

La contribution des atomes d'hydrogène a été négligée pour les molécules d'eau. Les calculs sont effectués sur ordinateur PDP 11-34 utilisant les programmes *SDP* (Enraf-Nonius, 1980).

**Discussion.** Une projection (010) de la structure est représentée sur la Fig. 1. Les coordonnées atomiques et les coefficients d'agitation thermique isotropes sont donnés dans le Tableau 1.\* Les anions cycliques de la maille sont reliés entre eux par les atomes de cobalt. L'ensemble des octaédres de coordination des atomes de cobalt et des groupements cycliques  $P_4O_{12}$  forment un enchaînement linéaire infini parallèle à la direction *c* et de période l'anion complexe  $[Co(H_2O)_2P_4O_{12}]^{2-}$ . Les atomes d'argent possèdent dans cette structure la coordinence 6. Leurs polyèdres de coordination mettent en commun le sommet O(E42). Ag(1)O<sub>6</sub> partage en outre l'arête O(E11)–O(E21) avec l'octaèdre Co(1)O<sub>6</sub>, alors que Ag(2)O<sub>6</sub> se lie à l'octaèdre Co(2)O<sub>6</sub> par la face O(E31)–O(E41)–O(W2). L'ensemble des cations associés définit un enchaînement infini perpendiculaire à la direction *c* (Fig. 2), tout en assurant la cohésion entre les chaînes précédentes. Les distances et angles des liaisons dans l'anion cyclique et les polyèdres de coordination des cations associés sont rassemblés dans le Tableau 2. L'anion cyclique possède la pseudo-

\* Les listes des facteurs de structure et des facteurs d'agitation thermique anisotrope ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 51486: 22 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

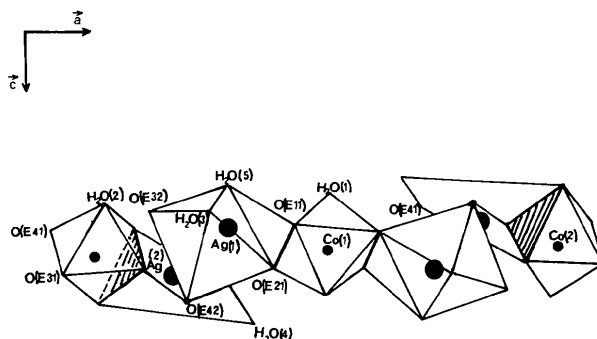


Fig. 2. Enchaînement des polyèdres de coordination des cations associés.

symétrie *m*. Les pseudo-miroirs sont parallèles au plan *ab* et placés en  $z = \frac{1}{4}$  et  $\frac{3}{4}$ . Les vibrations thermiques des atomes d'argent sont très anisotropes; leurs ellipsoïdes sont aplaties le long de la direction *a* de l'enchaînement.

#### Références

- Enraf-Nonius (1980). *Structure Determination Package*. Enraf-Nonius, Delft, Pays-Bas.  
*International Tables for X-ray Crystallography* (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel Kluwer Academic Publishers, Dordrecht.)  
 JOUINI, A. & DURIF, A. (1983). *C. R. Acad. Sci. Sér. II*, **297**, 573–575.  
 JOUINI, A., DURIF, A. & DABBABI, M. (1985). *J. Solid State Chem.* **60**, 6–12.  
 JOUINI, A., SOUA, M. & DABBABI, M. (1987). *J. Solid State Chem.* **69**, 135–144.

*Acta Cryst.* (1989). **C45**, 365–367

## The Structure of SrRuO<sub>3</sub> by Time-of-Flight Neutron Powder Diffraction

BY C. W. JONES, P. D. BATTLE\* AND P. LIGHTFOOT

*Department of Inorganic and Structural Chemistry, Leeds University, Leeds LS2 9JT, England*

AND W. T. A. HARRISON†

*Neutron Division, Rutherford-Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England*

(Received 4 July 1988; accepted 7 October 1988)

**Abstract.** SrRuO<sub>3</sub>,  $M_r = 236.7$ , orthorhombic, *Pbnm*. At  $T = 300$  K:  $a = 5.5670$  (1),  $b = 5.5304$  (1),  $c =$

$7.8446$  (2) Å,  $V = 241.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 6.510$  g cm<sup>-3</sup>. Final  $R_f = 8.4\%$ ,  $R_p = 3.08\%$ ,  $R_{wp} = 3.23\%$ ,  $\chi^2 = 2.47$ . The structure has been refined from high-resolution time-of-flight neutron powder diffraction data. It is a distorted, pseudo-cubic perovskite of the GdFeO<sub>3</sub> type.

\* Author to whom correspondence should be addressed.

† Present address: Department of Chemistry, University of California, Santa Barbara, California 93106, USA.

Table 1. Atomic coordinates and anisotropic thermal parameters for SrRuO<sub>3</sub> at room temperature

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>23</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>12</sub>	
Sr	4( <i>c</i> )	-0.0027 (3)	0.0157 (4)	$\frac{1}{2}$	0.61 (6)	0.74 (7)	0.71 (8)	0	0	0.00 (6)
Ru	4( <i>b</i> )	$\frac{1}{2}$	0	0	0.50 (6)	0.42 (6)	0.63 (8)	-0.04 (8)	-0.19 (9)	-0.02 (7)
O1	8( <i>d</i> )	0.7248 (2)	0.2764 (2)	0.0278 (2)	0.57 (5)	0.69 (5)	1.06 (6)	-0.03 (6)	0.27 (6)	-0.20 (5)
O2	4( <i>c</i> )	0.0532 (4)	0.4966 (5)	$\frac{1}{2}$	1.10 (8)	1.00 (9)	0.40 (9)	0	0	0.13 (10)

Table 2. Bond lengths (Å) and bond angles (°) for SrRuO<sub>3</sub> at room temperature

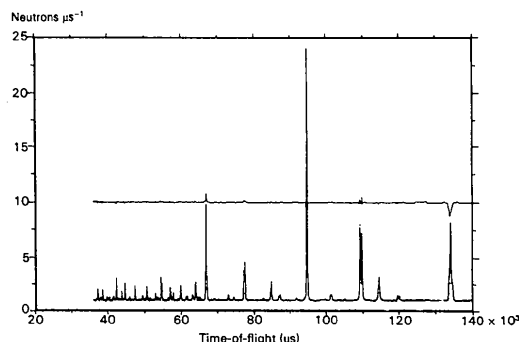
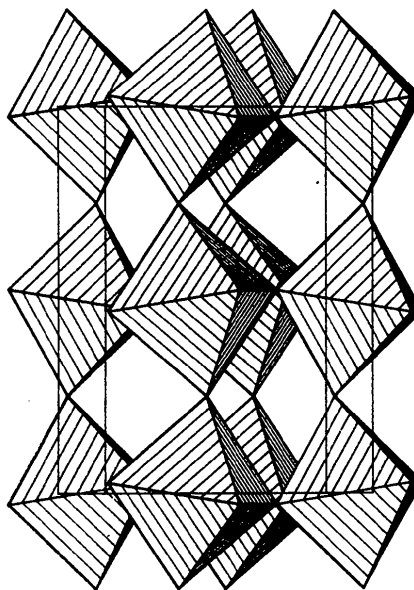
Ru—O octahedra	
Ru—O1	1.987 (2) (× 2)
Ru—O1	1.981 (2) (× 2)
Ru—O2	1.983 (2) (× 2)
O1—Ru—O2	
O1—Ru—O2	91.09
O1—Ru—O1	90.04
O1—Ru—O1	90.41
Sr—O polyhedra	
Sr—O1	2.724 (4) (× 2)
Sr—O1	2.770 (4) (× 2)
Sr—O1	2.514 (4) (× 2)
Sr—O2	2.505 (4)
Sr—O2	2.678 (4)

**Introduction.** SrRuO<sub>3</sub> is a distorted, pseudo-cubic perovskite first reported (Randall & Ward, 1959) to be an orthorhombic phase of the GdFeO<sub>3</sub> (Geller, 1956) type. It is a metallic conductor [ $\rho = 2.75 \times 10^{-4} \Omega \text{ cm}$  at 300 K (Bouchard & Gillson, 1972)] which orders ferromagnetically below  $T_c \sim 160 \text{ K}$  (Callaghan, Moeller & Ward, 1966).

Recent advances in powder diffraction instrumentation have now made feasible detailed structural studies of such phases, which involve relatively small deviations from cubic symmetry. The current study was undertaken in order to provide a basis for future work on the magnetic structure of the phase.

**Experimental.** A pure polycrystalline sample of SrRuO<sub>3</sub> was prepared by conventional solid-state methods. Stoichiometric quantities of dried RuO<sub>2</sub> and spectroscopic grade SrCO<sub>3</sub> were ground together in an agate mortar and fired in pellet form, firstly at 1073 K for 24 h, and then for a further 6 d at 1473 K. Two intermediate regrindings were undertaken in order to ensure the homogeneity of the final product. On the final firing cycle, the sample was slow-cooled to 673 K over a period of 24 h. X-ray diffraction of the product confirmed the presence of a perovskite-like phase, with no observable impurities.

Time-of-flight neutron diffraction data were collected at room temperature on the High-Resolution Powder Diffractometer (HRPD) at ISIS, Rutherford-Appleton Laboratory. Approximately 10 g of sample were loaded in a vanadium container, and data collected between 30 000 and 140 000  $\mu\text{s}$  in time-of-flight, over a total period of about 6 h. After summation and normalization of the data, the region

Fig. 1. The observed, calculated and difference diffraction profiles of SrRuO<sub>3</sub> at room temperature.Fig. 2. Polyhedral representation of the RuO<sub>3</sub> framework of SrRuO<sub>3</sub>, viewed along a direction 10° away from [100].

35 000–140 000  $\mu\text{s}$ , corresponding to an approximate *d*-spacing range of 0.7–2.8 Å and hence including 328 Bragg intensities, was used in the profile refinement. The background was fitted by a five-term Chebyshev polynomial, the five parameters being included as variables in the least-squares procedure. Peak shapes were described by a complex function incorporating Gaussian, Lorentzian and two exponential contributions. The former two peak-shape parameters were

refined, the latter two being fixed by instrumental characteristics. In addition to these parameters, a zero-point error, cell parameters and atomic and anisotropic thermal parameters for all atoms were refined, giving a total of 39 variables during the final cycles. The program *VDELSQ*, incorporating sub-routines from the Cambridge Crystallographic Sub-routines Library package (Brown & Matthewman, 1987), and *GENIE* spectrum manipulation software (David *et al.*, 1986) were used for all data analysis. Atomic coordinates for the isomorphous  $\text{La}_2\text{NiRuO}_6$  (Battle & Jones, 1987) were used as a starting model for the refinement, in space group *Pbnm*; the systematic absences of this space group were consistent with those observed in our data. A smooth refinement was achieved, with convergence at the final agreement factors  $R_I = 8.4\%$ ,  $R_p = 3.0\%$ ,  $R_{wp} = 3.2\%$ . The statistically expected *R* factor,  $R_{exp}$ , was 2.5%, leading to a goodness-of-fit index  $\chi^2$  ( $= |R_{wp}/R_{exp}|^2$ ) of 2.47. All the *R* factors are defined in the original paper of Rietveld (1969). The most obvious discrepancy between the observed and calculated diffraction profiles occurs at  $d \sim 2.6 \text{ \AA}$ ; we have no convincing explanation for this anomaly.

**Discussion.** Final atomic coordinates and anisotropic temperature factors are given in Table 1, and selected bond distances and angles in Table 2. The phase adopts an orthorhombic,  $\text{GdFeO}_3$ -like perovskite structure with final, refined cell parameters  $a = 5.5670$  (1),  $b = 5.5304$  (1) and  $c = 7.8446$  (2)  $\text{\AA}$ . A plot of the final observed, calculated and difference profiles for the

Rietveld refinement is shown in Fig. 1,\* and a polyhedral representation (Fischer, 1985) of the distorted perovskite structure in Fig. 2. All bond lengths lie within chemically sensible limits, the Ru—O bond lengths being comparable to those in other  $\text{Ru}^{\text{IV}}$  oxides, for example  $\text{RuO}_2$  [ $2 \times 1.942 \text{ \AA}$  and  $4 \times 1.984 \text{ \AA}$  (Boman, 1970)].

We are grateful to the SERC for financial support.

\* A list of numerical data corresponding to Fig. 1 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51563 (84 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

#### References

- BATTLE, P. D. & JONES, C. W. (1987). *Mater. Res. Bull.* **22**, 1623–1627.  
 BOMAN, C. E. (1970). *Acta Chem. Scand.* **24**, 116–122.  
 BOUCHARD, R. J. & GILLSON, J. L. (1972). *Mater. Res. Bull.* **7**, 873–878.  
 BROWN, P. J. & MATTHEWMAN, J. C. (1987). Rutherford–Appleton Laboratory Report RAL-87-010.  
 CALLAGHAN, A., MOELLER, C. W. & WARD, R. (1966). *Inorg. Chem.* **5**, 1572–1576.  
 DAVID, W. I. F., JOHNSON, M. W., KNOWLES, K. J., MORETON-SMITH, C. M., CROSBIE, G. D., CAMPBELL, E. P., GRAHAM, S. P. & LYALL, J. S. (1986). Rutherford–Appleton Laboratory Report RAL-86-102.  
 FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.  
 GELLER, S. (1956). *J. Chem. Phys.* **24**, 1236–1239.  
 RANDALL, J. J. & WARD, R. (1959). *J. Am. Chem. Soc.* **81**, 2629–2631.  
 RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

*Acta Cryst.* (1989). **C45**, 367–371

## The Structure of Ferric Oxonium Bis(hydrogenphosphate), $\text{Fe}^{3+} \cdot (\text{H}_3\text{O})^+ \cdot 2(\text{PO}_4\text{H})^{2-}$

BY IVO VENCATO

*Departamento de Física, Universidade Federal de Santa Catarina, 88049 Florianópolis, SC, Brazil*

ENRICO MATTIEVICH AND LÍGIA DE F. MOREIRA

*Instituto de Física, Universidade Federal do Rio de Janeiro, 21941 Rio de Janeiro, RJ, Brazil*

AND YVONNE P. MASCARENHAS

*Instituto de Física e Química de São Carlos, Universidade de São Paulo, 13560 São Carlos, SP, Brazil*

(Received 3 March 1988; accepted 14 October 1988)

**Abstract.** The new synthetic compound with  $M_r = 266.8$  is monoclinic,  $P2_1/c$ ,  $a = 5.191$  (2),  $b = 8.748$  (2),  $c = 14.448$  (2)  $\text{\AA}$ ,  $\beta = 94.81$  (2) $^\circ$ ,  $V = 653$  (1)  $\text{\AA}^3$ ,  $Z = 4$ ,  $D_x = 2.69 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) =$

$0.71073 \text{ \AA}$ ,  $\mu = 26.6 \text{ cm}^{-1}$ ,  $F(000) = 520$ , room temperature, final  $R = 0.058$  for 976 observed reflections. The structure consists of  $\text{Fe}^{3+}$  ions coordinated by  $(\text{PO}_4\text{H})^{2-}$  ligands forming interconnected octahedra