**Ab-initio Quantum Mechanical Study of Akdalaite (5Al$_2$O$_3$$\cdot$H$_2$O): Structure and Vibrational Spectrum.**

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**Abstract.** The structure and the vibrational spectrum of akdalaite (5Al$_2$O$_3$$\cdot$H$_2$O, also known as tohdite) have been investigated at the periodic ab-initio quantum-mechanical level by using a high quality Gaussian type basis set and the hybrid B3LYP Hamiltonian with the CRYS TA L06 code. Three space groups proposed in the literature, namely $P6_3mc$ and its two $P31c$ and $Cmc2$ subgroups, have been considered, obtaining essentially the same energy (the largest total energy difference is 0.2 kJ/mol per cell) and geometry. The harmonic frequencies at the $\Gamma$ point have been computed. Isotopic substitution and graphical representation permit a complete classification of normal modes in terms of simple models (octahedra and tetrahedra modes, hydrogen stretching and bending). The Al-O octahedra and tetrahedra modes appear below 880 cm$^{-1}$, Al-OH bending modes are located in the range 870-900 cm$^{-1}$, and OH stretching modes are at 3330-3400 cm$^{-1}$.

1. Introduction

The present work is part of a systematic investigation, with quantum mechanical tools, of the energetic, structural and vibrational features of Al hydroxides. The latter exhibit the general formula (Al$_2$O$_3$$\cdot$nH$_2$O), where $n$ stands for the degree of hydration. Many different stable structures exist [1, 2, 3, 4] corresponding to $n = 3$ (Al(OH)$_3$, present in four polymorphs: gibbsite, bayerite, doyleite and nordstrandite), $n = 1$ (boehmite or $\gamma$-AlOOH and diaspore or $\alpha$-AlOOH), and $n = 0.2$ (5Al$_2$O$_3$$\cdot$H$_2$O, akdalaite or tohdite). Two previous papers have been devoted to mono-hydroxides, diaspore [1] and boehmite.[5] In the present paper we extend the investigation to the compound with the lowest water content, akdalaite, that is rarely present in ores, but can easily be obtained by hydrothermal methods.[6, 8, 9, 10, 11] Experimental studies, aimed to determine the crystal structure and investigate the formation of stable alumina from the high temperature dehydration reaction (akdalaite$\rightarrow$ $\kappa$-Al$_2$O$_3$ $\rightarrow$ $\alpha$-Al$_2$O$_3$) are available.[6, 8, 9, 10, 11]

In the past the name “tohdite” were assigned to the 5Al$_2$O$_3$$\cdot$H$_2$O phase, synthesized for the first time by Yamaguchi et al.[8], whereas “akdalaite” was used to identify a natural phase, similar to

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Tohdite in almost all aspects, but corresponding to the 4Al₂O₃·H₂O phase. Crystallographic data of akdalaite derived from powder XRD experiments have been recently found to be in error,[7] and akdalaite has been found to correspond to the natural counterpart of tohdite. On the basis of these considerations, the Commission on New Minerals and Mineral Names (CNMMN) decided to retain the name of akdalaite for the 5Al₂O₃·H₂O phase.

In the present work, we explore the structural and vibrational properties of akdalaite:[1] three space groups proposed in the literature will be considered, namely P6₃/mn and two of its subgroups, P31c and Cmc2₁. When possible, a comparison with the experimental data is carried out.

As regards previous studies, the structure and the relative stability with respect to α-Al₂O₃·H₂O have been simulated by Digne et al.[2] by applying the PBE DFT scheme as implemented in SIESTA,[12, 13], a computer code that adopts a truncated Gaussian type basis set. Neither calculated, nor experimental IR and Raman data are available.

The paper is organised as follows. In section II we summarise the method employed for our calculations. The equilibrium geometries are discussed and compared to experiment in section III. Section IV is devoted to the vibrational analysis, with subsections discussing the various regions of the spectrum. Finally, in the last section, the main conclusions and perspectives are summarized.

2. Computational methods

The present calculations have been performed with CRYSTAL06,[14] a periodic ab initio all-electron program that uses a Gaussian type basis set. For Al, O and H, 8-621G(d), 8-411G(d) and 211G(p) contractions[1, 5, 15, 16, 17] have been used, respectively. The hybrid B3LYP Hamiltonian has been adopted.[1, 5, 18, 19, 20, 21] The level of accuracy in evaluating the Coulomb and Hartree-Fock exchange series is controlled by five parameters,[14] for which the 7 7 7 14 values have been adopted. The DFT exchange-correlation contribution to B3LYP is evaluated by numerical integration over the unit cell volume. The accuracy in the integration can be measured by quoting the error in the integrated electronic charge in the unit cell (∆e) = 4.6·10⁻⁵ |e| for a total of 260 electrons).

Further details about the grid generation and its influence on the accuracy and cost of calculation can be found in refs.[1, 19, 20, 22]

The reciprocal space was sampled according to a regular sublattice with a shrinking factor equal to 6, corresponding to the choice of 52 (Cmc2₁), 34 (P31c) and 28 (P6₃/mc) independent k points in the irreducible Brillouin zone. The gradient with respect to the atomic and cell coordinates is evaluated analytically[23, 24, 25] and equilibrium atomic positions are determined by using the Broyden-Fletcher-Goldfarb-Shanno scheme for Hessian updating.[26, 27, 28, 29] We refer to ref.[18] for details about the frequency harmonic calculation; further details concerning isotopic substitution, IR intensity, treatment of the OH anharmonicity and animation of modes can be found in ref.[1].

Manipulation and visualisation of structures have been performed with the MOLDRAW program.[30] The web page[31] presenting the akdalaite vibrational modes for the three space groups has been realised by using the Jmol[32] engine and the WEBVIB[33] script.

3. Structure

Akdalaite consists of oxygen planes stacked in the A-B-A-C-A.. sequence[8] (see figures 1 and 2). There are 10 Al atoms in the unit cell, eight of them occupy octahedral and two tetrahedral cavities. On the basis of their XRD experiments, Yamaguchi et al.[8] proposed two possible space groups: P31c (number 159, C₃₁ᵥ) and P6₃/mc (186, C₆₃ᵥ). The DFT study carried out by Digne et al.[2] proposes a third space group, namely Cmc2₁ (number 36, C₂ᵥ), as the most probable at 0 K (1.2 kJ/mol more stable than P6₃/mc from their calculations). They indicate H atoms,
not considered in XRD experiments, as the main responsibles for the symmetry reduction: the $x$ and $y$ coordinates of H atoms are constrained in $P31c$ and $P6_3mc$ groups, whereas only the $x$ coordinate is constrained in $Cmc2_1$. More generally, all the $y/b$ constraints on Al and O atoms are removed when passing from $P6_3mc$ (or $P31c$) to $Cmc2_1$, and so the whole structure is allowed to relax.

The number of point symmetry operators is 12 ($P6_3mc$), 6 ($P31c$) and 4 ($Cmc2_1$), and both $P31c$ and $Cmc2_1$ are $P6_3mc$ subgroups. In all the considered space groups the unit cell, hexagonal for $P31c$ and $P6_3mc$ and orthorhombic for $Cmc2_1$, contains 28 atoms, corresponding to the formula unit $5\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$; the asymmetric unit of $Cmc2_1$ consists of 4 Al, 6 O and 1 H atoms (the $x/a$ fractional coordinate is constrained for 3 Al, 4 O and H atoms), whereas 3 Al, 4 O and 1 H build the $P6_3mc$ and $P31c$ asymmetric unit (the $x/a$ and $y/b$ fractional coordinates are constrained for 2 Al, 2 O and H atoms in both space groups).

In the present study the three structures have been optimized; cell parameters, bond lengths and angles turn out to be extremely similar (see table 1; due to the orthorhombic crystal system, the $b$ parameter is different for $Cmc2_1$). The small geometry differences involve extremely small differences in the electronic energies (see table 1). For this reason, we will use the structure corresponding to the $P6_3mc$ space group as a reference for describing the akdalaite geometry.

Table 1. Calculated and experimental[8] structures. The electronic energy per cell, $E_{el}$, of the $Cmc2_1$ space group is used as a reference. The number into parentheses corresponds to the experimental $b$ value in the hypothesis of $Cmc2_1$ space group. Al-O$_{min}$ is the shortest Al-O bond length (tetrahedral Al-O), Al-O$_{max}$ is the largest one (octahedral Al-O); HB indicates the hydrogen bond length.

| Sym. Op. | $P6_3mc$ | $P31c$ | $Cmc2_1$ | Expt. [8] |
|----------|----------|---------|----------|-----------|
| Atoms    | 28       | 28      | 28       | 28        |
| $a$/Å    | 5.6153   | 5.6153  | 5.6152   | 5.576     |
| $b$/Å    | 5.6153   | 5.6153  | 9.7264   | 5.576 (9.66) |
| $c$/Å    | 8.8247   | 8.8249  | 8.8242   | 8.768     |
| $V_{ol.}$/Å$^3$ | 240.977  | 240.984 | 240.969  | 236.1     |
| O-H/Å   | 0.980    | 0.980   | 0.980    | -         |
| HB/Å    | 2.19     | 2.20    | 2.19-2.20| -         |
| HÖH/°   | 132.7    | 132.7   | 132.7    | -         |
| Al-O$_{min}$/Å | 1.81     | 1.81    | 1.81     | 1.72-1.60 |
| Al-O$_{max}$/Å | 2.04     | 2.04    | 2.04     | 1.95      |
| $E_{el.}$/kJ/mol | +0.16   | +0.20   | 0.0      | -         |

The eight Al hexacoordinated atoms in the unit cell form, in $P6_3mc$, two different kind of irregular AlO$_6$ octahedra:

- six Al$_a$ atoms (general position, grey colour in figures): Al$_a$-O=1.84-1.97 Å; four O atoms are two-by-two symmetry related; one O atom (at 1.92 Å) is directly linked to hydrogen and two (at 1.84 Å) are acceptors of weak hydrogen bonds;
- two Al$_b$ atoms (special position, green colour in figures): Al$_b$-O=1.86-2.04 Å; O atoms are three-by-three symmetry related and three of them (Al-O=1.86 Å) are hydrogen bond acceptors.

The remaining two Al$_c$ atoms (special position, yellow colour in figures) are tetracoordinated, with three symmetry related and one independent oxygen atoms at 1.81-1.83 Å. Some of the distances and angles are shown in figure 1 on the left. The $P31c$ structure mainly differs from
Figure 1. Akdalaite fragments. Left: coordination of the irreducible Al atoms (Al$_a$: grey, Al$_b$: green, Al$_c$: yellow, O: red, H: white); the dot line indicates the weak hydrogen bond, the black bold line the 6$_3$ symmetry axis. Right: the hydrogen cavity. Distances: Å; angles: degrees.

Figure 2. Akdalaite bulk structure: oxygen layers are organized in a ABAC type-sequence (see text).
P6₃mc in the symmetry relations among oxygen atoms. In Cmc2₁ the Alₐ group splits into two families of symmetry related octahedra; distances and angles remain, however, unchanged.

The Mulliken analysis provides a schematic (and in part arbitrary) description of the charge distribution in the unit cell in terms of charge and bond population data, and permits spending a few words about the different character of Al-O bonds. Net charges associated to Alₐ, Alₐ, and Alₐ are +1.99, +2.02 and +1.84[|e|], respectively; ionicity is then lower for tetrahedral than for octahedral Al-O bonds. This is confirmed by the overlap population data, ranging from +0.004 to +0.106[|e|] for lₐ,ₗ-O (1.84-2.04 Å) and from +0.109 to +0.135[|e|] for Al₁-O (1.81-1.83 Å). The charge of the O atoms linked to Al atoms only is −1.30/−1.32[|e|], whereas it increases to −1.04[|e|] for O atoms directly linked to hydrogen. The hydrogen charge is +0.59[|e|], and the overlap population of the O-H bond, +0.246[|e|] confirms its strong covalent character.

The macrostructure of akdalaite is shown in figure 2. The A, B, and C oxygen layers are indicated, and the ABACA... sequence can easily be visualized (note that there is no link between the A,B,C oxygen layer labels and the a, b, c Al subscripts). Two different Alₐ octahedra sheets can be individuated (see the grey sheets in figure 2): Alₐ atoms lie between A and B or A and C oxygen layers alternatively. Similar considerations hold for the sheet containing Alₐ and Alₐ polyhedra (green and yellow sheets in figure 2), and two different sheets are then observed. Oxygen atoms linked to hydrogen atoms belong to the A layer; in particular, a sort of cavity is observed in correspondence of each H atom pointing from an Alₐ sheet to a B or C layer (see figure 1 on the right).

4. Frequency analysis

The decomposition of the reducible representation built on the basis of the Cartesian coordinates of the unit cell atoms gives the following symmetry assignment of the 84 normal modes:

\[
\Gamma^{Cmc2_1} = 25A_1 + 17A_2 + 25B_1 + 17B_2 \\
\Gamma^{P31c} = 14A_1 + 14A_2 + 28E \\
\Gamma^{P6_3mc} = 11A_1 + 3A_2 + 11B_1 + 3B_2 + 14E_1 + 14E_2
\] (1)

The three lowest frequencies (A₁, B₁ and B₂ for Cmc2₁; E and A₁ for P31c; E₁ and A₁ for P6₃mc) correspond to pure translations and are null.

The P31c and P6₃mc spectra essentially coincide. Small differences are observed between P6₃mc and Cmc2₁ in the high frequency part of the spectrum: in Cmc2₁ the harmonic OH stretching and bending modes are shifted towards higher frequencies by 26 and 11 cm⁻¹ respectively. All the other modes are the same for both space groups. The P6₃mc spectrum, shown in table 2, will then be used as a reference for the present discussion.

The three typical regions characterizing the Al hydroxide spectra[1, 5] have been individuated also for akdalaite: the Al-Oₐ region (200-880 cm⁻¹, n=4.6), the Al-OH bending region (870-900 cm⁻¹) and the OH stretching region (over 3000 cm⁻¹). As mentioned above, we have not been able to find any experimental study of the vibrational properties of akdalaite to compare with the present computational results.

4.1. The OH modes

Two OH groups are present in the unit cell; the distance between them is, however, large (H-H=5.61 Å) and then their interaction limited. As a consequence, the stretching and the bending bands are quite narrow (25 and 15 cm⁻¹ respectively). Due to the light mass of hydrogen, 6 ”hydrogen modes” are separated from the remaining part of the spectrum: OH stretching modes, at 3550 and 3525 cm⁻¹, and Al-OH bending modes at 885, 885, 871 and 871 cm⁻¹.
The effect of the isotopic substitution[1, 16] on the full set of frequencies confirms the different nature of the 6 highest modes: when H atoms are replaced by D, the 6 hydrogen modes are shifted by 156 cm$^{-1}$ (Al-OH bending modes) or by as much as 965 cm$^{-1}$ (OH stretching modes). The shift of modes not involving H atoms is on the contrary always smaller than 35 cm$^{-1}$.

In previous papers,[1, 5, 16, 17, 22, 34] the effect of anharmonicity on the OH stretching modes has been studied at the B3LYP level, obtaining excellent results when hydrogen is not involved in strong hydrogen bonds. The OH stretching anharmonicity has been calculated for akdalaite with the same approach: an anharmonic constant $\omega_{e\chi e} = 97.4$ cm$^{-1}$ has been obtained, and the OH stretching frequencies are then bathochromically shifted by about 195 cm$^{-1}$ (see ah frequencies in table 2). This result can be compared with the ones shown in Table 1 of ref.[1], where the calculated $\omega_{e\chi e}$ constants for different systems are listed: for non H-bonded[16, 17, 22] systems $\omega_{e\chi e}$ ranges from 76 to 90 cm$^{-1}$, and increases respectively to 130 and 216 when weak (Be(OH)$_2$[34], OH=2.15 Å) and strong ($\alpha$-AlOOH[1], OH=1.69 Å) H bonds are present. In akdalaite, the calculated H bond distance is 2.19 Å, and so the calculated $\omega_{e\chi e}$ value is coherent with the interpretation proposed in ref.[1].

4.2. The octahedra modes

The low frequency part of the spectrum (from 200 to 880 cm$^{-1}$) corresponds to the AlO$_n$ octahedra and tetrahedra modes. Roughly speaking, this part of the spectrum can be further divided in three zones (see animation [31]): modes below 300 cm$^{-1}$ are rotations of the polyhedra; the 300-600 cm$^{-1}$ region corresponds mainly to bending modes, whereas stretching modes occupy the highest part of the spectrum, between 550 and 880 cm$^{-1}$. These three zones are not separated by gaps, and the classification of modes in the three groups (rotations, bending, stretching) is qualitative rather than quantitative, and many modes are of mixed nature.

One of the specific features of akdalaite is the presence of Al atoms with two different...
coordinations, namely octahedra \( \text{Al}_6 \) and \( \text{Al}_8 \) and tetrahedra \( \text{Al}_4 \). The question then arises concerning the possible separation of the modes of the two polyhedra, namely \( \text{AlO}_4 \) and \( \text{AlO}_6 \). In order to try to answer this question, we used different tools, including analysis of the eigenvectors, isotopic substitution on the Al atoms of the two kinds, animation of the modes [31]. It turns out that \( \text{AlO}_4 \) and \( \text{AlO}_6 \) are both involved in all modes, although the relative contribution vary to a certain amount from mode to mode. This mixing is not surprising, as the subunits are strongly interrelated in the akdalaite structure. From figure 2 one can easily guess that the deformation in the tetrahedra cannot be independent of the displacement of the octahedra atoms, and vice versa.

5. Conclusions and perspectives
The three space groups proposed in the literature for akdalaite \( (P6_3mc \) and its two subgroups \( P31c \) and \( Cmc2_1 \) have been considered; it turns out that the additional geometrical freedom available in \( P31c \) and \( Cmc2_1 \) is not exploited, as the three optimized structures coincide nearly exactly, and the three total energies differ by no more than 0.2 kJ/mol, much less than in the previous study with SIESTA.[12, 13]

In the akdalaite structure, at variance with respect to all other hydroxides, Al atoms appear in edge-sharing \( \text{AlO}_6 \) octahedra as well as in vertices-sharing \( \text{AlO}_4 \) tetrahedra; in the vibrational spectrum it is however impossible to clearly identify modes belonging to one or to the other polyhedron. Hydrogen atoms are essentially isolated, and non involved in hydrogen bonds, as documented by the O-H stretching frequency.

Extension of this study to \( \text{Al(OH)}_3 \) hydroxides and to various alumina forms is in progress, that will permit to investigate the thermodynamic stability of the various hydrated compounds.

Acknowledgements
C.Z.W. thanks Mexican CONACYT for financial support (Project SEP05-46983) and Institute for Scientific Interchange (ISI) CRT Foundation for a Lagrange Senior Fellowship at the University of Turin.

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