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STRUCTURE OF INORGANIC COMPOUNDS

Accurate Crystal Structure Refinement of Natrolite and Localization of Free Water

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Abstract—Crystals that contain water molecules spaced by distances excluding their chemical interaction are model systems for studying the so-called "water ferroelectricity": ordering of polar water molecules, interacting via electric dipole bonds. Natrolite crystal $Na_2(Al_2Si_3O_{10})(H_2O)_2$, which contains water molecules localized in cages (isolated cavities) formed by framework ions, has been investigated by X-ray diffraction (XRD) analysis at 93 K (sp. gr. $Fdd2$, $Z = 8$, $a = 18.24822(6)$ Å, $b = 18.59561(8)$ Å, $c = 6.57868(4)$ Å, $R1(|F|)/wR2(|F|) = 1.149/1.294\%$, and $\Delta\rho_{\min}/\Delta\rho_{\max} = -0.19/0.17$ e/Å^3 for 11 145 independent reflections). Hydrogen atomic parameters have been refined in the anisotropic approximation of atomic displacements, which made it possible to determine the orientation of water molecules. The mineral under investigation is a model object for spectroscopic analysis of water ferroelectricity.

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INTRODUCTION

Traditionally, nanoinclusions (atoms or molecules) in minerals with pores and channels have been of interest for geologists. These media can be used in practice, e.g., as matrices for storing radioactive waste and as molecular filters. Recently, researchers have been interested in these objects from the fundamental point of view, because inclusions may interact in a special way. In particular, the systems with inclusions in the form of polar water molecules have attracted attention. In the absence of chemical interaction, short-range mutual ordering of the dipole moments of water molecules may occur because of the long-range electric dipole forces. This phenomenon may manifest itself in various (both inorganic and biological) systems.

The ordered state of water molecules in a beryl crystal was revealed recently using spectroscopic analysis [1]. These systems cannot be investigated if the atomic parameters of water molecules and hydrogen atoms entering their composition are unknown. Accurate and reliable information about the characteristics of hydrogen atoms is important for studying the energy of atomic interactions in technological, biological, and pharmaceutical materials. On the whole, the role of hydrogen in chemistry, biology, and medicine can hardly be overestimated. The most important problem of materials science is the development of hydrogen-storage devices, which may help in solving many climatic and ecological problems.

Despite the importance of this subject and the interest of researchers in it [2, 3], the difficulties in determining accurately the coordinates of hydrogen atoms based on X-ray diffraction (XRD) data are well known. In the XRD analysis, one must take into account the mismatch between the maximum in the electron density distribution of a hydrogen atom and the center of hydrogen nucleus because of the chemical interaction in water molecule. It is not surprising then that the corresponding distances found based on XRD data in routine studies are much shorter than those obtained in neutron diffraction analysis, where proton serves a scattering center. The determination of hydrogen atom displacement parameters in the anisotropic approximation is even more difficult. To get around this problem, it is usually recommended to use neutron diffraction, which cannot be considered a cost-effective solution. It should be emphasized that the lengths of H–O bonds and hydrogen atomic displacements in the anisotropic approximation, obtained by analyzing neutron diffraction databases, should not be absolutized. Because of the instrumental limitations (primarily, relatively large neutron wavelength and, correspondingly, low resolution in interplanar distances), neutron diffraction data are not always reliable. In addition, the purpose of a specific study is most often not restricted to diagnostics of hydrogen atoms; therefore, neutron diffraction analysis may be insufficiently accurate in some cases.

An interesting alternative was proposed in the series of studies by Madsen, which was implemented on the SHADE web-server [4]. In some cases, one can assume that hydrogen atom displacements have two components, one of which is due to the partition of hydrogen atom in the common vibrations of surrounding atoms, and the other presents its intrinsic displacements [5]. The latter are estimated based on neutron diffraction data, and the common vibrations are calculated using the TLS procedure [6]. This means that the method can be applied to molecular crystals, and the minimum condition for its applicability is to satisfy the Hirshfeld rigid-bond test [7]. For the crystal under study, this method is inapplicable in both criteria.

The general approach to the solution of complex problems related to the parameter refinement for structural models, based on experimental data using minimization methods, similar to the least-squares method, is to increase the number and variety of measurements [8]. Due to the physics of X-ray scattering from a vibrating atom, large-angle scattering is most informative for determining the atomic displacements. Having considered additionally the contributions from high-angle reflections in the structural model refinement, one can increase significantly the reliability of determining the atomic displacement parameters (especially, the anharmonic ones).

According to the approach [8], the structural model of cordierite mineral was refined as $(Mg_{1.643}Mn_{0.001}Fe_{0.137}Al_{0.104}Ca_{0.002})Al_3(Al_{0.921}Si_{5.079})O_{18} \cdot [(H_2O)_{0.756}Na_{0.041}K_{0.001})]$ (a simplified chemical formula is $(Mg,Fe,Al)_2Al_4Si_5O_{18}$), and the coordinates of alternating water and carbon dioxide molecules, located in vertical channels at the level $z = 1/4$, were determined in [9]. It was shown that there are several orientations of water molecules with intense inter-orientational transitions. Specifically, ordered orientations of H_2O molecules (forming a long-range-order network) are unlikely to exist in the temperature range of 91–295 K. Along with physicochemical reasons, the localization of water molecules in cordierite is hindered by their small amount: many of unit cells do not contain H_2O and CO_2 molecules; the site occupancies by water and carbon dioxide molecules are ~9 and ~12%, respectively.

The object of this study is a crystal of natrolite: hydrated aluminosilicate zeolite $(Na_2Al_2Si_3O_{10} \cdot 2H_2O$, orthorhombic sp. gr. $Fdd2$). The zeolite-group minerals, described by the general formula $(M^+,M^{2+}_{0.5})_x[Al_xSi_yO_{2(x+y)}](H_2O)_n$, are crystalline compounds, whose structure is characterized by a framework consisting of linked tetrahedra, each formed by four oxygen atoms surrounding a cation [10]. In the case of natrolite, the main structural block is a fragment consisting of two AlO_4 and three SiO_4 tetrahedra. This framework contains open cavities in the form of channels and cages (isolated voids). The voids are filled with extraframework cations (Na^+ in our case) and water molecules. In nature, natrolite is often found in the form of transparent columnar crystals, jointly with analcime $(NaAlSi_2O_6) \cdot H_2O$.

There are several minerals in the natrolite subgroup of zeolite group. In addition to natrolite, paranatrolite $(Na_2Al_2Si_3O_{10} \cdot 3H_2O$, monoclinic sp. gr. Cc) and tetranatrolite (or gonnardite, $(Na,Ca)_{16}[Al_{19}Si_{21}O_{80}] \cdot nH_2O$, tetragonal sp. gr. $I\bar{4}2d$) are also of interest. The relationship of the structures in the natrolite subgroup had been widely discussed in [11–13]. Paranatrolite [14] and tetranatrolite [15] were found in Quebec, Canada. In Russia, paranatrolite was discovered for the first time in the Lovozero and Khibiny massifs [16]. The paranatrolite structure was refined using the XRD data in [17] within the anisotropic approximation of hydrogen atom displacements. The hydrogen atom coordinates were obtained by neutron diffraction analysis [18] and fixed during refinement. The reasons for stabilizing the paranatrolite structure were discussed in [19].

Tetranatrolite is the product of paranatrolite dehydration (note that the dehydration reaction is reversible [20]). Hydration/dehydration of natrolite under pressure not only causes structural transformation [21], but also leads to the formation of well-ordered one-dimensional chains of water molecules [22]. The tetranatrolite crystal structure was studied in [23]. Temperature variations in the tetranatrolite structure were analyzed in [24]. Natrolite belongs to the orthorhombic system and has selected directions, based on which one can draw unambiguous conclusions about the orientation of dipole moments of water molecules. In contrast to cordierite, water molecules in this mineral occupy regular cage cells of the framework (i.e., exhibit complete occupancy), which should facilitate characterization of water molecules.

The natrolite structure was determined for the first time using XRD analysis in [25, 26]. In view of the complexity of structural analysis of this mineral, studies were carried out several times [27, 28]. In [29], hydrogen atom positions in the natrolite structure were determined, and a network of hydrogen bonds was constructed based on difference Fourier electron density maps using modern equipment. The O–H distances found in [29] are obviously underestimated. The estimation was carried out based on 8136 measured and 1495 independent reflections at the obtained model–experiment goodness of fit $R1(|F|) = 2.85\%$ for the reflections with statistically significant intensities ($I > 2\sigma(I)$). This accuracy is insufficient for the detailed analysis of the orientations of dipole moments of water molecules in a natrolite crystal. We should also note the results of [30], where ordering of water molecules in natrolite was initiated under pressure. Hydration/dehydration of natrolite was studied in [31]. The most reliable data on the positional parameters of hydrogen atoms were obtained using neutron diffraction analysis [32]; however, the hydrogen atom displacement parameters are somewhat overestimated, possibly, because of the insufficient resolution ($\sin\theta/\lambda \leq 1.05$ Å^{-1}, 2176 independent reflections, $R1(F^2) = 5.4\%$). Thus, the accurate refinement of natrolite structure is an urgent problem.

The purpose of this work was to determine the atomic structure of mineral natrolite with an accuracy sufficient for obtaining water molecule parameters by the XRD method. In the methodical plan, we intended to formulate recommendations facilitating the structural diagnostics of water molecules and hydrogen atoms in crystals.

EXPERIMENTAL

Natrolite sample was purchased online (the origin country of is India). A sample in the form of an ellipsoid with axes 0.30 and 0.38 mm long was prepared for XRD analysis. XRD experiment was performed on an Xcalibur diffractometer (Rigaku Oxford Diffraction) with an EOS S2 CCD detector (MoK_α radiation with a wavelength $\lambda = 0.71073$ Å; the nominal temperature is 87 K). The sample was cooled using a Cobra Plus cryosystem (Oxford Cryosystems) with an open cold nitrogen flow directed to the sample. To carry out low-temperature XRD experiments on this equipment, one must take into account that there is a temperature gradient between the temperature sensor mounted in a cryostreamer nozzle and the sample (spaced by up to 12 mm from the sensor). A calibration performed in [33] showed the real sample temperature to be 93 K. A representative dataset was experimentally obtained: the reciprocal-space coverage was more than 99.5% at the maximum reflection-scattering angle $\theta = 74.4^{\circ}$ and data redundancy of more than five.

The integral intensities were calculated based on the diffraction patterns using the CrysAlisPro software [34]. The data processing included the following stages: consideration of the geometric features of measurements (Lorenz correction) and beam polarization correction; diffractometer calibration [35, 36]; absorption correction for ellipsoidal samples [37]; and correction for thermal diffuse scattering [38] with elastic constants [39]. Equivalent reflections were averaged using the average-intensity estimation by nonparametric statistics [40], and the half-wavelength contribution was refined [41]. The extinction correction was not introduced, because (in contrast to [32]) it barely affects the refinement procedure. The introduction of all corrections and refinement of structure parameters were performed using the ASTRA software [42]. Fourier syntheses of electron density were constructed using the Jana2006 program [43]. The graphical constructions were obtained using the Diamond [44] and Vesta [45] software. The details of the X-ray experiment and structure refinement parameters for natrolite at 93 K are listed in Table 1. The atomic coordinates, equivalent isotropic rms values of atomic displacements, and anisotropy of atomic displacements (ellipsoidality ε [46]) are summarized in Table 2. The structural data were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1999308).

Table 1. Crystallographic characteristics, details of the X-ray experiment, and structure refinement parameters for the natrolite crystal $Na_2(Al_2Si_3O_{10})(H_2O)_{28}$

T, K	93
a, b, c, Å	18.24822(6)*, 18.59561(8), 6.57868(2)
V, Å^3	2232.39(1)
μ, mm^{-1}	0.721
Diffractometer	Xcalibur EOS S2 CCD
Radiation; λ, Å	MoK_α; 0.71073
Scan mode	ω
Ranges of indices h, k, l	$-49 \leq h \leq 48$, $-48 \leq k \leq 45$, $-17 \leq l \leq 17$
θ_{max}, deg	74.4
Number of measured reflections	57484
Redundancy**	5.04
$\langle\sigma(F^2)/F^2\rangle$	0.0253
$R1_{av}(F^2)/wR2_{av}(F^2)$, %	1.49/1.40
Number of reflections/refined parameters	11145/130
$R1(\lvert F\rvert)/wR2(\lvert F\rvert)$, %	1.149/1.294
S	1.00
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	–0.19/0.17

* Precision declared by the diffractometer software, which exceeds by a factor of about 10 the real accuracy, obtained, e.g., in repeated experiments.

** Redundancy is the ratio of the number of measured reflections to the number of independent reflections used in refinement. The averaging-precision criteria are as follows: $\langle\sigma(F^2)/F^2\rangle = \{\sum_i[\sigma(F^2)/F^2]\}/N \approx \{\sum_i[\sigma(F^2)]/\sum_i[F^2]\}$, $R1_{av}(F^2) = \sum_j[\sum_i|F_i^2 - \langle F^2\rangle|]/\sum_j[\sum_i\langle F^2\rangle]$, and $wR2_{av}(F^2) = \sqrt{}\{\sum_j[\sum_i w(F_i^2 - \langle F^2\rangle)^2]/\sum_j[\sum_i w(\langle F^2\rangle)^2]\}$. The refinement-precision criteria are $R1(|F|) = \sum||F_{obs}| - |F_{calc}||/\sum|F_{obs}|$ and $wR2(|F|) = \sqrt{}\{\sum w(|F_{obs}| - |F_{calc}|)^2/\sum w(F_{obs})^2\}$.

RESULTS AND DISCUSSION

Determination of the Natrolite Structure

The parameters of the framework, consisting of AlO_4 and SiO_4 tetrahedra, were determined easily. The initial structural model was taken from [32]. Note that the origins of coordinates in [29, 32] differ. It was

Table 2. Atomic coordinates, equivalent thermal parameters U_{eq}, and ellipsoidalities ε [46] of atomic displacements in the natrolite crystal at 93 K

Atom	Site	x/a	y/b	z/c	U_{eq}, Å^2	ε
Si1	8*a*	0	0	0	0.003436(14)	0.0051
Si2	16*b*	0.152745(3)	0.211672(3)	0.622566(11)	0.003246(9)	0.0033
Al1	16*b*	0.036861(4)	0.094183(4)	0.615131(13)	0.003358(11)	0.0028
Na1	16*b*	0.220688(6)	0.030672(6)	0.617389(19)	0.006896(19)	0.0068
O1	16*b*	0.022139(9)	0.068983(9)	0.86666(3)	0.00634(2)	0.0191
O2	16*b*	0.069250(8)	0.182731(8)	0.60946(3)	0.00452(2)	0.0179
O3	16*b*	0.098442(9)	0.035421(9)	0.50070(3)	0.00597(2)	0.0104
O4	16*b*	0.205712(9)	0.152434(10)	0.72476(3)	0.00585(3)	0.0186
O5	16*b*	0.179917(9)	0.227874(10)	0.38981(3)	0.00652(3)	0.0173
O6	16*b*	0.05612(2)	0.18976(2)	0.11096(6)	0.00905(7)	0.0074
H1	16*b*	0.0513(4)	0.14340(18)	0.0433(9)	0.019(2)	0.0407
H2	16*b*	0.10281(18)	0.1913(4)	0.1794(9)	0.015(2)	0.0484

Occupancies of all atomic sites are unity.

found that natrolite is crystallized into the sp. gr. *Fdd*2 with the following unit-cell parameters: a = 18.24822(6) Å, b = 18.59561(8) Å, and c = 6.57868(4) Å; Z = 8.

Within the framework, one can select a fragment consisting of three SiO_4 and two AlO_4 tetrahedra. Two $Si2O_4$ tetrahedra with a cation at the level $z \sim 0.373$ and two AlO_4 tetrahedra at the level $z \sim 0.615$ form four-membered rings. They are linked by the fifth $Si1O_4$ tetrahedron ($z = 0$). The fragments are arranged in the form of continuous chains along the c axis (Fig. 1a). Columns or needles, which form crystals during growth, are elongated in this direction. In the perpendicular directions, chains are linked by oxygen atoms. Channels in the structure contain two sodium ions and two water molecules. Na^+ ions are surrounded by four O^{2-} ions and two H_2O molecules (Fig. 1b).

It is known that zeolites belong on the whole to the group of nonstoichiometric crystallohydrates, which exhibit high variability in composition. Nevertheless, natrolite samples with weak Si–Al disordering were described [47]. A similar case is considered in this study. SiO_4 and AlO_4 tetrahedra share the O2–O3 and O2–O4 edges with Na prisms (Fig. 1a). O6 atoms, which do not have nearest cation neighbors (except for two Na^+ ions), occupy the two remaining vertices of Na prisms. The weaker bonds of O6 atoms with SiO_4 and AlO_4 tetrahedra are hydrogen bonds O6–H1···O1 and O6–H2···O5 with lengths of 1.884(5) and 2.088(5) Å, respectively (Fig. 1c). Therefore, the water molecule H1–O6–H2 can be considered as a group that is not very rigidly linked with the framework.

Thus, the atomic configuration in natrolite exhibits the following features. On the one hand, water molecules are connected with the framework and are present in a sufficient large amount in its cells (nanopores) (in contrast to the case of cordierite crystal [9], where it was necessary to localize a trace amount of free water in channels). At the same time, hydrogen atoms are terminal, and the electric dipole interaction between water molecules may be quite sufficient for rotation and ordering of both hydrogen atoms and water molecules as a whole. The network of water molecules in the cells of natrolite framework (Fig. 2) allows for summation of the electric dipole contributions from individual molecules.

Formation of the Atomic Model of Water Molecules in Natrolite

Is the sensitivity of structural analysis sufficient for refining the parameters of water molecule using a conventional model of independent atoms? Generally, the anisotropic atomic displacement parameters (ADPs) of hydrogen are determined in neutron diffraction experiments and fixed in XRD analysis. Rather promising are the results of [48], where a possibility of accurate localization of hydrogen atoms using XRD data was reported. To this end, one must use complex electron density models: multipole model [49] or Hirshfeld atom refinement [50].

The following question should be answered: to what extent one can increase the amount of experimental data instead of complicating simulation? The general rule for increasing the amount of data necessary for making results more reliable [8] is as follows: an increase in the number of measured high-angle reflections increases the accuracy in determining ADPs. In any model, hydrogen ADPs can be refined in the anisotropic approximation only in rare cases of especially accurate experimental data, obtained using the following tools: careful sample preparation, sam-

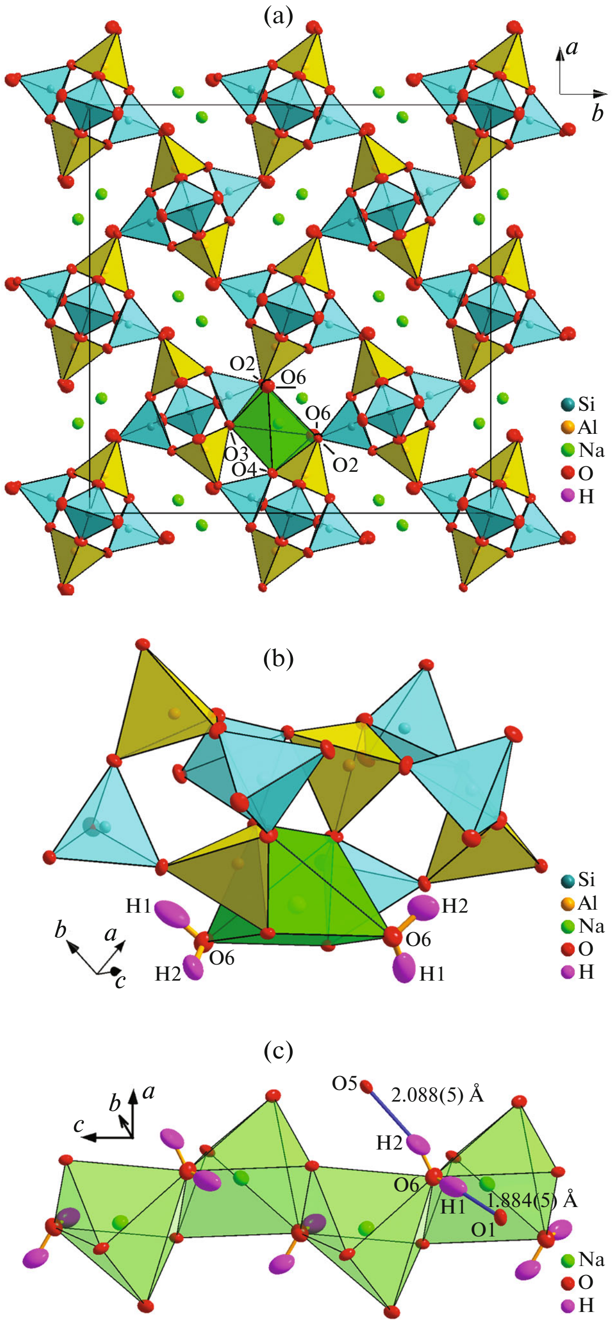

Fig. 1. Structure of mineral natrolite: (a) general motif as a framework composed of fragments formed by (dark) three SiO_4 and (bright) two AlO_4 tetrahedra, linked by triangular Na prisms (one prism is shown, hydrogen atoms are omitted); (b) two fragments consisting of SiO_4 and AlO_4 tetrahedra, Na^+ ions are located in the void between them, their oxygen environment is a prism, and the water molecule H1–O6–H2 is in an isolated cell; and (c) water molecules H1–O6–H2 surround Na^+ ions, which form elongated chains along the cell axis *c* (the oxygen atom O6 is bounded moderately with only two nearest sodium atoms). The boundaries of ADP ellipsoids are calculated for the probabilities of (a) 99 and (b, c) 90%.

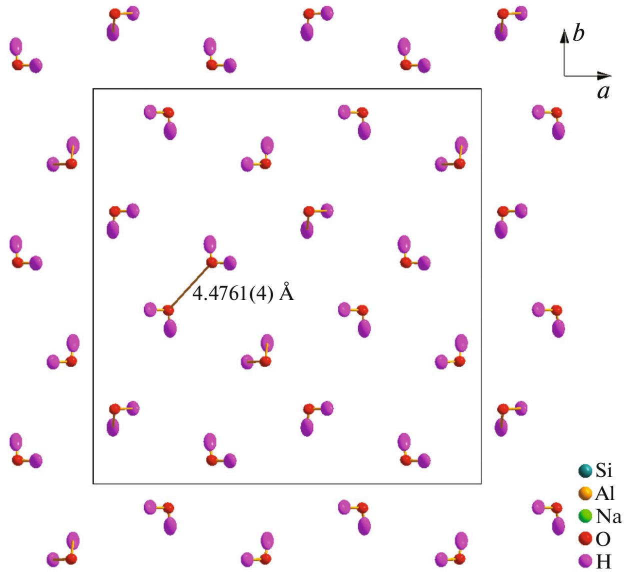

Fig. 2. Motif of the water-molecule network in natrolite. The boundaries of ADP ellipsoids of are calculated for a probability of 95%.

ple cooling, and increase in the number of measured reflection intensities. The data collection time was increased to 122 h upon extremely slow scanning of high-angle reflections (260 s/deg). The XRD experiment was carried out under rare conditions: long duration; high resolution in interplanar distance ($\sin\theta/\lambda \le$ 1.36 $Å^{-1}$); and redundancy of more than five, which was sufficient to cover the reciprocal space by 99.55% at this ultrahigh resolution. These conditions made it possible to measure a large number of the reflection intensities, which yielded in final refinement 11 145 independent reflections (averaged at low reliability factor $R1_{av}(F^2)$ = 1.49%), obtained after reduction of intensities (removal of contributions from all effects accompanying elastic coherent diffraction). In particular, the thermal diffuse scattering correction decreases the refinement *R* factors by 0.02–0.03% and improves the statistical criteria for high-angle reflections.

Due to accurate corrections, even the incomplete structural model of natrolite, which contains 10 atoms and 87 parameters (with hydrogen atoms disregarded), was refined to the criteria $R1(|F|)/wR2(|F|)$ = 1.208/1.470%. In the difference Fourier electron density map, peaks H1 and H2 were found in the vicinity of the O6 atom at distances of 0.859 and 0.964 Å, respectively. The maximum height of these peaks was $\Delta\rho_{max}$ = 0.3 e/$Å^3$ (Fig. 3a). After the refinement of hydrogen atom parameters in the isotropic approximation (with constraints imposed on the O–H distances), the difference density was reduced and refinement *R* factors were significantly statistically decreased at a confidence level of 0.9999 [51]. The H2 and H1 atoms are located, respectively, above and

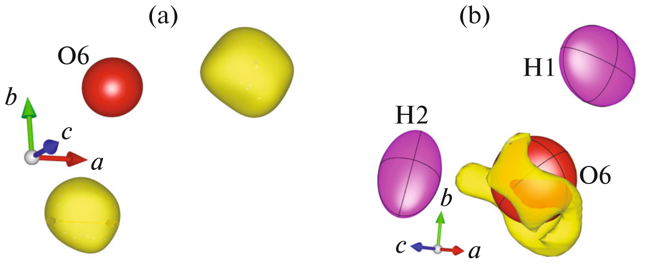

Fig. 3. Three-dimensional difference electron density map in the vicinity of water molecule: (a) with hydrogen atoms disregarded in the model (the oxygen atom O6 in the anisotropic approximation and isosurfaces of hydrogen atoms with a boundary of 0.2 e/Å^3) and (b) in the final model (hydrogen atoms have anisotropic ADPs, the oxygen atom O6 is refined in the anharmonic approximation).

below the horizontal plane passing through the center of the O6 atom. The transition to anisotropic ADPs for hydrogen atoms improved additionally the criteria. Nevertheless, large displacements U_{eq} of the O6 atom were observed at surprisingly small anisotropy (ellipsoidality ε [46]) and significant residual density in the vicinity of this atom. The terminal nature of the H_2O molecule does not exclude possibility of its anharmonic displacement. The expansion of the model to take into account the anharmonic component of O6 displacements up to the fourth rank was related to the attempt to improve the model goodness of fit and difference-map purity. This was implemented only partially: there remains a small residual density in the region of the O6 atom (Fig. 3b). The anharmonic model was chosen for another (main) reason: the values of hydrogen ADPs was decreased one and a half times (Fig. 4a). The Hamilton–Fisher test [51] reliably confirmed the statistical significance of the expanded models: addition of hydrogen atoms in the isotropic approximation to the structural model, transition to anisotropic displacements of hydrogen atoms, and transition to anharmonic displacements of oxygen atoms O6. The structure refinement was finished at a precise level (a = 18.24822(6) Å, b = 18.59561(8) Å, c = 6.57868(4) Å, sp. gr. $Fdd2$, Z = 8, $\sin\theta/\lambda \le 1.35$ Å^{-1}; $R1(|F|)/wR2(|F|)$ = 1.149/1.294%, $\Delta\rho_{min}/\Delta\rho_{max}$ = –0.19/0.17 e/Å^3) for a set of 11 145 independent reflections, including 1169 reflections with $F^2 < 2\sigma(F^2)$.

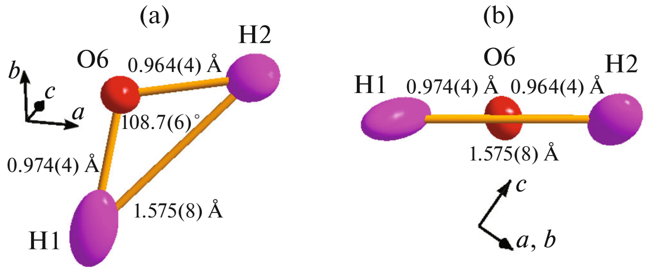

Fig. 4. (a) Geometry and (b) orientation of water molecules in the natrolite crystal.

Let us discuss the reliability of the hydrogen-bond parameters obtained in this refinement. To this end, we will compare the results from three sources: this study and [29, 32] (Table 3). Unique study [32] was performed on a neutron point-detector diffractometer at 20 K. This study and [29] were carried out on X-ray CCD diffractometers of one generation, produced approximately at the same time. It can easily be seen that the results of this study and [32] are close and their accuracies are comparable. The results of [29] exhibit a much worse relative precision and sometimes incorrect magnitudes, because experimental data of insufficiently high resolution were used in it.

The above example clarifies the limitedness of some conclusions and recommendations related to the determination of hydrogen-bond parameters in crystals based on XRD data. The analytical materials devoted to the estimation of the parameters of hydrogen atoms in crystals are generally based on the data on organic crystals, where, at best, the resolution is up to d = 0.6 Å and the model reliability factor is as low as $R1(|F|)$ > 2–3%. In this study, the resolution is d =

Table 3. Comparison of the hydrogen bond parameters in the natrolite crystal

Reference	O6–H···O*n*	O6–H, Å	H···O*n*, Å	O6···O*n*, Å	O6–H···O*n*, deg
[32]	O6–H1···O1	0.974(2)	1.877(2)	2.830(1)	165.6(2)
[32]	O6–H2···O5	0.964(2)	2.103(2)	2.999(1)	153.8(2)
[29]	O6–H1···O1	0.73(4)	2.38(4)	3.009(3)	144(4)
[29]	O6–H2···O5	0.66(4)	2.21(4)	2.848(3)	162(5)
This study	O6–H1···O1	0.974(4) 0.906(4)*	1.884(5)	2.8304(4)	163.2(6)
This study	O6–H2···O5	0.964(4) 0.892(4)*	2.088(5)	2.9951(4)	156.2(5)

* At free refinement of all atomic coordinates.

0.36 Å and the relative reliability factor is $R1(|F|) = 1.1\%$. Moreover, when a conventional refinement criterion ($F > 4\sigma(F)$) is used, we obtain R factors of less than 0.8% for about 9000 reflections. The data of such high precision are rarely included in reviews and tests and do not affect statistics; therefore, the potential of refining hydrogen atom parameters using reliable data, similar to those obtained in this study, remains unknown.

To perform structural diagnostics of natrolite, which is necessary for spectroscopy and quantum-mechanical calculations, one had to solve two problems: find correct oxygen–hydrogen distances and describe hydrogen atom displacements in the anisotropic approximation. The oxygen–hydrogen distances were refined using the restrictions imposed on them in correspondence with the neutron diffraction data obtained in [32]. Removal of restrictions and full-matrix refinement gives rise to somewhat shorter O–H distances (Table 3); however, they remain within the average values of O–H bond lengths (0.9–1.0 Å). These distances correspond to the results of neutron diffraction experiments deposited with the Cambridge Crystallographic Data Centre [52] and lie in the range of values characteristic of the charge density studies using the multipole model or the Hirshfeld atom refinement [48].

The anisotropic ADPs of both hydrogen atoms were obtained in free refinement without restrictions. Thus, both complex problems are solved using the XRD data obtained under laboratory conditions, without neutron diffraction experiments. However, the determination of O–H distances still requires additional methodological investigations. Evident advantages can easily be obtained when passing to a laboratory Ag-radiation source with a shorter wavelength and increasing the number of measurements by 30–50%.

Can piezoelectric ordering of water molecules in a natrolite crystal be detected? This question can be answered using spectroscopic analysis. A structural analysis only makes it possible to estimate the potential possibility of this phenomenon, which can be made conveniently by comparing with the results of studying a similar problem in a cordierite crystal [9]. Water molecules in cordierite are located in relatively lacy channels. The minimum distance between water oxygen atoms is 4.674 Å. Their number is small: approximately only a tenth part of cells contain water molecules. Therefore, the effective water–water distance is significantly longer, and the electrical field formed by this system of dipoles is expected to be relatively weak. The thermal motion of atoms at room and liquid-nitrogen temperatures can easily disorder this structure. Dipoles are ordered only at temperatures below 3 K [9]. On the one hand, water molecules in natrolite are connected with the framework and, therefore, one should expect their orientation along the long-range fields of the entire lattice (rather than alignment with respect to each other). On the other hand, water-oxygen atoms O6 are located closer to each other than in cordierite (d(O6–O6) = 4.4761(4) Å), and the degree of nanopore filling with water molecules is higher. Moreover, these atoms are detached: bonds of moderate strength are implemented between them and Na^+ cations (d(Na–O6) = 2.3802(4) Å). The equivalent isotropic rms displacements of O6 atoms are unusually large (0.009 against 0.004–0.006 Å^2 for other five oxygen atoms). Even the anharmonic model of displacements of O6 atoms does not remove completely the residual electron density in the vicinity of O6. The Hirshfeld rigid-bond test [7] for the natrolite structure is not satisfied for only the O6, H1, and H2 atoms. In addition, there is a not quite rigid Na–O2 bond of the Na^+ cation bound with water molecule (the nearest atom is O2 at a distance of 2.49723(15) Å). Thus, water molecules are indeed weakly bound with the framework, due to which they can be ordered. The directions of preferred hydrogen atomic vibrations and dipole-moment direction can clearly be observed (Fig. 4b). In essence, a water molecule is a terminal group, and one might expect it have additional degrees of freedom in comparison with purely framework anions.

Thus, the XRD data indicate that natrolite mineral is a convenient object for studying water ferroelectricity by spectroscopic methods, because this mineral contains a bulk three-dimensional network of polar water molecules with some degree of mobility.

CONCLUSIONS

Accurate XRD analysis of water-containing mineral natrolite ($Na_2(Al_2Si_3O_{10})(H_2O)_2$), which is a promising candidate for studying the water ferroelectricity by spectroscopic methods, was carried out. The electric dipole ordering of polar water molecules is an important process in many phenomena in animate and inanimate nature.

The structural analysis yielded experimental data of ultrahigh resolution, large amount, and high completeness and precision: $\sin\theta/\lambda \le 1.36$ Å^{-1}; $R1(|F|)/wR2(|F|) = 1.149/1.294\%$, $\Delta\rho_{\min}/\Delta\rho_{\max} = -0.19/0.17$ e/Å^3. The atomic structure parameters were refined based on the dataset consisting of 11 145 independent reflections for the model from 130 refined parameters (about 86 measurements per parameter). A complete dataset was used, which included 1169 reflections with $F^2 < 2\sigma(F^2)$ (without rejection of weak and defect reflections).

The crystallochemical analysis revealed signs of weakness of the bonds of water molecules with the framework. A complex problem of localization of hydrogen atoms in water molecules was solved in the anisotropic approximation of atomic displacements. The found parameters of water molecules are in good agreement with the neutron-diffraction results, and their reliability exceeds significantly that of known XRD data.

The study was successful due to the use of efficient original techniques based on the method of interexperimental comparison [8]. The analysis of the literature and authors's experience gave grounds to suggest that the main reason for the failure in determining correct hydrogen bonds parameters in crystals from XRD data is the lack of high-resolution measurements (rather than objective limitations related to the physics of X-ray scattering, as was believed).

The obtained data on the orientation of water molecules, their motif, and degree of freedom of their vibrations made it possible to conclude that natrolite is a convenient object for studying the water ferroelectricity by spectroscopic methods. The necessary data for carrying out molecular-dynamic calculations and planning spectroscopic studies are accumulated in this structural study.

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REFERENCES

1. B. P. Gorshunov, V. I. Torgashev, E. S. Zhukova, et al., Nat. Commun. **7**, 12842 (2016).
2. P. Müller, R. Herbst-Irmer, A. L. Spek, et al., *Hydrogen Atoms,* in Crystal Structure Refinement: A Crystallographer's Guide to SHELXL, Ed. by P. Müller (International Union of Crystallography Texts on Crystallography) (Oxford Univ. Press, New York, 2006), No. 8, Ch. 3.
3. A. A. Hoser, M. Paulina, P. M. Dominiak, and K. Wozniak, Acta Crystallogr. A **65**, 300 (2009).
4. A. O. Madsen, J. Appl. Crystallogr. **39**, 757 (2006).
5. P. Munshi, A. O. Madsen, M. A. Spackman, et al., Acta Crystallogr. A **64**, 465 (2008).
6. V. Schomaker and K. N. Trueblood, Acta Crystallogr. B **24**, 63 (1968).
7. F. L. Hirshfeld, Acta Crystallogr. A **32**, 239 (1976).
8. A. P. Dudka, Crystallogr. Rep. **47** (1), 152 (2002).
9. A. P. Dudka, M. A. Belyanchikov, V. G. Tomas, et al., Poverkhn.: Rentgenovskie, Sinkhrotronnye. Neitr. Issled. **63** (7), 1 (2020).
10. D. S. Coombs, A. Alberti, T. Armbruster, et al., Can. Mineral. **35**, 1571 (1997).
11. G. Artioli and E. Galli, Am. Mineral. **84**, 1445 (1999).
12. H. T. Evans, J. A. Konnert, and M. Ross, Am. Mineral. **85**, 1808 (2000).
13. Y. Lee, J. A. Hriljac, J. B. Parise, and T. Vogt, Am. Mineral. **91**, 247 (2006).
14. G. Y. Chao, Can. Mineral. **18**, 85 (1980).
15. T. T. Chen and G. Y. Chao, Can. Mineral. **18**, 77 (1980).
16. A. P. Khomyakov, G. E. Cherepivskaya, and M. G. Mikheeva, Dokl. Akad. Nauk SSSR, **288** (1), 214 (1986).
17. F. Pechar, Cryst. Res. Technol. **23** (5), 647 (1988).
18. F. Pechar, W. Schafer, and G. Will, Z. Kristallogr. **164**, 19 (1983).
19. Y. Lee, J. A. Hriljac, J. B. Parise, and T. Vogt, Am. Mineral. **90**, 252 (2005).
20. Yu. V. Seryotkin and V. V. Bakakin, Eur. J. Mineral. **19**, 593 (2007).
21. Y. Lee, T. Vogt, J. A. Hriljac, et al., J. Am. Chem. Soc. **124**, 5466 (2002).
22. Y. Lee, C. D. Martin, J. B. Parise, et al., Nano Lett. **4** (4), 619 (2004).
23. M. G. Mikheeva, D. Yu. Pushcharovskii, A. P. Khomyakov, and H. A. Yamnova, Kristallografiya **31** (3), 434 (1986).
24. Y. Lee, J. A. Hriljac, and T. Vogt, Am. Mineral. **90**, 247 (2005).
25. W. H. Taylor, C. A. Meek, and W. W. Jackson, Z. Kristallogr. **84**, 373 (1933).
26. W. M. Meier, Z. Kristallogr. **113**, 430 (1960).
27. N. E. Ghermani, C. Lecomte, and Y. Dysausoy, Phys. Rev. B **53**, 5231 (1996).
28. W. H. Baur, D. Kassner, C.-H. Kim, and N. H. Sieber, Eur. J. Mineral. **2**, 761 (1990).
29. F. Capitelli and M. G. Derebe, J. Chem. Crystallogr. **37**, 583 (2007).
30. Yu. V. Seryotkin, A. Yu. Likhacheva, and S. V. Rashchenko, J. Struct. Chem. **57** (7), 1377 (2016).
31. H.-W. Wang and D. L. Bish, Eur. J. Mineral. **22**, 271 (2010).
32. G. Artioli, J. V. Smith, and A. Kvick, Acta Crystallogr. C **40**, 1658 (1984).
33. A. P. Dudka, I. A. Verin, and E. S. Smirnova, Crystallogr. Rep. **61** (4), 692 (2016).
34. Rigaku Oxford Diffraction, *CrysAlisPro Software System, Version 1.171.40.64* (Rigaku Corporation, Oxford, UK, 2019).
35. A. Dudka, J. Appl. Crystallogr. **43** (6), 1440 (2010).
36. A. P. Dudka, Crystallogr. Rep. **60** (4), 601 (2015).

37. A. P. Dudka, Crystallogr. Rep. **50** (6), 1068 (2005).

38. A. P. Dudka, M. Kh. Rabadanov, and A. A. Loshmanov, Kristallografiya **34** (4), 818 (1989).

39. C. Sanchez-Valle, S. V. Sinogeikin, Z. A. D. Lethbridge, et al., J. Appl. Phys. **98**, 053508 (2005).

40. A. P. Dudka, Crystallogr. Rep. **63** (6), 1051 (2018).

41. A. Dudka, J. Appl. Crystallogr. **43**, 27 (2010).

42. A. Dudka, J. Appl. Crystallogr. **40**, 602 (2007).

43. V. Petricek, M. Dusek, and L. Palatinus, Z. Kristallogr. **229** (5), 345 (2014).

44. K. Brandenburg, *Diamond. Ver. 3.1* (Crystal Impact GbR, Bonn, Germany, 1999).

45. K. Momma and F. Izumi, J. Appl. Crystallogr. **44**, 1272 (2011).

46. A. P. Dudka and B. V. Mill', Crystallogr. Rep. **59** (5), 689 (2014).

47. P. S. Neuhoff, S. Kroeker, L.-S. Du, et al., Am. Mineral. **87**, 1307 (2002).

48. M. Woinska, S. Grabowsky, and P. M. Dominiak, Sci. Adv. **2**, e1600192 (2016).

49. N. K. Hansen and P. Coppens, Acta Crystallogr. A **34**, 909 (1978).

50. S. C. Capelli, H.-B. Bürgi, B. Dittrich, et al., IUCr J. **1**, 361 (2014).

51. W. Hamilton, Acta Crystallogr. **18**, 502 (1965).

52. F. H. Allen and I. J. Bruno, Acta Crystallogr. B **66**, 380 (2010).

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