

The c axis of the present structure is three times longer than that of the simple tetragonal unit cell of rutile. The intensities of hkl reflections with $l = 3n$ are strong, while those with $h = 3n \pm 1$ are extremely weak indicating that the structure is a superstructure of the rutile structure. A superstructure having three unit cells of the rutile structure is referred to as the trirutile structure. The trirutile cell is indicated by the broken lines in Fig. 1. However, the normal trirutile structure requires an ordered arrangement of metal atoms. The scheme of cation distribution in the present structure is intermediate between disordered rutile-type and ordered trirutile-type. The occupancies of the Fe and Nb atoms in the $M(1)$ and $M(2)$ sites are nearly equal. The $M(3)$ site is mainly occupied by the Nb atom, while the Fe occupancies in the $M(1)$ and $M(2)$ sites are twice as large as that of the $M(3)$ site. This reflects on the metal-metal distances along the c axis (see Table 2): the $M(1)$ – $M(2)$ distance is shorter than $M(2)$ – $M(3)$ or $M(3)$ – $M(1)$. These observations indicate that a slight ordering of the metal atoms exists in the structure. In addition, the present crystal gave rather diffuse diffraction spots. Since the crystal was synthesized by the floating-zone method under conditions of high temperature >1823 K, rapid growth rate 5 mm h^{-1} , and rapid cooling, these synthetic conditions may disturb the ordering of the metal atoms. As a result, this substance has a structure intermediate between rutile and trirutile types.

Valence bond sums $\sum c_i$ were calculated using the parameters of Brown & Wu (1976) and are listed in Table 1. The valence sums for O(1), O(2), and O(3) are 1.99, 1.97, and 1.92, respectively, and are slightly smaller than 2.00 of the ideal valence for O^{2-} ions. The Mössbauer study showed a small existence of the

trivalent Fe atom in the present compound (Tokizaki & Sugitani, 1984). It is considered that vacancies occur in the cation site to balance the charge, though no estimation of vacancies was taken into account in the present study.

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Structure of a New Form of Rubidium Dihydrogenphosphate, RbH_2PO_4

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Abstract. $M_r = 182.4$, monoclinic, $P2_1/a$, $a = 9.606$ (5), $b = 6.236$ (5), $c = 7.738$ (5) Å, $\beta = 109.07$ (5)°, $V = 438.1$ Å³, $Z = 4$, $D_x = 2.765$ Mg m⁻³, $\lambda(\text{Ag } K\alpha) = 0.5608$ Å, $\mu = 6.598$ mm⁻¹, $F(000) = 344$, $T = 293$ K, final $R = 0.032$ for 695 independent reflexions. This salt is closely related to

the monoclinic form of CsH_2PO_4 and its atomic arrangement may be considered as a superstructure of this salt, identical to the intermediate form of RbD_2PO_4 . The PO_4 tetrahedra are interconnected by H bridges [O...O distances 2.518 (11) and 2.518 (5) Å, and O–H...O angles 156 (10) and 171 (11)°].

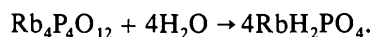
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Introduction. The tetragonal form of RbH_2PO_4 has until now been the only one stable at room temperature. According to Blinc, O'Reilly, Peterson & Williams (1969) a monoclinic form occurs at 359 K and seems to be isomorphous with monoclinic RbD_2PO_4 . This intermediate form of RbD_2PO_4 stable between 317 and 377 K has recently been investigated (Hagiwara, Itoh, Nakamura, Komukae & Makita, 1984).

In the present work we describe a new form of RbH_2PO_4 closely related to the monoclinic RbD_2PO_4 . The accurate location of the H atoms explains some ambiguities observed in the description of the deuterium-bond scheme of RbD_2PO_4 by Hagiwara *et al.* (1984).

Experimental. Single crystals of monoclinic RbH_2PO_4 have been prepared by a process using the hydrolytic cleavage of rubidium tetrametaphosphate:



An aqueous solution of rubidium tetrametaphosphate is heated at 333 K until it is converted into a gel. This gel is then kept at room temperature in a water-saturated atmosphere. After several days, the first crystals of monoclinic RbH_2PO_4 appear. Their general aspect is quite similar to calcite rhombohedra. The yield of such a process is very poor.

D_m not measured. Prismatic crystal $0.16 \times 0.16 \times 0.16$ mm. Philips PW 1100 diffractometer. Systematic absences: $h0l$, $h = 2n$; $0k0$, $k = 2n$. 17 reflections ($12 < \theta < 14^\circ$) for refining the unit-cell dimensions. ω scan. 1409 reflexions measured ($3 < \theta < 30^\circ$), $\pm h, k, l$, $h_{\text{max}} = 16$, $k_{\text{max}} = 11$, $l_{\text{max}} = 13$. Scan width 1.20° , scan speed $0.02^\circ \text{ s}^{-1}$, total background measuring time 20 s. Lorentz-polarization correction, no absorption correction. Classical methods for structure determination: Patterson and successive Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F) for non-hydrogen atoms. Unit weights. Total number of unique reflexions 1331. Final refinement with 695 reflexions corresponding to $F_o > 3\sigma_F$. Final $R = 0.032$ ($wR = 0.037$). For the complete set of unique reflexions (1331) $R = 0.056$. $S = 1.301$. Max. $\Delta/\sigma = 0.17$. * Max. peak height in final difference Fourier synthesis $0.65 \text{ e } \text{\AA}^{-3}$. No extinction correction. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius (1977) *SDP* used for all calculations. H atoms from difference Fourier map, refined isotropically.

Discussion. Final atomic coordinates, B_{eq} values for non-hydrogen atoms and B_{iso} for H atoms are reported

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42026 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in Table 1 while the main interatomic distances and bond angles are given in Table 2.

Table 1. Final atomic parameters for RbH_2PO_4 , with e.s.d.'s in parentheses

For non-H atoms $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} or B_{iso} (\AA^2)
Rb	0.28464 (6)	0.2383 (1)	0.26559 (8)	2.44 (1)
P	0.4823 (1)	0.2458 (4)	0.7577 (2)	1.66 (2)
O(1)	0.4452 (4)	0.7551 (10)	0.3979 (5)	2.31 (8)
O(2)	0.9307 (5)	0.5839 (8)	0.0944 (7)	2.54 (9)
O(3)	0.6751 (4)	0.8198 (9)	0.3312 (7)	2.97 (11)
O(4)	0.0010 (6)	0.9747 (9)	0.1618 (7)	3.20 (10)
H(1)	0.501 (9)	0.55 (1)	0.07 (1)	4. (2)
H(2)	0.346 (9)	0.74 (2)	0.37 (1)	5. (2)

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in the PO_4 tetrahedron and the RbO_8 polyhedron

The PO_4 tetrahedron				
P	O(1)	O(2)	O(3)	O(4)
O(1)	1.575 (4)	2.515 (6)	2.460 (5)	2.513 (7)
O(2)	107.2 (3)	1.550 (5)	2.533 (6)	2.537 (7)
O(3)	106.3 (2)	112.4 (3)	1.499 (4)	2.540 (7)
O(4)	107.3 (3)	110.1 (3)	113.1 (3)	1.545 (6)

The RbO_8 polyhedron			
Rb—O(1)	3.387 (5)	Rb—O(3)	3.038 (5)
Rb—O(1)	3.017 (3)	Rb—O(3)	3.051 (5)
Rb—O(2)	3.083 (5)	Rb—O(4)	3.056 (6)
Rb—O(2)	2.996 (5)	Rb—O(4)	3.043 (6)

Table 3. Main interatomic distances (\AA) and bond angles ($^\circ$) in the hydrogen-bond scheme

	O—H	H...O	O—O	O—H...O	P—O—H
O(4)—H(1)...O(4)	0.71 (8)	1.85 (7)	2.518 (11)	156 (10)	101 (2)
O(1)—H(2)...O(3)	0.91 (8)	1.61 (8)	2.518 (5)	171 (11)	122 (5)

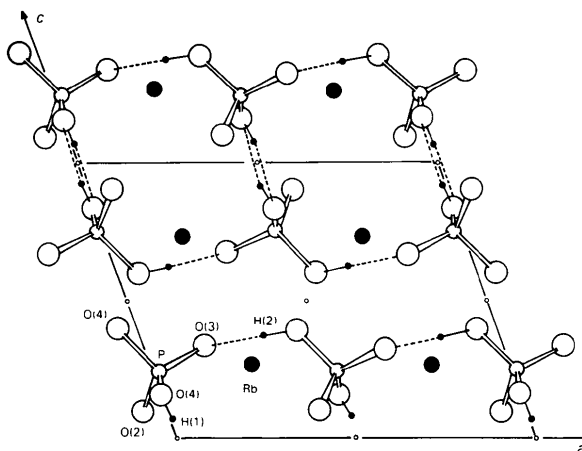


Fig. 1. Projection of the atomic arrangement of RbH_2PO_4 along *b*.

Table 3 presents the main features of the hydrogen-bonding scheme. Fig. 1 is a projection of the atomic arrangement along **b**. This structure, a very simple network of PO₄ tetrahedra interconnected by hydrogen bridges, is in fact a superstructure of the CsH₂PO₄ arrangement (Matsunaga, Itoh & Nakamura, 1980), by doubling the *a* axis. If only the non-hydrogen atoms are considered, the title compound is exactly similar to the intermediate form of RbD₂PO₄ described by Hagiwara *et al.* (1984), but the distribution found by these authors for two of the D atoms seems questionable. The first D atom connecting the PO₄ tetrahedra along **a** is found to be very close to our values for H(2):

0.346	0.74	0.37	(present work)
0.34	0.749	0.372	(Hagiwara <i>et al.</i> , 1984)

and has a low temperature-factor value (0.6 Å²). The last two D atoms are located by these authors on two

inversion centers at $\frac{1}{2}, \frac{1}{2}, 0$ and $\frac{1}{2}, 0, 0$ and are affected by abnormally large thermal factors (25· and 32· Å²). In the title compound, the two H atoms are located in one general position of the space group *P2₁/a* (0.501, 0.55, 0.07) with a normal temperature factor, suggesting a revision of the D location in RbD₂PO₄.

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Structure du Tétrarsulfure de Dierbium(III) et d'Europium(II), EuEr₂S₄

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Abstract. *M_r* = 614.74, orthorhombic, *Pbnm*, *a* = 14.151 (3), *b* = 11.861 (3), *c* = 3.939 (1) Å, *V* = 661.14 (21) Å³, *Z* = 4, *D_m*(293 K) = 6.1 (1), *D_x* = 6.18 (2) Mg m⁻³, *Mo Kα*, *λ* = 0.71069 Å, *μ* = 36.6 mm⁻¹, *F*(000) = 1052, *T* = 293 K, *R* = 0.046 for 1087 independent reflections. The compound has the CaFe₂O₄ structure. The Eu atoms have eightfold prismatic coordination [trigonal prism (Eu–S 3.05 to 3.07 Å) with Eu contacts to two other S atoms in the equatorial plane of the prism (Eu–S 3.23 and 3.28 Å)] and the Er atoms have sixfold octahedral coordination (Er–S 2.65 to 2.73 Å).

Introduction. Les composés du type *ML₂Se₄* (*M* = Eu, Sr, Ba; *L* = lanthanoïde) sont décrits par Souleau & Guittard (1968) et les structures de sulfures ternaires de scandium du type ferrite de calcium sont étudiées par IJdo (1982) à partir de diagrammes de poudre, mais faute de monocristaux convenables, aucune étude aux rayons X n'a pu être effectuée. Des monocristaux de EuEr₂S₄ ont pu être préparés par action de H₂S sur une préparation obtenue par mélange de Eu₂O₃ + 2Er₂O₃ à 1473 K. Les cristaux se sont formés au cours du chauffage de ce composé sous argon vers 2073 K.

Partie expérimentale. Monocristal de couleur grise, parallélépipède de dimensions 92 × 118 × 108 μm; masse volumique mesurée par pycnométrie à 293 K; 15 réflexions utilisées pour affiner les paramètres de la maille, *θ* variant de 11,53 à 23,96°; 1445 réflexions indépendantes; (sin*θ*)/*λ* ≤ 0,70 Å⁻¹; *h* 0 à 21, *k* 0 à 17, *l* 0 à 5; diffractomètre automatique à quatre cercles Syntex; balayage ω–2*θ*, angles –0,7° + 2*θ*₁ à 0,7° + 2*θ*₂, *θ*₁ et *θ*₂ étant les angles de diffraction correspondant respectivement aux longueurs d'onde *Kα*₁ et *Kα*₂ du molybdène; 1087 réflexions telles que *I* > 3σ(*I*); l'écart-type σ(*I*) sur la mesure de l'intensité *I* est déduit de l'écart-type σ_{*c*} sur le taux de comptage et de l'écart-type relatif σ_{*i*} sur la variation des réflexions de référence par la relation: σ(*I*) = (σ_{*c*}² + σ_{*i*}²*I*²)^{1/2}; écart-type relatif sur l'instabilité égal à 0,025 déterminé avec l'intensité des réflexions de référence 630 et 400 vérifiées toutes les 50 mesures; *I* corrigées des facteurs de Lorentz–polarisation et mises à l'échelle absolue par la méthode statistique de Wilson; correction d'absorption réalisée au moyen du programme de J. A. Ibers d'après la méthode analytique décrite par de Meulenaer & Tompa (1965), max. et min. du facteur de transmission 0,18 et 0,085; résolution de la structure