

## The Crystal Structure of RbHSeO<sub>4</sub>: A Neutron Diffraction Study of the Paraelectric Phase

IRMÈLA BRACH, DEBORAH J. JONES,\* AND JACQUES ROZIÈRE†

*Laboratoire des Acides Minéraux, LA 79, CNRS, Université des Sciences et Techniques du Languedoc, Place E. Bataillon, 34060 Montpellier, Cedex, France*

Received January 11, 1983; in revised form March 18, 1983

The structure of the paraelectric phase of RbHSeO<sub>4</sub> has been determined at 387 K by neutron diffraction. The structure consists of chains of hydrogen bonded SeO<sub>4</sub> groups extending along the crystallographic *b* axis. Two different hydrogen bonds have been characterized, with O–O distances of 2.524(4) and 2.583(3) Å. In the shorter O–H–O hydrogen bond the hydrogen atom is disordered, suggesting that the ordering of hydrogen participates directly in the phase transition to the ferroelectric phase.

Ferroelectricity in rubidium and ammonium hydrogen selenates (henceforth RHSe and AHSe) has recently been discovered (1, 2). The crystals are isomorphic in the corresponding phases: triclinic in the ferroelectric phase and monoclinic in the paraelectric phase. They belong to a class of ferroelectric materials of formula MeHBX<sub>4</sub> which includes the well-known rubidium and ammonium hydrogen sulphates (3).

However, particular interest in the selenate subfamily arises from several properties: (i) the crystals are not isomorphic with the corresponding ferroelectric sulphates, (ii) the hydrogen bond network is parallel to the ferroelectric axis, and (iii) the phase transition mechanism probably involves ordering of hydrogen atoms.

X-ray diffraction studies have established the crystal structures of RHSe and

AHSe in both their ferroelectric and paraelectric phases (4–7). In particular, an extremely short O–H–O bond of 2.35 Å has been reported for RHSe in its paraelectric phase (5).

This neutron diffraction study of the paraelectric phase of RHSe was carried out to determine the proton density distribution in the hydrogen bond network and to provide precise atomic coordinates which are essential for the understanding of the nature of the phase transition.

### Experimental

#### (a) Data

Crystals of RbHSeO<sub>4</sub> were prepared as previously described (1). Large crystals were grown by slow evaporation of H<sub>2</sub>O from a saturated solution at 303 K. The crystal selected had a volume of 61 mm<sup>3</sup>. The X-ray lattice parameters in the nonconventional body-centered monoclinic cell used in this neutron diffraction study were

\* On leave from the Dept. of Chemistry, King's College, University of London, Strand, London WC2R 2LS, England.

† Author for correspondence.

$\text{RbHSeO}_4$ :  $M = 229.4$ , space group  $I2$ ,  $a = 19.443(5) \text{ \AA}$ ,  $b = 4.629(3) \text{ \AA}$ ,  $c = 7.635(3) \text{ \AA}$ ,  $\gamma = 90.78(1)^\circ$ ,  $V = 687.1 \text{ \AA}^3$  at  $387 \text{ K}$ ,  $Z = 6$ .

The nonconventional space group of the X-ray study (5) was retained to emphasize the pseudoorthorhombic symmetry of the crystal and its similarity to the nonisomorphous structures of  $\text{RbHSO}_4$  and  $\text{NH}_4\text{SO}_4$ .

Full three-dimensional data were collected at the high flux reactor at the Institut Laue-Langevin, Grenoble (8). Reflections numbering 1479 were measured at  $387 \pm 2 \text{ K}$  up to  $\sin \theta/\lambda = 0.8$  with a neutron wavelength of  $0.840 \text{ \AA}$  using the  $\theta$ - $2\theta$  step scan technique. Data reduction was carried out with the minimum  $\sigma(I)/I$  method (9). Structure factors were derived by correcting for

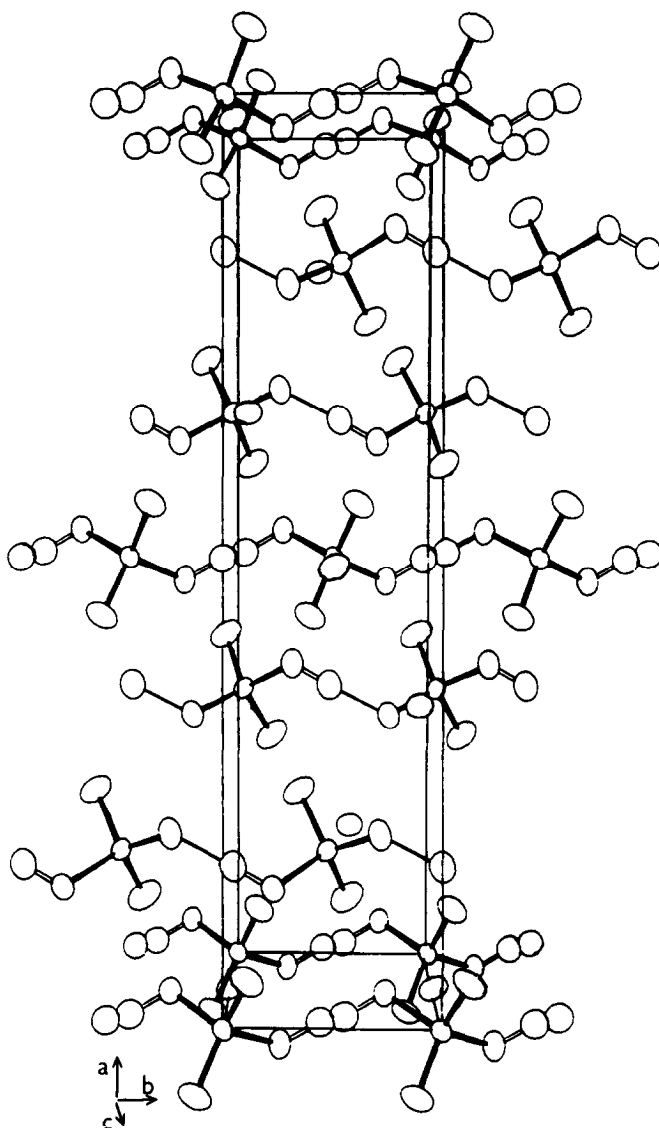


FIG. 1. View down the  $c$  axis showing the chains extending along  $b$ .

TABLE I

ATOMIC COORDINATES ( $\times 10^{-4}$ ) WITH ESD'S IN PARENTHESES. THE TEMPERATURE FACTOR ( $\times 10^{-5}$ ) IS OF THE FORM  $T = \exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$

	x	y	z	$B_{eq}$ (Å <sup>2</sup> )	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Rb(2)	0	0	5129(4)	2.93(1)	173(5)	4186(105)	1114(39)	191(19)	0	0
Rb(3)	1656(1)	5834(3)	9142(3)	2.86(1)	148(3)	3935(68)	1247(27)	-9(11)	-13(9)	-49(40)
Se(2)	0	0	0	1.84(1)	120(4)	1954(60)	867(25)	-86(12)	0	0
Se(3)	1674(1)	4686(2)	4237(3)	2.02(1)	127(3)	2086(44)	1008(20)	69(8)	-41(8)	-211(29)
O(5)	633(1)	1177(5)	8841(4)	3.29(1)	194(5)	4669(97)	1242(37)	-323(11)	160(11)	-144(46)
O(7)	294(1)	7448(5)	1346(4)	2.92(1)	210(5)	2235(66)	1570(37)	8(14)	184(11)	190(42)
O(9)	1325(1)	2133(4)	2865(4)	3.32(1)	226(5)	2614(82)	1841(44)	-41(16)	-273(13)	-379(48)
O(10)	1046(1)	5694(5)	5459(4)	3.79(1)	238(6)	5500(117)	1330(37)	407(21)	168(13)	298(56)
O(11)	1939(1)	7223(4)	2911(4)	3.12(1)	227(5)	2541(70)	1598(39)	-123(15)	140(12)	-65(46)
O(12)	2299(1)	3295(6)	5301(4)	4.14(1)	244(6)	5175(109)	1863(50)	460(20)	-373(15)	-830(62)
H(1)	1582(2)	237(7)	2936(7)	3.73(1)	251(9)	3312(142)	1948(72)	-85(30)	-45(22)	-418(84)
H(2)	35(4)	5561(13)	1265(8)	3.19(1)						

absorption effects and the Lorentz factor ( $\mu_c = 0.5 \text{ cm}^{-1}$ ). The minimum and maximum transmission factors were 0.80 and 0.88, respectively. Averaging all equivalent data gave 953 independent reflections with an "agreement factor" between equivalent reflections of 4%.

### (b) Structure Refinements

The previously derived X-ray atomic parameters (5) were used initially in a least squares refinement, providing sufficient phase information to locate the hydrogen

atoms from a difference Fourier map. Two types of hydrogen site were found: one, designated H(1), in a special position on a twofold symmetry axis, the other, designated H(2), in a general position. It was clear from the Fourier map that H(1) was suffering from extremely high and anisotropic thermal motion and therefore a disorder model for this hydrogen atom was intro-

TABLE II

HYDROGEN BOND DISTANCES (Å) AND ANGLES (°) (THE SUPERScript INDICATES THE SYMMETRY OPERATION THROUGH THE TWOFOLD SYMMETRY AXIS)

O(7)-O(7)'	2.525(4)
O(7)-H(1)	1.005(7)
O(7)-H(1)'	1.526(6)
H(1)-H(1)'	0.535(11)
Se(2)-O(7)-H(1)	113.8(4)
Se(2)-O(7)-H(1)'	118.5(3)
O(7)-H(1)-O(7)'	172.0(7)
O(9)-O(11)	2.583(3)
O(9)-H(2)	1.017(4)
O(11)-H(2)	1.568(4)
Se(3)-O(9)-H(2)	111.6(3)
Se(3)-O(11)-H(2)	119.6(2)
O(9)-H(2)-O(11)	175.1(5)

TABLE III

COMPARISON OF INTERATOMIC DISTANCES (Å) AND ANGLES (°) OF SeO<sub>4</sub> GROUPS IN AMMONIUM AND RUBIDIUM HYDROGEN SELENATES

	AHSe <sup>a</sup>	RHSe
Se(2)-O(7)	1.664(4)	1.672(2)
Se(3)-O(5)	1.617(5)	1.605(2)
O(7)-Se(2)-O(5)	108.2(3)	108.1(1)
O(7)-Se(2)-O(7)	104.6(3)	104.1(2)
O(5)-Se(2)-O(5)	112.2(3)	113.1(2)
O(7)-Se(2)-O(5)	111.8(3)	111.5(1)
Se(3)-O(11)	1.630(5)	1.629(3)
Se(3)-O(12)	1.611(6)	1.604(3)
Se(3)-O(9)	1.709(6)	1.713(3)
Se(3)-O(10)	1.615(5)	1.610(3)
O(11)-Se(3)-O(12)	112.4(3)	111.7(1)
O(11)-Se(3)-O(9)	104.1(3)	103.7(2)
O(11)-Se(3)-O(10)	111.9(3)	112.6(1)
O(12)-Se(3)-O(9)	108.9(3)	109.2(1)
O(12)-Se(3)-O(10)	113.7(4)	113.9(2)
O(9)-Se(3)-O(10)	105.1(4)	105.0(1)

<sup>a</sup> From Aleksandrov *et al.* (6).

TABLE IV  
INTERATOMIC DISTANCES (Å)  
AROUND THE RUBIDIUM IONS

Rb(2)–O(10) <sup>a</sup>	2.878(3)
Rb(2)–O(10) <sup>b</sup>	
Rb(2)–O(5)	3.134(3)
Rb(2)–O(5) <sup>c</sup>	
Rb(2)–O(7) <sup>a</sup>	3.175(2)
Rb(2)–O(7) <sup>b</sup>	
Rb(2)–O(9)	3.244(3)
Rb(2)–O(9) <sup>c</sup>	
Rb(2)–O(10)	3.317(4)
Rb(2)–O(10) <sup>c</sup>	
Rb(3)–O(5)	2.922(3)
Rb(3)–O(12) <sup>d</sup>	2.944(3)
Rb(3)–O(11) <sup>e</sup>	2.998(4)
Rb(3)–O(11) <sup>f</sup>	3.015(3)
Rb(3)–O(10)	3.052(2)
Rb(3)–O(5) <sup>g</sup>	3.203(3)
Rb(3)–O(7) <sup>e</sup>	3.234(3)
Rb(3)–O(9) <sup>e</sup>	3.576(4)
Rb(3)–O(12)	3.404(3)
Rb(3)–O(12) <sup>f</sup>	3.486(4)

Note: Symmetry operations implied by the superscripts are

- a: (x, y – 1, z),  
 b: (–x, 1 – y, z),  
 c: (–x, –y, z),  
 d: (½ – x, 1 – y, ½ + z),  
 e: (x, y, 1 + z),  
 f: (½ – x, ½ – y, ½ + z),  
 g: (x, 1 + y, z).

duced in the refinements. A full matrix least squares refinement with anisotropic temperature factors for all atoms, except the half-hydrogen, which was given an isotropic thermal parameter, led to the values of agreement indices:  $R(F_o) = 0.066$ ,  $R(F_o^2) = 0.11$ ,  $R_w(F_o^2) = 0.27$ ,  $(R(F_o) = \sum |F_o| - |F_c| / \sum |F_o|)$ ;  $R(F_o^2) = \sum |F_o^2 - F_c^2| / \sum |F_o^2|$ ;  $R_w(F_o^2) = |\sum w_i |F_o^2 - F_c^2|^2 / \sum w_i F_o^4|^{\frac{1}{2}}$  with  $w_i^{-1} = \sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.02 F_o^2)^2$ ;  $\sigma_c$  is determined by counting statistics.

At this point it was apparent that the data suffered from severe extinction effects; therefore an isotropic secondary extinction parameter was refined and the 39 most intense reflections were excluded from the

last cycles of refinement. The final discrepancy indices were  $R(F_o) = 0.036$ ,  $R(F_o^2) = 0.059$ ,  $R_w(F_o^2) = 0.076$  for 940 reflections. In all refinements the values assumed for the coherent neutron scattering amplitudes for Rb, Se, O, and H were 0.708, 0.797, 0.580, and –0.374, respectively (units of  $10^{-12}$  cm) (10). Observed and calculated structure factor amplitudes are available on demand.

## Results and Discussion

The positional and thermal parameters of all atoms are given in Table I. Relevant bond distances and angles are given in Tables II–IV.

To facilitate comparison between the X-ray and neutron diffraction derived parameters, the numbering scheme is the same as that used by Waskowska *et al.*, (5); Fig. 1 shows the contents of one unit cell.

We have found the structure to be grossly as reported in Ref. 5. It consists of distorted  $\text{SeO}_4$  tetrahedral groups linked into chains in the direction of the *b* axis by hydrogen bonds. Such chains repeat themselves over the whole crystal cell and are connected via the rubidium ions. Two different hydrogen bonds exist in the structure. One of them crosses a twofold symmetry axis with the hydrogen atom located either on the symmetry element or disordered in half-occupied positions. No symmetry restriction is imposed on the other hydrogen bond.

However, compared with the three-dimensional refinements of the X-ray study, the errors derived in the positions of the oxygen atoms are reduced in the present work by a factor of approximately five. Moreover, in spite of the high e.s.d.'s reported in the X-ray study, some of the oxygen atoms' positional parameters disagree by more than  $6\sigma$ . We therefore think that the results presented in this neutron diffraction study give more reliable information, in particular with respect to the  $\text{SeO}_4$

groups' geometry and the hydrogen bond lengths, which are most important for the understanding of the mechanisms of phase transition and spontaneous polarization.

The details of hydrogen bonding are illustrated in Fig. 2 and summarized in Table II.

Contrary to the results of the X-ray diffraction study, no evidence for a very short bond is found from our neutron diffraction results. The hydrogen bond across the two-fold symmetry axis is 2.524(4) Å long, which is considerably longer (0.17 Å) than the previously reported O–O distance (5). In this hydrogen bond the proton is disordered across two sites with equal occu-

pancy. Refinements of the half-hydrogen positional parameters gave an O–H distance of 1.005(7) Å and a separation of 0.53(1) Å between the two half-occupied sites. In contrast a fully ordered proton is found in the second hydrogen bond with an O–O distance of 2.583(3) Å and an O–H distance of 1.017(4) Å. In the triclinic ferroelectric phase, the symmetry restriction on the shorter hydrogen bond is relaxed and the phase transition mechanism should involve ordering of the proton in this hydrogen bond. Therefore the transition is probably of nearly one-dimensional character with chainlike ordering parallel to the ferro-

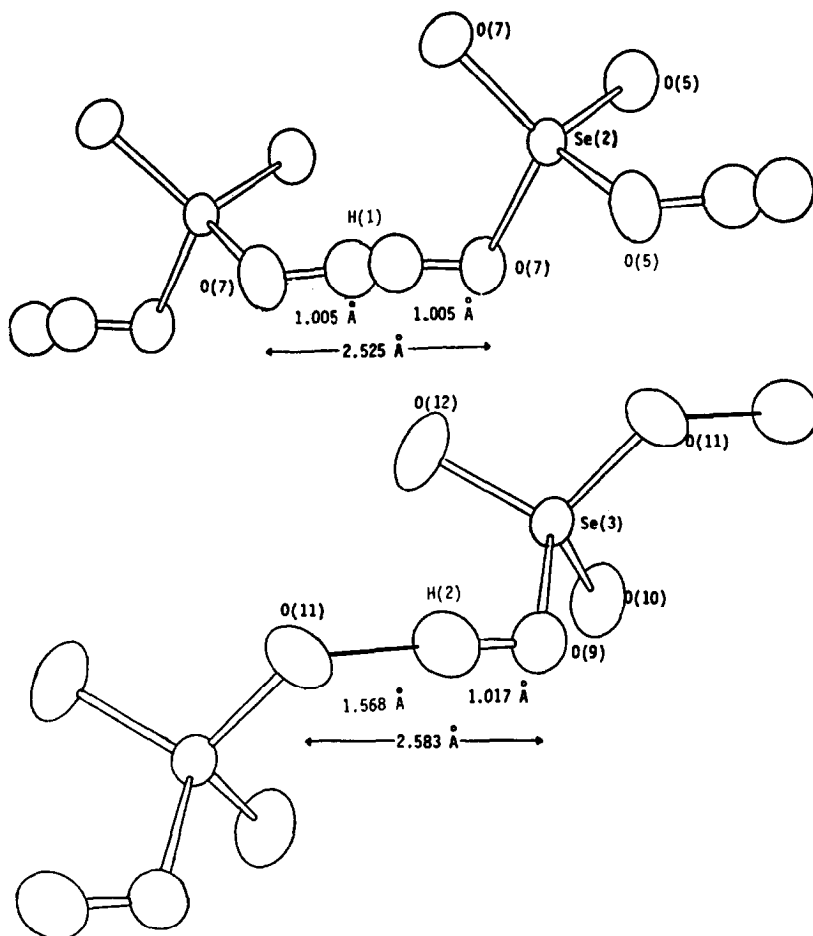


FIG. 2. The geometry of the two types of hydrogen bonded chain.

electric  $b$  axis. The hydrogen bonding scheme in RHSe is very similar to that of the isomorphic paraelectric phase of AHSe described in the room temperature X-ray diffraction study of Aleksandrov *et al.* (6).

While in the present study the longer hydrogen bond is definitely asymmetrical, with the proton localized at one oxygen, in AHSe, Aleksandrov *et al.* found this hydrogen bond to be disordered. However, consideration of the Se–O bond lengths can give additional information about possible disorder in AHSe. In RHSe, a pure Se–O bond is 1.60 to 1.63 Å long and a pure Se–OH bond is about 1.71 Å long; an Se–O bond of 1.67 Å corresponds to a 50–50% disorder of the hydrogen. As shown in Table III bond lengths and bond angles pertinent to the  $\text{SeO}_4$  tetrahedra in RHSe agree in a very satisfactory way with the values given for AHSe (6). Therefore, there is little doubt that the proton distribution in the hydrogen bonds is essentially the same in the two crystals.

### Acknowledgments

We thank Professor L. Sobczyk (Institute of Chemistry, University of Wrocław) for suggesting this study

and for stimulating discussion. We acknowledge the support staff of ILL (Grenoble, France) and express particularly our thanks to J. Allibon, Dr. M. S. Lehmann, and Dr. G. Bentley for their kind assistance. D.J.J. thanks the Royal Society of Great Britain and the French C.N.R.S. for the award of a European Exchange Fellowship.

### References

1. R. POPRAWSKI, J. MROZ, Z. CZAPLA, AND L. SOBCZYK, *Acta Phys. Pol. A* **55**, 641 (1979).
2. Z. CZAPLA, T. LIS, AND L. SOBCZYK, *Phys. Status Solidi A* **51**, 609 (1979).
3. F. JONA AND G. SHIRANE, "Ferroelectric Crystals," Pergamon, Oxford, 1962.
4. A. WASKOWSKA, S. OLEJNIK, A. LUKASIEWICZ, AND T. GŁOWIAK, *Acta Crystallogr. Sect. B* **34**, 3344 (1978).
5. A. WASKOWSKA, S. OLEJNIK, A. LUKASIEWICZ, AND Z. CZAPLA, *Cryst. Struct. Commun.* **9**, 663 (1980).
6. K. S. ALEKSANDROV, A. I. KRUGLIK, S. V. MISYUL, AND M. A. SIMONOV, *Kristallografiya* **25**, 1142 (1980).
7. A. I. KRUGLIK, S. V. MISYUL, AND K. S. ALEKSANDROV, *Dokl. Akad. Nauk. SSSR* **255**, 344 (1980).
8. J. ALLIBON AND M. S. LEHMANN, ILL Internal Reports, 79AL53T, 1979.
9. M. S. LEHMANN AND F. K. LARSEN, *Acta Crystallogr. Sect. A* **32**, 580 (1974).
10. G. E. BACON, *Acta Crystallogr. Sect. A* **28**, 357 (1972).