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Triclinic—Cubic Phase Transition and Negative Expansion in the Actinide IV (Th, U, Np, Pu) Diphosphates

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ABSTRACT: The AnP2O7 diphosphates (An = Th, U, Np, Pu) have been synthesized by various routes depending on the stability of the AnIV cation and its suitability for the unusual octahedral environment. Synchrotron and X-ray diffraction, thermal analysis, Raman spectroscopy, and 31P nuclear magnetic resonance reveal them as a new family of diphosphates which probably includes the recently studied CeP2O7. Although they adopt at high temperature the same cubic archetypal cell as the other known MP2O7 diphosphates, they differ by a very faint triclinic distortion at room temperature that results from an ordering of the P2O7 units, as shown using high-resolution synchrotron diffraction for UP2O7. The uncommon triclinic—cubic phase transition is first order, and its temperature is very sensitive to the ionic radius of AnIV. The conflicting effects which control the thermal variations of the P–O–P angle are responsible for a strong expansion of the cell followed by a contraction at higher temperature. This inversion of expansion occurs at a temperature significantly higher than the phase transition, at variance with the parent compounds with smaller MIV cations in which the two phenomena coincide. As shown by various approaches, the P–O b–P linkage remains bent in the cubic form.

INTRODUCTION

In 1935, Levi and Peyronel revealed the existence of a wide family of MIVP2O7 diphosphates, whose structure can be thought of as a rock-salt-like array of P2O7 units and MIV cations in octahedral coordination.1,2 Since then an abundant amount of literature has established the ability of this structure to host nearly any tetravalent cation, including some which almost never occur in a six-oxygen coordination like the two end members: SiIV and ThIV, coord. VI (r (SiIV) = 0.40 Å; r (ThIV) = 0.94 Å, coord. VI). In the early works the structure at room temperature was believed to be cubic (space group Pa-3, Z = 4, a ≈ 8 Å), but since the late 1960s, progress in diffraction techniques and other analytical methods have revealed superstructures for M = Si,3,7 Ti,8,9 and Ce10 resulting from an ordering of the bent P2O7 units. In this family, ZrP2O7 offers perhaps one of the most remarkable examples of a long-debated crystal structure. After Hagman et al. (1969)14 and Chaunac (1971)15 confirmed Levi’s model, Khosrovani et al. proposed in 1996 a 3 × 3 × 3 superstructure, still cubic, exhibiting unusual P–O–P angles of 180°.16 Ten years later, Birkedal et al.17 and Stinton et al.18 demonstrated that the superstructured cell was orthorhombic with all the P–O–P linkages bent at 141–149°. However, despite the validity of Levi’s model at room temperature often being questioned, most authors agree about the existence of this simple cubic form at high temperature,13,19,20 which will be referred to in the following as the "archetype".

Although less known than the other members of the family, the AnP2O7 (An = Th, U, Np, Pu) diphosphates have been studied during the past two decades in the frame of the exploration of the AnO2–P2O5 systems to evaluate the interest of phosphate-based matrices in the back-end of the nuclear fuel cycle.24–28 First considered as potential host matrices for the long-term minor actinides’ immobilization, these diphosphates showed two critical structural weaknesses, i.e., the presence of a bridging oxygen (O3 in the O3P2O5 unit) prone to protonation and the limited thermal stability of the big actinide cations in octahedral coordination.29 Besides,
development of spent nuclear fuel reprocessing led to the reinvestigation of the chemistry of actinide phosphates as products of the reaction with tributyl phosphate. However, available data remain limited because of the radioactivity hazards which restrict considerably both their availability and their use.

The actinide diphosphates also show several points of fundamental interest. From a structural point of view, the presence of high-radius cations like UIV and particularly ThIV in a 6-fold oxygen environment stable up to about 1000 °C is an exceptional feature from which unusual physical properties can be expected, like thermal expansion. In contrast to the other diphosphates, the title compounds are still considered to adopt Levi's simple cubic model. However, routine X-ray powder diffraction performed during our preliminary work showed anomalous peak profiles which suggested a complex and still unknown modification of the archetype. Synchrotron diffraction has been used to address this point.

In previous work, the room-temperature forms, supposedly cubic, were generally referred to as "α" to be distinguished from a would-be orthorhombic high-temperature variety termed β. The transition between both phases was reported to be reversible between 800 and 1000 °C for ThP2O7 and near 750 °C for UP2O7. However, despite being similar in composition to a diphosphate, the β form recently appeared to correspond to isomeric An2(PO4)(PO3O10) instead. Moreover, the symmetry of the room-temperature form of the true AnP2O7 diphosphates appears questionable. Thus, this misleading terminology will be replaced in the present work by naming the different forms after their crystal system, for example, c-UP2O7 for the cubic one. Indeed, nothing was known about a possible polymorphism in spite of two early dilatometric experiments made several decades ago on ThP2O7 and UP2O7, ceramics, which demonstrated an inversion of the thermal expansion. Now, such a phenomenon, one of the most popular topics related to the other MP2O7, is commonly associated to a probable phase transition to the archetype form. However, White et al., studying recently CeP2O7, suggested that this transition occurred below the inversion temperature. In the present work, a wide range of analytical methods was used in order to contribute to this debate by measuring precisely the thermal expansion of the AnP2O7 and characterizing the evolution of their crystal structure.

### EXPERIMENTAL SECTION

Owing to the toxicity and/or low radioactivity of the title compounds, all experiments except NMR and synchrotron diffraction on samples containing thorium or depleted uranium were carried out with special facilities in gloveboxes for radionuclides at ITU and ICSM.

**Synthesis.** Powder samples of the compounds were obtained following different synthesis routes adapted to both the stability of the AnIV cation in the octahedral environment and its tendency to oxidize or reduce. All actinide reagents were previously laboratory prepared.

As stated previously, pure ThP2O7 seems difficult to obtain by the wet chemistry synthesis. In previous work, the room-temperature forms, supposedly cubic, were generally referred to as "α" to be distinguished from a would-be orthorhombic high-temperature variety termed β. The transition between both phases was reported to be reversible between 800 and 1000 °C for ThP2O7 and near 750 °C for UP2O7. However, despite being similar in composition to a diphosphate, the β form recently appeared to correspond to isomeric An2(PO4)(PO3O10) instead. Moreover, the symmetry of the room-temperature form of the true AnP2O7 diphosphates appears questionable. Thus, this misleading terminology will be replaced in the present work by naming the different forms after their crystal system, for example, c-UP2O7 for the cubic one. Indeed, nothing was known about a possible polymorphism in spite of two early dilatometric experiments made several decades ago on ThP2O7 and UP2O7, ceramics, which demonstrated an inversion of the thermal expansion. Now, such a phenomenon, one of the most popular topics related to the other MP2O7, is commonly associated to a probable phase transition to the archetype form. However, White et al., studying recently CeP2O7, suggested that this transition occurred below the inversion temperature. In the present work, a wide range of analytical methods was used in order to contribute to this debate by measuring precisely the thermal expansion of the AnP2O7 and characterizing the evolution of their crystal structure.

#### Table 1. Main Acquisition and Refinement Parameters and Crystallographic Data for t- and c-UP2O7

<table>
<thead>
<tr>
<th>Parameter</th>
<th>t-UP2O7</th>
<th>c-UP2O7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Form</strong></td>
<td>t-UP2O7</td>
<td>c-UP2O7</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>25 °C</td>
<td>600 °C</td>
</tr>
<tr>
<td><strong>Diffractometer</strong></td>
<td>ESRF ID31</td>
<td>Siemens D8</td>
</tr>
<tr>
<td><strong>Wavelength, Monochromator</strong></td>
<td>0.35409 Å, Si (111)</td>
<td>1.5405 Å, Ge (111)</td>
</tr>
<tr>
<td><strong>2θ scan range, step</strong></td>
<td>23–30°, 0.001°</td>
<td>15–118°, 0.007°</td>
</tr>
<tr>
<td><strong>Obsd Refs</strong></td>
<td>10027</td>
<td>164</td>
</tr>
<tr>
<td><strong>I-dependent profile parameters</strong></td>
<td>125, 13</td>
<td>11, 6</td>
</tr>
<tr>
<td><strong>Conventional reliability factors</strong></td>
<td>Rp = 0.078, Rwp = 0.11, Rsigma = 0.037, Rwp = 0.056, Rp = 0.065, Rw = 0.093</td>
<td>Rp = 0.075, Rwp = 0.099, Rsigma = 0.047, Rw = 0.048</td>
</tr>
<tr>
<td><strong>Cryst. syst., Space group</strong></td>
<td>triclinic, P1 (no. 1)</td>
<td>cubic, Pa3 (no. 205)</td>
</tr>
<tr>
<td><strong>Cell parameters</strong>, volume</td>
<td>a = 8.6180(2) Å, b = 8.6326(3) Å, c = 8.6349(2) Å</td>
<td>V = 644.69(7) Å³</td>
</tr>
<tr>
<td></td>
<td>α = 89.929(2)°, β = 90.174(2)°, γ = 90.089(2)°</td>
<td>α = 90.089(2)°</td>
</tr>
<tr>
<td><strong>Fw, Z, Density</strong></td>
<td>411.96, 4, 4.26</td>
<td>411.96, 4, 4.24</td>
</tr>
</tbody>
</table>

To take into account possible systematic errors, esd's given by the refinement program have been multiplied by 10.
High-Temperature X-ray Powder Diffraction. Diffraction experiments above room temperature (HTXRD) were carried out under He flow on a conventional diffractometer equipped with a heating platinum holder. Temperature was calibrated according to the transition point of UP2O7, measured by DSC. Samples were studied at various temperatures from room temperature to 800 °C (500 °C for PuP2O7 because of the reduction of PuIV under He that led to formation of PuIIIPO4) with counting times and scan ranges depending on whether the pattern was to be used for measuring the cell parameters and peak width or refine the crystal structure (only in the cubic model). See Table 1 for experimental conditions in the latter case. A complete series of long XRD measurements was carried out on ThP2O7 in order to follow the thermal evolution of the P–P and Th–P distances.

Differential Scanning Calorimetry. DSC measurements of UP2O7 were performed under He flow at a heating/cooling rate of 15 °C min−1 on a Netzsch STA 409 A Cell analyzer.

31P Nuclear Magnetic Resonance. 31P NMR experiments on UP2O7 were conducted using a Bruker 400 MHz spectrometer operating at a Larmor frequency of 161.97 MHz. The sample was packed in a 4 mm zirconia rotor and spun at a magic-angle spinning (MAS) rate of 9 kHz. 31P chemical shifts were referenced to the signal from H31PO4 (80% aqueous solution) at 0 ppm. Temperature calibration was made prior to experiments using the temperature dependence of the 207Pb resonance of PbNO3. Correction factors were input into the Bruker software to correct temperature-induced field variations. The temperature was then calibrated according to the DSC measurements of UP2O7, carried out on a conventional apparatus equipped with an edge filter and using a Nd:YAG laser (Yvon Aramis apparatus equipped with an edge filter and using a 355 nm, 45 mW). Samples were placed in a platinum crucible and brought to the chosen temperature at a rate of 5 °C min−1 on a Netzsch STA 409 A Cell analyzer.

High-Temperature Micro-Raman Spectroscopy. HT-μ-Raman spectra of ThP2O7 and UP2O7 were collected with a Horiba-Jobin Yvon Aramis apparatus equipped with an edge filter and using a Nd:YAG laser (λ = 532 nm, 45 mW). Samples were placed in a platinum crucible and brought to the chosen temperature at a rate of 5 °C min−1. HT-μ-Raman spectra were then recorded after a few minutes of thermal stabilization. The laser beam was focused on the sample using an Olympus BX41 microscope, resulting in a spot area of about 1 μm2. Several locations were investigated at the surface of each sample, usually considering a dwell time of 30 s and an average of 4 scans. Band areas were finally determined from a Gaussian–Lorenzian fitting using the Peakfit 4.12 software.

RESULTS AND DISCUSSION

Crystal Structures of t- and c-UP2O7. The search for the crystal unit cell in the low-temperature form was initiated by careful examination of the synchrotron diffraction pattern taken at −173 °C, which exhibits the strongest deviation from the cubic model. No other peaks except those corresponding to residual U(UO2)(PO4)2 (≤0.7%) were observed, thus demonstrating the absence of a superstructure. Electron diffraction recently led to the same conclusion for ThP2O7. However, all peaks of the prototype cell showed anomalous profiles indicating a very faint cell distortion. The a, b, and c cell edges were evaluated from the 3-fold split 200 reflection and then used for a Le Bail (profile matching) refinement with Fullprof to determine the α, β, and γ angles. Although these parameters only faintly deviate from the archetype, the triclinic nature of the low-temperature form (t-UP2O7) appears clearly in the complex splitting of all the reflections except those with indices (h00), (0k0), and (00l) (Figure 1).

In the archetype form, the single bridging oxygen O1 of the P–O–P linkage is often considered to lie on the inversion center at (1/2,1/2,1/2), resulting in anomalous short bridging P–O distances (1.48–1.52 Å) and high thermal factors for O1 (Bo1 = 7–13 Å2). In a more realistic model, O1 is supposed to be distributed around this special position to take into account the bending of the P–O1–P linkage commonly observed in diporphosphates. Should these units order at low temperature, then the inversion center disappears. Thus, we built the starting triclinic model by expanding the atomic positions of the cubic set into the P1 space group, that is, with the 40 atoms of the 4 UP2O7 units in general positions. The refinement was performed with Fullprof. Despite the high number of peaks measured, the overlaps resulting from the pseudosymmetry and the strong contrast between the electron densities of U and O led us to impose soft restraints on the highly predictable P–O and P–O distances. Using Breze’s bond valence parameters and assuming bond strengths of 1 for P–O and 4/3 for P–O, the restraints were set, respectively, at 1.60 and 1.50 Å. Likewise, one common thermal factor was refined for all 8 P atoms, 1 for the 24 nonbridging oxygens, and 1 for the 4 bridging oxygens. The refined crystal structure is shown in Figure 2.

![Figure 1. Twelve-fold splitting of the 311 reflection in the final Rietveld plot of the synchrotron diffraction pattern of t-UP2O7 (red dots, experimental; black line, calculated, sum of the 12 peaks; lower green plot, difference curve). (Inset) Same region observed by laboratory XRD.](image)

![Figure 2. Crystal structures of triclinic t-UP2O7 (left) and cubic c-UP2O7 (right, showing the oxygen atoms on their mean position).](image)

The unit cell parameters of the t form confirm the nearly cubic geometry that was not detected in previous studies on UP2O7, based only on conventional XRD. The final positions of the cations are very close to those of the cubic model (Δx = 0.007 Å for uranium and ≤ 0.138 Å for phosphorus), so the faint triclinic distortion of the cell...
results in a splitting into peaks of similar intensities, as shown by decomposition of the cubic 311 peak into 12 nearly equal reflections (Figure 1). The shifts of the oxygen atoms are far stronger, but the unrestrained U–O distances and O–P–O angles are satisfactory (Table 2).

Table 2. Selected Cation–Anion Distances and Angles for t-UP2O7 (−173, 25 °C) and c-UP2O7 (600 °C)\(^{a}\)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>U–O (Å)</th>
<th>P–O(_b–P) (deg) (^{b})</th>
<th>U–P (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>−173</td>
<td>2.20(2)–2.27(3)</td>
<td>135(2)–140(2)</td>
<td>3.57(1)–3.76(1)</td>
</tr>
<tr>
<td>25</td>
<td>2.21(3)–2.28(3)</td>
<td>136(2)–142(3)</td>
<td>3.55(1)–3.73(1)</td>
</tr>
<tr>
<td>600</td>
<td>2.276(6)</td>
<td>139(2)</td>
<td>3.65(6)</td>
</tr>
<tr>
<td>T (°C)</td>
<td>P–O(_b) (Å)</td>
<td>P–O (Å)</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-----------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>−173</td>
<td>1.60(5)–1.61(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1.60(3)–1.61(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>1.60(4)</td>
<td>1.402(5)</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Ob is a bridging oxygen and O a nonbridging one. \(^{b}\)Esd's are underestimated because of the restraints on the P–O\(\_b\) distances.

The four independent P\(_2\)O\(_7\) units show a staggered conformation with a strong bending of the P–O\(\_b–P\) linkages. The bond angles are in good agreement with those determined from the Raman spectra using Lazarev's empirical correlation rule based on the \(\nu_\delta\) (P–O\(\_b–P\)) and \(\nu_{\pi}\) (P–O–P) stretching wavenumbers (about 140° at 20 °C). They are also comparable to the 137° angle of Cabeza's room-temperature cubic model featuring split positions for O\(\_b\). The binding of the P–O–P linkages results in a strong distortion of the PO\(_4\) tetrahedra. Typically, as shown in Figure 3 for the P\(_2\)O\(_7\) unit near (1/2,1/2,1/2), the O\(\_b–P\) angles involving a nonbridging O on the same side as the opposite phosphorus are higher than the other ones. This asymmetric distortion justifies a posteriori the choice of acentric space group Pl instead of P–1. This ordered model is also validated by the moderate thermal factor of the bridging oxygens (\(B_{O\_b} = 5.0(4) \text{ Å}^2\) at 20 °C, common to the four O\(\_b\)’s), comparable to that of the nonbridging ones (3.9(1) \(\text{Å}^2\)).

As will be shown below, UP\(_2\)O\(_7\) transforms to the cubic archetype form (c-UP\(_2\)O\(_7\)) at high temperature. This structure was refined from a conventional X-ray pattern on the basis of Levi’s cubic model (space group Pa-3, U (0,0,0), P (x,y,z) and nonbridging O (x,y,z)), but particular attention was paid to the location of bridging O\(_b\) (near (1/2,1/2,1/2)), which monitors the bending of the unique P–O\(\_b–P\) linkage. A Fourier synthesis of the observed structure factors at 600 °C was made introducing all atoms but O\(_b\) to obtain an electron density map of the (111) mid-distance plane perpendicular to the P–P (3-fold) axis (Figure 4). This reveals a dense and homogeneous annular zone centered on (1/2,1/2,1/2), which accounts for the delocalization of O\(_b\) about 0.56 Å away from the inversion center. This distribution of O\(_b\) in the archetype confirms that a ring-like model, even discontinuous, with off-centered positions is more satisfactory than an ellipsoidal model with a maximum probability of the presence at the center, in agreement with the absence of \(\pi\) bonding. P–O\(_b–P\) was estimated at about 139° on the basis of the P–P distance, assuming P–O\(_b\) = 1.60 Å. Although the nonbridging oxygen atoms are also affected by the disorder as shown by the anomalous short P–O distances, they are too close to the heavy uranium atoms to be observed in the same way as O\(_b\).

Other AnP\(_2\)O\(_7\). According to XRD, the other AnP\(_2\)O\(_7\) compounds (An = Th, Np, Pu) also exhibit broadened peaks without any evidence of a superstructure, but the distortion appears more intense when the An\(^{IV}\) cation is small (i.e., extremely faint for ThP\(_2\)O\(_7\), but clearly visible for PuP\(_2\)O\(_7\)). On this basis, the AnP\(_2\)O\(_7\) can be supposed to adopt also the triclinic symmetry at room temperature. In this way, the actinide cations differ from smaller ones like Si\(^{IV}\), Ti\(^{IV}\), and Zr\(^{IV}\), whose diphosphates have a 3 × 3 × 3 cubic or orthorhombic superstructure.\(^{3,8,17,18}\) On the other hand, White et al. using synchrotron diffraction recently noted a faint distortion of the CeP\(_2\)O\(_7\),\(^{13}\) and proposed a triclinic cell with parameters remarkably analogous to those of UP\(_2\)O\(_7\), considering both the metric distortion (0.20% vs 0.20% for the latter) and the maximum deviation from the right angle (0.17° vs 0.17°), also with two nearly equal cell edges. Thus, owing to the similar ionic radius of the tetravalent cation (rCe\(^{IV}\) = 1.01 Å; 1.00 ≤ rAn\(^{IV}\) ≤ 1.08 Å in 6-fold coordination\(^{3}\)), CeP\(_2\)O\(_7\) is probably isotopic with the title compounds.

Triclinic–Cubic Phase Transition of UP\(_2\)O\(_7\). A single endothermal peak (starting 155 °C, rev. 155 °C) is visible on
the DSC curve (Figure 5). Although intense, this transition shows a negligible hysteresis. HTXRD, less accurate than synchrotron diffraction, does not allow deconvolution of the strongly overlapped peaks of the triclinic form and following the thermal evolution of the six cell parameters. However, measurement of the integral width (IFWHM) of four strong composite peaks revealed a continuous decrease on heating, followed by a sudden break near the transition point (Figure 6).

Figure 5. Differential scanning calorimetry analysis of UP₂O₇: heating (upper) and cooling (lower) plots.

Figure 6. Thermal variation of average cell parameter a (black, left scale) of UP₂O₇, and integral widths of four composite diffraction peaks in the 45° ≤ 2θ ≤ 57° range (colors, right scale). a, h, k, and l refer to the cubic lattice.

At higher temperatures, all IFWHMs remain nearly constant and equal to that of a corundum standard, thus proving the cubic symmetry of the archetype and the probable absence of an intermediate form. As shown on the same figure, the t–c transition of UP₂O₇ is also associated with a marked increase of the cell edge, like for CeP₂O₇ in agreement with the first-order nature of the transition observed by DSC.

Further evidence of the t–c transition is given by ³¹P NMR. At low temperature, t-UP₂O₇ shows a complex spectrum, where the peaks of the eight independent phosphorus sites present in the triclinic cell strongly overlap (Figure 7). Consequently, a best-fit simulation of the ³¹P spectra over the whole temperature range could not reasonably be performed. The presence of heavy uranium atoms in the neighborhood also results in an anisotropic chemical shift and numerous rotation bands. The chemical shift appears very sensitive to temperature (0.49 ppm °C⁻¹ from linear fit), probably due to the strong thermal expansion of the cell, as described in the following section. However, the most remarkable thermal transformation of the NMR spectrum is the collapse of each grouping into a single peak upon reaching the cubic form at 155 °C, in agreement with the presence of phosphorus in a single site of the archetype form.

The transition temperatures of the other AnP₂O₇ (Table 3) were determined from the inflection point of the expansion curves as shown thereafter. To summarize, this phenomenon can be described according to three criteria: the first-order character, shown by DSC and the discontinuity of the cell volume; the order–disorder character, evidenced by the presence of heavy uranium atoms in the neighborhood also results in an anisotropic chemical shift and numerous rotation bands. The chemical shift appears very sensitive to temperature (0.49 ppm °C⁻¹ from linear fit), probably due to the strong thermal expansion of the cell, as described in the following section. However, the most remarkable thermal transformation of the NMR spectrum is the collapse of each grouping into a single peak upon reaching the cubic form at 155 °C, in agreement with the presence of phosphorus in a single site of the archetype form.

Table 3. Effect of the Ionic Radius of MIV on the Temperatures of Transition and Inversion of Expansion for Several MP₂O₇⁺

<table>
<thead>
<tr>
<th>Cation</th>
<th>ZrIV</th>
<th>PuIV</th>
<th>CeIV</th>
</tr>
</thead>
<tbody>
<tr>
<td>r_MIV (Å)</td>
<td>0.86</td>
<td>1.00</td>
<td>1.01</td>
</tr>
<tr>
<td>T_trans (°C)</td>
<td>290</td>
<td>180(5)</td>
<td>160(10)</td>
</tr>
<tr>
<td>T_inv (°C)</td>
<td>450</td>
<td>400</td>
<td>400</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cation</th>
<th>NpIV</th>
<th>UIV</th>
<th>ThIV</th>
</tr>
</thead>
<tbody>
<tr>
<td>r_MIV (Å)</td>
<td>1.01</td>
<td>1.03</td>
<td>1.08</td>
</tr>
<tr>
<td>T_max (°C)</td>
<td>160(10)</td>
<td>155(2)</td>
<td>85(5)</td>
</tr>
<tr>
<td>T executes (°C)</td>
<td>400</td>
<td>330</td>
<td>200</td>
</tr>
</tbody>
</table>

*Our estimation from ref 13 expansion curve; these authors state 115–175 °C. Inversion temperatures are estimated from the thermal expansion graphs (Figure 9).
delocalization of $O_b$; the direct change from triclinic to cubic (HTXRD, $^{31}$P NMR), unless a possible intermediate form occurs in a very narrow range of temperature near the transition. This very uncommon increase of the order of symmetry by a factor of 24 is comparable to that between the cubic $3 \times 3 \times 3$ and the $1 \times 1 \times 1$ cells$^{27}$ but higher than that between the orthorhombic $Pbca$ $3 \times 3 \times 3$ and the cubic $1 \times 1 \times 1$ cells of $ZrP_2O_7$ ($\sim 7.1$).$^{17,18}$

Thermal Expansion and Contraction. The thermal variation of the cubic/pseudo-cubic cell parameter $a$ was determined for the $AnP_2O_7$ diphosphates ($An = Th, U, Np, Pu$) by HTXRD and Rietveld analysis (Figure 8). Except at the highest temperatures, the expansion of the cell edge of $ThP_2O_7$ is in fair agreement with the dilatometric curve recorded on a ceramic by Laud et al. in 1971.$^5$ Note also the superimposability of the expansion curves of $NpP_2O_7$ and $CeP_2O_7$,$^{13}$ which, beyond the similarity of the ionic radii ($r_{\text{CeIV}} = r_{\text{NpIV}} = 1.01$ Å), can be seen as further evidence for a probable isotopy.

For all the other compounds the coefficient of thermal expansion (CTE) is strongly positive at low temperature and then becomes negative. For instance, $ThP_2O_7$ shows a nearly perfect linear contraction between 400 and 900 °C with a CTE $\alpha = -3.5 \times 10^{-6}$ °C$^{-1}$ ($R = 0.999$), an extremely rare value over such a wide range. One can compare this behavior to those of $ZrP_2O_7$, $ZrV_2O_7$, and their solid solutions$^{19,20,52}$ which also exhibit a strong expansion at low temperature. However, at variance with the $AnP_2O_7$, the transition is marked by a sharp break followed by a moderate but still positive expansion for $ZrP_2O_7$ (a moderate contraction for the vanadium-rich forms). In all the cases, the low or negative expansion observed above the transition point is typical of a thermal rocking of the corner-connected $\text{MO}_6$ and $\text{PO}_4$ polyhedra, even though these units sustain some distortion in this phenomenon and cannot be treated as rigid.$^{19}$ However, no explanation was found in the literature for the strong positive expansion that precedes the inversion in all these compounds.

As clearly observed for $UP_2O_7$, the jump in the domain of positive expansion corresponds to the change of symmetry, which obviously occurs below the inversion. Thus, these two phenomena should be considered as definitely distinct in the $AnP_2O_7$, like in $CeP_2O_7$.$^{13}$ On the other hand, the break in the expansion curve of the $ZrP_2O_7$–$ZrV_2O_7$ solid solutions matches with the transition to the archetypal form.$^{20}$ Indeed, differences in behavior are conceivable because the low-temperature distortions of these two families of diphosphates are also different.

We tried to explain the remarkable variations of the CTE considering the evolution of the crystal structure over a wide range of temperature. In $ThP_2O_7$, which has the lowest transition point, the triclinic distortion can be considered as faint enough to be ignored in the Rietveld refinement, which was performed therefore in the cubic model, whatever the temperature. Because the oxygen atoms are light, distant from their ideal positions in the triclinic form and subject to strong thermal displacements in the cubic form, the cation–oxygen distances were not considered as reliable enough to follow the evolution of the crystal structure. Conversely, the unambiguous positions of $Th$ and $P$ in the two domains allow consideration of the $Th$–$P$ and $P$–$P$ distances as suitable for this purpose.

The thermal rocking of the corner-connected $ThO_6$ and $PO_4$ polyhedra is the probable cause of the moderate but continuous decrease of the $Th$–$P$ distance in both $t$ and $c$ forms (Figure 9), although the intensity of this contraction is limited by the expectedly faint thermal expansion of the $Th$–$O$ bond. This contraction is also observed between $-173$ and $25$ °C by synchrotron diffraction in the triclinic domain of $UP_2O_7$ (Table 2). On the other hand, the expansion of the covalent $P$–$O$ bonds can be considered as negligible, so the intense and nonmonotonous variations of the $P$–$P$ distance only result from the two modes of deformation of the $P$–$O_b$–$P$ linkage: the stretching at low temperature and tetrahedra rocking at high temperature, which rule the expansion of the whole cell by their intensity.

We can propose an explanation for the expansion in the low-temperature domain on the basis of Birkedal's DFT model, in
which the energy of an isolated staggered $P_2O_7$ unit was calculated as a function of the $P-O-P$ angle.\textsuperscript{17} Figure 10 shows the anharmonic potential well, whose minimum corresponds to the equilibrium angle at 0 K. The energy increases very rapidly when the angle decreases, whereas the slope is much lower at high angles. From this model we can infer that the average value of the $P-O_b-P$ angle increases with energy $\Delta E$. Thus, assuming $\Delta E = kT$, the $P-O_b-P$ linkage should expand on heating in the same way as the thermal expansion of a chemical bond $A-B$ arises from the asymmetry of the potential well of $E_{A-B}$ vs $d_{A-B}$. Note that the $P-O_b-P$ angle actually observed in ThP$_2$O$_7$ has a very similar behavior up to the transition point (Figure 10, inset).

Although some improvements could be performed by taking into account the interactions with the tetravalent cation and the torsion of the $P_2O_7$ unit, the DFT model offers an interesting insight into the interactions with the tetravalent cation and the diphosphate unit. Therefore, this mode remains active in the cubic form. The crossing of the inversion barrier, predicted to occur above 160 °C by DFT, conceivably results in intense variations of the angle. A wide dispersion of the phonon modes can be expected as well as a shortening of the coherence length, which both contribute to the broadening of the signal observed.

In the archetypal form, the annular distribution of $O_b$ around the inversion center allows a rocking of the corner-connected tetrahedra. Actually, this effect starts at the transition point, as shown by the inflection of the $P-P$ expansion curve (Figure 9). At higher temperatures, the rocking becomes more intense and prevails over the stretching of the $P-O_b-P$ angle, resulting in a negative definite expansion of both the $P-P$ linkage and the cell edge. Thermal rocking, a common feature in corner-connected arrays of polyhedra, is known as one of the most efficient ways to achieve zero or negative thermal expansion.\textsuperscript{19} As shown in Figure 9, the conflicting effects, each of them predominant in a domain of temperature, do not govern only the expansion of the $P_2O_7$ unit but also that of the cell. For this reason, the expansion plots of the five compounds (Figure 8) show roughly similar slopes at high temperature. However, in agreement with the previous mechanism, An$^{IV}$ cations smaller than Th$^{IV}$ form stronger An--O bonds, more resistant to thermal disorder, so the temperatures of $t$--c transition and inversion of expansion logically increase when the ionic radius of An$^{IV}$ decreases (Table 3).

Although negative thermal expansion is a very rare property among crystalline solids, several recent studies have pointed out the outstanding tendency of the phosphates of tetravalent actinides to contract over wide ranges of temperature. For example, whereas zirconium oxophosphate $Zr_2O(OPO_4)_3$ has been known since 1985 for its ultralow expansion ($+1.5 \times 10^{-6}$...
for providing facility for working with actinides.

The unequaled high-radius, high-valence expansion is the high valence of the actinide which makes the An–O bond strong and therefore only faintly sensitive to temperature. Globally, the unequaled high-radius, high-valence combination makes this family an attractive field of research for low and negative expansion mechanisms.

ASSOCIATED CONTENT

Rietveld plot and CIF file of the t-\(\text{UP}_2\text{O}_7\) structure solved from synchrotron diffraction and \(^{31}\text{P}\) NMR shift in \(\text{UP}_2\text{O}_7\) plotted against sample temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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