Crystal structure of vyacheslavite, U(PO₄)(OH), solved from natural nanocrystal: a precession electron diffraction tomography (PEDT) study and DFT calculations†

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The crystal structure of the U(Ⅳ)-phosphate mineral vyacheslavite has been solved from precession electron diffraction tomography (PEDT) data from the natural nano-crystal and further refined using density-functional theory (DFT) calculations.Vyacheslavite is orthorhombic, with the space group Cmca, with \( a = 6.96 \) Å, \( b = 9.07 \) Å and \( c = 12.27 \) Å, \( V = 775 \) Å\(^3\) (obtained from PEDT data at 100 K). Z = 8. Its structure is a complex heteropolyhedral framework consisting of sheets of UO₂(OH) and PO₄ polyhedra, running parallel to (001), interconnected by additional PO₄ polyhedra. There is an (OH) group associated with the U(Ⅳ) polyhedron. The question of \( \text{H}_2\text{O} \) presence within the small cavities of the framework has been addressed by the DFT calculations, which have proved that vyacheslavite does not contain any significant amount of \( \text{H}_2\text{O} \) at room temperature.

Materials and methods

Sample

The sample investigated in this study was removed from the specimen containing vyacheslavite that originates from the Menzenschwand (Krunkelbach) uranium deposit, Black Forest Mountains, Germany. The matrix of the specimen consists of quartz, which crystallized into cavities. The pyramidal...
terminations of quartz are covered by limonite overgrown by dark-green to the green crust of vyacheslavite (Fig. 1A). The nanocrystal used in this study (Fig. 1B) was separated from the dark-green parts of the crust.

Single-crystal electron diffraction

For transmission electron microscopy (TEM) investigations, small pieces of vyacheslavite crystals were mildly crushed and deposited on a Cu-grid with a thin film of holey amorphous carbon. The grid was plunged into liquid nitrogen and then transferred to a Philips CM120 electron transmission microscope (TEM) (acceleration voltage of 120 kV, LaB6) using a Gatan cryo-transfer holder. Precession electron diffraction tomography (PEDT) data sets of non-oriented patterns were recorded at 100 K on several crystals with the precession device Nanomegas Digistar and a side-mounted CCD camera Olympus Veleta with 14 bit dynamic range. The precession angle was set to 1° and a tilt step of 1° as well. A condenser aperture of 10 μm and low illumination setting (spot size 7) were used to reduce the electron dose. PEDT data were analyzed using computer programs PETS and Jana2006. For each data set, the result is a list of hkl-indices with associated intensities and estimated standard deviations based on counting statistics. The analysis of the PEDT data at 100 K gives an orthorhombic unit cell with standard deviations based on counting statistics. The analysis programs PETS and Jana2006.

The dynamical refinement including hydrogen is significant and does not provide any improvement of further information.

Density-functional theory (DFT) calculations

We augmented out experiments with density-functional-theory (DFT) computations to validate the structure refinements. All computations are performed within the context of 3D periodic DFT as implemented in the software package VASP. Electrons were treated within the all-electron like PAW framework. The plane-wave cutoff energy \( E_{\text{cut}} = 520 \text{ eV} \) was adopted following previous computations on \( \text{UO}_2 \). The \( k \)-point grid was chosen as \( 4 \times 4 \times 2 \), taken into account the asymmetry of the lattice. DFT computations result in a metallic ground state, inconsistent with the green crystal colour. However, charge neutrality suggests that uranium is in an open shell +4 oxidation state. Therefore, we adopted a Hubbard+U approach to treat the open shells on uranium. We tested two sets of Hubbard+U parameters, \( U - J = 3 \text{ eV} \) and \( U - J = 6 \text{ eV} \), and applied to the uranium 5f-states. Both sets share, that crystals are predicted to be insulating and that the magnetic moment is largely confined to uranium. The computed magnetic moment per uranium ion is \( m = 2 \mu_\text{B} \), consistent with two unpaired electrons and an uranium +4 oxidation state. Moreover, our computations show that the finite atomic magnetic moment can be attributed to the uranium f-shell. Since the results for the two Hubbard+U parameter sets are indistinguishable, we report below only results for \( U - J = 3 \text{ eV} \). The void spaces in vyacheslavite may accommodate water molecules and the formation of superimposed is a difference-Fourier map of electron-density, with highlighted maxima corresponding to H1 atom.
an extended hydrogen bonding network is possible. In order to address water solubility in vyacheslavite we included van der Waals corrections as parameterized within the opt88-vdW functional.22 Unless noted otherwise, we fixed the simulation cell at the experimental geometry. In addressing the water solubility in vyacheslavite, an initial model of the water array is needed. For this purpose, we adopted a two-step process. In the first step we placed the oxygen in the water molecules and for fixed oxygen location we found the rotational equilibrium orientation of the water molecules based on electrostatic forces and derived torques (we assumed a TIP3P water model and formal charges of +4, +5, +1, and −2, for U, P, H, and O, respectively), using the TORQUE method.23 We determined the rotational equilibrium for 150 randomly chosen initial water configurations, in order to identify possible different water orientations. In a second step, we determined the H₂O position using DFT+U+vdW. Since the structure models obtained at different levels of the DFT theory calculations are differing only insignificantly (Fig. 3a and b), we further report (atom coordinates) the DFT+U model only. Results of the DFT calculations are given in the ESI (Tables S3a, b, S4a and b).

Results

General structural architecture as revealed from PEDT

The structure of vyacheslavite revealed from electron-diffraction data contains one U site, one P site, four O sites, and one H site. The structural model obtained at 100 K is similar to the model at the room temperature for the synthetic phase.9 At our case, the bond-valence calculations and stoichiometry considerations suggest that H-atom missing in the previous determination is associated with the O4 position and was successfully localized suggesting that H-atom missing in the previous determination is the bond-valence calculations and stoichiometry considerations subsequently con­

erved by our DFT computations.

The structure of vyacheslavite contains UIV cation coordinated in the form of a distorted square antiprism. One of the ligands is, in fact, a protonized O atom (O4); thus, the UO₇(OH)polyhedra share edges with each other and adjacent PO₄ tetrahedra to form chains extending parallel to [100]. The chains polymerize along the [010] by sharing edges between UO₂(OH)polyhedra, and by UO₂(OH)polyhedra sharing corners with the PO₄ tetrahedra of the adjacent chains. The structure thus contains complex uranium phosphate sheets running parallel to (001). These are interlinked by PO₄ tetrahedra that share corners with UO₂(OH) polyhedra from the next layer. The result is a framework, which contains cavities (of ~2 Å in diameter) that may host some H₂O. Nevertheless, no assignable residual electron density could be reasonably associated with additional O atoms (Fig. 2). The structural formula obtained for the natural vyacheslavite is, therefore, U⁴⁺[OH]₂[PO₄]₃, Z = 8. Based on the structure study of natural nanocrystal it is not likely that vyacheslavite contains H₂O.

Crystal structure based on DFT calculations

DFT computations were used to address the stability of the crystal structure. For simplicity, we did not include any interstitial water molecules (see below) and addressed the geometry of the O–H group only. Placing hydrogen in a general (8f) site allows for multiple solutions describing a cone with the oxygen at its apex. We constrain the initial O–H vector to be parallel to [001] and having a length of 1.0 Å. During the relaxation, the hydrogen rotated in the (y, z)-plane, to a final position ~21.0° off the [001] axis. In order to test the uniqueness of our DFT solution, we performed a second calculation, where the initial H–O vector was constraint to the (y, z)-plane as well but on the opposite side of the intersection of the (y, z)-plane and the cone. Upon relaxation, the O–H vector rotated back to the first solution. This result can be rationalized by considering the bond geometry of the unstable site, that is characterized by a comparatively short and repulsive d(U–…H) = 2.35 Å. If released from this (unstable) position, the hydrogen bond array evolves toward a lower energy state that is 17 meV per hydrogen lower in energy and d(U–…H) = 2.95 Å. The final orientations of the O–H vectors differ by less than 0.003 Å with an average final 8f position of (0, 0.399, 0.668). The vdW corrected computations corroborate the presence of a single position-H orientation. Thus, the DFT computations support the existence of a single fully occupied hydrogen (8f) site for –OH formation, consistent with our electron diffraction observations (Fig. 3a and b).

Uptake of H₂O based on DFT calculations

The determination of water solubility depends on the balance of chemical potentials of water in the crystal and water in the surrounding chemical environment. Our X-ray and electron diffraction observations do not show any evidence for extensive intercrystalline H₂O. We performed two sets of computations to shed light on the water solubility: DFT+U only, as well as DFT+U+vdW. In contrast to the –OH hydrogen placement, described above, with a strong affinity for single oxygen, H₂O is a charge neutral molecular unit that is bonded to the surrounding crystal through hydrogen bonds. To place the H₂O molecules in a rational fashion, we placed its oxygen at the (8e) site and explored the initial water orientation of eight water
molecules through the TORQUE method. We tested 150 randomly chosen initial orientations to explore the possibility of multiple equilibrium orientations. The analysis shows the existence of two equilibrium orientations that are symmetrically related through an inversion operation about the oxygen in each water molecule. Each hydrogen bond array (8H2O molecules) consists of hydrogen atoms in (16g) sites, and the two hydrogen atoms per water molecule are connected to surrounding crystal by $d(O-H-O) = 1.29 \text{ Å}$ and $1.68 \text{ Å}$ and O-H-O angles of 160° and 155°, respectively. Since the two equilibrium orientations are symmetrically equivalent, we picked one and generated the remaining hydrogen atoms by applying the space group operations to this set. The resulting eight H2O configurations were used as the initial configuration for our DFT computations: we retained subsets of these eight water molecules to explore the energetics of water solubility, similar to that given elsewhere.25 We performed computations for 0, 1, 2, 3, and 8 water molecules in the unit cell, at the DFT+U+vDw level, where only water molecules are relaxed for otherwise fixed experimental structure, we find that water solubility is an unfavourable endo- thermic process. Thus, the water solubility is predicted to be zero. If the structure is allowed to relax for fixed lattice, we observe a limited solubility of water with a maximum of stabilization energy of ~0.28 eV/H2O for 2H2O molecules in the unit cell. The hydrogen bonding array is slightly asymmetric, $d(O-H1) = 0.979 \text{ Å}$, $d(H1-O1) = 2.10 \text{ Å}$, and $d(O-H2) = 1.019 \text{ Å}$, and $d(H2-O2) = 2.09 \text{ Å}$. Moreover, for the H2 atom, we find an additional short H2-O bond of length 1.52 Å, which links the water molecules to the hydroxyl group coordinating uranium, and explains the unequal intramolecular O-H bond length. If the water content is increased to 3H2O, we find that the average (H-O) distance increases to 1.64 Å. This 7.7% increase of $d(H\cdot\cdot\cdot O)$, attributed to increased repulsion between like ion pairs, leads to a less favourable energy for water solubility. Therefore, even without vibrational effects, the solubility is not expected to extend beyond 3/8 H2O molecules pfu, leading to the nominal chemical formula: U[PO4](OH)0.375H2O. Thus, the water solubility may be over-estimated by energy-only based calculation, since entropy is expected to facilitate H2O release with increasing temperature. Moreover, allowing for relaxation of atomic positions for fixed experimental lattice shows that the H2O molecule migrates to the nearest uranium atom and increases its coordination number from 8 to 9, an effect of the small size of the cavity. For computation with the $n = 8$ case, $d(U-O)$ ranges from 2.198 Å to 2.782 Å, and the U-OH2 bond length is 2.595 Å. Furthermore, if we consider the oxygen coordination of the ninth coordinating oxygen (OH2), we can estimate local distortions. For the PEDT refined structure (Tables S1 and S2†) we identified the (four) oxygen ions of the uranium polyhedra that form the neighbours in the corresponding $n = 8$ computation of OH2. The four O-O distances are: 2.804 Å, 3.109 Å, 2.674 Å, and 2.980 Å. The corresponding distances for $n = 8$ are 3.010 Å, 3.587 Å, 2.718 Å, and 3.334 Å, with distortions that could be as high as ~14% of the bond length. Such a large distortion is far beyond the PEDT resolution limit and would have been resolved during our structure refinement. Even in the case of $n = 1$, we find significant distortions, 2.848 Å, 3.548 Å, 2.718 Å, and 3.334 Å. To conclude, the energetics obtained from the DFT computations support low if any water solubility at room temperature, consistent with our PEDT observations. Similarly, the DFT calculations predict significant changes of some of the U-O bond distances, and a coordination change from 8 to 9. None of these predicted changes has been observed in our experiments providing further evidence of very limited if any H2O solubility in vyacheslavite.

Implications

Current structure determination on vyacheslavite proved that the crystal data given originally were correct and that natural vyacheslavite has the same structure as the synthetic phase and contains small cavities that occasionally may host some molecular H2O. Nevertheless, based on DFT calculations the water uptake at room temperature is not thermodynamically favoured. Furthermore, our conclusions have not closed the controversy between the status of vyacheslavite and lermontovite as mineral species. Lermontovite is reported to have a formula U[PO4](OH). H2O, thus only slightly differing from that of vyacheslavite, nevertheless its structure remains unknown.26 Although based on current results, it is clear that the structure of lermontovite is entirely different from that of vyacheslavite, the volume of the cavity that can potentially host some additional H2O in vyacheslavite-like structures is small. Therefore we conclude that lermontovite is most probably based upon sheet structure, similarly to, e.g., béhounekite,27 since the reported unit-cell volume of lermontovite, ~1850 Å3 is much higher than that of vyacheslavite, ~780 Å3. Furthermore, the type material for lermontovite is not defined; therefore the conclusions of the original analyses cannot be verified.

Conflicts of interest

There are no conflicts to declare.

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