent only OH, then one obtains the formula $NaFe_9^{3+}M_{5x}(OH)_{12}(H_2O)_2(PO_4)_6$, with 30 negative charges. As mentioned above, the refinement indicated the possibility of a partially occupied Na site. If confirmed, this would complicate matters further, but would also fit into the picture of an overall non-stoichiometric formula. The suggested simplified formula of kidwellite is therefore $Na(Fe^{3+},M)_{9+x}(OH)_{11}(H_2O)_3(PO_4)_6$, where M = Fe^{3+}, Cu^{2+} or other metal cation, and $x \approx 0.3$. This formula also reflects the fact that the mineral contains no zeolitic ('free') water. As no H atoms could be detected in the refinement, the suggested hydrogen bonds (Table 4) are only tentative. Nonetheless, the suggested donor-acceptor distances indicate that the hydrogen bonds are seemingly rather weak, with the

exception of the short bond Oh(14)···Ow(19), 2.610(8) Å.

'Laubmannite' and its relation to kidwellite

The structure solution shows that 'laubmannite' as defined by Moore (1970) is a valid, but presently unnamed species which clearly deserves a species name. The space group $Pbcm$ suggested by Moore (1970) is confirmed, although the formula had to be completely revised (see below).

'Laubmannite' has a complex framework structure comprising four Fe atoms, three P atoms, 17 O atoms, ~13 H atoms (four of which were detectable during the refinement of LAUB2), and two cation sites, $M(1)$ and $M(2)$, with very low occupancies (Table 7). As in

kidwellite, all four Fe atoms are [6]-coordinated by O atoms to form distorted FeO_6 octahedra (Fig. 3). The main building units are a dimer composed of two face-sharing $Fe(1)O_6$ and $Fe(2)O_6$ octahedra, a dimer composed of two edge-sharing $Fe(3)O_6$ octahedra and a dimer composed of two corner-sharing $Fe(4)O_6$ octahedra. Both Fe(1)/Fe(2)- and Fe(3)-based dimers also occur in kidwellite, whereas the Fe(4)-based dimer contrasts with the Fe(4)/Fe(5)/Fe(4)-based trimer of kidwellite. Two equivalent face-sharing $Fe(1)O_6$-$Fe(2)O_6$ dimers are connected via one common terminal edge to form a unique tetramer extended parallel to the c axis (Figs 3,4).

Linkage between the FeO_6-based building units is achieved by corner-sharing with adjacent FeO_6 octahedra and by corner-linkage to PO_4 tetrahedra
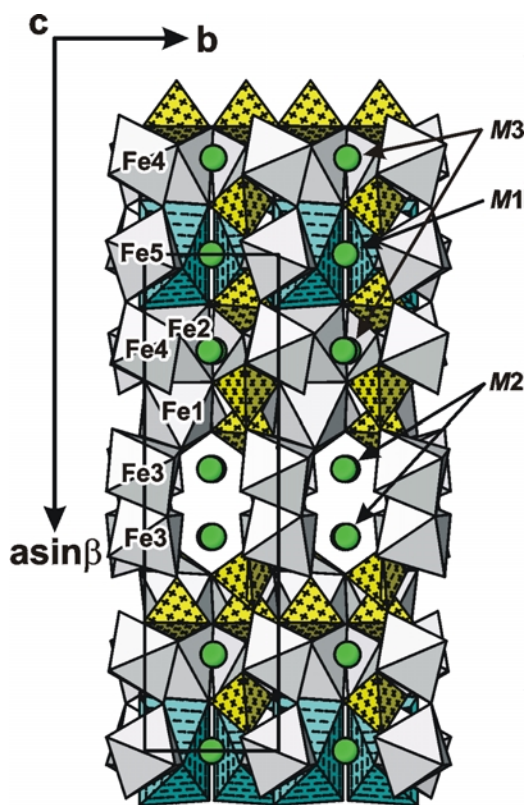
FIG. 2. View of the crystal structure of kidwellite along [001], showing the partially occupied sites $M(1)$, $M(2)$ and $M(3)$ (green spheres), all of which are located in channels of the framework, and have strongly distorted 'octahedral' coordinations. The important role of these sites is discussed in the text. Legend otherwise as for Fig. 1. Compare Fig. 4.
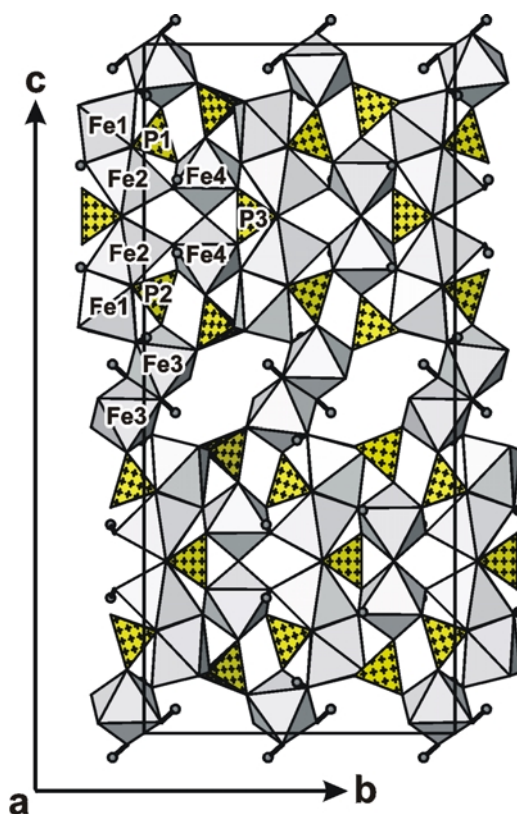
FIG. 3. The crystal structure of 'laubmannite' (Moore, 1970) projected along [100], i.e. the short ~5.1 Å axis. The FeO_6-based building units (face-sharing dimer, edge-sharing dimer and corner-sharing dimer) are easily recognized in this view (compare Figs 1 and 5). O−H bonds are drawn as thin lines. Legend otherwise as for Fig. 1.
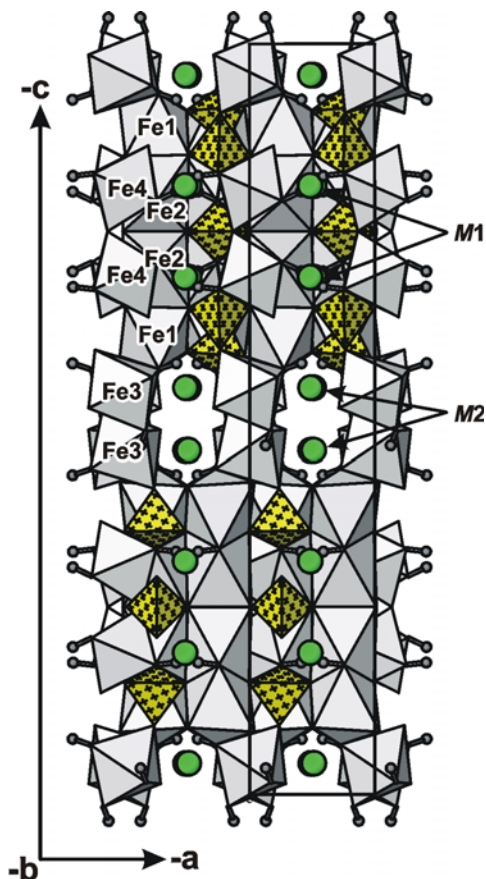
FIG. 4. View of the crystal structure of 'laubmannite' along [010], showing the partially occupied sites $M(1)$ and $M(2)$ (green spheres). Both sites are located in channels of the framework, and have strongly distorted [5+1] [$M(1)$] and 'octahedral' [$M(2)$] coordinations. Compare also with Fig. 2.

(Figs 3,4). The P(1) site contains ~13% As substituting for P, the P(3) site ~5% As, whereas the P(2) site is basically As-free (Table 7). As a result, the average P−O bond lengths in the P(1)-, P(2)- and P(3)O$_4$ tetrahedra are 1.555, 1.530 and 1.547 Å, respectively (Table 9). In the As-free LAUB1 the corresponding value of the average P(1)−O bond length is, as expected, considerably lower: 1.542 Å. The PO$_4$ tetrahedra show different degrees of geometrical distortion, which, as a comparison between LAUB2 and LAUB1 shows, is unrelated to the As content of LAUB2. The P(2)O$_4$ tetrahedron is the least distorted (P−O range: 1.521(3) to 1.539(3) Å). Both the P(1)O$_4$ and P(3)O$_4$ tetrahedra show

considerable distortions, with bond length ranges of 1.536(3) to 1.570(3) Å for P(1), and 1.528(3) to 1.568(4) Å for P(3), respectively. Again, this is in accordance with the observed As-for-P substitution on these two sites.

Average Fe−O bond lengths for Fe(1) to Fe(4) are 2.016, 2.072, 2.013 and 2.012 Å, respectively. Bond-valence calculations indicate that Fe(1), Fe(3) and Fe(4) are occupied by Fe^{3+} only, whereas the average Fe valency of Fe(2) is ~2.5+ (Table 10). The average Fe(2)−O distance, 2.072 Å (Table 9), also provides evidence that Fe(2) is occupied by a mixture of ferrous and ferric iron in an approximate ratio of 1:1. According to Baur (1981), average Fe^{2+}−O and Fe^{3+}−O bond lengths in oxide iron compounds are 2.138 and 2.011 Å, respectively. The length of an 'ideal' ($Fe_{0.5}^{2+}Fe_{0.5}^{3+}$)−O bond, 2.075 Å, is indeed very close to the average Fe(2)−O bond length in 'laubmannite'.

The relatively short Fe(1)−Fe(2) distance in the face-sharing dimer, 2.924(1) Å, makes it understandable that only this dimer accepts Fe^{2+}, but not the other, edge- and corner-sharing dimers: if it would host only Fe^{3+} cations, electrostatic cation repulsion across the shared face would be much stronger and could lead to severe intrapolyhedral strain. In kidwellite, which contains only Fe^{3+} ions in an otherwise very similar face-sharing dimer, the Fe(1)−Fe(2) distance is considerably longer, 2.967(2) Å, as would be expected from a stronger repulsion across the shared face. The dark greenish to greenish brown colour and the strong pleochroism of 'laubmannite' is due to Fe^{2+}-Fe^{3+} charge transfer within the face-, edge- and corner-sharing dimeric units, typical of ferric-ferrous iron phosphates (Moore, 1970).

The three-dimensional framework of 'laubmannite' hosts narrow channels parallel to the a and b axes, as in kidwellite. In one of these channels, a further cation site, $M(1)$, with a very low occupancy (~3%, if refined as Cu) and a strongly distorted [5+1]-coordination is located in a void between two Fe(4)O$_6$ octahedra (Fig. 4, Table 9). A second cation site, $M(2)$, with an equally low occupancy (~2%) but a distorted 'octahedral' coordination, is present in a different channel (Fig. 4, Table 9). As in kidwellite, both Cu^{2+}, Fe^{3+} and other minor metal cations might be present on these two sites. The $M(1)$ site has two fairly short distances to Fe(4), 2.44(3) and 2.74(3) Å. Similarly, the $M(2)$ site has fairly short distances to Fe(3). Thus, repulsive forces

will preclude any high occupancy of the two M sites, comparable to the situation of the three partially occupied M sites in kidwellite. If one takes the $M(1)$ site into account for the description of the framework connectivity, chains of face-sharing, alternating $Fe(M(1))O_6$ octahedra running along the ~5.1 Å axis (a-axis) would result. Similar iron-deficient octahedral chains are known in lipscombite, $(Fe^{2+},Mn^{2+})Fe_2^{3+}$ $(PO_4)_2(OH)_2$ (Vencato et al., 1989). Partial occupancies of Fe sites have also been encountered in other iron phosphates: examples include rockbridgeite (Moore, 1970), whitmoreite (Moore et al., 1974), and synthetic $Fe^{2+}Fe_2^{3+}(PO_3OH)_4$ $(H_2O)_4$ (Vencato et al., 1986). As in kidwellite, all those O atoms which are most underbonded (O(1), O(2), O(8), O(9); Table 10) receive small bond-valence contributions from the two M sites (Table 9).

The chemical formula of 'laubmannite' obtained from the structure model is distinctly different from that suggested by Moore (1970). Judging from the bond-valence sums of the O atoms, five of them represent OH groups [Oh(12), Oh(13), Oh(14), Oh(15) and Oh(17)], whereas Ow(16), with only 0.38 v.u., is part of a H_2O molecule (Tables 9, 10). If one also takes into account the occupancy of the Fe(2) site ($Fe^{3+}:Fe^{2+} \approx$ 1:1), and the two partially occupied M sites, the accurate structural formula is $(Fe^{3+},Fe^{2+})_2Fe_6^{3+}M_{4x}(OH)_9(H_2O)_2(PO_4)_5$, where $M = Fe^{3+}$, Cu^{2+} or other metal cation, and $x \approx$ 0.02. This formula has 23.16 positive charges if only Cu^{2+} is present on the two M sites, and 24 negative charges. If only Fe^{3+} would occupy the M sites, a sum of 23.24 positive charges would result. However, the bond-valence sum of Oh(14), 0.87 v.u., could indicate that there might also be small amounts of water on this site and, consequently, <24 negative charges. Oh(14) does not accept any hydrogen bonds and can, therefore, not increase its bond-valence sum through hydrogen bonding. The non-stoichiometric nature of the formula is thus comparable to that in kidwellite.

The idealized formula of 'laubmannite' is $(Fe^{3+},Fe^{2+},M)_{8+x}(OH,H_2O)_9(H_2O)_2(PO_4)_5$, where $M = Fe^{3+}$, Cu^{2+} or other metal cation, and $x \approx$ 0.1. This formula has a distinctly lower Fe:P ratio (1.60) than the originally proposed formulae, $Fe_3^{2+}Fe_6^{3+}(PO_4)_4(OH)_{12}$ (Frondel, 1949) and $Fe_9(PO_4)_4(OH)_{15}$ (Moore, 1970), and is intermediate between that of beraunite and kidwellite (both 1.50) and that of rockbridgeite and dufrénite

(both 1.67). The similar ratios explain indirectly the often close association of 'laubmannite' with these other iron phosphates. The suggested hydrogen bonding scheme in 'laubmannite' (Table 9), which is based on the four detected H positions, shows that the hydrogen bonds are rather weak, with donor−acceptor distances all >2.75(4) Å, similar to the situation in kidwellite (see above).

A powder diffraction pattern calculated from the structure model is in good agreement with that given by Moore (1970) (see also ICDD-PDF 22-283). The calculated density, 3.37 g/cm^3 is relatively close to the value of 3.33 g/cm^3 measured for the laubmannite type material of Frondel (1949), which, however, represented a mixture of different iron phosphates (Moore, 1970; Dunn, 1990). 'Laubmannite' material from Buckeye Mountain, Arkansas, characterized by Moore (1970) gives a calculated density of 3.41 g/cm^3 on the basis of the formula $Fe_9(PO_4)_4(OH)_{15}$. The presently determined formula, $(Fe^{3+},Fe^{2+})_2Fe_6^{3+}(PO_4)_5(OH)_8(H_2O)_3$, results in a lower calculated density because it has a lower Fe:P ratio than that suggested by Moore (1970).

Relation to other iron phosphates and explanation of epitaxial intergrowths

The structure determinations of kidwellite and 'laubmannite' do not confirm the assumption of Moore (1970) that both minerals contain clusters composed of three face-sharing $(Fe^{2+},Fe^{3+})O_6$ octahedra ('h-clusters'), which are present in the crystal structures of dufrénite and rockbridgeite (Moore, 1970). The conclusion of Moore (1970) was based on his observation that the occurrence of ~13 and ~5.1 Å axes are a common feature of several fibrous iron phosphates such as barbosalite, lipscombite, dufrénite, souzalite, rockbridgeite, beraunite, 'laubmannite' and kidwellite, and that his single-crystal study of 'laubmannite' had given the unit-cell parameters $a = 13.95$, $b = 30.77$, $c = 5.16$ Å. Moore (1970) observed that the ~13 and ~5.1 Å axes always lie in the plane of dense polyhedral slabs.

The lengths of the a axis in 'laubmannite', 5.17 Å, and the b axis in kidwellite, 5.19 Å, are, in a rather fortuitous way, very similar to the those of the other iron phosphates mentioned. In rockbridgeite, the length of the 5.17 Å axis is defined by the length of a face-sharing dimer, while in dufrénite the length of the 5.13 Å axis

represents the added lengths of two parallel polyhedral edges of an FeO_6 octahedron and a PO_4 tetrahedron (Moore, 1970). In both rock-bridgeite and dufrénite the elongation of the 'h-cluster' is perpendicular to the respective $\sim$5.1 Å axes.

Although 'laubmannite' does not contain 'h-clusters', the general connectivity in its structure also results in a thick polyhedral slab in the a-b plane, i.e. in the plane of the 5.17 and 14.0 Å axes. Adjacent slabs are connected solely via the edge-sharing dimer $Fe(3)O_6-Fe(3)O_6$. The cleavage observed on (010) may be explained by the fact that the weakest (i.e. corner-sharing) links are in a plane parallel to (010) (Fig. 3). In kidwellite, a similar, thick polyhedral slab is present in the b-c plane, i.e. again in the plane of the 5.19 and 14.0 Å axes. This slab includes the NaO_6 polyhedron, and therefore differs from that in 'laubmannite'. The cleavage reported for kidwellite is parallel to the (100) plane (Moore and Ito, 1978). Thus, it may be explained by the comparatively weak bonds involving the NaO_6 octahedron and the corner-sharing trimer (Fig. 1).

The frequently observed epitaxial intergrowth of kidwellite and 'laubmannite' and also inter-growths with other fibrous iron phosphates (see section 'Previous work') are explained by the overall similarity of the crystal structures.

Figure 5 gives a direct comparison of the similarly arranged, FeO_6-based units in kidwellite and 'laubmannite' in views perpendicular to the 5.1 Å axis, i.e. the morphological growth axis of both minerals (compare also Figs 2 and 4). It can be seen that the 'insertion' of the Na site in kidwellite induces, by comparison to 'laubmannite', a disruption of the edge-linkage of the two adjacent, face-sharing dimers. Simultaneously, an additional FeO_6 octahedron is inserted between the two octahedra of the corner-sharing dimer to form the trimer in kidwellite. The resulting inserted layer is shown within a dashed box in Fig. 5. The similarity of the polyhedral building units and their arrangement makes it easy to understand that structural adaptations to changes in growth conditions (e.g. Fe:P ratio and Na^+ activity in the solution, pH, Eh) of the fibrous iron phosphates discussed here can be accomplished by only small modifications of the polyhedral clusters (dimers, trimers, chains) and their interconnection (corner-, edge- or face-sharing).
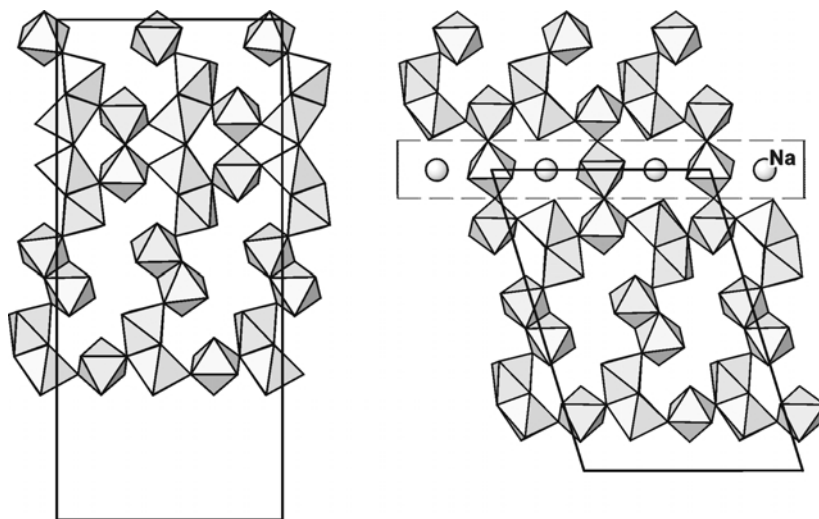
Acknowledgements

FIG. 5. Comparison of the FeO_6-based building units in 'laubmannite' (left) and kidwellite (right) in views along the short $\sim$5.1 Å axes, which represent the growth axes in both species. The similarity explains the often observed epitaxial intergrowths between both species and other related fibrous iron phosphates (see text for details and compare also with Figs 2 and 4).

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