Nordgauite, $MnAl_2(PO_4)_2(F,OH)_2 \cdot 5H_2O$, a new mineral from the Hagendorf-Süd pegmatite, Bavaria, Germany: description and crystal structure

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ABSTRACT

Nordgauite, $MnAl_2(PO_4)_2(F,OH)_2 \cdot 5H_2O$, is a new secondary phosphate from the Hagendorf-Süd pegmatite, Bavaria, Germany. It occurs as white to off-white compact waxy nodules and soft fibrous aggregates a few millimetres across in altered zwieselite−triplite. Individual crystals are tabular prismatic, up to 200 μm long and 10 μm wide. Associated minerals include fluorapatite, sphalerite, uraninite, a columbite−tantalite phase, metastrengite, several unnamed members of the whiteite−jahnsite family, and a new analogue of kingsmountite. The fine-grained nature of nordgauite meant that only limited physical and optical properties could be obtained; streak is white; fracture, cleavage and twinning cannot be discerned. $D_{meas.}$ and $D_{calc.}$ are 2.35 and 2.46 g cm^{-3}, respectively; the average RI is $n = 1.57$; the Gladstone-Dale compatibility is -0.050 (good). Electron microprobe analysis gives (wt.%): CaO 0.96, MgO 0.12, MnO 14.29, FeO 0.60, ZnO 0.24, Al_2O_3 22.84, P_2O_5 31.62, F 5.13 and H_2O 22.86 (by CHN), less F=O 2.16, total 96.50. The corresponding empirical formula is $(Mn_{0.90}Ca_{0.08}Fe_{0.04}Zn_{0.01}Mg_{0.01})_{\Sigma 1.04}Al_{2.01}(PO_4)_2[F_{1.21},(OH)_{0.90}]_{\Sigma 2.11} \cdot 5.25H_2O$. Nordgauite is triclinic, space group $P\bar{1}$, with the unit-cell parameters: $a = 9.920(4)$, $b = 9.933(3)$, $c = 6.087(2)$ Å, $\alpha = 92.19(3)$, $\beta = 100.04(3)$, $\gamma = 97.61(3)°$, $V = 584.2(9)$ Å^3 and $Z = 2$. The strongest lines in the XRD powder pattern are [d in Å (I) (hkl)] 9.806 (100)(010), 7.432 (40)(1$\bar{1}$0), 4.119 (20)(210), 2.951 (16)(0$\bar{3}$1), 4.596 (12)(2$\bar{1}$0), 3.225 (12)(220) and 3.215 (12)(121). The structure of nordgauite was solved using synchrotron XRD data collected on a 60 μm × 3 μm × 4 μm needle and refined to $R_1 = 0.0427$ for 2374 observed reflections with $F > 4\sigma(F)$. Although nordgauite shows stoichiometric similarities to mangangordonite and kastningite, its structure is more closely related to those of vauxite and montgomeryite in containing zig-zag strings of corner-connected Al-centred octahedra along [011], where the shared corners are alternately in *cis* and *trans* configuration. These chains link through corner-sharing with PO_4 tetrahedra along [001] to form (100) slabs that are interconnected via edge-shared dimers of MnO_6 polyhedra and other PO_4 tetrahedra.

Introduction

A diverse suite of phosphate minerals, including eleven new species, has been characterized from the zoned granite pegmatite of Hagendorf-Süd in Bavaria, Germany (49º39′1″N, 12º27′35″E). Known since the late 19th century, the pegmatite has been mined for feldspar and, since the 1950s, for lithium-rich triphylite, although it is now closed. The zone rich in primary phosphate minerals, chiefly triphylite, zwieselite, wolfeite, fluorapatite and hagendorfite, and their alteration products, occurs above the quartz core of the pegmatite (Mücke, 1981). Complex parageneses for the various primary and secondary phosphate minerals have been presented and described by Strunz *et al*. (1976) and Mücke (1981).

In his discussion of the secondary phosphates from Hagendorf, Mücke (1981) distinguished between "newly formed" and "transformation" phases. The former (such as strunzite and laueite) are generally idiomorphic crystals deposited in druses and cavities, whereas the latter were defined as mostly compact, earthy polycrystalline masses, which were largely uncharacterized. The new mineral, nordgauite, described here, is an example of such a phase. The name and data for nordgauite have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2010-040). The mineral is named for Nordgau, the oldest name for that part of northeastern Bavaria in which Hagendorf is situated, and where mining has taken place since the 13th century. As several different specimens were used in data collecting, there is no single type specimen. Co-types are housed in the collections of Museum Victoria, Melbourne, Australia, registered numbers M48795 and M51231.

Occurrence, mineral assemblage and paragenesis

The specimens on which nordgauite occurs were collected by one of the authors (EK) in 1975−6, between the 60 and 67 m levels of the mine (Keck, 1983). They consist of fragments of etched, pinkish brown zwieselite−triplite containing irregular cavities up to a few cm across. Nordgauite occurs in the cavities as fine-grained compact nodular masses and soft, finely fibrous hemispherical aggregates and coatings a few mm thick (Fig. 1). Etched fragments of pale-grey fluorapatite are associated with the zwiese-

lite. A number of other minutely crystallized minerals occur as drusy crusts and coatings. Some of these are difficult to identify, but include strengite, strunzite or laueite and fluellite. Uraninite, sphalerite and a columbite−tantalite-series mineral are also present. On one specimen, colourless prismatic crystals lining etch cavities have been identified as a new CaMnMn end-member of the whiteite group. Enclosed within the nordgauite are minute clusters of white-ite−jahnsite crystals showing marked compositional zonation. More details of these whiteite phases are presented in a separate paper (Grey *et al*., 2010). On the same specimen, spherical aggregates of nordgauite are encrusted with tabular prisms of what appears to be a new analogue of kingsmountite.

Nordgauite has formed as a late-stage hydrothermal phase in the secondary phosphate suite, the end-product of the decomposition of zwieselite−triplite. Decomposition is likely to have involved reaction with F-rich acidic solutions. Several parageneses for secondary phosphates from Hagendorf, based on zwieselite decomposition and the presence or absence of rockbridgeite, were established by Mücke (1981). Nordgauite and its associated phases represent a distinct assemblage in the former paragenetic sequence.

Physical and optical properties

The compact nodules of nordgauite are off-white to white with an earthy to slightly waxy lustre

FIG. 1. Compact, off-white nordgauite in altered pinkish zwieselite–triplite. The main mass is 10 mm across. Note the thin white fibrous rims around the edge of the mass (co-type specimen M51231).
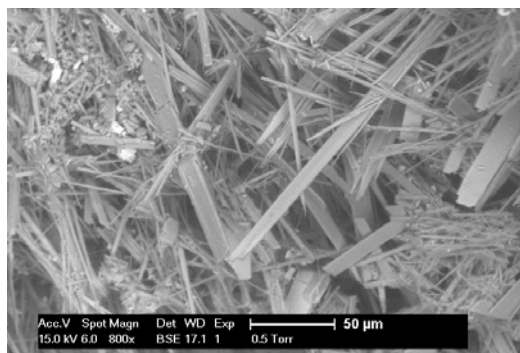
FIG. 2. SEM image of nordgauite crystals on the margins of the nodular compact form (co-type specimen M48795).

(Fig. 1). They are very fine-grained, but in places show a thin fibrous outer crust, which SEM examination reveals as consisting of individual ribbon-like crystals up to 200 μm long and 10 μm wide (Fig. 2). The soft, finely fibrous aggregates and coatings are snow-white and silky. The streak is white. Properties such as cleavage, fracture, twinning and parting cannot be discerned. The dominant form (ribbon face) is (100). The density of the compact variety was measured using a sink/float method in sodium polytungstate solution with water, yielding 2.35 g cm^{-3}. This is slightly lower than the calculated density of 2.46 g cm^{-3}, probably due to a small degree of porosity in the measured fragments. The mode of occurrence of nordgauite precludes any detailed investigation of its optical properties. All that could be determined is that it is biaxial with an average RI of $n = 1.57$.

Chemical composition

Grains of the compact form of nordgauite were mounted and polished for microprobe analysis using a Cameca SX50 instrument at the University of Melbourne, operating in WDS mode, at 15 kV and 20 nA. The beam was defocused slightly to 5 μm and the sample moved during the analyses. Standards used were wollastonite (Ca), periclase (Mg), Mn metal, sphalerite (Zn), hematite (Fe) corundum (Al) and fluorapatite (P, F). Water in the compact form was determined using a Carlo Erba 1106 automatic CHN analyser in the Research School of Chemistry, Australian National University, Canberra. Analytical details are shown in Table 1. Using the average of eight analyses, the empirical formula for the compact form of nordgauite, based on 2.00 P atoms and charge balance, is $(Mn_{0.90}Ca_{0.08}Fe_{0.04}Zn_{0.01}Mg_{0.01})_{\Sigma1.04}$ $Al_{2.01}(PO_4)_{2.0}[F_{1.21},(OH)_{0.90}]_{\Sigma2.11}\cdot5.25H_2O$. The simplified formula is $MnAl_2(PO_4)_2(F,OH)_2\cdot5H_2O$.

The soft, fibrous form of nordgauite was analysed using a JEOL 8500 Hyperprobe operated

TABLE 1. Microprobe analyses and empirical formulae for nordgauite.

Oxide	1	2		3	4
CaO	0.96	0.70	Ca	0.08	0.05
MgO	0.12	0.04	Mg	0.01	–
MnO	14.29	14.27	Mn	0.90	0.86
ZnO	0.24	0.38	Zn	0.01	0.02
FeO	0.60	0.45	Fe	0.04	0.03
Al_2O_3	22.84	22.89	Al	2.01	1.92
P_2O_5	31.62	33.17	P	2.00	2.00
F	5.13	2.89	F	1.21	0.65
H_2O (CHN)	22.86	n.d.	OH	0.90	1.03
$-F=O$	2.16	1.22	H_2O	5.25	–
Total	96.50	73.77			

1. Compact nordgauite (wt.%, average of eight) (Cameca SX50; see text), with H_2O by CHN.
2. Fibrous nordgauite (wt.%, average of eight) (JEOL 8500) (H_2O not determined).
3. Formula for analysis 1 based on 2 P atoms and with charge balance.
4. Formula for analysis 2 based on 2 P atoms and with charge balance.
n.d.: not determined

in WDS mode with lower accelerating voltage (12 kV) and beam current (2 nA) but without beam defocusing. Standards used were fluorite (Ca, F), $AlPO_4$ (P), $MgAl_2O_4$ (Mg, Al), sphalerite (Zn), hematite (Fe) and Mn metal. The data are very similar to those for the compact form (see Table 1), but with significantly lower F contents. Calculation of the empirical formula on the same basis shows that OH is dominant over F in the site they share. The soft fibrous form is, therefore, the OH-analogue of nordgauite and represents a new species. Further investigations are underway to characterize it fully.

X-ray crystallography

Powder X-ray diffraction and transmission electron microscopy

Powder X-ray diffraction (XRD) data were obtained on the compact variety of nordgauite using a Philips diffractometer, equipped with a graphite monochromator and employing Co-$K\alpha$ radiation. The X-ray tube was operated at 40 kV and 40 mA with 1º divergent and scatter slits, a 0.3 mm receiving slit and Soller slits. Step-scan intensity data were collected over the range 5 to 140º2¡, using a step size of 0.02º and a step counting time of 10 s. Powder data (in Å for Co-$K\alpha$) are given in Table 2. A triclinic unit cell was obtained by indexing the powder pattern using the Ito method as implemented by Visser (1969). The cell parameters were refined using *CELREF* (Laugier and Bochu, 2003), giving the following values:

a = 9.920(4), b = 9.933(3), c = 6.087(2) Å, α = 92.19(3), β = 100.04(3), γ = 97.61(3)º, V = 584.2(9) Å^3 and Z = 2, in $P\bar{1}$; a:b:c 0.9987:1:0.6128 (from unit-cell dimensions).

Prior to the discovery of fibrous crystals large enough for investigation by synchrotron XRD, electron diffraction (ED) patterns were taken on crystal fragments using a JEOL 4000EX transmission electron microscope (LaB$_6$ source and spherical aberration coefficient of 1.06 mm). The microscope was operated at 400 kV, using parallel illumination geometry to minimize beam damage. A [100] zone ED pattern and the corresponding image of the crystal are shown in Fig. 3. This confirms that the plane of the ribbon-like crystals is (100) and that the c axis is aligned along the length of the ribbon. ED patterns obtained by tilting about b* verified the other cell parameters. Based on the refined cell

parameters, together with the average RI and calculated density, the Gladstone-Dale compatibility (Mandarino, 1981) $(1-Kp/Kc)$ = -0.050 (rated as good) using the empirical formula for nordgauite.

TABLE 2. Powder XRD data for nordgauite.

| I/I_o	$d_{(obs)}$	$d_{(calc)}$	h	k	l
100	**9.806**	9.822	0	1	0
40	**7.432**	7.435	1	$\bar{1}$	0
2	6.457	6.449	1	1	0
2	5.983	5.980	0	0	1
2	5.566	5.556	$\bar{1}$	0	1
3	5.265	5.256	0	$\bar{1}$	1
8	4.961	4.971	0	1	1
5	4.797	4.789	$\bar{1}$	$\bar{1}$	1
10	4.650	4.652	1	$\bar{2}$	0
12	**4.596**	4.602	2	$\bar{1}$	0
3	4.469	4.464	1	$\bar{1}$	1
20	**4.119**	4.112	2	1	0
4	4.057	4.068	1	1	1
3	3.933	3.929	$\bar{2}$	1	1
3	3.912	3.918	0	$\bar{2}$	1
2	3.689	3.684	0	2	1
2	3.642	3.638	$\bar{1}$	$\bar{2}$	1
2	3.630	3.623	1	$\bar{2}$	1
7	3.468	3.465	2	0	1
3	3.421	3.418	2	$\bar{1}$	1
12	**3.225**	3.224	2	2	0
12	**3.215**	3.217	1	2	1
3	3.134	3.135	2	1	1
2	3.081	3.079	$\bar{3}$	0	1
3	3.051	3.052	$\bar{2}$	$\bar{2}$	1
12	2.976	2.976	1	3	0
16	**2.951**	2.951	0	$\bar{3}$	1
6	2.908	2.908	2	$\bar{3}$	0
10	2.869	2.867	$\bar{1}$	1	2
5	2.799	2.799	0	3	1
5	2.792	2.793	$\bar{1}$	$\bar{3}$	1
5	2.777	2.778	$\bar{2}$	0	2
4	2.651	2.65	3	$\bar{1}$	1
5	2.627	2.628	0	$\bar{2}$	2
2	2.591	2.592	$\bar{1}$	$\bar{2}$	2
3	2.553	2.552	1	3	1
3	2.548	2.549	2	3	0
2	2.359	2.359	2	0	2
3	2.000	2.000	1	3	2
3	1.997	1.998	$\bar{1}$	$\bar{1}$	3
4	1.936	1.936	$\bar{2}$	$\bar{1}$	3
4	1.933	1.933	5	0	0

Seven strongest lines in bold.
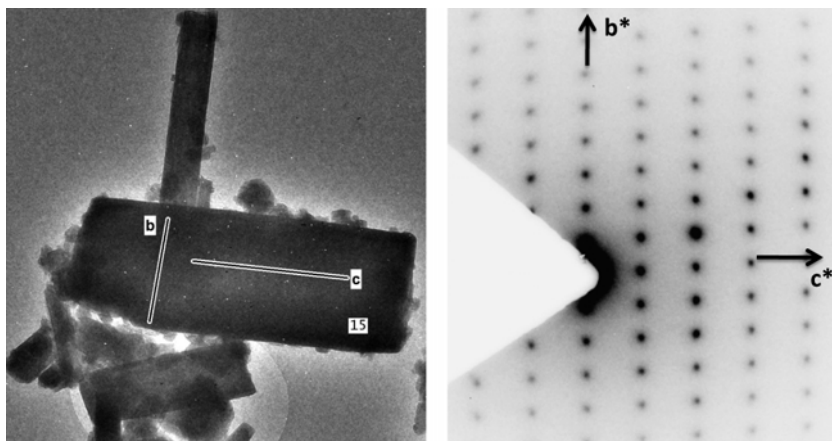
FIG. 3. [100] zone ED pattern for nordgauite with corresponding image of crystal.

Single-crystal synchrotron data collection and structure refinement

A 60 μm × 3 μm × 4 μm needle extracted from a slightly coarser zone of fibrous crystals surrounding compact nordgauite was used for data collection on the macromolecular beam line MX2 of the Australian Synchrotron. Data were collected using an ADSC Quantum 315r detector and monochromatic radiation with a wavelength of 0.71086 Å. The crystal was maintained at 100 K in an open-flow nitrogen cryostream. Phi and omega scans were employed with framewidths of 1° and a counting time per frame of 1 s. A total of 365 frames was collected. Further data-collection and refinement details are summarized in Table 3. The intensity data sets were processed to produce data

TABLE 3. Crystal data and structure refinement for nordgauite.

Structural formula	$Mn(H_2O)_2[Al_2(F,OH)_2(H_2O)_2(PO_4)_2]\cdot H_2O$
Formula weight	428.94
Temperature	100 K
Wavelength	0.71086 Å
Space group	$P\bar{1}$ (No. 2)
Unit-cell dimensions	$a = 9.887(2)$ Å $\alpha = 92.70(1)°$
	$b = 9.796(2)$ Å $\beta = 99.83(1)°$
	$c = 6.054(2)$ Å $\gamma = 97.10(1)°$
Volume	571.9(3) Å^3
Z, ρ (calc.)	2, 2.491 mg/m^3
Absorption coefficient	1.689 mm^{-1}
Crystal size	60 μm × 3 μm × 4 μm
°2θ range	2.11−29.63
Limiting indices	$-13 \leqslant h \leqslant 13,\ 0 \leqslant k \leqslant 13,\ -8 \leqslant l \leqslant 8$
Reflections collected / unique	10902 / 2818 [$R_{int} = 0.0622$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2818 / 0 / 219
Goodness-of-fit on F^2	0.933
Final R indices [$F>4\sigma(F)$]	$R_1 = 0.0427,\ wR_2 = 0.1151$
R indices (all data)	$R_1 = 0.0513,\ wR_2 = 0.1212$
Extinction coefficient	0.085(6)
Largest diff. peak and hole	0.929 and -0.626 e/Å^3

files which were analysed in *WinGX* (Farrugia, 1999). The structure solution was made using *SIR-92* (Altomare *et al.*, 1993) and the refinement was made using SHELXL-97 (Sheldrick, 2008).

The location of all non-hydrogen atoms was obtained by direct methods and refinement with isotropic displacement parameters gave $R_1 = 0.074$ for 2374 observed reflections $[F > 4\sigma(F)]$. A difference Fourier map revealed the presence of 10 H atoms. A plot of the structure showed that eight of these were associated with water molecules coordinated to Al and Mn atoms, and two others corresponded to a water molecule occupying a cavity site. The positions of the latter were smeared due to disorder and/or thermal motion and their positions were fixed during the refinement. The coordinates of the other eight H atoms were refined. The final refinement, with anisotropic displacement parameters for Al, Mn and O/F and isotropic displacement parameters for H atoms, converged to $R_1 = 0.0427$ for 2374 observed reflections. Other refinement details are given in Table 3, while atomic coordinates and equivalent isotropic displacement parameters are reported in Table 4. Tables of anisotropic displacement parameters and observed and calculated structure factors have been deposited with the journal and can be downloaded from www.minersoc.org/ pages/e_journals/dep_mat_mm.html.

Description of the structure

A projection of the structure of nordgauite along the 6 Å *c* axis in Fig. 4 shows that a key structural

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for nordgauite. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| Atom	x	y	z	U_{eq} ($\mathring{A}^2$)
Mn	5912(1)	4114(1)	3502(1)	17(1)
P(1)	8916(1)	7300(1)	7074(1)	13(1)
P(2)	6689(1)	4390(1)	9183(1)	14(1)
Al(1)	0	5000	0	11(1)
Al(2)	0	0	5000	13(1)
Al(3)	7963(1)	7182(1)	1841(2)	12(1)
O(1)	7961(2)	6899(2)	4824(4)	16(1)
O(2)	7981(2)	7456(2)	8815(4)	14(1)
O(3)	9847(2)	8665(2)	6996(4)	16(1)
O(4)	9892(2)	6220(2)	7707(4)	15(1)
O(5)	8152(2)	4215(2)	8860(4)	16(1)
O(6)	6007(2)	3091(2)	98(4)	19(1)
O(7)	5843(2)	4725(2)	6950(4)	17(1)
O(8)	6722(2)	5539(2)	1068(4)	15(1)
F(1)	9084(2)	8831(2)	2610(3)	20(1)
F(2)	9466(2)	6235(2)	1914(3)	16(1)
Ow1	8239(3)	576(3)	5524(5)	21(1)
Ow2	6402(2)	8210(3)	1723(4)	18(1)
Ow3	4573(3)	2194(3)	3759(5)	24(1)
Ow4	7906(3)	3354(3)	4509(5)	20(1)
Ow5	7476(3)	746(3)	9839(5)	30(1)
H(11)	8100(60)	1390(60)	5140(100)	41(15)
H(12)	8050(70)	490(80)	6520(130)	60(20)
H(21)	6560(60)	8950(60)	1310(100)	42(15)
H(22)	5690(50)	7820(50)	1130(80)	25(12)
H(31)	4420(50)	2000(50)	5120(100)	31(13)
H(32)	3750(80)	2270(70)	2880(120)	70(20)
H(41)	8520(60)	3490(50)	3580(90)	37(14)
H(42)	8170(60)	3580(60)	5770(110)	49(17)
H(51)	8380	890	10560	47(16)
H(52)	7240	1590	9950	90(30)
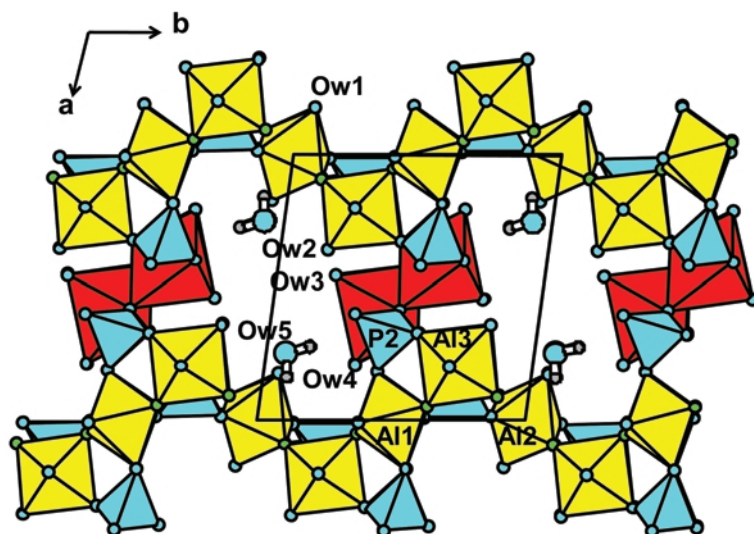
FIG. 4. Projection of the structure of nordgauite along [001].

element is a zig-zag chain of corner-connected octahedra occupied by Al. The corner-sharing anion sites are occupied predominantly by F, and are alternately in *cis* and *trans* configurations. The sequence of octahedra is *trans* $Al(2)\Phi_6 - cis$ $Al(3)\Phi_6 - trans$ $Al(1)\Phi_6 - cis$ $Al(3)\Phi_6$ (Φ = O, F, H_2O), where $Al(1)$ and $Al(2)$ occupy special sites at $[0,\frac{1}{2},0]$ and $[0,0,\frac{1}{2}]$ respectively. A view of the structure along the *a* axis in Fig. 5 shows that the octahedral chain direction is [011]. Figure 5 shows that the octahedral chains are interconnected by *trans* corner-sharing of the $Al(3)\Phi_6$ octahedra with $P(1)O_4$ tetrahedra to form slabs parallel to (100). The corner-sharing of the
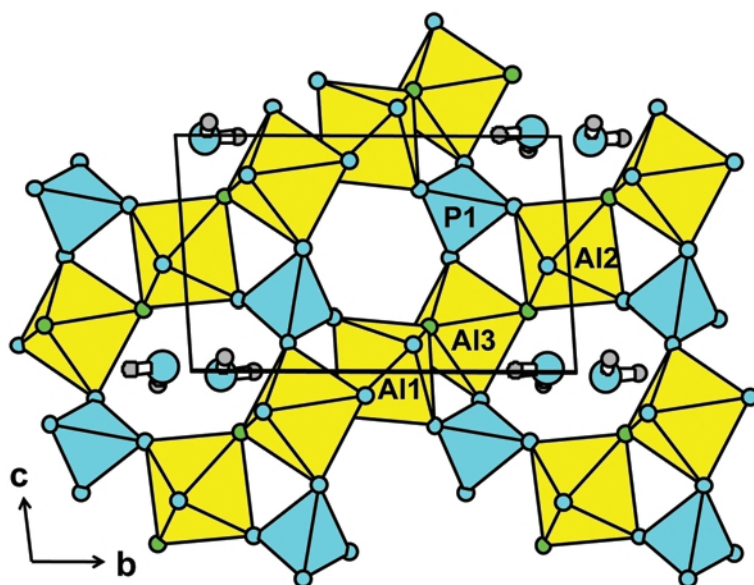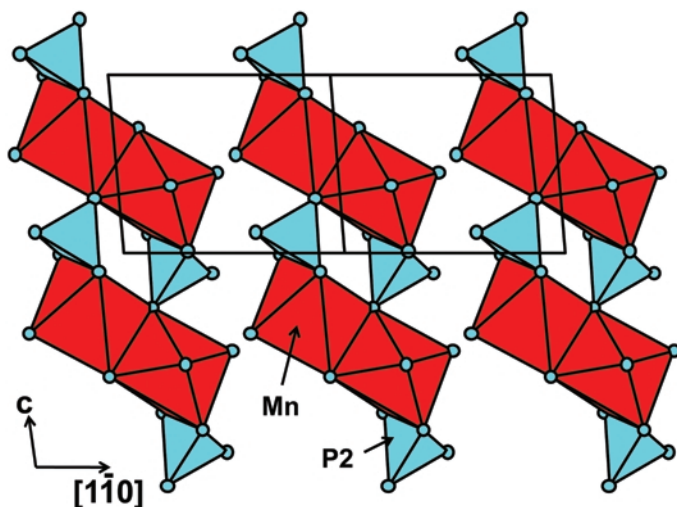

FIG. 5. Connectivity of $Al\Phi_6$ octahedra and $P(1)O_4$ tetrahedra in (100) slabs in nordgauite.

Fig. 6. Connectivity of $Mn\Phi_6$ octahedra and $P(2)O_4$ tetrahedra, viewed along $[\bar{1}\bar{1}0]$.

polyhedra gives rise to two types of six-sided channels, bounded by polyhedral edges for polyhedra centred on Al(2)–Al(3)–P(1)–Al(2)–Al(3)–P(1) and Al(1)–Al(3)–P(1)–Al(1)–Al(3)–P(1), respectively. The former channels are occupied by water molecules, Ow5, whereas the latter are blocked by Mn-centred octahedra on either side and are empty.

Figure 4 shows that the (100) slabs of corner-connected $Al\Phi_6$ and $P(1)O_4$ polyhedra are connected along [100] *via* corner-sharing with dimers of edge-shared $Mn\Phi_6$ octahedra and with $P(2)O_4$ tetrahedra. The articulation of the $Mn\Phi_6$ and $P(2)O_4$ polyhedra is seen more clearly in the $[\bar{1}\bar{1}0]$ projection in Fig. 6. Pairs of $Mn\Phi_6$ octahedra share edges, and each octahedron shares a second edge with $P(2)O_4$ tetrahedra to form chair-type tetramers. The tetramers inter-connect by corner-sharing between $P(2)O_4$ and $Mn\Phi_6$ to form ladder-like chains along [001]. The connection between the Mn-P(2) chains and the Al-P(1) slabs is *via* corner sharing of $P(2)O_4$ with $Al(1)\Phi_6$ and $Al(3)\Phi_6$ as shown in Fig. 4.

Polyhedral bond lengths, given in Table 5, show that the $Al\Phi_6$ and PO_4 polyhedra are all regular, with small ranges of bond lengths and with angular deviations from ideal geometry of only a few degrees. The $Mn\Phi_6$ polyhedron has a relatively narrow range of bond lengths, 2.16 to 2.27 Å, but the angles are strongly distorted from ideal octahedral geometry, with *cis* Φ–Mn–Φ angles in the range 64.9 to 124.3° and *trans* Φ–Mn–Φ angles varying from 144.0 to 169.8°. The strongly

distorted angles all involve O(8), which partici-pates in edge sharing between $P(2)O_4$ and $Mn\Phi_6$, as well as corner sharing with $Al(3)\Phi_6$. The $Mn\Phi_6$ octahedron has two unshared corners, Ow3 and

TABLE 5. Selected bond lengths (Å) for nordgauite.

Mn–O(7)	2.159(3)	Al(1)–F(2) (×2)	1.822(2)
–O(7)′	2.176(2)	–O(4) (×2)	1.872(2)
–Ow3	2.190(3)	–O(5) (×2)	1.892(2)
–Ow4	2.193(3)	<Al1–O>	1.862
–O(8)	2.255(2)	Al(2)–O(3) (×2)	1.832(2)
–O(6)	2.270(3)	–F(1) (×2)	1.834(2)
<Mn–O>	2.207	–Ow1 (×2)	1.966(3)
		<Al2–O>	1.877
Mn–P(2)	2.863(1)		
P(1)–O(1)	1.523(2)	Al(3)–F(1)	1.834(2)
–O(2)	1.530(3)	–F(2)	1.842(2)
–O(3)	1.535(2)	–O(1)	1.840(2)
–O(4)	1.536(2)	–O(2)	1.867(3)
<P1–O>	1.531	–O(8)	1.887(2)
		–Ow2	1.938(3)
		<Al3–O>	1.868
P(2)–O(5)	1.522(2)		
–O(6)	1.537(2)		
–O(7)	1.535(2)		
–O(8)	1.557(3)		
<P2–O>	1.538		

Ow4, and the Al(2)Φ_6 and Al(3)Φ_6 octahedra each have one unshared corner, Ow1 and Ow2. The Al−Ow distances are considerably longer than the other Al−Φ distances, whereas for the MnΦ_6 octahedron, the Mn−Ow distances are intermediate between other Mn−O distances (Table 5). Based on the different forms of water molecules, the structural formula for nordgauite is: Mn(H$_2$O)$_2$[Al$_2$(F,OH)$_2$(H$_2$O)$_2$(PO$_4$)$_2$]·H$_2$O.

Hydrogen bonding in nordgauite

Bond lengths and angles for the H bonds in nordgauite are given in Table 6. Both H atoms of each of the five water molecules participate in a H bond, either to Ow of other water molecules, or to phosphate oxygen atoms. With the exception of O(6), shared between two MnΦ_6 octahedra, the distances from H to acceptor atoms are all considerably shorter when the acceptor is a phosphate oxygen atom, relative to the acceptor being another water molecule. The angle that H makes with donor and acceptor atoms lies in a relatively narrow range, 156 to 176°. The H bonds involve O−O distances in the range 2.59 to 3.08 Å, which correspond to medium to weak bonds (Libowitzky, 1999).

Relation to other species

Two other rare minerals occurring in the Hagendorf Süd pegmatite have similar stoichiometry to nordgauite, although with more structural water and with OH dominant over F. Mangangordonite (Leavens and Rheingold,

1988; Leavens *et al*., 1991) and kastningite (Schlüter *et al*., 1999) are triclinic dimorphs with the same end-member formula, MnAl$_2$(PO$_4$)$_2$(OH)$_2$.8H$_2$O. Their structures, however, differ from that for nordgauite in being based on 7 Å chains of *trans* corner-connected AlΦ_6 octahedra.

The zigzag chains of alternating *cis* and *trans* corner-connected AlΦ_6 octahedra are also found in montgomeryite, Ca$_2$Mg$_{0.5}$(H$_2$O)$_6$ [Al$_2$(OH)$_2$(PO$_4$)$_3$] (Moore and Araki, 1974), and in vauxite, Fe(H$_2$O)$_2$[Al$_2$(OH)$_2$(PO$_4$)$_2$]·2H$_2$O (Baur and Rao, 1968), both of which have nearly orthogonal 10 Å (= *a*) and 6 Å axes (= *c*) in common with nordgauite. In montgomeryite, the *cis*-connected AlΦ_6 octahedra in the chains share opposite corners with PO$_4$ tetrahedra along the 6 Å *c* axis to form (010) slabs that are topologically identical to the (100) slabs in nordgauite. Similar slabs, parallel to (010), are formed in vauxite, but with the difference that the *trans*-connected AlΦ_6 octahedra share opposite edges with FeΦ_6 octahedra to form edge-shared octahedral chains along the 6 Å axis. These chains alternate with the chains of corner-shared AlΦ_6 and PO$_4$ polyhedra along [100]. In nordgauite and montgomeryite, these sites are occupied by Fe, and in vauxite they are empty. Nordgauite differs from montgomeryite and vauxite predominantly in the chemistry and structure of the interslab region. Its structure is unique in having chains of edge-shared tetramers, PO$_4$-MnΦ_6-MnΦ_6-PO$_4$, as connecting units between the slabs of corner-connected AlΦ_6 and PO$_4$ polyhedra.

TABLE 6. Hydrogen bonds (Å and °) in nordgauite.

D−H....A	D−H	H...A	D...A	<(DHA)
Ow1−H(11)...Ow4	0.86(6)	2.01(6)	2.864(4)	174(5)
Ow1−H(12)...Ow5	0.67(8)	2.19(8)	2.843(4)	166(8)
Ow2−H(21)...Ow5[i]	0.79(6)	2.18(6)	2.937(4)	164(6)
Ow2−H(22)...O(6)[ii]	0.78(5)	1.82(5)	2.595(3)	176(5)
Ow3−H(31)...Ow2[iii]	0.89(6)	2.21(6)	3.078(4)	166(5)
Ow3−H(32)...O(2)[iii]	0.91(7)	1.89(8)	2.800(3)	176(7)
Ow4−H(41)...O(4)[iv]	0.90(6)	1.86(6)	2.745(4)	166(5)
Ow4−H(42)...O(5)	0.77(7)	1.95(7)	2.689(4)	160(6)
Ow5−H(52)...O(6)[v]	0.889(3)	2.031(3)	2.877(4)	158.7(2)
Ow5−H(51)...O(3)[vi]	0.916(3)	1.880(2)	2.744(4)	156.4(2)

Symmetry codes: (i) *x*, *y*+1, *z*−1; (ii) −*x*+1, −*y*+1, −*z*; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*+2, −*y*+1, −*z*+1; (v) *x*, *y*, *z*+1; (vi) −*x*+2, −*y*+1, −*z*+2

Acknowledgements

References

Altomare, A., Cascarano, G., Giacovazzo, C. and Guagliardi, A. (1993) Completion and refinement of crystal structures with SIR92. *Journal of Applied Crystallography*, **26**, 343−350.

Baur, W.H. and Rao, B.R. (1968) The crystal structure and the chemical composition of vauxite. *American Mineralogist*, **53**, 1025−1028.

Farrugia, L.J. (1999) WinGX suite for small-molecule single-crystal crystallography. *Journal of Applied Crystallography*, **32**, 837−838.

Grey, I.E., Mumme, W.G., Neville, S.M., Wilson, N.C. and Birch, W.D. (2010) Jahnsite-whiteite solid solutions and associated minerals in the phosphate pegmatite at Hagendorf-Süd, Bavaria, Germany. *Mineralogical Magazine*, **74**, 969−978.

Keck, E. (1983) Phosphatmineralien und deren Auftreten in verschiedenen Teufen im Pegmatite von Hagendorf-Süd. *Aufschluss*, **34**, 307−316.

Laugier, J. and Bochu, B. (2004) Chekcell: Graphical powder indexing cell and space group assignment software, http://www.ccp14.ac.uk/tutorial/lmgp/.

Leavens, P.B. and Rheingold, A.L. (1988) Crystal structures of gordonite, $MgAl_2(PO_4)_2(OH)_2$ $(H_2O)_6 \cdot 2H_2O$, and its Mn analogue. *Neues Jahrbuch für Mineralogie Monatshefte*, **1988**, 265−270.

Leavens, P.B., White, J.S. Jr., Robinson, G.W. and Nelen, J.A. (1991) Mangangordonite, a new phosphate mineral from Kings Mountain, North Carolina and Newry, Maine, USA. *Neues Jahrbuch für Mineralogie Monatshefte*, **1991**, 169−176.

Libowitzky, E. (1999) Correlation of O−H stretching frequencies and O−H···O hydrogen bond lengths in minerals. *Monatshefte für Chemie*, **130**, 1047−1059.

Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *The Canadian Mineralogist*, **19**, 441−450.

Moore, P.B. and Araki, T. (1974) Montgomeryite, $Ca_4Mg(H_2O)_{12}[Al_4(OH)_4(PO_4)_6]$: Its crystal structure and relation to vauxite, $Fe_2^{2+}(H_2O)_4[Al_4(OH)_4(H_2O)_4(PO_4)_4] \cdot 4H_2O$. *American Mineralogist*, **59**, 843−850.

Mücke, A. (1981) The paragenesis of the phosphate minerals of the Hagendorf pegmatite − a general view. *Chemie der Erde*, **40**, 217−234.

Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112−122.

Schlüter, J., Klaska, K.-H., Friese, K. and Adiwidjaja, G. (1999) Kastningite, $(Mn,Fe,Mg)Al_2(PO_4)_2(OH)_2 \cdot 8H_2O$, a new phosphate mineral from Waidhaus, Bavaria, Germany. *Neues Jahrbuch für Mineralogie Monatshefte*, **1999**, 40−48.

Strunz, H., Tennyson, C. and Mücke, A. (1976) Mineralien von Hagendorf (Ostbayern). *Aufschluss*, **27**, 329−340.

Visser, J.W. (1969) A fully automated program for finding the unit cell from powder data. *Journal of Applied Crystallography*, **2**, 89.