

Structural study of the high and low temperature phases of the proton conductor $\text{Rb}_3\text{H}(\text{SeO}_4)_2$

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Abstract

The crystal structures of $\text{Rb}_3\text{H}(\text{SeO}_4)_2$ have been determined in the rhombohedral proton conducting phase at 498 K and in the monoclinic ordered phase at 298 K by means of neutron powder diffraction. Special emphasis is given to the determination of accurate positions for the light atoms. The proton conduction mechanism in the high temperature phase is discussed with respect to the results of the structure refinement.

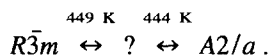
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1. Introduction

$\text{Rb}_3\text{H}(\text{SeO}_4)_2$ (TRHSe) belongs to the family of $\text{M}_3\text{H}(\text{XO}_4)_2$ with $\text{M} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$ and $\text{X} = \text{S}, \text{Se}$. This family is well-known for possessing proton conducting phases with rhombohedral symmetry. The two-dimensional proton conductivity results from a disorder of the hydrogen atoms among partly occupied symmetry equivalent positions. All members of the family show one or more phase transitions into phases of lower order with monoclinic or triclinic symmetry. Most of these phase transitions are of ferroic, ferroelastic as well as ferroelectric, nature.

For TRHSe up to now two phases have been described, a disordered proton conducting phase with space group $R\bar{3}m$ for temperatures above 449 K [1] and an ordered phase below 444 K with space group $A2/a$ [2] (Fig. 1). It has been suggested that an inter-

mediate phase possibly exists in a narrow temperature range of a few degrees [3]; but this is not the topic of the present work. Differential thermal analysis and precise lattice parameter measurements [4] seem to prove the existence of such a phase. Its structure is still unknown. The “complete” phase sequence for TRHSe should be



The proton conduction is one of the outstanding features of this compound. Nevertheless, precise positions of the hydrogen atoms have not been determined as “only” X-ray single crystal experiments were performed in the work cited above (and this is true for most other compounds belonging to this proton conductor family). It is essential to know these positions in order to understand the proton conduction mechanism.

Neutron scattering, with its sensitivity for light atoms, is one of the most powerful tools for investigating such structural details. Therefore we have reinves-

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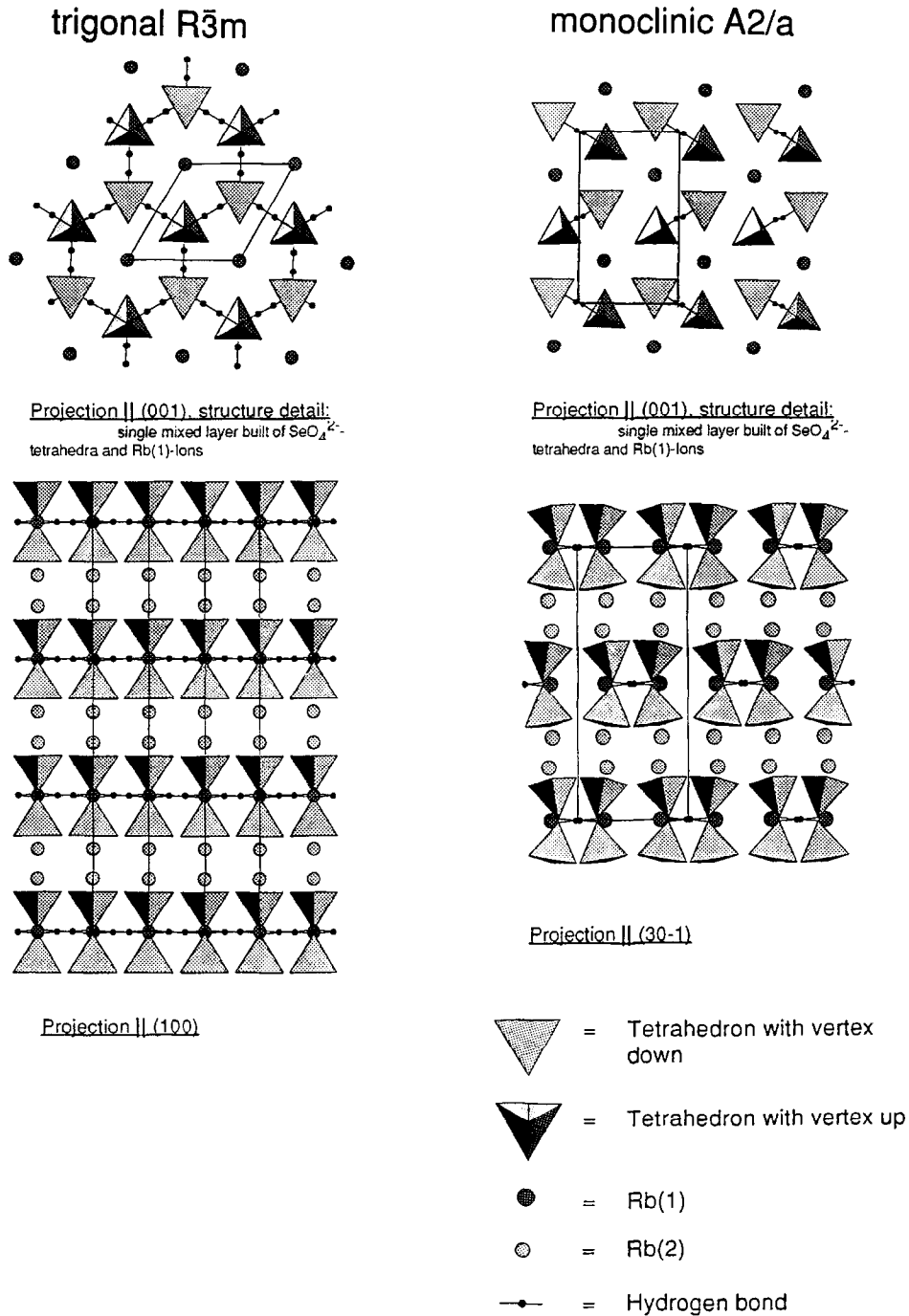


Fig. 1. Schematic pictures of the rhombohedral high (above 449 K) and monoclinic low temperature (below 444 K) phase of TRHSe. The positions of the hydrogens determined in this study are already included. Proton conduction in the high temperature phase takes place in a two-dimensional hydrogen sublattice (upper left) located between two sublayers of selenate tetrahedra pointing with their vertices towards the sublattice. In the rhombohedral phase the hydrogens are randomly distributed over all possible H-bridges in the conducting plane with an occupancy of one third, whereas the monoclinic phase is ordered.

tigated the structure of TRHSe with its H-sublattice by means of neutron powder diffraction experiments. Its results will be discussed in the following with special emphasis on elucidating the proton conduction mechanism.

2. Experimental

2.1. Crystal growth

Single crystals with sizes up to 10 mm³ were prepared by slow evaporation of an aqueous solution containing stoichiometric quantities of Rb₂CO₃ (99.99% Alfa No. 976345) and H₂SeO₄ (Merck No. 12325) with H₂O (Merck No. 15333) in a ratio of 0.3 (2-molar solution of H₂SeO₄). The high quality of the crystals and the purity have been proved by single crystal precession photographs and Guinier powder diffractograms, respectively, which show unambiguously the monoclinic room temperature phase of Rb₃H(SeO₄)₂. No impurity phases were detected. The weight ratio between Se and Rb was shown by electron microprobe to be about 0.65 (ideal=0.616). As the standards available only roughly reflected the composition, the deviation from the ideal ratio is perhaps not surprising.

2.2. Neutron powder diffraction

The neutron powder diffraction experiments on Rb₃H(SeO₄)₂ were performed on the flat-cone diffractometer E2 (498 K) and on the powder diffractometer E3 (298 K) at the 10 MW research reactor BERII at the Hahn-Meitner-Institut in Berlin. Both diffractometers are situated on thermal neutron beam tubes. They are equipped with a BF₃ filled multicounter with 400 wires separated by 0.2° which covers simultaneously 80° in 2-θ. To improve the angular resolution the multicounter was used in two different angular positions differing by 0.1°. By this the resulting diffraction pattern contains 800 equidistant points separated by 0.1°. The sample was enclosed in a vanadium cylinder 50 mm in height and 8 mm in diameter.

For the room temperature investigation on E3 a vertical focussing germanium monochromator (311) was chosen with λ = 1.851 Å. The collimation was 15' in front of and 30' behind the monochromator. The total measuring time was 16 h (8 h per step).

For the high temperature investigation the sample was mounted in an ILL "orange type" furnace cryostat. In addition we moved to the flat cone diffractometer E2 because of its radial-collimator in front of the multicounter which cuts off all scattered neutrons coming from the aluminium shielding of the furnace. Again a germanium monochromator (311) was used, but in this case with λ = 1.221 Å. A 10' collimator in front of the monochromator was chosen to attain the best possible resolution. Measuring time was 8 h per step.

2.3. Data analysis

The Rietveld analysis was carried out by employing the program PROFIL [5]. Initial structural parameters were taken from Ref. [2].

3. Results and discussion

3.1. The high temperature phase of TRHSe at 498 K

The neutron powder diffractogram measured at 498 K and the graphical result of the Rietveld refinement are shown in Fig. 2 (upper part). The proton conduction in the high temperature phase induces strong librations of the SeO₄ tetrahedra due to the formation and breaking of hydrogen bridges (see e.g. [1] and [6]). Improvements of the refinement procedure taking qualitative account of essential features of such librations have been achieved by applying (compare Table 1): a split position for O(2) among three equivalent positions; anisotropic atomic displacement factors for O(1). The results of the refinement concerning structural and important instrumental parameters are listed in Table 1. The coordinates of the heavier atoms including the oxygens are in good agreement with literature data given there.

Given the complex interactions in the structure, the model refined is probably oversimplified and does not always quantitatively reflect the real atomic displacements in the structure. This is expressed e.g. by the relatively low atomic displacement factors for O(2) and the hydrogen and, what is more important and will be discussed later, the short O(2)–H distance of 0.78(3) Å (compare Table 3). It is worthwhile to mention that the standard structure refinement programs

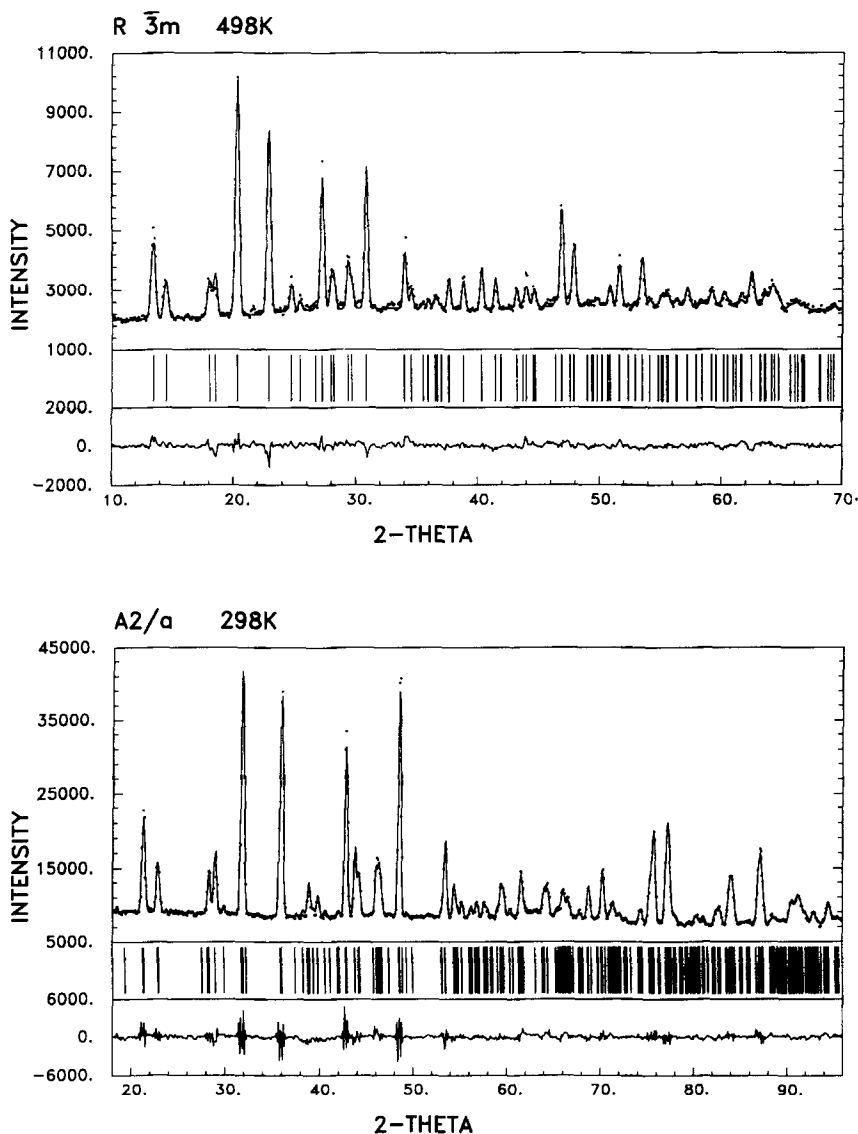


Fig. 2. Results of the Rietveld analysis of neutron powder experiments of TRHSe at 498 K in the high temperature proton conducting phase (upper part) and at 298 K in the low temperature ordered phase (lower part). The diffractograms were recorded at the research reactor BERII at the Hahn-Meitner-Institut in Berlin. The observed and calculated patterns as well as the difference plot are shown.

currently available do not offer the possibility of a more precise description of complex atomic motions, such as anisotropic librations coupled to the translational movement of protons within hydrogen bonds. An attempt to achieve this is in progress in our group.

Nevertheless, our approach should be sufficient to get a first insight into the proton conduction mechanism in TRHSe.

3.2. The proton conduction in the high temperature phase of TRHSe

In order to describe the proton conduction mechanism it is necessary to take a closer look at the bonding geometry of the hydrogen and oxygen atoms directly involved in the process. These are illustrated in Fig. 3 (compare Table 3). The O(2) atoms (at the tetrahe-

dron tops) are disordered among three distinct equivalent positions. The distance between these sites is 0.84(1) Å, and the distance from any one of them to the average position is 0.484(6) Å. The distance O(2)–O(2) between closest sites of neighbouring selenate apical oxygen atoms amounts to 2.58(1) Å. This is a typical value for a hydrogen bridge with a double minimum potential. Proton conduction in this context could happen via a fairly standard mechanism based on two consecutive processes (see e.g. Ref. [7]): (1) translational motion within the double minimum potential; (2) breaking of a hydrogen bridge and formation of a new neighbouring one, i.e. “rotational” motion of the hydrogen between adjacent hydrogen bridges.

Both processes are shown in Fig. 3. In TRHSe the average occupancy of each hydrogen bridge in the planar proton conducting layer is one third. The energetically most favourable and therefore most probable arrangement may be expected to be that, where the four potential H-bonds adjacent to a given hydrogen bridge are deprived of protons (i.e. “empty”), next-nearest O–O pairs possess a proton and are thus forming H-bonds. This situation cannot however be permanent in the presence of proton conduction. The conduction process requires the appearance of “defects”, for instance by the temporary creation of nearest-neighbour (nn) H-bonds, nn “empty” O–O bonds or by the partial occupation of interstitial sites, such as in between two oxygens of selenate tetrahedra, but outside of the main conducting plane. In other proton conductors with similar structural units interstitial sites have

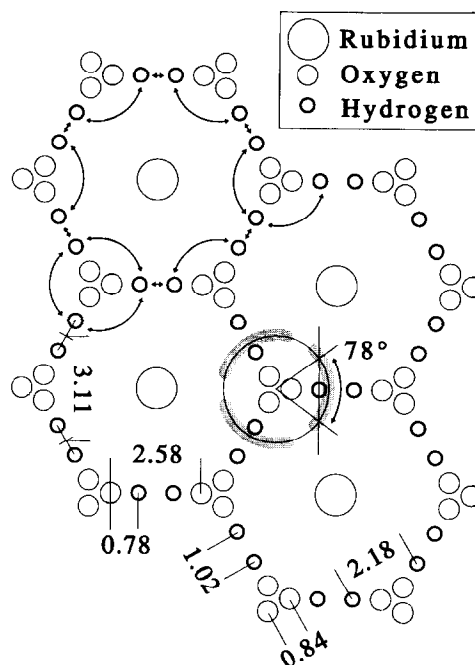


Fig. 3. Schematic picture of the proton conducting layer in the two-dimensional proton conductor TRHSe determined from Rietveld analysis of neutron powder data taken at 498 K. The translational and “rotational” motions (upper left) as well as the displacements of the hydrogen atoms, as derived from the bond length shortening (center), are shown. Important bond distances are given (in Å units).

been found [8]. We tried in vain to find such interstitial sites in the refinement procedure of TRHSe. Therefore the proton residence time in such sites, if they exist, must be very small. Nevertheless, in order to explain

Table 1

Important instrumental and structural parameters of the Rietveld refinement of the neutron powder investigation of TRHSe at 498 K. E2-diffractometer, HMI, $\lambda = 1.221$ Å. Space group $R\bar{3}m$, hexagonal setting: $a = 6.1291(1)$ Å, $c = 22.656(5)$ Å, $V = 737.1$ Å³, $u = 1.6(2)$, $v = -1.1(1)$, $w = 0.28(2)$. Calculated density 3.672 g/cm³.

| | This study | | | | Literature data [1] | | | |
|-------|------------|------------|-----------|-----------|---------------------|------------|------------|---------|
| | x/a | y/b | z/c | B | x/a | y/b | z/c | B |
| Rb(1) | 0.0 | 0.0 | 0.0 | 4.9(6) | 0.0 | 0.0 | 0.0 | 4.49(9) |
| Rb(2) | 0.0 | 0.0 | 0.2024(6) | 4.5(4) | 0.0 | 0.0 | 0.20308(4) | 4.90(7) |
| Se | 0.0 | 0.0 | 0.4092(5) | 3.6(3) | 0.0 | 0.0 | 0.41020(4) | 3.78(7) |
| O(1) | 0.1450(3) | -0.1450(3) | 0.5711(5) | see below | 0.1458(3) | -0.1458(6) | 0.5687(2) | 5.9(3) |
| O(2) | 0.046(1) | -0.046(1) | 0.338(1) | 2.9(8) | 0.041(2) | -0.041(2) | 0.3384(3) | 5.4(7) |
| H | 0.452(3) | 0.548(3) | 0.000(4) | 2(2) | - | - | - | - |

Atom B[1, 1] B[2, 2] B[3, 3] B[1, 2] B[2, 3] B[3, 1]

O(1) 4.5(2) 4.5(2) 13(1) 3.8(5) 0.8(1) -0.8(1)

Occupancies for O(2) = 0.33333 and for H = 0.16667.

R-factors: $R_{wp} = 15.6\%$, $R_{exp} = 6.1\%$, $R_1 = 13.7\%$.

the proton motion in TRHSe we would like to retain this third process as plausible: (3) movements of the hydrogens between structural sites and interstitial sites.

The complex proton diffusion mechanism will be discussed in more detail in [9] but within the present context the refined too short O–H distance of 0.78(3) Å needs some explanation. The breaking and formation of hydrogen bridges requires strong displacements of the hydrogens which could have the effect of an apparent bond length shortening due to the refinement model used. If we assume that the distance of 0.78(3) Å corresponds to the center-of-gravity of the proton's probability density distribution, this would imply a quite plausible O–H librational amplitude of about $\pm 39^\circ$ (calculated with an ideal value of an O–H bond of 1.0 Å; see the center of Fig. 3).

3.3. The low temperature phase of TRHSe at 298 K

The neutron powder diffractogram measured at 298 K and the graphical result of the Rietveld refinement are shown in Fig. 2 (lower part). The results of the refinement concerning structural and important instrumental parameters are listed in Table 2; again the structural parameters are in good agreement with literature data.

The structure of the low temperature phase is possibly reflected also in instantaneous local arrangements of the high temperature phase, which would be seen if one could take a snapshot. In this context it is convenient to compare the bonding parameters. The geometry of the hydrogen bridge in the rhombohedral and the

Table 3

Important interatomic distances and angles for the hydrogen bridge in the high temperature phase at 498 K as well as in the low temperature phase at 298 K of TRHSe as determined from Rietveld analysis of neutron powder data.

| | 498 K | 298 K ^a |
|------------------|------------------|---------------------------|
| O(2)–O(2) | 2.58(1) | 2.51(3) |
| O(2)–H | 0.78(3) | 1.1(1) |
| H–H | 1.02(3) | 0.4(1) |
| \angle O–H···O | 173(10) | 171(18) |
| Rb(1)–O(1) | 2.947(8) | 2.991 |
| Rb(1)–O(2) | 3.325(6) | 3.286 |
| Rb(2)–O(1) | 3.176(5) | 3.064 |
| Rb(2)–O(2) | 3.11(3) | 3.09(2) |
| O(1)–O(2) | 2.47(2); 2.89(2) | 2.61(3); 2.65(4); 2.70(4) |

^a For the low temperature phase some of the values are necessarily mean values.

monoclinic phase is presented in Table 3. As already mentioned the O(2)–H distance for the high temperature phase is apparently too small and reflects the shortcomings of the applied model for the oxygen and hydrogen disorder. In the low temperature phase the O(2)–H distance amounts to 1.1(1) Å which is a typical value for an O–H bond. Therefore the O–H librational amplitudes are much smaller than in the high temperature phase.

The O–H···O angle deviates in both phases not significantly from 180° but with a tendency towards lower angles. It is important to note that the hydrogen atoms are possibly displaced from the proton conducting plane as the hydrogen situated at a top of the selenate tetrahedron is rotated slightly away from the selenium

Table 2

Important instrumental and structural parameters of the Rietveld refinement of the neutron powder investigation of TRHSe at 298 K. E3-diffractometer, HMI, $\lambda = 1.851$ Å. Space group $A2/a$, unique axis b : $a = 10.491(1)$ Å, $b = 6.0955(9)$ Å, $c = 15.441(1)$ Å, $\beta = 102.89(1)^\circ$, $V = 962.5$ Å³, $u = 0.70(8)$, $v = -0.64(9)$, $w = 0.24(2)$. Calculated density 3.749 g/cm³.

| | This study $A2/a$ | | | | Literature data [2] | | | |
|-------|-------------------|----------|-----------|--------|---------------------|-----------|------------|---------|
| | x/a | y/b | z/c | B | x/a | y/b | z/c | B |
| Rb(1) | 0.25 | 0.748(5) | 0.0 | 2.7(4) | 0.25 | 0.7521(2) | 0.0 | 1.92(6) |
| Rb(2) | 0.653(2) | 0.742(3) | 0.1957(7) | 2.4(3) | 0.65176(7) | 0.7343(1) | 0.19486(4) | 2.17(5) |
| Se | 0.462(1) | 0.227(3) | 0.1150(6) | 2.5(3) | 0.46199(6) | 0.2267(1) | 0.11638(4) | 1.45(4) |
| O(1) | 0.403(2) | 0.018(5) | 0.155(1) | 1.9(3) | 0.3986(5) | 0.0172(7) | 0.1567(3) | 2.2(6) |
| O(2) | 0.442(2) | 0.178(3) | 0.006(1) | 3.0(5) | 0.4406(5) | 0.1767(8) | 0.0061(3) | 2.7(7) |
| O(3) | 0.620(2) | 0.243(4) | 0.1572(6) | 2.1(6) | 0.6190(4) | 0.2413(8) | 0.1547(3) | 2.3(7) |
| O(4) | 0.3878(6) | 0.456(4) | 0.128(1) | 3.3(7) | 0.3879(5) | 0.4535(7) | 0.1286(4) | 2.6(6) |
| H | 0.006(8) | 0.033(8) | 0.00(1) | 6(2) | 0.0 | 0.0 | 0.0 | 7(4) |

R-factors: $R_{wp} = 14.9\%$, $R_{exp} = 3.0\%$, $R_1 = 6.8\%$.

ion. This arrangement might support the migration of hydrogens into interstitial sites.

4. Conclusion

For the first time hydrogen positions have been determined by means of neutron powder Rietveld refinement for TRHSe in the rhombohedral high temperature proton conducting phase and in the low temperature phase. Standard structure refinement programs presently available do not permit a precise description of the proton and oxygen density distribution in the high temperature phase. Despite this shortcoming, the data given here allow a general description of the mechanism of proton conduction: it is a complex interaction of hydrogen and oxygen displacements combined with the breaking and formation of hydrogen bridges.

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