The Layered Uranyl Silicate Mineral Uranophane- β : Crystal Structure, Mechanical Properties, Raman Spectrum and Comparison with the α -Polymorph[†]

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The crystal structure, elastic properties and Raman spectrum of the layered calcium uranyl silicate pentahydrate mineral uranophane- β , $\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_6(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, are studied by means of first-principles solid-state methods and compared with the corresponding information for the α polymorph. The availability of the energy optimized full crystal structure of uranophane- β , including the positions of the hydrogen atoms, made possible the computation of its elastic properties and Raman spectrum by using the theoretical methodology. An extended set of relevant mechanical data is reported. Uranophane- β is shown to be a weak and ductile mineral and, consequently, is mechanically very different from the α polymorph which is a hard and brittle material. Uranophane- β exhibits the important negative Poisson's ratio (NPR) and the negative linear compressibility (NLC) phenomena. The experimental Raman spectrum of uranophane- β is obtained from a natural mineral sample from pegmatite Perus, São Paulo, Brazil and compared with the spectrum determined theoretically. Since both spectra are in very good agreement, the theoretical methods are employed to assign the Raman spectrum. Three weak bands of the experimental spectrum of this mineral, located at the wavenumbers 2302, 2128 and 2042 cm^{-1} , are identified as combination bands. The Raman spectrum of uranophane- β is also compared with that of the α polymorph. While they are rather similar, the detailed analysis reveals a significant number of differences. Finally, the relative thermodynamic stability of the α and β polymorphs is evaluated. The α polymorph is more stable than the β polymorph at zero pressure and temperature by -12.0 kJ/mol.

1 Introduction

Uranyl silicate minerals are one of the most abundant uranyl minerals on the Earth's surface.^{1–3} These minerals are invariably found as a result of the oxidation and dissolution/precipitation processes occurring in uranium-bearing ore deposits^{4–7} and are among the most relevant components of the paragenetic sequence of secondary phases arising from the corrosion of spent nuclear fuel (SNF).^{8–12} The characterization and the investigation of the long-term stability of the uranyl silicate phases under the various environmental conditions is extremely important to understand the composition and evolution of the complex assemblages of uranyl minerals found at uranium deposits.^{1–3,13}

While the α -polymorph of the calcium uranyl silicate pentahydrate mineral uranophane, $\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_6(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, is one of the earliest known uranyl mineral, described in

1853 by Websky,^{14–15} the β -polymorph was observed by the first time by the Czech mineralogist Radim Nováček in 1935,^{16–17} almost a century later. Whereas uranophane- α is the most abundant uranyl silicate mineral and has been identified in nearly all major and most of the minor uranium deposits in the world, the β -polymorph is significantly less frequent. From the structural complexity point of view,¹⁸ it has been suggested that uranophane- β could be even more stable than the α -polymorph,¹⁹ the larger abundance of the latter being attributable to the fact that its formation may be kinetically favored due to the largest simplicity of its crystal structure. This paper shows that this is not true. A rigorous evaluation of their relative thermodynamic stability shows that uranophane- α is slightly more stable. Despite of its smaller abundance and stability, uranophane- β is an important uranyl silicate phase whose properties have not been studied in sufficient detail.^{16–17,19–24} For example, its crystal structure, initially studied by Smith and Stohl²⁰ in 1972 and Viswanathan and Harneit²¹ in 1986, was determined in a complete way, including the positions of the hydrogen atoms in its unit cell, only one year ago by Plášil.¹⁹ The main purpose of this work is to determine and analyze in detail the mechanical properties and Raman spectrum of this mineral which, as far as we are concerned, have not been reported.

The crystal structure of uranophane- β is studied in this work by means of first-principles solid-state methods based on density functional theory using large plane wave basis sets and

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[†] Electronic Supplementary Information (ESI) available: (a) Interatomic distances in uranophane- β ; (b) Comparison of the experimental X-ray diffraction powder patterns of uranophane- α and β ; (c) Images of the atomic motions in the Raman active vibrational normal modes of uranophane- β ; (d) Comparison of the experimental Raman spectra of uranophane- α and β ; (e) Computed positions of the atoms in the unit cell of uranophane- β (CIF file). See DOI: 10.1039/x0xx00000x

pseudopotentials in order to describe the internal atomic electrons.²⁵ The structural results obtained in this work confirmed the crystal structure of uranophane- β proposed experimentally¹⁹ and allowed for the computation of its mechanical properties and Raman spectrum, because their determination using the first-principles theoretical solid-state methods requires the knowledge of the full energy optimized crystal structure. As is well known, the mechanical properties, including the compressibility (the inverse of bulk modulus), the Young and shear moduli, the Poisson's ratio, the isotropy, ductility and hardness indices and the elastic wave velocities, are among the most important properties characterizing a given mineral phase or material.^{26–28} In this work, the computed mechanical properties of uranophane- β are compared extensively with those of the α -polymorph.

Due to the radiotoxicity of uranyl ion containing minerals, which complicates the handling of these materials under security conditions, one of the main analytical techniques used for their safe characterization is Raman spectroscopy.^{29–49} This technique does not need a special preparation of the samples, a very small amount of sample is required and it is non-destructive. Raman spectroscopy is today a sophisticated technique which, combined with microscopy techniques, allows to perform a surface characterization of the mineral samples because it permits to make spectroscopic studies in localized placements of the surface of these materials.⁴⁸ Besides, Raman spectroscopy may also be used in situ to perform spectroscopic studies of the effect of temperature on these materials and to study their thermal stability.⁴⁹ Raman spectroscopy provides a great amount of information about the crystal structure of the material being considered because the locations of the Raman bands are generally connected to specific types of vibrational motions which are only possible for particular structural environments. However, for the extraction of this information, a precise assignment of the bands in the Raman spectra to specific vibrational motions is required and the assignments of the Raman spectra of uranium minerals are usually incomplete and unreliable since they have been performed using purely empirical arguments. The situation has changed significantly in recent times, since the use of the first principles theoretical methodology has allowed to assign rigorously the Raman spectra of a large series of uranyl containing minerals.^{49–57} In this work, the Raman spectrum of uranophane- β is recorded from a natural crystal and computed using theoretical solid state methods. The resulting spectrum is fully assigned and compared with the Raman spectra of the α -polymorph. The theoretical methods have been used not only as a complement of the experimental techniques allowing the determination of the incompletely known crystal structures of uranyl containing materials^{55,57–60} and the precise assignment of their Raman spectra,^{49–57} but also as powerful predictive tool of their thermodynamic, mechanical and optical properties.^{50,52–55,57–73}

This paper is organized as follows. The experimental and theoretical solid-state methods employed in this work are described in Section 2. The results of the present paper are given and discussed in Section 3. The calculated crystal structure of uranophane- β is reported in Section 3.1 and the

computed X-ray powder pattern is given in Section 3.2. The mechanical properties and mechanical stability of uranophane- β are studied in Section 3.3. In Section 3.4, the Raman spectrum of uranophane- β is recorded from a natural mineral specimen and the results are compared with the Raman spectrum of this mineral computed using Density Functional Perturbation Theory (DFPT). The assignment of the bands in this spectrum is also performed in this Section. The relative thermodynamic stability of the α - and β -polymorphs is obtained in Section 3.5. Finally, in Section 4 the main conclusions of this paper are presented.

2 Materials and methods

2.1 Experimental

The natural crystal investigated in this paper originates from the pegmatite Perus, São Paulo, Brazil. The crystal was extracted from a sample composed of dark yellow transparent prismatic crystals up to 1 mm in length. Raman spectroscopy was used to characterize the uranophane- β crystals. The Raman spectrum was recorded for incident radiation perpendicular to the direction of elongation of crystals and collected in the range 4000–45 cm^{-1} using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope. The Raman signal was excited by an unpolarized red 633 nm He-Ne gas laser and detected by a CCD detector. The experimental parameters were: 100x objective, 10 s exposure time, 100 exposures, 50 μm pinhole spectrograph aperture and 8 mW laser power level. The eventual thermal damage of the measured point was excluded by visual inspection of excited surface after measurement, by observation of possible decay of spectral features in the start of excitation and checking for thermal downshift of Raman lines. The instrument was set up by a software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser frequency calibration) and standardized white-light sources (intensity calibration). Spectral manipulations were performed using the Omnic 9 software (Thermo Scientific). Since the sample studied is a well-formed single-crystal of uranophane- β , the risk of the presence of impurities is very low.

2.2 Theoretical solid-state methods

The Cambridge Serial Total Energy Program (CASTEP),⁷⁴ a module of the Materials Studio program suite,⁷⁵ was utilized in order to model the uranophane- β crystal structure. The Perdew-Burke-Ernzerhof (PBE) energy-density functional⁷⁶ supplemented with Grimme's empirical dispersion correction⁷⁷ (the so called DFT-D2 approach) was employed. Standard norm-conserving pseudopotentials⁷⁸ from CASTEP code were used for the Ca, Si, O and H atoms in the unit cell of uranophane- β . However, for the U atom a relativistic norm-conserving pseudopotential generated from first principles^{50–51} was employed. This pseudopotential has been proven extensively in the research of uranyl containing materials.^{49–65}

The unit-cell dimensions and shape and all atomic positions in uranophane- β were optimized by means of the Broyden–

Fletcher–Goldfarb–Shanno (BFGS) technique.⁷⁹ A plane wave kinetic energy cut-off parameter of $\epsilon = 950$ eV and a k -mesh⁸⁰ of $4 \times 2 \times 2$ were employed. These calculation parameters are similar to those used in previous studies^{49–65} and were required in order to attain well converged crystal structures, energies and elastic properties. The X-ray powder diffraction patterns were generated⁸¹ from the optimized crystal structures using the software REFLEX included in Materials Studio software suite.⁷⁵ It must be emphasized that the full crystal structure of uranophane- β , including the locations of the hydrogen atoms, was first obtained using theoretical methods in 2016^{51,50} using small calculation parameters. The present energy-optimized structure was determined using this previous theoretical structure as initial input and without *a priori* knowledge of the experimental crystal structure.¹⁹

The theoretical calculation of the Raman spectrum of uranophane- β was performed by using density functional perturbation theory.^{82–84} This method was also employed in a series of previous works^{49–57,85–87} leading to consistently accurate descriptions of the vibrational spectra. No scaling procedures, commonly used to correct the computed infrared vibrational frequencies and Raman shifts for the anharmonicity and remaining approximations used in the theoretical treatment employed,⁸⁸ were applied. Hence, the calculated values of the Raman shifts and intensities correspond to the harmonic approximation of the interatomic force field.

The stiffness tensor^{26–28} elements, required to calculate the mechanical properties and to study the mechanical stability of the uranophane- β crystal structure, were determined from stress-strain relationships using the finite deformation method.⁸⁹ This method, which has been successfully utilized for the computation of the elastic response of solid materials,^{28,53–55,57,59–61,64,101–104} appears to be more efficient for this purpose than the energy based methods and DFPT.⁸⁹ The computation of the mechanical properties of this mineral was quite expensive due to the long size of its unit cell and the fact that the required finite structure deformations lead to unsymmetrical crystal structures. The last feature imposes that all the required calculations must be carried out without exploitation of the crystal symmetry. Despite of the difficulty, the convergence and accuracy of the calculated properties was carefully evaluated by employing increasingly more complex sets of calculation parameters and different energy density functionals. The results obtained were essentially the same when sufficiently accurate calculation parameters were employed and therefore must be reproducible.

The bulk modulus and its pressure derivatives were determined by fitting the lattice volumes and associated pressures to a fourth-order Birch-Murnaghan equation of state.⁹⁰ The lattice volumes near of the optimized equilibrium geometry were determined by optimizing the uranophane- β crystal structure under the effect of sixteen different external pressures with values in the range -1.0 to 9.0 GPa. The resulting pressure-volume data were then adjusted to the chosen equation of state using Angel's EOSFIT 5.2 code.^{91–92} The optimization of the crystal structure of uranophane- β under pressure was also performed using the BFGS technique. The spatial

representations of the elastic properties of uranophane- β as a function of the orientation of the applied strain were performed with the EIAM software.⁹³

The use of Hubbard correction⁹⁴, improving the description of the strong Coulomb repulsion between electrons in f orbitals, was also assessed in this work. As shown in Section 3, this correction, making significant improvements in the description of uranium containing systems in which uranium acts with IV oxidation state,^{94–98,66,71} appears not to be required in the present case. In fact, for a large series of materials in which uranium acts with VI oxidation state, the standard DFT description provides very accurate results for their structures and properties.^{49–70,72–73,99–100}

3 Results and discussion

3.1 Crystal structure

For the classification of the naturally occurring uranyl silicates, the uranium to silicon ratio can be used effectively, since it partially determines the type of structural fundamental building blocks (structural units) of these minerals.¹⁰⁵ Most uranyl silicate minerals have a 1:1 uranium to silicon ratio and are layered materials.^{105–106} Soddyite has 2:1 uranium to silicon ratio and possesses a framework crystal structure.^{107,105–106} Weeksite^{108–109}, haiweeite^{110–111} and coutinhoite¹¹² display a uranium to silicon ratio of 2:5 and complicated layered and mixed layered-framework crystal structures. There are nine uranyl silicate minerals, uranophane- α and β , sklodowskite, cuprosklodowskite, boltwoodite, natroboltwoodite, kasolite, oursinite and swamboite, representing the uranophane group on the basis of the 1:1 uranium to silicon ratio and the same uranophane anion sheet topology.^{106,113–117} The layers in the uranyl silicate minerals of the uranophane group have a net negative charge and stack up with cations in the interlayer spaces to provide charge balance within the structure. This topology is also at the basis of the structure of a large series of phosphates, arsenates, selenates, vanadates, and molybdates.^{118–123}

The computed crystal structure of uranophane- β is shown in Figure 1 and may be compared with that of uranophane- α given in Figure S.1 of the Supplementary Information.⁵⁴ As can be seen in these Figures, uranium atom displays pentagonal bipyramidal coordination¹²⁴ in uranophane. The uranyl silicate layers, $[(\text{UO}_2)(\text{SiO}_4)]_n^{2n-}$, are composed of UO_7 pentagonal bipyramids and SiO_3OH tetrahedra. The uranyl polyhedra share two edges to form chains expanding along $[001]$ direction ($[010]$ in the α -polymorph). These chains are connected through silicate tetrahedra which share an edge with one adjacent chain and a vertex with another. The free vertex in the silicate tetrahedra contains the hydroxyl ion and points towards the interlayer spaces. One of the main differences between both polymorphs¹⁹ is that whereas the free vertices of the SiO_3OH tetrahedra distributed in a given row along $[010]$ direction in an uranyl silicate layer of the α -polymorph (Figure S.1.A) point uniformly towards the same interlayer space, they alternate in the rows directed along $[001]$ in the β form (Figure 1.A), that is, they point alternatively towards the upper and lower interlayer spaces.

Fig. 1. Computed crystal structure of uranophane- β : (A) View of two uranyl silicate layers and the corresponding interlayer space from [100]; (B) View of a uranyl silicate layer from [010]. Color code: U-Blue, Si-Brown, O-Red, H-White, Ca-Yellow.

The charge compensating cation in both uranophanes is calcium and it is located, together with the water molecules, in the interlayer space. Another important difference between both polymorphs, is that while two uranyl silicate sheets are connected by $\text{CaO}_2(\text{OH})(\text{H}_2\text{O})_4$ polyhedra in uranophane- α (Figure S.1.A), they are linked through $\text{CaO}_3(\text{OH})(\text{H}_2\text{O})_4$ polyhedra in the β form (Figure 1.A). Therefore, the coordination number of Ca to O is equal to seven for the α -polymorph and eight for the β -polymorph. The ligands of the Ca atom consist in four structural interlayer water molecules, two uranyl oxygen atoms (three in uranophane- β) and one hydroxyl ion from the SiO_3OH tetrahedra. One of the five water molecules in the formula unit of uranophane (α or β) is not structural but free. It is out of the Ca coordination polyhedra and held in the structure by hydrogen bonding only. Hydrogen bonds reinforce the bonding between the layers, the Ca atoms and the interlayer water molecules.

The unit cell of uranophane- β has monoclinic symmetry, space group $\text{P}12_1/\text{c}1$ (no. 14, $Z = 4$). The unit cell is very large and contains 136 atoms: 8 U, 8 Si, 4 Ca, 68 O and 48 H. In the computations, 640 valence electrons must be described explicitly. The number of valence electrons per atom are 14, 4, 10, 6 and 1 electrons for U, Si, Ca, O, and H, respectively, corresponding to the valence electron configurations: U: $6s^2 6p^6 6d^1 5f^3 7s^2$, Si: $3s^2 3p^2$, Ca: $3s^2 3p^6 4s^2$, O: $2s^2 2p^4$, and H: $1s^1$. Table 1 shows the final unit-cell parameters, volumes and densities obtained compared with the corresponding experimental values of Viswanathan and Harneit²¹ and Plášil.¹⁹ The agreement obtained using the DFT-D2 approach was quite satisfactory, the difference in the computed volume and density with respect to the experimental values being only about 3.0%, despite of the great complexity of the crystal structure of uranophane- β . The introduction of dispersion corrections improved significantly the computed crystal structure since as it can be seen in the first line of the table, the difference in the computed volume and density obtained using the uncorrected PBE energy-density functional was significantly larger (5.1 %).

The crystal structure was also optimized by adding the Hubbard correction with the parameter, $U_{\text{eff}} = 4.0$ eV, determined by Weck *et al.*⁹⁷ for uranium dioxide. The results, given in Table 1, show that the Hubbard correction does not introduce significant changes to the computed crystal structure. Since, the introduction of Hubbard correction does not improve the description of uranophane- β significantly, it was not used to obtain the properties and spectra of this mineral.

Table S.1 (Supplementary Information) reports the computed values of a selected set of interatomic distances compared with the corresponding experimental data from the recently determined crystal structure.¹⁹ Uranophane- β has two structurally (symmetrically) independent U and Si atoms and only one structurally independent interlayer Ca atom in its crystal structure. The two O uranyl atoms situated in apical positions of the pentagonal bipyramids have U-O distances of 1.807(4) and 1.807(4) Å for U1 and 1.803(3) and 1.808(4) Å for U2. These distances agree very well with the computed values of 1.829 and 1.830 Å for U1 and 1.819 and 1.836 Å for U2. The differences are of the same order as those obtained in previous works for uranophane- α ⁵⁴ and soddyite,⁵³ and smaller than those obtained for the same type of distances in several uranyl minerals as schoepite,⁵⁵ becquerelite⁵⁹ and kasolite.⁵⁷ The remaining five O atoms lie in the equatorial plane with average U-O distances of 2.34 Å for U1 and 2.36 Å for U2, which compare very well with the theoretical values of 2.35 Å and 2.36 Å. These values are in excellent agreement with the average value of 2.37 Å reported by Burns *et al.*¹¹⁵ for the same type of uranium coordination polyhedra in a large set of well-defined crystal structures. The average Si-O distances are 1.63 and 1.62 Å for Si1 and Si2 and also compare very well with the calculated values of 1.64 and 1.64 Å. Finally, the Ca-O distances are also well described, the experimental and computed average Ca-O distances being 2.45 and 2.44 Å, respectively. The precise locations of the atoms in the crystal structure of uranophane- β are given as Supplementary Information in a file of CIF (Crystallographic Information File) type.

3.1.1 Density of states, band gap and frontier band functions

The computed density of states of uranophane- β is displayed in Figure 2. As may be seen, the calculations predict correctly the uranophane- β is an insulator with a band gap of 2.68 eV. The frontier band functions of uranophane- β , that is, the highest occupied (ψ_{320}) and lowest unoccupied (ψ_{321}) one-electron wavefunctions, are plotted in Figure 3. Clearly, the highest occupied band function is mainly localized on the oxygen atoms bridging the uranium and silicon atoms in the uranyl silicate layers and has predominantly p character with nodes in the positions of these oxygen atoms. On the other hand, the lowest unoccupied band function is localized in the uranium atoms and has predominantly f character. The fact that f functions are unoccupied and are separated by about 3 eV from the highest occupied one electron state explains in a clear manner why the Hubbard correction is unimportant in uranophane- β .

Fig. 2. Computed density of states of uranophane- β .

3.2 X-ray powder diffraction pattern

The X-ray powder diffractogram of uranophane- β was determined⁸¹ from the optimized and experimental¹⁹ crystal structures using the software REFLEX included in Materials Studio package⁷⁵ with $CuK\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$). The results are compared in Figure 4 with a true experimental X-ray diffraction pattern of uranophane- β given in the Record R060962 from RRUFF database,¹²⁵⁻¹²⁶ corresponding to a natural mineral sample from Teofilo Otoni, Minas Gerais, Brazil. The agreement between the computed and experimental patterns is acceptable.

Table 1. Computed unit-cell parameters of uranophane- β . The experimental and theoretical values correspond to room temperature and 0 K, respectively.

Parameter	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (deg)	β (deg)	γ (deg)	Vol. (Å ³)	Dens. (g/cm ³)
PBE	6.6827	15.9007	14.1290	90.0	90.15	90.0	1501.3467	3.788
DFT-D2	6.6499	15.7633	14.0502	90.0	90.47	90.0	1472.7538	3.862
DFT-D2+U	6.6499	15.7634	14.0503	90.0	90.47	90.0	1472.7784	3.862
Exp. ²¹	6.632	15.443	13.966	90.0	91.38	90.0	1429.9546	3.988
Exp. ¹⁹	6.62620(10)	15.4553(3)	13.9506(2)	90.0	91.4390(10)	90.0	1428.2291	3.983

Fig. 3. Frontier band functions in uranophane- β : (A) Highest occupied band function; (B) Lowest unoccupied band function. Color code: U-Blue, Si-Brown, O-Red, H-White, Ca-Green.

Fig. 4. X-ray diffraction powder patterns of uranophane- β . The upper pattern has been determined from the calculated geometry. The intermediate pattern was obtained from the experimental geometry.¹⁹ Finally, the lower diffractogram is the experimental pattern of a natural mineral sample from Teofilo Otoni, Minas Gerais, Brazil, taken from the record R060962 of the RRUFF database.¹²⁵⁻¹²⁶

The experimental X-ray diffraction pattern of uranophane β from the RRUFF database¹²⁵⁻¹²⁶ (record R060962) is compared in Figure S.2 (Supplementary Information) with the experimental pattern of the α -polymorph from a natural sample from Wölsendorf deposit, Upper Palatinate, Bavaria, Germany (record R070584 from the RRUFF database). As can be observed, although the patterns of both polymorphs are relatively similar, they may be distinguished from the X-ray data.

3.3 Elastic properties and mechanical stability

3.3.1 Elasticity tensor and mechanical stability

The symmetric elasticity tensor for a crystalline material with monoclinic space symmetry has thirteen non-vanishing independent tensor elements, C_{ij} .^{26,868} The computed values of these elements are provided in Table 2. The indices of the elements of the elasticity tensor are expressed using the standard Voigt notation in which a pair of Cartesian indices are contracted into a single integer $1 \leq i \leq 6$: $xx \rightarrow 1$, $yy \rightarrow 2$, $zz \rightarrow 3$, $yz \rightarrow 4$, $xz \rightarrow 5$, $xy \rightarrow 6$. For monoclinic symmetry, the generic necessary and sufficient Born condition¹²⁷⁻¹²⁸ for mechanical stability of a crystal structure is that all eigenvalues of the matrix representation of the C tensor be positive.¹²⁸ Hence, a numerical diagonalization of the C matrix was carried out. Since all the eigenvalues were found to be positive, the crystal structure of uranophane- β is mechanically stable.

Table 2. Computed elastic constants of uranophane- β . All the values are given in GPa.

ij	C_{ij}
11	140.67
22	122.31
33	135.97
44	16.90
55	14.29
66	13.58
12	37.05
13	36.60
15	-29.52
23	30.06
25	-11.83
35	-20.16
46	-4.50

3.3.2 Elastic properties

By using the Voigt,¹²⁹ Reuss¹³⁰ and Hill¹³¹ approaches, the elastic properties of uranophane- β polycrystalline aggregates were computed. The Hill approximation provided the best comparison of the calculated bulk modulus, $B = 51.79 \pm 2.91$ GPa, with that determined from the equation of state (see the Section 3.3.4). The results obtained for a set of elastic properties of uranophane- β in the Hill approximation, together with the results obtained in a previous work⁵⁴ for uranophane- α , are reported in Table 3. The calculated ductility index is $D = 2.38$. Hence, uranophane- β is a ductile material¹³²⁻¹³³ while the α -polymorph is brittle ($D = 1.62$). The calculated Vickers hardness, $H = 1.39$, corresponds to a weak material¹³⁴ in contrast to uranophane- α which is a hard mineral ($H = 6.33$). As observed in Table 3, the universal anisotropy index¹³⁵ of uranophane- β is very large, $A^U = 5.51$, and, therefore, it is mechanically very anisotropic whereas uranophane- α has a very low elastic anisotropy ($A^U = 0.81$). This result is quite

surprising due to the relative structural similarity of both polymorphs. Due to the well-known correlation between the values of the elastic anisotropy and the difference between the minimum and maximum values of the Poisson's ratio when all the possible directions of the applied strain are considered,^{93,136} uranophane- β was considered to be a strong candidate to display the negative Poisson's ratio phenomenon.^{28,101-104,137-142} Moreover, since negative values of the Poisson's ratio are frequently accompanied by the negative linear compressibility phenomenon,^{28,101-104,143-148} the mechanical behavior of uranophane- β was investigated in the search for both negative mechanical phenomena.

Table 3. Computed mechanical properties of uranophane- β and uranophane- α ⁵⁴ determined using the Hill approximation. The values of the bulk, shear and Young moduli (B , G and E) are given in GPa.

	Property	Uranophane- β	Uranophane- α ⁵⁴
B	Bulk modulus	51.79	59.20
G	Shear modulus	21.74	36.52
E	Young modulus	57.21	90.88
ν	Poisson's ratio	0.32	0.24
D	Ductility index	2.38	1.62
H	Hardness index	1.39	6.33
A^U	Universal anisotropy	5.51	0.81

The transverse and longitudinal elastic wave velocities in uranophane- β were also estimated using the calculated elastic constants.⁶⁸ The values found were $V_L = 4.573$ km/s and $V_T = 2.701$ km/s using the computed bulk and shear moduli and the calculated crystal density of 3.862 g/cm³ (see Table 1).

3.3.3 Negative Mechanical Phenomena in uranophane- β

The dependence of the mechanical properties of uranophane- β as a function of the direction of the applied strain was visualized using the EIAM computer program.⁹³ This software was employed to generate detailed spatial representations of the most important elastic properties which are plotted in Figure 5. The corresponding pictures were also obtained for uranophane- α . Although the mechanical properties of the α -polymorph were computed in a previous work,⁵⁴ the dependence of these properties as a function of the applied strain was not analyzed. The results are displayed in Figure 6. In this figure, the y and z axes were interchanged to compare the α and β polymorphs in the correct way because their unit cell space symmetries orient the axes differently. As can be observed in Figure 5 and Figure 6, while the dependence of the Young and shear moduli with respect to the direction of the applied strain are quite similar for both polymorphs, the pictures corresponding to the compressibility and Poisson's ratio are strongly different. In fact, uranophane- β exhibits significant negative compressibilities at the first sight (the red surface in Figure 5.A). The minimum value of the linear compressibility is $k_{min}^V = -11.04$ TPa⁻¹. Uranophane- β also displays negative Poisson's ratios but the minimum value of this property ($\nu_{min} = -0.11$) is small. The values of the minimum and maximum compressibilities and Poisson's ratios in uranophane- β as well as the directions of the applied strains leading to these minimum and maximum elastic properties are given in Table 4 and Table 5, respectively.

Fig. 5. Elastic properties of uranophane- β as a function of the orientation of the applied strain: (A) Compressibility; (B) Young modulus; (C) Shear modulus; (D) Poisson's ratio. The maximum values of the compressibility, Young modulus, shear modulus and Poisson's ratio are 32.21 TPa^{-1} , 135.36 GPa , 51.11 GPa and 1.37 , respectively.

Fig. 6. Elastic properties of uranophane- α as a function of the orientation of the applied strain: (A) Compressibility; (B) Young modulus; (C) Shear modulus; (D) Poisson's ratio. The maximum values of the compressibility, Young modulus, shear modulus and Poisson's ratio are 9.14 TPa^{-1} , 142.97 GPa , 55.28 GPa and 0.49 , respectively.

3.3.3 Equation of state and bulk modulus pressure derivatives

By optimizing the crystal structure of uranophane- β under the effect of sixteen different external isotropic pressures, the unit-cell volumes near the equilibrium geometry were determined. The calculated volume-pressure data were fitted to a fourth-order Birch-Murnaghan⁹⁰ equation of state (EOS) utilizing the EOSFIT 5.2 code.⁹¹⁻⁹² The fitted EOS parameters are the bulk modulus and its first two pressure derivatives. The values found are given in Table 6. The value obtained for bulk modulus at the temperature of 0 K, $B = 51.57 \pm 1.08 \text{ GPa}$, is in excellent agreement with that obtained from the elastic constants, $B = 51.79 \pm 2.91 \text{ GPa}$.

Table 4. Minimum and maximum compressibilities of uranophane- β at zero pressure and temperature. The directions for the corresponding external strains are also given.

k_{min}^V	U_{k-min}	k_{max}^V	U_{k-max}
-11.04	(0.68, 0.0, -0.73)	32.21	(0.73, 0.0, 0.68)

Table 5. Minimum and maximum Poisson's ratios of uranophane- β at zero pressure and temperature. The directions for the associated longitudinal and transverse directions are also given.

ν_{min}	$U_{\nu-min}^L$	$U_{\nu-min}^T$
-0.11	(-1.00, 0.0, 0.06)	(-0.06, 0.0, -1.00)
ν_{max}	$U_{\nu-max}^L$	$U_{\nu-max}^T$
1.37	(0.70, 0.0, -0.71)	(-0.71, 0.0, 0.70)

Table 6. Computed bulk modulus and pressure derivatives of uranophane- β derived from the EOS. The values of the bulk modulus computed from the elastic constants are also given in the last row of the table for comparison.

Property	Value
EOS	
$B \text{ (GPa)}$	51.57 ± 1.08
B'	3.85 ± 1.90
$B'' \text{ (GPa}^{-1}\text{)}$	2.77 ± 3.52
χ^2	0.001
Elastic constants	
$B \text{ (GPa)}$	51.79 ± 2.91

3.4 Raman spectroscopy

The Raman spectrum of uranophane- β was recorded from a natural specimen of this mineral from the pegmatite Perus, São Paulo, Brazil. The recorded spectrum was compared with the spectrum computed by using DFPT. The Raman intensities¹⁴⁹ are proportional to the Raman scattering efficiency, S ,

$$\frac{dS_{\sigma}}{d\Omega} = \frac{(\omega_0 - \omega_{\sigma})^4}{c^4} |\mathbf{e}_s \cdot \boldsymbol{\alpha}^{\sigma} \cdot \mathbf{e}_0|^2 \frac{h}{2\omega_{\sigma}} (n_{\sigma} + 1) \quad (1)$$

where ω_0 and ω_{σ} are the frequencies of the incoming and scattered photons, $\boldsymbol{\alpha}^{\sigma}$ is the Raman tensor of a particular mode σ , and $\mathbf{e}_s$ and $\mathbf{e}_0$ are the orientations of the scattered and incident light, respectively. The dependence on temperature is given by the factor:

$$n_{\sigma} = \frac{1}{e^{h\omega_{\sigma}/k_B T} - 1} \quad (2)$$

The theoretical spectrum was determined by computing the Raman tensors at the optimized crystal structure and using expression (1) for incident laser radiation with wavelength $\lambda = 633 \text{ nm}$ and $T = 298 \text{ K}$. The experimental and theoretical spectra are in very good agreement as shown in Figure 7 and, consequently, the theoretical results were employed to assign the bands in the experimental Raman spectrum. In Figure S.3 (Supplementary Information), images of the atomic motions in the Raman active vibrational modes are given.

The Raman spectrum was analyzed separately in four different wavenumber regions: (i) OH stretching vibration region from 2750 to 3650 cm^{-1} (Figure 7.D); (ii) H_2O bending region from 1500 to 1750 cm^{-1} (Figure 7.C); (iii) uranyl (UO_2^{2+}) and silicate (SiO_4^{4-}) fundamental vibrations region from 590 to 1250 cm^{-1} (Figure 7.B); and (iv) low-wavenumber region from 75 to 590 cm^{-1} (Figure 7.A). The resolution of the bands in the experimental Raman spectrum into components was carried out using a method described recently⁵⁷ and is shown in Figure S.4 of the Supplementary Information. Some types of atomic motions in the Raman active vibrational normal modes of

uranophane- β which are localized within the uranyl and silicate fragments are shown in Figure 8. Finally, three additional weak bands were observed between the OH stretching and H₂O bending regions. These bands are described after the discussion of the bands of the four main regions (Section 3.4.5). The Raman shifts of the experimental and theoretical spectra, the computed band intensities and the assignments performed in this work are given in Table 7.

Although several versions of the experimental Raman spectrum of uranophane- β were available from RRUFF database¹²⁵⁻¹²⁶ and these spectra were very useful in the initial steps of the present study, they cover only a very small wavenumber range and were not accurate enough for our purposes.

3.4.1 OH stretching vibrations region

Figure 7.D shows the Raman spectrum of uranophane- β in the hydroxyl stretching region which, as can be observed from the theoretical results, has a very complex structure. The complexity is expected from the dense hydrogen bonding network in the interlayer space of uranophane- β . The experimental spectrum displays a wide band having eight main band components located at the following wavenumbers: (i) band *a*: 3524 cm⁻¹; (ii) band *b*: 3477 and 3458 cm⁻¹; (iii) band *c*: 3379 and 3340 cm⁻¹; (iv) band *d*: 3230 cm⁻¹; (v) band *e*: 3177 cm⁻¹; (vi) band *f*: 3087 cm⁻¹; (vii) band *g*: 2978 cm⁻¹; and (viii) band *h*: 2759 cm⁻¹. These bands are reproduced theoretically at (i) band *a*: 3621 cm⁻¹; (ii) band *b*: 3379 and 3362 cm⁻¹; (iii) band *c*: 3307 and 3304 cm⁻¹; (iv) band *d*: 3221 cm⁻¹; (v) band *e*: 3160 cm⁻¹; (vi) band *f*: 3090 cm⁻¹; (vii) band *g*: 3006 cm⁻¹; and (viii) band *h*: 2797 cm⁻¹.

3.4.2 H₂O bending region

Figure 7.C displays the experimental and theoretical spectra of this region. The experimental spectrum contains three different bands at 1672, 1644 and 1633 cm⁻¹. These three bands correspond to the water molecule bending bands obtained in the theoretical calculations at the wavenumbers 1705, 1671 and 1612 cm⁻¹.

3.4.3 Uranyl (UO₂²⁺) and silicate (SiO₄⁴⁻) fundamental vibrations region

The first two bands in the experimental spectrum of this region, denoted as *o* and *p*, appear at 1210 and 1042 cm⁻¹, respectively, and are reproduced satisfactorily at 1190 and 1057 cm⁻¹. The first is assigned to SiOH bending vibrations localized SiO₃OH tetrahedra in which the hydroxyl ion is free, that is does not belong to the calcium atom coordination polyhedra, $\delta(fr - SiOH)$. The second is ascribed to SiOH bending vibrations localized SiO₃OH tetrahedra whose hydroxyl ions are coordinated with interlayer Ca atoms, $\delta(co - SiOH)$. The $\delta(fr - SiOH)$ and $\delta(co - SiOH)$ vibrational motions are illustrated in Figure 8 (see Figure 8.F and Figure 8.G, respectively). The next two experimental bands are located at 979 and 970 cm⁻¹ and appear in the theoretical spectrum at 984 and 967 cm⁻¹. The following experimental band, placed at 962 cm⁻¹, corresponds to a pair of theoretical bands at 947 and 943 cm⁻¹ which are too close to be resolved experimentally. All these three bands are assigned to SiOH bending vibrations and

water librations but in these cases the bending vibrations are not localized in *fr* or *co* SiO₃OH fragments (both types of fragments are involved simultaneously).

The experimental band located at 942 cm⁻¹ is calculated to be at 928 cm⁻¹ and attributed to combination of SiOH bending and SiO bond stretching vibrations and water librations. The band located at 881 cm⁻¹ corresponds to three theoretical bands which are weak and again are too close to be resolved experimentally. The calculated wavenumbers of these bands are 906, 897 and 895 cm⁻¹. The first one is assigned to uranyl UO and SiO bond stretchings, SiOH bending vibrations and water librations. The second one is ascribed to uranyl UO bond stretching vibrations and water librations and, finally, the third one to SiOH bending vibrations and water librations. Due to the symmetry loss in uranophane- β , the stretching vibrational motions in the uranyl ion involved in the bands at 906 and 897 cm⁻¹ cannot be classified as symmetric or antisymmetric. However, these bands are placed at wavenumbers close to those of the uranyl antisymmetric vibrations in many uranyl containing materials.^{38-42,150} As can be seen for example in Figure 8.A (and in Figure S.3 of the Supplementary Information), the contribution of uranyl UO bond stretching motions to the Raman active normal modes of uranophane- β is quite small.

The band located at 846 cm⁻¹ corresponds to the theoretical bands at 859 and 844 cm⁻¹. Both bands are attributed to combinations of SiOH bending and SiO bond stretching vibrations and water librations. The three bands at 796, 791 and 771 cm⁻¹ are calculated to be at 795, 793 and 764 cm⁻¹. The first of these bands is assigned to uranyl UO and SiO bond stretching, SiOH bending vibrations and water librations. The second and the third ones must be assigned to uranyl UO bond stretching vibrations, SiOH bending vibrations and water librations. As in the case of the bands located at 906 and 897 cm⁻¹, the uranyl UO bond stretching motions involved in these bands cannot be classified as symmetric and their contribution of these motions to the corresponding normal modes is very small. The experimental band at 740 cm⁻¹ correspond to three theoretical bands located at 735, 732 and 715 cm⁻¹, the three bands being assigned to SiOH bending vibrations and water librations. Finally, the bands located at 635 and 624 cm⁻¹ are reproduced theoretically at 648 and 646 cm⁻¹, both bands being attributable to water librations only. The band predicted theoretically at 597 cm⁻¹, also attributed to water librations, is probably too weak to be observable experimentally.

3.4.4 Low-wavenumber region

The first band of this region is located at 555 cm⁻¹. It is very well reproduced theoretically at 544 cm⁻¹ and assigned to water librations. The next experimental band at 539 cm⁻¹ corresponds to two theoretical bands located at 523 and 514 cm⁻¹, which are both assigned to OSiO (see Figure 8.H) and SiOH bending vibrations and water librations.

Fig. 7. Experimental and theoretical Raman spectra of uranophane- β : (A) Region: 75-590 cm^{-1} ; (B) Region: 590-1250 cm^{-1} ; (C) Region: 1500-1750 cm^{-1} ; (D) Region: 2900-3650 cm^{-1} .

Fig. 8. Uranyl and silicate atomic motions in the Raman active vibrational normal modes of uranophane- β : (A) Uranyl UO bond stretching, $\nu(\text{UO}_2^{2+})$; (B) Uranyl rotation, $\rho(\text{UO}_2^{2+})$; (C) Uranyl bending, $\delta(\text{UO}_2^{2+})$; (D) Uranyl deformation, $\gamma(\text{UO}_2^{2+})$; (E) SiO bond stretching, $\nu(\text{SiO})$; (F) SiOH bending, $\delta(\text{fr} - \text{SiOH})$; (G) SiOH bending, $\delta(\text{co} - \text{SiOH})$; (H) OSiO bending, $\delta(\text{OSiO})$; (I) Umbrella silicate deformation, $\text{Um}(\text{SiO}_4^{4-})$; (J) Silicate bending $\delta(\text{SiO}_4^{4-})$; (K) Silicate deformation $\gamma(\text{SiO}_4^{4-})$.

The bands at 473 and 441 cm^{-1} are calculated at 462 and 455 cm^{-1} . They are ascribed to a combination of SiO stretching, SiOH bending and umbrella-like silicate vibrations and water librations (see Figures 8.E and Figure 8.I). The bands at 406 and

390 cm^{-1} are associated to the calculated bands placed at 391 and (369, 346) cm^{-1} . The first one is assigned to silicate and SiOH bending vibrations, translations of the structural water molecules and librations of the free water molecules. The second one is attributed to SiOH bending vibrations and water librations. The following three bands encountered at 313, 281 and 275 cm^{-1} are reproduced theoretically at 306, 281, 267 cm^{-1} . They are assigned to a combination of silicate deformations, SiOH bending vibrations, water librations and three different atomic motions localized in the uranyl ion which may be clearly distinguished from Figure 8.B, Figure 8.C and Figure 8.D. These motions are the uranyl rotation, $\rho(\text{UO}_2^{2+})$, the uranyl bending, $\delta(\text{UO}_2^{2+})$, and the uranyl deformation, $\gamma(\text{UO}_2^{2+})$, motions. The bending and rotation motions involve displacements of the uranyl oxygens out of the uranyl axis in the same and opposite directions and in the deformation motion each oxygen atom displaces in a different direction. The bands at 259, 232, 215, 193, 176, 147, 123 and 86 cm^{-1} are calculated at 240, (235, 225), (218, 214), 195, 179, 166, (135, 128) and 90 cm^{-1} . These bands are ascribed to the combinations of motions given in detail in Table 7. The accurate reproduction of these eight bands and its detailed assignment is a very satisfactory achievement due to the excellent quality of first-principles theoretical treatment. As it is well-known, the assignment of low wavenumber bands of solid materials is generally not possible from empirical arguments because the corresponding bands do not exist in gas-phase molecules or liquid state systems.

Table 7. Experimental and calculated band wavenumbers in the Raman spectrum of uranophane- β , calculated intensities and assignments.

Band Name	Exp. Raman shift (cm ⁻¹)	Calc. Raman shift (cm ⁻¹)	Irr. Rep. (C _{2h})	Int. (Å ⁴)	Assignment
OH stretching region					
<i>a</i>	3523.9	3621	<i>A_g</i>	1554.00	$\nu(\text{OH})$
<i>b</i>	3477.1	3379	<i>A_g</i>	703.94	"
	-	3378	<i>B_g</i>	665.61	"
	3457.7	3362	<i>A_g</i>	4133.93	"
<i>c</i>	3378.7	3307	<i>A_g</i>	1527.23	"
	3339.8	3304	<i>B_g</i>	1472.65	"
<i>d</i>	3229.6	3221	<i>A_g</i>	4666.45	"
		3195	<i>B_g</i>	509.94	"
<i>e</i>	3177.3	3160	<i>A_g</i>	1904.57	"
<i>f</i>	3087.3	3105	<i>A_g</i>	1240.24	"
		3090	<i>A_u</i>	2568.61	"
<i>g</i>	2978.5	3006	<i>A_g</i>	1028.88	"
<i>h</i>	2758.7	2797	<i>A_g</i>	2588.39	"
<i>i</i>	2302.0	-	-	-	$\nu_1 + \nu_2 = 1672.4 + 634.8 = 2307.2 [l + u]$
<i>j</i>	2128.4	-	-	-	$\nu_1 + \nu_2 = 1643.6 + 472.8 = 2116.4 [m + z]$
<i>k</i>	2041.6	-	-	-	$\nu_1 + \nu_2 = 1643.6 + 389.9 = 2033.5 [m + \alpha]$
HOH bending region					
<i>l</i>	1672.4	1705	<i>A_g</i>	33.44	$\delta(\text{HOH})$
<i>m</i>	1643.6	1671	<i>A_g</i>	61.56	"
		1641	<i>A_g</i>	11.41	"
<i>n</i>	1633.4	1612	<i>A_g</i>	10.62	"
Fundamental UO_2^{2+} and SiO_4^{4-} vibrations region					
<i>o</i>	1209.6	1190	<i>A_g</i>	44.35	$\delta(\text{fr} - \text{SiOH})$
<i>p</i>	1042.2	1057	<i>A_g</i>	155.18	$\delta(\text{co} - \text{SiOH})$
<i>q</i>	979.0	984	<i>A_g</i>	72.02	$\delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
	970.4	967	<i>A_g</i>	145.74	"
	961.7	947	<i>A_g</i>	304.35	"
		943	<i>A_g</i>	92.97	"
	942.4	928	<i>A_g</i>	1206.66	$\delta(\text{SiOH}) + \nu(\text{SiO}) + \text{l}(\text{H}_2\text{O})$
<i>r</i>	880.7	906	<i>A_g</i>	137.99	$\nu(\text{UO}_2^{2+}) + \delta(\text{SiOH}) + \nu(\text{SiO}) + \text{l}(\text{H}_2\text{O})$
		897	<i>A_g</i>	76.94	$\nu(\text{UO}_2^{2+}) + \text{l}(\text{H}_2\text{O})$
		895	<i>A_g</i>	74.61	$\delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
<i>s</i>	846.0	859	<i>A_g</i>	74.94	$\delta(\text{SiOH}) + \nu(\text{SiO}) + \text{l}(\text{H}_2\text{O})$
		844	<i>A_g</i>	48.39	"
<i>t</i>	795.8	795	<i>A_u</i>	871.39	$\nu(\text{UO}_2^{2+}) + \delta(\text{SiOH}) + \nu(\text{SiO}) + \text{l}(\text{H}_2\text{O})$
	791.0	793	<i>A_g</i>	141.95	$\nu(\text{UO}_2^{2+}) + \delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
	770.8	764	<i>A_g</i>	1821.40	"
	739.9	735	<i>A_g</i>	975.29	$\delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
		732	<i>A_g</i>	277.10	"
		715	<i>A_g</i>	181.10	"
<i>u</i>	634.8	648	<i>A_g</i>	215.52	$\text{l}(\text{H}_2\text{O})$
	624.2	646	<i>B_g</i>	13.21	"
<i>v</i>		597	<i>A_g</i>	30.95	$\delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
Low wavenumber region					
<i>x</i>	554.8	544	<i>A_g</i>	11.39	$\text{l}(\text{H}_2\text{O})$
<i>y</i>	539.4	523	<i>A_g</i>	36.20	$\delta(\text{OSiO}) + \delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
		514	<i>A_g</i>	77.02	"
<i>z</i>	472.8	462	<i>A_g</i>	98.05	$\nu(\text{SiO}) + \delta(\text{SiOH}) + \text{Um}(\text{SiO}_4^{4-}) + \text{l}(\text{H}_2\text{O})$
	441.0	455	<i>A_g</i>	81.86	"
<i>α</i>	406.2	391	<i>A_g</i>	126.66	$\delta(\text{SiO}_4^{4-}) + \delta(\text{SiOH}) + \text{T}(\text{st} - \text{H}_2\text{O}) + \text{l}(\text{fr} - \text{H}_2\text{O})$
	389.9	369	<i>A_u</i>	58.79	$\delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
		346	<i>A_g</i>	49.37	"
<i>β</i>	313.0	306	<i>A_g</i>	37.23	$\rho(\text{UO}_2^{2+}) + \gamma(\text{SiO}_4^{4-}) + \delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
	280.9	281	<i>A_g</i>	35.60	$\delta(\text{UO}_2^{2+}) + \gamma(\text{SiO}_4^{4-}) + \delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$ "
<i>γ</i>	275.2	267	<i>A_g</i>	58.94	$\gamma(\text{UO}_2^{2+}) + \gamma(\text{SiO}_4^{4-}) + \delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
	258.8	240	<i>A_g</i>	39.91	$\gamma(\text{UO}_2^{2+}) + \delta(\text{SiOH}) + \text{T}(\text{H}_2\text{O})$
<i>δ</i>	231.8	235	<i>A_g</i>	12.04	$\gamma(\text{UO}_2^{2+}) + \delta(\text{SiOH}) + \text{T}(\text{H}_2\text{O})$
		225	<i>B_g</i>	18.49	$\gamma(\text{UO}_2^{2+}) + \gamma(\text{SiO}_4^{4-}) + \delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
<i>ε</i>	215.4	218	<i>A_g</i>	13.37	"
		214	<i>B_g</i>	25.34	$\rho(\text{UO}_2^{2+}) + \gamma(\text{SiO}_4^{4-}) + \delta(\text{SiOH}) + \text{l}(\text{H}_2\text{O})$
	193.2	195	<i>B_g</i>	7.55	"
<i>η</i>	175.8	179	<i>B_g</i>	6.76	"
<i>θ</i>	146.9	166	<i>B_g</i>	10.43	"
<i>λ</i>	122.8	135	<i>B_g</i>	7.40	$\gamma(\text{UO}_2^{2+}) + \gamma(\text{SiO}_4^{4-}) + \delta(\text{SiOH}) + \text{T}(\text{H}_2\text{O})$
		128	<i>A_g</i>	6.48	$\gamma(\text{UO}_2^{2+}) + \delta^{op}(\text{UO}_{eq}) + \text{T}(\text{OH}^-) + \text{T}(\text{H}_2\text{O})$
<i>μ</i>	86.43	90	<i>A_g</i>	10.11	$\text{T}(\text{UO}_2^{2+}) + \gamma(\text{SiO}_4^{4-}) + \delta(\text{SiOH}) + \text{T}(\text{H}_2\text{O})$

Fig. 9. Experimental Raman spectra of uranophane- β mineral in the wavenumber region from 2000 to 2500 cm^{-1} . Three weak peaks are observed at wavenumbers 2302.0, 2128.4 and 2041.6 cm^{-1} .

The bands at 473 and 441 cm^{-1} are calculated at 462 and 455 cm^{-1} . They are ascribed to a combination of SiO stretching, SiOH bending and umbrella-like silicate vibrations and water librations (see Figures 8.E and Figure 8.I). The bands at 406 and 390 cm^{-1} are associated to the calculated bands placed at 391 and (369, 346) cm^{-1} . The first one is assigned to silicate and SiOH bending vibrations, translations of the structural water molecules and librations of the free water molecules. The second one is attributed to SiOH bending vibrations and water librations. The following three bands encountered at 313, 281 and 275 cm^{-1} are reproduced theoretically at 306, 281, 267 cm^{-1} . They are assigned to a combination of silicate deformations, SiOH bending vibrations, water librations and three different atomic motions localized in the uranyl ion which may be clearly distinguished from Figure 8.B, Figure 8.C and Figure 8.D. These motions are the uranyl rotation, $\rho(\text{UO}_2^{2+})$, the uranyl bending, $\delta(\text{UO}_2^{2+})$, and the uranyl deformation, $\gamma(\text{UO}_2^{2+})$, motions. The bending and rotation motions involve displacements of the uranyl oxygens out of the uranyl axis in the same and opposite directions and in the deformation motion each oxygen atom displaces in a different direction. The bands at 259, 232, 215, 193, 176, 147, 123 and 86 cm^{-1} are calculated at 240, (235, 225), (218, 214), 195, 179, 166, (135, 128) and 90 cm^{-1} . These bands are ascribed to the combinations of motions given in detail in Table 7. The accurate reproduction of these eight bands and its detailed assignment is a very satisfactory achievement due to the excellent quality of first-principles theoretical treatment. As it is well-known, the assignment of low wavenumber bands of solid materials is generally not possible from empirical arguments because the corresponding bands do not exist in gas-phase molecules or liquid state systems.

3.4.5 The 1750–2750 cm^{-1} region

Apparently, in the spectral region between the OH stretching and H_2O bending regions, that is from 1750 to 2750 cm^{-1} , there are not Raman bands. However, a focused view on the region from 2000 to 2500 cm^{-1} (Figure 9) shows the presence of three

additional very weak bands located at 2302, 2128 and 2042 cm^{-1} . These bands are absent in the theoretical Raman spectrum and are identified as combination bands as detailed in Table . As mentioned in the next section, these bands are analogous to three bands observed in the Raman spectrum of uranophane- α that appear in the same region but at quite different wavenumbers.

3.4.6 Comparison of the Raman spectra of the α - and β -polymorphs.

Figure S.5 of the Supplementary Information gives a comparison of the Raman spectra of two mineral samples of uranophane- α and β taken from the RRUFF database.^{125–126} As can be appreciated, their Raman spectra are quite analogous. However, as it will be seen, many differences in the Raman spectra of these compounds may be found when they are observed in detail.

Table S.2 (Supplementary Information) contains a comparison of the present experimental Raman spectrum of uranophane- β and four different Raman spectra of natural samples uranophane- α published by Frost *et al.*^{38–39} in 2006. These natural samples are the first from the Shaba province (Democratic Republic of Congo, DRC),³⁸ and the other three ones from Shaba (DRC), the Poisson Canyon, New Mexico (USA) and the Eagle Pass, West Texas (USA).³⁹

The uranophane- β bands f (OH bond stretching), l , m , n (HOH bending), q_1 , q_2 (SiOH bending) and u_1 (water librations) are not observed or are very weak in uranophane- α . Likewise, the uranophane- α bands located at about 3310, 1500, 1370, 1270, 296, 268, 212, 137 and 112 cm^{-1} are not found for uranophane- β . In the α -polymorph, the combination bands i and k are displaced towards larger and smaller wavenumbers, respectively, and the j band appears at nearly the same location. Similarly, several bands as the g (OH bond stretching), o and p (SiOH bending) ones are red-shifted to smaller wavenumbers by about 79, 41 and 37 cm^{-1} , respectively.

3.3 Relative thermodynamic stability of the uranophane α - and β -polymorphs

The determination of the relative stability of two closely related stable polymorphic forms of a given crystalline material is a relatively difficult matter from the theoretical point of view because one must assure that the theoretical treatment of both forms is very well balanced to avoid possible artifacts. This is due to the fact that the evaluation of the relative stability involves the subtraction of energy quantities associated to the two polymorphs which are expected to be very close. Thus, one should use comparable unit cells and employ exactly the same methods (the same energy density functional and the same dispersion correction method if applied) and calculation parameters (in our case the same plane wave basis set and k -mesh). Besides, the convergence criteria used in the crystal structure optimizations must be not only the same for both forms but also more stringent than in the evaluation of the majority of material properties. Finally, vibrational zero point corrections should be taken into account.

The unit cell of uranophane- β was reoptimized using hyperfine convergence criteria (a convergence threshold of 0.002 eV/Å in the atomic forces was selected) and the optimized unit cell of uranophane- α determined in our previous work⁵⁴ was doubled and reoptimized using exactly the same calculation parameters and convergence criteria as for the β form. The use of a $1 \times 2 \times 1$ supercell for the α -polymorph assures that exactly the same chemical composition of the unit cells was employed for the treatment of both polymorphic forms. The zero point vibrational energies were also evaluated. From the results we obtain,

$$\begin{aligned}\Delta G^{\alpha-\beta}(P = 0 \text{ GPa}; T = 0 \text{ K}) &= G^{\alpha} - G^{\beta} \\ &= (E_{Tot}^{\alpha} - E_{Tot}^{\beta}) + (E_{Zp}^{\alpha} - E_{Zp}^{\beta}) \\ &= (-0.1237) + (-0.0006) = -0.1231 \text{ eV}\end{aligned}$$

Consequently, uranophane- α is 12.0 kJ/mol more stable than uranophane- β at zero pressure and temperature. The much larger abundance of the uranophane- α in nature should be the result not only from the larger thermodynamic stability but also from the larger simplicity of its crystal structure which makes its formation kinetically favored in line with the previous speculation made by Plášil.¹⁹

The small relative stability between the two polymorphic forms of uranophane is not the only example of near-degeneracy between two related uranyl containing materials having the same structural formula. An example is the α and β forms of barium uranyl phosphate¹⁵¹ and another one is the case of the Pmmn and Imm2 orthorhombic structures of rutherfordine uranyl carbonate mineral.⁵¹ In the last case, the X-ray diffraction patterns and Raman spectra are so close that they are almost indistinguishable using these techniques. Due to the smallness of the relative stability of these two orthorhombic structures, the simultaneous presence of both forms in nature was suggested.^{51,152}

4 Conclusions

The crystal structure of the layered calcium uranyl silicate pentahydrate mineral uranophane- β was studied by means of first-principles theoretical methods based on density functional theory. The calculated crystal structure and X-ray diffraction powder pattern were in good agreement with experimental data.¹⁹ From the energy optimized crystal structure, the elastic properties of uranophane- β were determined using the finite deformation method and compared with the elastic properties of the α -polymorph obtained in a previous paper.⁵⁴ An extended set of relevant mechanical data, including the bulk modulus and its pressure derivatives, the Young and shear moduli, the Poisson's ratio and the ductility, hardness and anisotropy indices was reported. The results show that uranophane- β is a weak and ductile mineral with a bulk modulus of about $B \sim 52$ GPa. While the bulk modulus is relatively similar to that of uranophane- α , $B \sim 59$ GPa,⁵⁴ the computed mechanical properties differ significantly despite of their structural similarity, the α -polymorph being a hard and brittle material. Uranophane- β is mechanically stable and its mechanical anisotropy is very large in contrast to the α -

polymorph which is very isotropic mechanically. While the dependence of the Young and Shear moduli with respect to the orientation of the applied strain is relatively similar for both polymorphs, the behavior of the compressibility and Poisson's ratio is very different. This work has revealed that, as a consequence of the large anisotropy, the mechanical behavior of uranophane- β is extremely anomalous and exhibits the important negative Poisson's ratio^{28,101-104,137-142} (NPR) and negative linear compressibility^{28,101-104,143-148} (NLC) phenomena. The magnitude of the lowest negative Poisson's ratio and compressibility are $\nu_{min} = -0.1$ and $k_{min}^V = -11.0 \text{ TPa}^{-1}$, respectively. While the first one is small, the NLC effect in uranophane- β is quite significant.

The experimental Raman spectrum of uranophane- β was recorded from a natural mineral sample from pegmatite Perus, São Paulo, Brazil and compared with the spectrum determined theoretically. Since both spectra were found to be in good agreement, the theoretical methods were employed to assign the experimental Raman spectrum. Besides, three weak bands of the experimental spectrum of this mineral, located at the wavenumbers 2302, 2128 and 2042 cm^{-1} , were identified as combination bands. Finally, the Raman spectrum of uranophane- β was compared with that of the α -polymorph. Although both spectra are very similar, the detailed analysis shows the existence of important differences between them which may be used as fingerprints useful to distinguish both polymorphs from the associated Raman spectra.

Finally, the relative thermodynamic stability of the α and β -polymorphs was evaluated. The α -polymorph is found to be more stable than the β -polymorph at zero temperature and pressure by -12.0 kJ/mol. Due to the larger thermodynamic stability and the larger simplicity of its crystal structure, the formation of uranophane- α is thermodynamically and kinetically favored. The evaluation of the relative stability of these materials as a function of temperature and pressure requires a quantitative determination of the Gibbs free energies from the corresponding thermodynamic functions (enthalpies and entropies). Exploratory theoretical calculations with small calculation parameters indicate that the relative thermodynamic stability increases as the temperature increases. However, the evaluation of the thermodynamic properties of both uranophane polymorphs requires the use of accurate parameter sets⁶¹⁻⁶² and should be pursued in the future.

Conflict of interest

There are no conflicts of interest.

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