distances O—acceptor and the angles acceptor—O—acceptor not being favorable for the formation of strong hydrogen bonds.

In a previous paper (Rigotti *et al.*, 1981) we reported the crystalline structure for the complete series of rare-earth decavanadates and wrongly described erbium decavanadate (Group III) as a 24-hydrate. It now seems reasonable to assume that structural differences between Groups III and IV are mainly due to the occupancy of a symmetry center by an interstitial water molecule, rather than by changes in the Ln^{3+} ionic radii, or any other inherent feature of the Ln^{3+} ions.

The authors thank Professor E. J. Baran for helpful discussions and CONICET, CICPBA and SUBCYT (R. Argentina) for financial support.

References

AHMED, F. R. & PIPPY, M. E. (1966). *NRC* Crystallographic Programs for the IBM 360 system. *NRC*22, revised June 1970. Division of Pure Physics, National Research Council of Canada, Ottawa.

BAUR, W. H. (1970). *Trans. Am. Crystallogr. Assoc.* **6**, 129–155.

BRINK, G. (1971). *Spectrochim. Acta Part A*, **28**, 1151–1155.

BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

DEBAERDEMAEKER, T., ARRIETA, J. M. & AMIGO, J. M. (1982). *Acta Cryst.* B**38**, 2465–2468.

DURIF, P. A., AVERBUCH-POUCHOT, M. T. & GUITEL, J. C. (1980). *Acta Cryst.* B**36**, 680–682.

EVANS, H. T. (1966). *Inorg. Chem.* **5**, 967–977.

GUGGENBERGER, L. J. & SLEIGHT, A. W. (1969). *Inorg. Chem.* **8**, 2041–2046.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

ITO, T. (1981). *Acta Cryst.* A**37**, 621–624.

JENSEN, S. J. (1968). *Acta Chem. Scand.* **22**, 647–652.

KNOP, O., WESTERHAUS, W. J. & FALK, M. (1980). *Can. J. Chem.* **58**, 867–874.

PIERCE-BUTLER, M. A. (1982). *Acta Cryst.* B**38**, 3097–3100.

RIGOTTI, G., PUNTE, G., RIVERO, B. E., ESCOBAR, M. E. & BARAN, E. J. (1981). *J. Inorg. Nucl. Chem.* **43**, 2811–2814.

SAF'YANOV, YU. N., KUZ'MIN, E. A. & BELOV, N. V. (1979). *Kristallografiya*, **24**, 767–771.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SWALLOW, A. G., AHMED, F. R. & BARNES, W. H. (1966). *Acta Cryst.* **21**, 397–405.

WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., p. 64. Oxford: Clarendon Press.

Acta Cryst. (1984). C**40**, 718–720

Structure of Monoclinic Rubidium Dideuteriumphosphate, RbD_2PO_4, in the Intermediate Phase

BY T. HAGIWARA, K. ITOH AND E. NAKAMURA

Faculty of Science, Hiroshima University, Hiroshima 730, *Japan*

AND M. KOMUKAE AND Y. MAKITA

Department of Applied Physics, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, *Japan*

(*Received* 17 *November* 1983; *accepted* 15 *December* 1983)

Abstract. $M_r = 184{\cdot}44$, monoclinic, $P2_1/c$, $a = 7{\cdot}683\,(1)$, $b = 6{\cdot}170\,(1)$, $c = 9{\cdot}560\,(1)$ Å, $\beta = 109{\cdot}10\,(1)°$, $V = 428{\cdot}2$ Å^3, $Z = 4$, $D_x = 2{\cdot}861$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 202{\cdot}16$ cm^{-1}, $F(000) = 344$, $T = 332$ K, $R = 0{\cdot}040$ for 500 unique reflections. The intermediate phase has a superstructure of the basic CsH_2PO_4 type. The shape of the PO_4 tetrahedron is rather regular. Two kinds of H atoms display extremely large thermal amplitudes of about 0·5 Å. PO_4 tetrahedra are connected by these H atoms to form a zigzag chain running along **b**.

Introduction. Monoclinic RbD_2PO_4 undergoes successive phase transitions at 377 and 317 K (Sumita, Osaka & Makita, 1981). It is known that the low-temperature phase is ferrielectric and the intermediate and the high-temperature phases are paraelectric (Osaka, Sumita & Makita, 1983). The crystal structure of the low-temperature phase was determined at room temperature by Makita, Sumita, Osaka & Suzuki (1981). However, the structures of the other phases have not yet been determined. It is necessary to investigate the structures of these higher-temperature phases in order to clarify the mechanism of the successive phase transitions from the structural point of view. We now report the crystal structure of the intermediate phase, as part of a continuing study of the mechanism of the successive phase transitions.

0108-2701/84/050718-03\$01.50

Table 1. *Positional parameters and thermal parameters* [$U_{eq}(\times 10^2)$ *for* Rb, P *and* O; $U_{iso}(\times 10^2)$ *for* D] *with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3.$$

	x	y	z	U_{eq}, U_{iso} (Å^2)
Rb	0·26385 (7)	0·26008 (8)	0·28046 (7)	3·61 (3)
P	0·2440 (2)	0·7464 (2)	0·5175 (2)	2·37 (5)
O(1)	0·4012 (5)	0·7455 (6)	0·4480 (5)	3·4 (2)
O(2)	0·3301 (6)	0·6900 (8)	0·6747 (5)	4·7 (1)
O(3)	0·1006 (5)	0·5802 (6)	0·4341 (5)	3·8 (1)
O(4)	0·1595 (6)	0·9705 (6)	0·4945 (6)	4·4 (1)
D(1)	0·372 (9)	0·749 (8)	0·34 (1)	0·6 (15)
D(2)	0	0·5	0·5	25 (18)
D(3)	0	0	0·5	32 (25)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Symmetry code: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $-x, 1-y, 1-z$; (iii) $-x, 2-y, 1-z$.

Rb–O(1)	3·397 (4)	P–O(1)	1·558 (5)
Rb–O(2^{i})	3·624 (5)	P–O(2)	1·472 (4)
Rb–O(3)	2·972 (5)	P–O(3)	1·525 (4)
Rb–O(4)	5·011 (4)	P–O(4)	1·513 (4)
Rb–D(1)	3·13 (5)		
O(1)···O(2^{i})	2·519 (6)	O(3)···O(3^{ii})	2·497 (7)
O(1)–D(1)	0·97 (9)	O(4)···O(4^{iii})	2·514 (7)
D(1)–O(2^{i})	1·57 (9)		
O(1)–P–O(2)	106·4 (2)	O(2)–P–O(3)	112·4 (3)
O(1)–P–O(3)	107·6 (2)	O(2)–P–O(4)	113·1 (3)
O(1)–P–O(4)	107·3 (3)	O(3)–P–O(4)	109·7 (2)
O(1)–D(1)–O(2^{i})	167 (5)		

Experimental. Colourless single crystals grown by evaporation of a heavy-water solution after several recrystallizations. D_m not determined. Spherical specimen, diameter 0·41 mm. Rigaku AFC-5 diffractometer. Systematic absences* $h0l$ for l odd, $0k0$ for k odd. 24 reflections in the range $48° < 2\theta < 63°$ for measuring lattice parameters. ω–2θ scan mode. 703 reflections measured with $2\theta < 120°$, 13 unobserved $[|F_o| < 2\sigma(|F_o|)]$. Lorentz–polarization correction, absorption correction, $\mu r = 4\cdot14$. Positions of Rb and P atoms from Patterson synthesis, O and D atoms from difference Fourier synthesis. Anisotropic full-matrix least-squares refinement, but isotropic thermal parameters for D atoms; $\sum w(|F_o| - |F_c|)^2$ minimized. Final $R = 0\cdot040$, $wR = 0\cdot051$; $w = 1\cdot5$ for $0\cdot5 < |F_o| \leq 3\cdot9$; $w = 1\cdot0$ for $3\cdot9 < |F_o| < 35\cdot7$. $(\Delta/\sigma)_{max}$ in final refinement cycle 0·21. Final difference Fourier map showed no peaks greater than 0·3 e Å^{-3}. No correction for secondary extinction. Scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). HITAC M-200 H computer. *UNICS* program system (Sakurai, 1967).

Discussion. Atomic parameters are given in Table 1 and interatomic distances and angles in Table 2.* The structure is depicted in Fig. 1. The PO_4 tetrahedra are connected to each other through three kinds of hydrogen bonds. One of them, associated with D(1), runs along **c** and the others, associated with D(2) and D(3), form a zigzag chain running along **b**. Assuming that $c/2$ translational symmetry in place of the real c glide leaves the lattice invariant, we obtain the CsH_2PO_4-type structure. Then RbD_2PO_4 in the intermediate phase is approximately isostructural to CsH_2PO_4 but the cell parameter c differs by a factor of two. P–O distances listed in Table 2 lie in the range 1·472 (4) to 1·558 (5) Å and O–P–O angles range from 106·4 (2) to 113·1 (3)°, indicating that the shape of the PO_4 tetrahedron is rather regular. As for the hydrogen bonds, the O(1)···O(2^{i}) distance of 2·519 (6) Å is appreciably shorter than the corresponding distance of about 2·54 Å in CsD_2PO_4 (Itoh, Hagiwara & Nakamura, 1983) while the O(3)···O(3^{ii}) distance of 2·497 (7) Å and the O(4)···O(4^{iii}) distance of 2·514 (7) Å are nearly the same as the corresponding distance of about 2·50 Å.

As shown in Table 1, we obtain a small value for the thermal parameter of the D(1) atom suggesting its harmonic thermal motion in the O(1)···O(2^{i}) bond. On the other hand, remarkably large values for D(2) and D(3) imply their disordered motion in their associated O···O bonds. It should be noted that the thermal parameters of the P and O atoms are considerably larger than those in the structure of the low-temperature phase (Suzuki, Arai, Sumita & Makita, 1983). To give an insight into this difference, we calculated the thermal

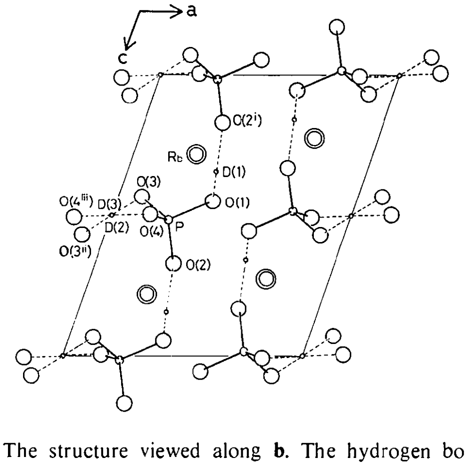

Fig. 1. The structure viewed along **b**. The hydrogen bonds are drawn with broken lines.

---

* The previously reported space groups $P2_1/m$ (Makita, Sumita, Osaka & Suzuki, 1981) and $P2_1/n$ (Osaka, Sumita & Makita, 1983) are incorrect.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39131 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parameters U_{eq} extrapolated to 322 K from the structure of the low-temperature phase on the basis of the harmonic model for thermal vibrations. The estimated values are $U_{eq}(P) = 1{\cdot}53$, $U_{eq}[O(1)] = 2{\cdot}8$, $U_{eq}[O(2)] = 3{\cdot}3$, $U_{eq}[O(3)] = 2{\cdot}9$ and $U_{eq}[O(4)] = 3{\cdot}1 \times 10^{-2}$ Å^2. It turns out that the observed values of U_{eq} at 322 K listed in Table 2 are still greater than the calculated ones by several tens of per cent or more. This fact suggests that the PO_4 tetrahedra in the intermediate phase are disordered while they are ordered in the low-temperature phase, indicating an order–disorder-type phase transition at 317 K.

Suzuki *et al.* (1983) reported that the high-temperature phase has the space group $P2_1/m$ with the basis lattice parameters a_o, b_o, c_o. Therefore, it follows that the sequence of successive phase transitions is as follows: $P2_1/m$ $(a_o,b_o,c_o) \rightarrow P2_1/c$ $(a_o,b_o,2c_o) \rightarrow P2_1$ $(2a_o,b_o,2c_o)$ with decreasing temperature. The high-temperature phase transition can be interpreted by **b**-directed average atomic displacements alternately along **c** to destroy the reflection symmetry and to double the parameter *c*. The low-temperature phase transition is interpreted by **b**-directed average atomic displacements to form the sublattice structure and to double the parameter *a*. In fact, considerable atomic displacements along **b** are found by comparing the structure of the intermediate phase to that of the reported low-temperature phase. The observed ferrielectric activity along **b** can be understood by sublattice formation.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

ITOH, K., HAGIWARA, T. & NAKAMURA, E. (1983). *J. Phys. Soc. Jpn*, **52**, 2626–2629.

MAKITA, Y., SUMITA, M., OSAKA, T. & SUZUKI, S. (1981). *Ferroelectrics*, **39**, 1017–1020.

OSAKA, T., SUMITA, M. & MAKITA, Y. (1983). *J. Phys. Soc. Jpn*, **52**, 1124–1126.

SAKURAI, T. (1967). Editor. *Universal Crystallographic Computing System*. (*UNICS*). Tokyo: Japanese Crystallographic Association.

SUMITA, M., OSAKA, T. & MAKITA, Y. (1981). *J. Phys. Soc. Jpn*, **50**, 154–158.

SUZUKI, S., ARAI, K., SUMITA, M. & MAKITA, Y. (1983). *J. Phys. Soc. Jpn*, **52**, 2394–2400.

Acta Cryst. (1984). C**40**, 720–722

Structure of Ammonium Dihydrogenphosphite, $NH_4H_2PO_3$

BY ZDENĚK MELICHAR, BOHUMIL KRATOCHVÍL* AND JANA PODLAHOVÁ

Department of Inorganic Chemistry, Charles University, Albertov 2030, 128 40 *Praha* 2, *Czechoslovakia*

AND VÁCLAV PETŘÍČEK, KAREL MALÝ AND IVANA CÍSAŘOVÁ

Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 180 40 *Praha* 8, *Czechoslovakia*

(*Received* 24 *October* 1983; *accepted* 3 *January* 1984)

Abstract. $M_r = 99{\cdot}026$, monoclinic, $P2_1/c$, $a = 6{\cdot}273\,(1)$, $b = 8{\cdot}232\,(2)$, $c = 8{\cdot}902\,(2)$ Å, $\beta = 120{\cdot}11\,(2)^\circ$, $V = 397{\cdot}7\,(2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}672\,(3)$, $D_x = 1{\cdot}654$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}54$ mm^{-1}, $F(000) = 208$, $T = 298$ K. Final $R = 0{\cdot}055$ for 1155 unique reflections. HPO_3 tetrahedra are connected through O—H···O hydrogen bonds so that infinite chains of composition $(H_2PO_3)_n^{n-}$ are formed in the structure parallel to the *z* axis. The chains are further interwoven together by means of N—H···O hydrogen bonds originating from the NH_4^+ ions, forming a three-dimensional network.

Introduction. The preparation of $NH_4H_2PO_3$ has been described by Amat (1891), and Ebert & Grospietsch (1968) found exact conditions for its formation from the solubility diagram of the $(NH_4)_2HPO_3$–H_3PO_3–H_2O system at 298 K. Preliminary crystal data (cell dimensions, space group, density) were determined by Norbert, Brun, Maurin & Barnoyer (1971). A crystal-structure study of $NH_4H_2PO_3$ was undertaken as part of an investigation of hydrogenphosphites.

Experimental. Spherical crystal, $r = 0{\cdot}8$ mm, $\mu r = 0{\cdot}43$, absorption ignored, Hilger & Watts diffractometer, lattice parameters refined from the setting of 29 centered high-angle reflections, 1233 reflections

---

* Author to whom correspondence should be addressed.

0108-2701/84/050720-03$01.50