

**A NOVEL POTASSIUM-RICH VARIANT OF TINSLEYITE,
 $[K_{1.5}(H_2O)_{0.5}][Al_2(OH)\{(OH)_{0.5}(H_2O)_{0.5}\}(PO_4)_2]$**

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ABSTRACT

Crystals of a potassium-rich variant of the mineral tinsleyite were obtained by hydrothermal synthesis in the system $K_2O-Al_2O_3-P_2O_5-H_2O$. The new phase is monoclinic, space group $P2_1/n$, a 9.4352(7), b 9.5254(10), c 9.4309(7) Å, β 101.421(7)°, $Z = 4$. Its crystal structure was solved from single-crystal data collected at 193 K and refined to $R = 0.0293$, including positions of all hydrogen atoms. The crystal structure is built of units of four AlO_6 octahedra sharing edges and vertices. The octahedron units are cross-linked by PO_4 tetrahedra to form a three-dimensional framework with channels along the main crystallographic [010], [001] and [100] directions, where the large K^+ ions and H_2O molecules are distributed. The system of $O-H \cdots O$ asymmetric hydrogen bonds between H_2O molecules, hydroxyl groups and framework oxygen atoms provides additional cross-linking in the structure. We show that a change in the alkalinity of the mineral-forming system correlates with the composition of the crystallizing phase and simultaneously influences the character of hydrogen bonding. The new K-rich variety of the tinsleyite is suggested as a possible mineral species. We evaluate the crystal chemistry of the leucophosphate group of minerals and the related synthetic compounds.

Keywords: tinsleyite, hydrothermal synthesis, X-ray diffraction, crystal structure, hydrogen bonds, leucophosphate group, micro-porous compounds, $AlPO_4-15$, structural relations.

INTRODUCTION

The leucophosphate group, with the formula $AB_2[PO_4]_2(OH) \cdot 2H_2O$ ($A = NH_4, K$; $B = Al, Fe$) includes, in addition to leucophosphate $KFe_2[PO_4]_2(OH) \cdot 2H_2O$ (Moore 1972), the minerals tinsleyite, $KAl_2[PO_4]_2(OH) \cdot 2H_2O$, and spheniscidite, $(NH_4, K)(Fe, Al)_2[PO_4]_2(OH) \cdot 2H_2O$. According to Haseman *et al.* (1951), they form a continuous series of low-temperature solid solutions. These minerals are known to occur in two different paragenetic associations: as late products of the hydrothermal alteration of triphylite in granitic pegmatites, or as biominerals. Spheniscidite forms by the interaction of phosphate solutions derived from guano with micaceous and chloritic minerals in

soil under a penguin rookery (Wilson & Bain 1986). Tinsleyite was first described from the Tip Top granitic pegmatite, in South Dakota. It is found in pods of highly altered triphylite in the intermediate zone of the pegmatite in association with leucophosphate, on which it commonly occurs as a morphologically continuous overgrowth (Dunn *et al.* 1984). The crystal structure of tinsleyite was solved using a synthetic sample and refined to $R = 0.071$ (Dick 1999). We present here a novel potassium-rich variant of the mineral tinsleyite, which was synthesized under hydrothermal conditions in the course of our experimental study of pegmatite-related phosphates (Yakubovich & Urusov 1996, Yakubovich 2008a, 2008b). Its crystal structure was investigated by single-crystal X-ray diffraction.

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BACKGROUND INFORMATION

The first crystal-structure investigation of minerals of the leucophosphate group was done by Moore (1972); he studied leucophosphate from the Tip Top pegmatite. The structure was refined by Dick & Zeiske (1997), who used a synthetic crystal. They found hydrogen atom positions in leucophosphate $\text{KFe}_2[\text{PO}_4]_2(\text{OH})\cdot 2\text{H}_2\text{O}$ by Rietveld refinement based on powder neutron-scattering data. Shi *et al.* (2008) published results of the crystal-structure investigation of a mixed Fe,V variant of leucophosphate $\text{K(FeV)[PO}_4]_2(\text{OH})\cdot 2\text{H}_2\text{O}$, synthesized hydrothermally at 453 K. Diffraction studies and magnetic characterization showed that Fe and V in equal proportions are disordered over the crystallographic sites. It has been determined that the inclusion of V^{3+} cations renders the compound ferromagnetic, whereas the original vanadium-free leucophosphate is antiferromagnetic.

The crystal structure of the NH_4Fe end member spheniscidite, $(\text{NH}_4)\text{Fe}_2[\text{PO}_4]_2(\text{OH})\cdot 2\text{H}_2\text{O}$, was refined by Yakubovich & Dadashov (1992) using crystals grown from a hydrogel at 423 K. The positions of all hydrogen atoms were found and refined in an isotropic approximation. In 1994, the same structure was investigated by Cavellec *et al.* (1997). These authors showed that spheniscidite is an antiferromagnet built upon weakly ferrimagnetic ferric octamers. Three-dimensional magnetic order of the octameric units occurs below 10 K owing to relatively weak antiferromagnetic or ferromagnetic couplings originating from superexchange interactions through the PO_4 tetrahedral units. One more structural study of this compound was performed by Choudhury & Natarajan (1999). They showed that the samples exhibit reversible dehydration and good absorption properties. Magnetic susceptibility measurements in the region of 15–300 K indicated strong three-dimensional antiferromagnetic behavior below $T_N = 22$ K. Zhou *et al.* (2010) documented the crystal structure of a new “pseudopolymorph” in the spheniscidite family, $\text{NH}_4\text{Fe}_2[\text{PO}_4]_2(\text{OH})\cdot 2.5\text{H}_2\text{O}$, exhibiting spontaneous magnetization below 25 K, with additional 0.5 H_2O molecules compared to the formula of the mineral group $\text{AB}_2[\text{PO}_4]_2(\text{OH})\cdot 2\text{H}_2\text{O}$.

There are not many papers devoted to the structural investigation of tinsleyite, the third representative in the leucophosphate group. Its crystal structure was established and refined by Dick (1999). He used a synthetic crystal of composition $\text{KAl}_2[\text{PO}_4]_2(\text{OH})\cdot 2\text{H}_2\text{O}$, obtained by the reaction of gibbsite with a potassium phosphate solution of $\text{pH} = 7$ at 423 K. Two steps in the thermal loss of water, at 341 and 471 K were observed.

HYDROTHERMAL SYNTHESIS
OF $\text{K}_{1.5}\text{Al}_2[\text{PO}_4]_2(\text{OH})_{1.5}\cdot \text{H}_2\text{O}$

The new phase, with the previously unreported composition $\text{K}_{1.5}\text{Al}_2[\text{PO}_4]_2(\text{OH})_{1.5}\cdot \text{H}_2\text{O}$, was formed by hydrothermal synthesis in the system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ in a PTFE-lined stainless steel autoclave at a temperature of 553 K and a pressure of 100 bars, over a period of 20 days. The new compound was synthesized from a mixture of 0.5 g KH_2PO_4 , 0.5 g $\text{Al}(\text{OH})_3$ and 15 mL of water. The pH of the solution after crystallization was close to 7. The reaction products were colorless crystals with a prismatic shape up to 0.5 mm long and a white powder. The crystals were washed with water, dried and subjected to an EDX electron-microprobe study and to single-crystal X-ray diffraction. The amounts of K, P, Al and O in the samples were estimated by semiquantitative X-ray spectral analysis (JEOL JSM-6480LV, EDSINCA-Wave 500). The very small size of the crystal prevented getting a good sample surface necessary for a quantitative analysis. Nevertheless, the results of our X-ray-diffraction study in combination with the semiquantitative data on its composition leave no doubts about the additional K position in the crystal structure.

X-RAY CRYSTALLOGRAPHY
AND CRYSTAL-STRUCTURE REFINEMENT

The determination of unit-cell parameters and data collection were performed on an IPDS-II area detector system using $\text{MoK}\alpha$ radiation (graphite monochromator). The intensities were corrected for Lorentz and polarization effects, and a numerical absorption correction using the measured size and shape of the crystal was applied. In Table 1, we report the crystallographic characteristics of the new variant of tinsleyite and the experimental conditions of data collection and refinement. All calculations were performed with the SHELX programs (Sheldrick 2008). Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography (Prince 2004). The crystal structure was solved by direct methods in space group $P2_1/m$ and refined using the F^2 data to residuals $wR_2 = 0.0736$ (for all 2250 reflections), $R = 0.0293$ [for 1833 reflections with $I > 2\sigma(I)$], $S = 1.003$, using anisotropic displacement parameters. A possible case of pseudomorph twinning due to metrics close to an orthorhombic B lattice could be ruled out by tentative twin-refinement.

The positions of five independent H atoms were obtained by difference-Fourier techniques. As the H

TABLE 1. K-RICH VARIANT OF TINSLEYITE: CRYSTAL DATA AND DETAILS OF THE COLLECTION OF X-RAY-DIFFRACTION DATA AND STRUCTURE REFINEMENT

Crystal data	
Formula	$K_{1.5}Al_2[PO_4]_2(OH)_{1.5} \cdot H_2O$
Absorption μ [mm ⁻¹]	1.539
Space group, Z	$P2_1/n, 4$
Lattice constants	
a, b, c (Å)	9.4352(7), 9.5254(10), 9.4309(7)
β (°)	101.421(7)
V (Å ³)	830.81(12)
D_{calc} (g cm ⁻³)	2.767
Crystal size (mm)	0.10 × 0.09 × 0.08
Data collection	
Diffractometer	IPDS-II area detector system (Stoe)
Radiation	MoK α , graphite monochromator
Temperature (K)	193(2)
Scanning mode: omega scans	$\omega = 0-200.4^\circ$, $\delta\omega = 1.2^\circ$, 6 min/rec
Measuring range	max $\theta = 29.99^\circ$
Reflections (total)	8523
R_{int}	0.068
R_σ	0.047
Refinement	
Reflections unique	2250
Reflections observed [$I > 2\sigma(I)$]	1833
Parameters	170
Absorption correction	numerical
T_{max}, T_{min}	0.919, 0.885
Residuals	
R (observed reflections)	0.0293
R, wR_2 (all reflections)	0.0392, 0.0736
Goodness of fit S	1.004
$\delta\rho$ (max)/(min) (e/Å ³)	0.494/-0.504

positions are crucial for the assignment of O, OH and H₂O, they were refined with free isotropic displacement parameters, common by groups. The O–H bond lengths were fixed by hard restraints to an empirical value of 0.800(1) Å in order to obtain comparable H-bond geometries, not affected by arbitrary scatter of refined O–H bond lengths.

According to these localized hydrogen atoms, O9 forms an OH group bridging three Al atoms. At O10, two atoms of H could be located, but one of them (H3) has to be half-occupied because of interference with its equivalent, generated by a symmetry center (1/2,0,1/2). Thus O10 forms with 50% probability an OH group or a H₂O molecule. In this way, a charge-balanced formula is achieved. The size of the displacement ellipsoid of O10, which is quite normal, shows that the difference in Al–OH and Al–OH₂ bond lengths is too small for a refinement of split positions. Atom O11 proved to be a half-occupied H₂O molecule coordinated to both independent K ions. Both hydrogen atoms could be located in a difference-Fourier map. Free refinement of the occupancy factor resulted in 0.530(9). This parameter was fixed in the final cycles of refinement to the idealized value of 1/2 according to a disorder model including the potassium atom K2, as discussed below. No experimental indication of superstructure reflections has been observed; thus we consider the vacancies at O11 sites and the assignment of OH or H₂O at O10 as statistically distributed in the structure.

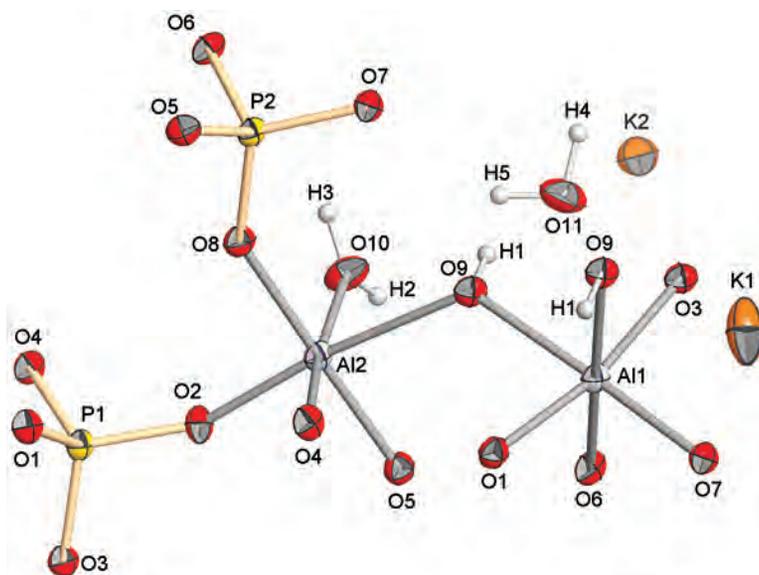


FIG. 1. The main structural elements of the K-rich variant of tinsleyite. Displacement ellipsoids are drawn at the 50% probability level.

Table 2 presents the final results of the atom positions and equivalent isotropic displacement parameters. The choices of the asymmetric unit and atom labels are taken to be as close as possible to that of tinsleyite (Dick 1999). Characteristic distances and angles are given in Table 3, geometric characteristics of hydrogen bonds in Table 4. A bond-valence calculation (Table 5) has been performed using the algorithm and parameters given by Brown & Altermatt (1985). Valence contributions of the H atoms were estimated from the O–O distances

following equations of Brown (1976) [the relationship between O–O distance and H–O (acceptor) bond valence is calculated from the O–H curve of Brown & Shannon (1973)]. Data from Table 5 clearly confirm the assignment of OH and H₂O ligands. A table of structure factors and a cif file are available from the Depository of Unpublished Data on the MAC website [document Tinsleyite variant CM50_559].

THE CRYSTAL STRUCTURE OF THE POTASSIUM-RICH VARIANT OF TINSLEYITE

The main structural elements of the title compound are shown in Figure 1. The Al³⁺ ions in two different positions are surrounded by O atoms, forming octahedra. The Al2 polyhedra have five close Al2–O distances that vary from 1.841(2) to 1.878(2) Å, and one longer distance, 2.219 (2) Å. The distortion of the Al1 octahedra is different: there are four distances lying in the interval 1.834(2)–1.905(2) Å and two longer distances, 1.984(2) and 2.011(2) Å (Table 3). The longest Al–O bonds for both Al atoms are to oxygen atoms of the hydroxyl groups O9–H1, which form a common edge of both octahedra. The pattern of distortion of the Al polyhedra is consistent with the bond-valence calculation (Table 5) and correlates with the distribution of hydrogen bonds (Tables 3, 4). The asymmetric unit of the structure includes two P sites in tetrahedral coordination. In the P1 tetrahedron, there is one short P1–O2 bond length of 1.511(1) Å and three similar bonds of about 1.54 Å. On the contrary, three close P2–O distances of about 1.52 Å and a longer one of 1.537(1) Å characterize the P2 polyhedron. Atoms K1 and K2 have K–O distances ranging from 2.759(2) to 3.295(2) Å for K1, and from 2.805(2) to 3.210(2) Å for the more regular centrosymmetric K2 polyhedron

TABLE 2. K-RICH VARIANT OF TINSLEYITE: ATOM COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}</i>
Al1	0.59812(6)	0.21233(6)	0.32170(7)	0.01431(14)
Al2	0.39343(6)	0.54272(5)	0.37218(7)	0.01362(14)
P1	0.79323(5)	0.01448(5)	0.15419(6)	0.01374(12)
P2	0.79228(5)	0.19176(4)	0.63950(6)	0.01323(12)
K1	0.51717(6)	0.15105(6)	0.85742(9)	0.04225(18)
K2	0.0	0.0	0.5	0.0626(4)
O1	0.94184(14)	0.08387(14)	0.20914(17)	0.0163(3)
O2	0.67123(15)	0.09581(14)	0.19799(18)	0.0182(3)
O3	0.76075(14)	0.00533(14)	-0.01157(16)	0.0166(3)
O4	0.70465(15)	0.36666(13)	0.28015(17)	0.0172(3)
O5	0.94750(15)	0.24627(14)	0.66752(17)	0.0173(3)
O6	0.78896(15)	0.04882(13)	0.71448(17)	0.0166(3)
O7	0.69021(15)	0.29077(13)	0.69719(17)	0.0166(3)
O8	0.74451(15)	0.16809(14)	0.47788(17)	0.0173(3)
O9	0.49908(15)	0.07691(16)	0.44906(17)	0.0161(3)
H1	0.448(3)	0.314(3)	0.482(4)	0.039(9)*
O10	0.48311(17)	0.07691(16)	0.3896(2)	0.0245(3)
H2	0.4046(19)	0.054(4)	0.347(4)	0.064(11)*
H3**	0.508(9)	0.033(9)	0.463(6)	0.064(11)*
O11**	0.2415(5)	0.1755(4)	0.5107(5)	0.0389(10)
H4**	0.235(7)	0.162(6)	0.593(2)	0.028(11)*
H5**	0.317(3)	0.139(6)	0.506(7)	0.028(11)

** Isotropic displacement parameters. ** Occupancy factor 0.5

TABLE 3. K-RICH VARIANT OF TINSLEYITE: INTERATOMIC DISTANCES (Å)

		Al1 octahedron		Al2 octahedron		P1 tetrahedron		P2 tetrahedron			
Al1 –	O1	1.905(2)	Al2 –	O2	1.841(2)	P1 –	O1	1.544(1)	P2 –	O5	1.527(1)
	O3	1.877(2)		O4	1.866(1)		O2	1.511(1)		O6	1.537(1)
	O6	1.834(2)		O5	1.863(2)		O3	1.535(2)		O7	1.523(1)
	O7	1.834(1)		O8	1.857(2)		O4	1.537(1)		O8	1.518(2)
	O9	1.984(2)		O9	2.219(2)						
	O9'	2.011(2)		O10	1.878(2)						
		K1 polyhedron				K2 polyhedron					
K1 –	O1	2.906(2)	K1 –	O5	3.272(2)	K2 –	O1	2.805(2) ×2			
	O2	2.932(2)		O6	3.273(2)		O4	3.210(2) ×2			
	O2'	3.295(2)		O7	2.774(2)		O5	2.925(2) ×2			
	O3	2.759(2)		O10	3.185(2)		O6	3.141(2) ×2			
	O4	2.899(2)		O11	2.844(4)		O8	2.867(1) ×2			
							O11	2.811(5)			

(Fig. 2). Half occupancy of the O11 position causes different coordination numbers of K^+ ions in the real structure. Thus, the coordination number of K1 may vary from nine to ten, whereas the coordination number of K2 is eleven with disordered O11 (see below).

The remarkable feature of this structure type is the occurrence of tetrameric units of four AlO_6 octahedra (Fig. 3). These centrosymmetric tetramers are built from two Al1 octahedra sharing an edge and two additional Al2 octahedra attached by corner sharing at each side of this common edge. The octahedral units are cross-linked by PO_4 tetrahedra to form a three-dimensional framework with channels along the main crystallographic [010], [001] and [100] directions, where the large K^+ ions and additional H_2O molecules are distributed (Figs. 3, 4). Compared with the crystal structure of tinsleyite, a second K position (K2) has been found in the present structure. It is on a $2a$ Wyckoff position at a symmetry center, at the center of the open channels parallel to the **b** axis of the unit cell (Fig. 2).

Compared to the mineral tinsleyite, the new variant differs not only in the quantity of K^+ cations in the framework channels, but also in the amount of H_2O and in the way it is distributed in the structure. The microporous character of the mixed anionic AlO_4-PO_4 framework seems to allow a limited number of interstitial atoms or molecules filling an extra framework space. Thus in the tinsleyite structure $|K(H_2O)| [Al_2(OH)(H_2O)(PO_4)_2]$ ($Z = 4$), there are one independent K^+ ion and one H_2O molecule per formula unit in the channels, whereas an additional special $2a$ Wyckoff position is occupied by the K^+ ion (K2) in the title compound. In the refinement, its displacement parameter became strongly anisotropic with elongation in the direction of the $H_2O-K_2-OH_2$ axis formed by H_2O molecule O11 and its symmetry-equivalent (Fig. 2). Refinement of the site-occupancy factor of O11 resulted in a value of 0.530(9). The K_2-O11 distance, 2.811 Å, is the shortest $K-O$ distances in the structure. Thus, we suppose that K2 is statistically displaced from the center of symmetry, away from O11. Atom O11 is half occupied, therefore, and this $K-OH_2$ unit is disordered over the symmetry center. We tried to refine the above disordered model, but the splitting of K was too small to achieve meaningful results. The structural formula of the new

phase is thus $|K_{1.5}(H_2O)_{0.5}| [Al_2(OH)\{(OH)_{0.5}(H_2O)_{0.5}\}(PO_4)_2]$ ($Z = 4$). It seems very important to note that the vacancies in the H_2O position depends on the K ion occurring in (or near) the special position $2a$. It suggests that the capacity of the minerals of the leucophosphate group to accommodate the K^+ (or NH_4^+ ions) is coupled with the H_2O content in the framework interstices, which is, thus, variable.

The localization and refinement of the hydrogen atoms have allowed the implementation of a rigorous interpretation of the peculiarities of the hydrogen bonds in this structure (Table 4: note that the $H \cdots Acceptor(A)$ distances and $O-H \cdots A$ angles refer to unified X-ray positions of H atoms). With $O \cdots O$ distances between 2.514(3) and 3.182(5) Å, they are classed as strong to weak. The system of $O-H \cdots O$ asymmetric hydrogen bonds between H_2O molecules, hydroxyl groups and framework oxygen atoms provides additional cross-linking in the structure (Fig. 5). Each tetrameric octahedral unit is connected by six neighboring tetramers in this way, thus strengthening the crystal structure. The hydroxyl group O9-H1 bridging three Al atoms plays the role of a donor providing hydrogen bonding to the H_2O molecule O11. This H_2O molecule participates in the coordination of both K polyhedra and also acts as a donor of two hydrogen bonds: one with an oxygen atom of the framework (O4), and another with an oxygen vertex of the Al1 octahedron O10 that forms with 50% probability an OH group or a H_2O molecule. Atom O10 is involved as a donor in the hydrogen bonding with a framework atom O6, and also plays both the roles of donor and of acceptor of the disordered $O10-H_3 \cdots O10'$ hydrogen bond. According to our results, hydroxyl groups substitute one half of H_2O molecules in the O10 vertices of Al2 octahedra to achieve a charge-balanced formula. The bond-valence calculation (Table 5) shows that the bond strengths on oxygen atoms O10 $[(OH)_{0.5}(H_2O)_{0.5}]$ are nearly equal to 2. It means that significant changes in the H atom content would infringe on the structure's stability. Consequently, we may assume that a change in the alkalinity of the mineral forming system correlates with the composition of the crystallizing phase and simultaneously influences the character of hydrogen bonding. The new K-rich variant of the tinsleyite has not been found in nature, but we suggest a possibility of its future discovery as a mineral species.

The crystal structure of one more synthetic compound $K_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)] \cdot xH_2O$ that belongs to the same group, has similar unit-cell parameters and the same space-group type, was published by Devi & Vidyasagar (1999). The authors did not locate the position of the hydrogen atoms, and achieved a charge-balanced formula for the compound by making the following assumptions: the two vertices forming the shared edge of AlO_6 octahedra are statistically populated by an O atom or by an OH group. One unshared

TABLE 4. K-RICH VARIANT OF TINSLEYITE: HYDROGEN-BOND GEOMETRY (Å, °)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$\angle D-H \cdots A$
O9-H1 \cdots O11	0.80	2.41(1)	3.182(5)	162(3)
O10-H2 \cdots O6	0.80	2.05(1)	2.827(2)	163(4)
O10-H3 \cdots O10'	0.80	1.73(2)	2.514(3)	165(9)
O11-H4 \cdots O4	0.80	1.864(7)	2.662(4)	175(6)
O11-H5 \cdots O10	0.80	2.17(3)	2.901(4)	152(6)

FIG. 2. Columns of K polyhedra in open channels parallel to the [010] direction.

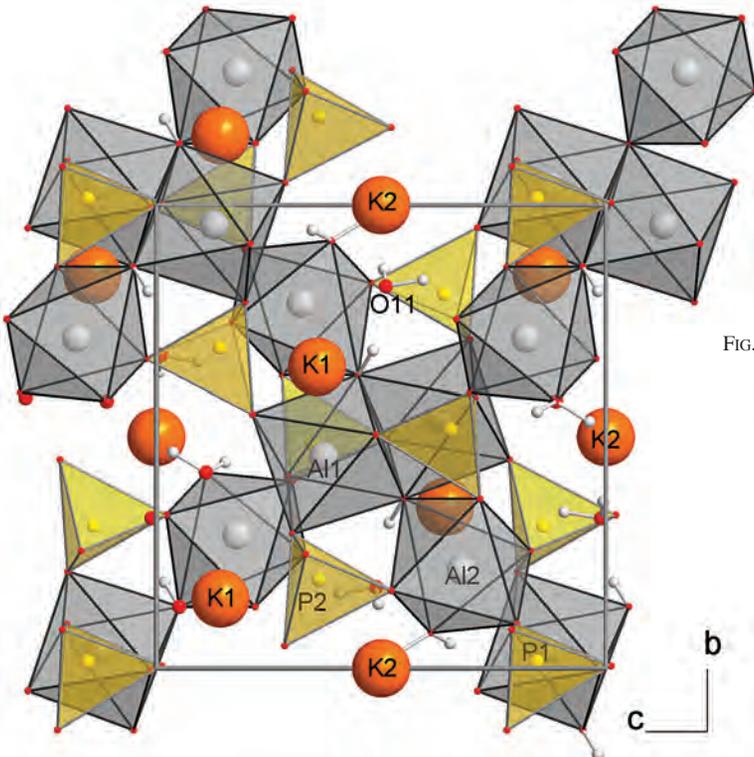
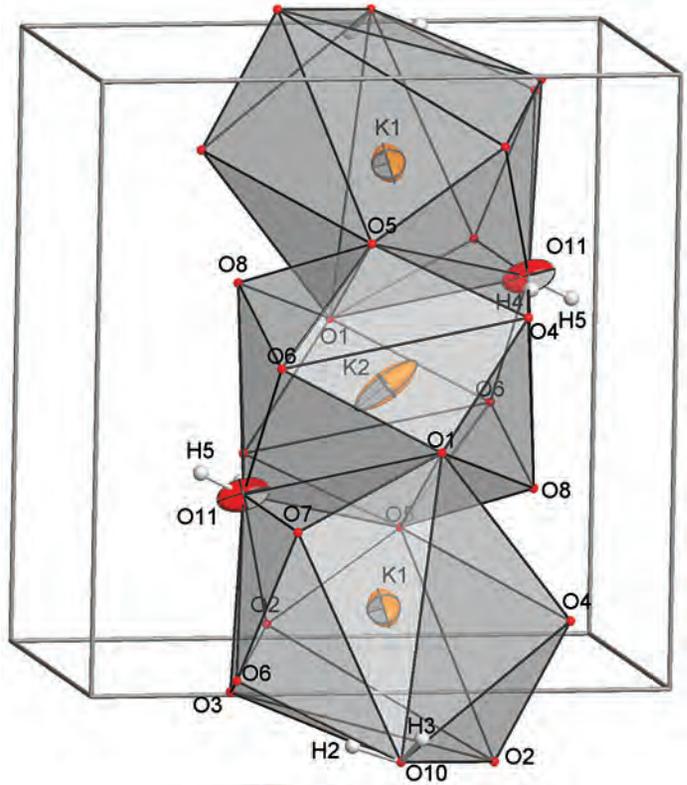


FIG. 3. The crystal structure of the K-rich variant of tinsleyite in projection along [100]. Grey: Al octahedra, yellow: P tetrahedra, large orange spheres: K^+ ions, small grey spheres: hydrogen atoms, red spheres: oxygen atoms.

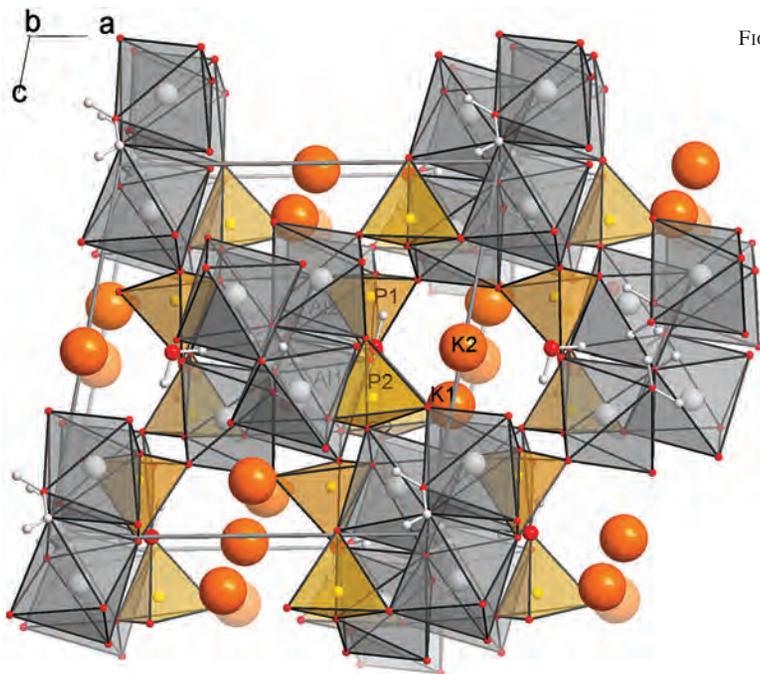
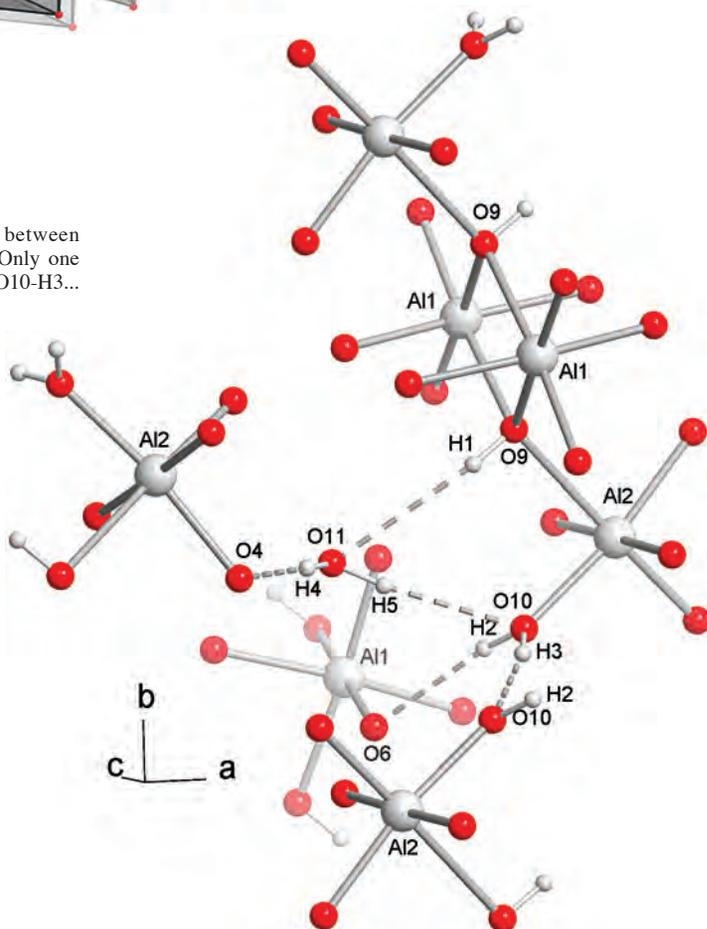


FIG. 4. The crystal structure of the K-rich variant of tinsleyite. View along the **b** axis. Color code as in Figure 3.

FIG. 5. Hydrogen bonds in the space between the tetrameric units of Al octahedra. Only one orientation of the disordered H-bond O10-H3...O10' is shown.



apical corner of the second symmetrically different AlO_6 octahedron is occupied by an H_2O molecule. They also considered the extra framework O atoms as "water of crystallization" ($x\text{H}_2\text{O}$ in the formula) in less than an ideal content of one. If the crystal-chemical formulae of both K-rich phases are written in the same way, they can be easily compared. Thus, the crystal structures of our tinsleyite variant, $|\text{K}_{1.5}(\text{H}_2\text{O})_{0.5}|[\text{Al}_2(\text{OH})\{(\text{OH})_{0.5}(\text{H}_2\text{O})_{0.5}\}(\text{PO}_4)_2]$ and that of Devi & Vidyasagar (1999), $|\text{K}_{1.5}(\text{H}_2\text{O})_x|[\text{Al}_2\{(\text{OH})_{0.5}\text{O}_{0.5}\}(\text{H}_2\text{O})(\text{PO}_4)_2]$ differ in the distribution of oxide, hydroxide ions and H_2O molecules on the vertices of the Al octahedra. We presume that these authors had the same potassium-rich variant of tinsleyite on hand, but could not write a correct formula for the crystal studied without finding and refining the positions of hydrogen atoms. Our introduction of the refined H atoms into the structure gives reasonable values of the bond-valence sums for all oxygen atoms under discussion (Table 5).

CRYSTAL CHEMISTRY OF RELATED COMPOUNDS

The title compound presents one more phase in the structural group of $\text{AlPO}_4\text{-15}$, with a three-dimensional anionic framework built from blocks of four Al octahedra and four P tetrahedra. The composition of $\text{AlPO}_4\text{-15}$ is $(\text{NH}_4)(\text{AlPO}_4)_2(\text{OH})(\text{H}_2\text{O})_2$, and the structure of this compound has been established simultaneously by Parise (1984) and Pluth *et al.* (1984). A charge-density analysis (Aubert *et al.* 2003) and first-principle calculations (Byrne *et al.* 2009) for this material were performed recently. Its crystal structure is built of $\text{AlO}_4(\text{OH})_2$ and $\text{AlO}_4(\text{OH})(\text{H}_2\text{O})$ octahedral building units. The four oxygen atoms around each Al are linked to P atoms, whereas the OH groups and

H_2O molecules either bridge between two Al atoms or are terminal. According to Chen *et al.* (1999), all the open-framework aluminophosphates crystallize in the presence of an organic template, and most of them involve the template in their structure. It means that templates play a critical role in the formation of these compounds. Although $\text{AlPO}_4\text{-15}$ forms from an aluminophosphate gel containing 1,4-diaminobutane, that component does not enter in the structure of $\text{AlPO}_4\text{-15}$, suggesting that during the crystallization, the 1,4-diaminobutane molecules disintegrate, releasing small NH_4^+ ions, which fill the micropores of the framework. Parnham *et al.* (2006) demonstrated that deep-eutectic solvents based on mixtures of urea and choline chloride can be used as reaction media and the source of the organic template in the synthesis of aluminophosphate materials, and of $\text{AlPO}_4\text{-15}$ in particular. In low-temperature synthesis experiments of the NH_4Fe end member of spheniscidite $|\text{NH}_4(\text{H}_2\text{O})|[\text{Fe}_2(\text{OH})\text{H}_2\text{O}(\text{PO}_4)_2]$ (Yakubovich & Dadashov 1992), we used a hydrogel containing an organic compound, urea or carbamide $\text{CO}(\text{NH}_2)_2$, which is found in the urine of mammalia, birds and some reptiles. In the presence of water, the urea gives off ammonia that enters the forming crystal structure. This is a usual way in which spheniscidite crystallizes in nature (Wilson & Bain 1986). However, two other minerals of the group, leucophosphite, $\text{KFe}_2[\text{PO}_4]_2(\text{OH}) \cdot 2\text{H}_2\text{O}$, and tinsleyite, $\text{KAl}_2[\text{PO}_4]_2(\text{OH}) \cdot 2\text{H}_2\text{O}$, do form without templates in hydrothermal conditions. Hydrothermal genesis of these minerals in pegmatites has been confirmed in several experimental works, including the present study.

The structural group of compounds under investigation includes a large spectrum of synthetic phases with different compositions, *e.g.*, containing Ga, Rb, Mo or

TABLE 5. K-RICH VARIANT OF TINSLEYITE: BOND-VALENCE DATA

atom	P1	P2	Al1	Al2	K1	K2	H1	H2	H3	H4	H5	Σ
O1	1.218		0.503		0.123	0.162 ₁₂						2.01
O2	1.332			0.598	0.115	0.043						2.09
O3	1.245		0.544		0.184							1.97
O4	1.241			0.558	0.126					0.24		2.16
O5		1.279		0.564	0.046	0.118 ₁₂						2.01
O6		1.241	0.611		0.046	0.065 ₁₂		0.16				2.12
O7		1.289	0.608		0.176							2.07
O8		1.303		0.573		0.137 ₁₂						2.01
O9			0.407	0.215			0.95					1.95
			0.378									
O10				0.542	0.058			0.84	0.30		0.13	2.07
									0.20			
O11					0.126	0.159	0.05			0.76	0.87	1.97
Σ	5.04	5.11	3.05	3.05	1.04	1.12	1	1	1	1	1	

The bond-valence sums are expressed in valence units. The symbol ₁₂ indicates a multiplication of the corresponding contributions in the columns due to symmetry.

TABLE 6. STRUCTURAL GROUP OF LEUCOPHOSPHITE (SPACE GROUP $P2_1/n$, $Z = 4$)

Mineral or synthetic phase	a (Å)	b (Å) β (°)	c (Å)	V (Å ³)	ρ _{calc} (g/cm ³)	R _{hkl}	Reference
Leucophosphite [K(H ₂ O)] [Fe ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.782(9)	9.658(9) 102.24(12)	9.751(9)	900	2.9	0.074	Moore (1972)
Tinsleyite [K(H ₂ O)] [Al ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.602(8)	9.532(6) 102.6(1)	9.543(11)	850	2.62	-	Dunn <i>et al.</i> (1984)
Spheniscidite [(NH ₄ , K)(H ₂ O)] [(Fe, Al) ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.75(1)	9.63(2) 102.6(1)	9.70(1)	889	3.08	-	Wilson & Bain (1986)
Leucophosphite, synthetic [K(H ₂ O)] [Fe ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.756(3)	9.664(3) 102.43(2)	9.769(4)	899.5	2.91	0.063	Dick & Zeiske (1997)
Fe, V analog of leucophosphite, synthetic [K(H ₂ O)] [FeV(OH)(H ₂ O)(PO ₄) ₂], sp. gr. $P2_1/c$	9.721(2)	9.650(2) 128.57(2)	12.198(4)	894.6	2.89	0.035	Shi <i>et al.</i> (2008)
Tinsleyite, synthetic [K(H ₂ O)] [Al ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.499(2)	9.503(2) 103.26(3)	9.535(2)	837.8	2.66	0.069	Dick (1999)
K-rich variant of tinsleyite, synthetic K ₁₋₅ Al ₂ [PO ₄] ₂ (OH) ₁₋₅ •H ₂ O*	9.4352(7)	9.5254(10) 101.421(7)	9.4309(7)	830.81	2.77	0.029	this work
NH ₄ , Fe analogue of spheniscidite, synthetic [NH ₄ (H ₂ O)] [Fe ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.819(2)	9.737(3) 102.82(3)	9.874(4)	920.5	2.69	0.034	Yakubovich & Dadashov (1992)
NH ₄ , Al analogue of spheniscidite synthetic (AlPO ₄ -15) [NH ₄ (H ₂ O)] [Al ₂ (OH)(H ₂ O)(PO ₄) ₂]** [(H ₃ O)(H ₂ O)] [Ga ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.562(2)	9.558(2) 103.616(5)	9.613(2)	853.9	2.45	0.024	Parnham <i>et al.</i> (2006)
[NH ₄ (H ₂ O)] [Ga ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.77(1)	9.64(1) 102.7(2)	9.68(1)	889	3	0.074	Mooney-Slater (1966)
[NH ₄ (H ₂ O)] [Ga ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.689(1)	9.703(1) 102.78(2)	9.788(1)	897.4	2.96	0.025	Loiseau & Ferey (1994)
[Rb(H ₂ O)] [Ga ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.6384(5)	9.6723(5) 102.465(1)	9.7512(5)	887.63	3.50	0.024	Beitone <i>et al.</i> (2002)
[NH ₄ (H ₂ O)] [V ₂ (OH)(H ₂ O)(PO ₄) ₂]	9.803(2)	9.688(2) 102.91(3)	9.858(2)	912.56	2.64	0.043	Soghomonian <i>et al.</i> (1998)
[NH ₄ (H ₂ O)] [Mo ₂ O ₂ (PO ₄) ₂]	9.780(10)	9.661(5) 102.17(8)	9.884(8)	914.8	3.27	0.029	King <i>et al.</i> (1991)

* Values of unit-cell parameters and volume correspond to a temperature of 193 K. ** Values of unit-cell parameters and volume correspond to a temperature of 150 K.

V (Table 6). All of them may formally be treated as derivatives based on the GaPO₄•2H₂O structure, where positions of hydroxonium ions in the framework channels correspond to the K, NH₄, or Rb positions in other phases, as one can see from the explicit formula [(H₃O)(H₂O)] [Ga₂(OH)H₂O(PO₄)₂].

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