Behavior of actinide dioxides under pressure: UO₂ and ThO₂

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The structural high-pressure properties of ThO₂ and UO₂ have been studied in diamond-anvil cells up to maximum pressures of 80 and 69 GPa, respectively. These results show that both thorium and uranium dioxides exhibit an identical sequence of structural transitions under pressure; both transform rather sluggishly to the cotunnite-type (orthorhombic *Pnma*) high-pressure structure. This study which was performed under better hydrostatic conditions than previous experiments has enabled us to determine reliable compressibility parameters for the two dioxides: ThO₂: $B_0=198(2)$ GPa and $B'_0=4.6(3)$; UO₂: $B_0=207(2)$ GPa and $B'_0=4.5(4)$. In the case of UO₂ the ambient pressure cubic phase was still found to be present at 69 GPa, which is in contradiction with earlier measurements. With regards to these results and re-calculations performed on other actinide dioxides PuO₂ and AmO₂, we obtain a different evolution of the bulk moduli through the actinide dioxide series.

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INTRODUCTION

These experiments form part of a general study looking at the influence of high pressures on the properties of fluoritetype compounds; in particular with respect to the role which 5f electrons play in bonding in these compounds. All of the AnO₂, with An=Actinide, crystallize in the (CaF₂-) type fluorite structure at ambient temperature and pressure. In this structure the cations are surrounded by eight equidistant anions forming the corners of a cube and consequently each anion is surrounded by four cations at the corners of a tetrahedron. The actinide atoms occupy the position 4a and the oxygen atoms position 8c of space group $Fm\overline{3}m$ and a particular feature of this structure is the presence of a large octahedral hole sited at position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

Previous high-pressure studies of $\bar{T}hO_2$ and UO_2 under pressure¹⁻³ performed using the energy dispersive x-ray diffraction (EDXRD) method were not able to determine precisely the high-pressure phase of UO_2 which could be indexed in either the *Pnma*² or *Cmcm* space group.¹ These experiments performed using the ADXRD method and synchrotron radiation combined with the use of N₂ as a better hydrostatic pressure transmitting medium enabled us to collect high-quality data whereby both the precise compressibility and the atomic positions of the high-pressure phase could be determined.

EXPERIMENTAL SETTINGS

A. Sample preparation

Fine white ThO₂ powder was produced by grinding semitransparent (pale-yellow) single crystals which were synthesized by high temperature solution growth at the Institute for Transuranium Element (ITU). This method is very good for growing refractory crystals. Crystallization is obtained, from solution of oxides in molten salts by transport in a gradient temperature (50 °C/cm); the solvent was lead vanadate (Pb₂V₂O₇) in small amount (36 g) and the nutritive element was oxide powder. This method gives small single crystals of around 8 mm³ after 7 days of growing. For UO₂, also synthesized at ITU, the method was different. Single crystals were obtained by chemical vapor transport using TeCl₄ as the transporting agent. Both methods of crystallization produce high-quality single crystals with well-formed natural faces. These two dioxides were characterized and their purity was verified by x-ray powder diffraction and a four-circle diffractometer.

B. High-pressure synchrotron diffraction

High-pressure ambient temperature studies of ThO₂ and UO₂ have been carried out on the beamline ID30 at the ESRF by ADXRD using a focused beam of high energy ($\lambda = 0.3738$ Å). Diffraction images were captured with an image plate detector or a CCD camera, and usually exposures of a few seconds were sufficient to obtain excellent diffraction data. The images were then integrated using the ESRF FIT2D software, which generates files for data analyses by Rietveld refinement using the FULLPROF program.⁴

Both compounds, consisting of a polycrystalline powder, were loaded in a Le Toullec–type membrane diamond-anvil cell (MDAC), using liquid nitrogen as the pressure transmitting medium, with a ruby ball as pressure calibrant. The only exception to this method was made for ThO₂ at very high pressure (i.e., above 55 GPa), in that case, we used a Cornell-type DAC, loaded with silicone oil and using copper powder as the pressure calibrant. Data was collected up to 80 and 69 GPa, respectively, for ThO₂ and UO₂.

RESULTS

A. Structural behavior of ThO₂

The initial lattice parameter of thorium dioxide at ambient pressure was found to be $a_0=5.6001(3)$ Å in good agreement with literature values.^{3,5} Around 34 GPa (Fig. 1) diffraction peaks appear between the 111 and 200 and before the 220



FIG. 1. ThO₂ powder diffraction pattern evolution with pressure. Around 34 GPa, peaks appear, belonging to the high-pressure phase. At 57 GPa, this phase is pure and is stable up to the maximum pressure of 80 GPa.

and 311 lines of the fluorite phase. This result is in agreement with high-pressure Raman spectroscopy⁶ which also shows a weak ThO₂ high-pressure phase peaks near 30 GPa. Lattice parameters were determined by full Rietveld refinement for all the 32 successive pressure steps. The highpressure phase was indexed in the (PbCl₂) cotunnite-type structure (orthorhombic structure, space group *Pnma*, *Z*=4). At 49 GPa the cubic phase was still found to be present and represents approximately 55% of the sample composition compared to the other phase, showing that the transition is still not complete.

When the transition starts, i.e., at 36 GPa, the orthorhombic lattice parameters are a=5.898(8) Å, b=3.600(3) Å, and c = 6.862(7) Å giving V = 145.7(3) Å³. The atoms are in the Th $(0.261, \frac{1}{4}, 0.111),$ (4c)in positions sites O $(0.163, \frac{1}{4}, 0.449)$ and the second O $(0.12, \frac{3}{4}, 0.27)$. Previously, Dancausse *et al.*³ made EDXRD measurements on ThO₂ with a laboratory x-ray source, and they observed the beginning of the transition at an upper critical pressure of 41.2 GPa. At this pressure, they obtained the following lattice parameters: a=5.90 Å, b=3.58 Å, and c=6.81 Å with V=143.84 Å³ slightly lower than ours. We conclude that they did not see the real beginning of the transition. In our case, the smoothness of the data obtained by ADXRD and synchrotron radiation allowed the analysis of the cotunnite phase to be performed from the beginning of its appearance, where it represents only a few percent of the sample. At low angles, diffraction peaks of the phase are very distinct from the cubic phase (Fig. 1), and could therefore be far better resolved than in the previous EDXRD experiments.

At \sim 57 GPa, the initial cubic structure completely disappears and only the cotunnite structure remains up to the



FIG. 2. Rietveld refinement of ThO₂ at 40 GPa (a) and 80 GPa (b). The round symbols correspond to the observed pattern, the full line to the calculated one, the line above to the difference between the observed and fitted profiles, and the ticks correspond to the reflection peak positions of the two phases, cubic $(Fm\bar{3}m)$ and orthorhombic (Pnma).

maximum pressure reached in this study, i.e., ~ 80 GPa. Figures 2(a) and 2(b) show the Rietveld refinements obtained at the beginning of the transition, when the high-pressure phase emerges at ~ 40 GPa and at 80 GPa when the sample is purely orthorhombic. At the highest pressure despite the broadening of the diffraction peaks, caused by the onset of nonhydrostaticity of the pressure transmitting medium, we were able to make a good refinement of the structure and reach $R_B = 3.2\%$.

Figure 3 shows the evolution with pressure of the lattice parameters across the fluorite to cotunnite phase boundary for ThO₂. In the high-pressure phase, the **a** axis is the most compressible and **c** the least compressible with the **b** axis following approximately the same evolution as **c**.

1. Compressibility of ThO₂

Figure 4 shows the relative volume V/V_0 evolution with pressure for ThO₂. The compressibility was determined for the cubic phase up to 20 GPa according to the Birch-Murnaghan equation of state (EOS),⁷ given below, giving



FIG. 3. Evolution with pressure of ThO_2 lattice parameters (a) and variation of relative lattice parameters (b). Beyond the transition zone the evolution of the relative lattice parameters appears to change.

values for the bulk modulus and its pressure derivative $B_0 = 198(2)$ GPa and $B'_0 = 4.6(3)$.

$$P = \frac{3}{2} B_0 \left[\left(\frac{V}{V_0} \right)^{-7/3} - \left(\frac{V}{V_0} \right)^{-5/3} \right] \\ \times \left\{ 1 - \frac{3}{4} (4 - B_0') \left[\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right] \right\}.$$

This bulk modulus value is much lower than the 262 GPa value determined by EDXRD in the previous study and established with a first derivative $B'_0=6.7$.³ This B_0 high value is probably caused by the experimental loading which was made with silicone oil as the pressure transmitting medium. It is now clearly established that silicone oil gives rise to overestimated bulk moduli due to its poor hydrostatic properties at low pressure.^{8–10} Before the EDXRD study made by Dancausse *et al.*,³ elastic constants calculations made by adiabatic acoustic measurements on ThO₂ single crystals¹¹ led to a bulk modulus at ambient temperature of 193 GPa, in reasonable agreement with our value.

Our bulk modulus value is very far from the 290 GPa theoretical value given by Kelly et al. in 1987,¹² but these calculations were made from the lattice parameters and total energy that do not take into account the 5f state. Although the 5f orbital is empty, this level widens in band and contributes, although only slightly, to the conduction band. By taking into account only the ionic character in ThO₂ bonding. Harding et al.¹³ in 1994 found a bulk modulus of 175 GPa, which is lower than our value. Thus it would seem that stronger interactions reinforce the material, making it more refractory to deformations and to structural changes under pressure. Recently, Li et al.14 recalculated the AnO2 bulk modulus and found for thorium dioxide: $B_0 = 220.8$ GPa and $B'_0=3.2$. If we increase the pressure derivative of the bulk modulus from 3.2 to our value 4.6, this will decrease the bulk modulus value down to ~ 211 GPa.

2. The transition zone

The structural phase transition in ThO_2 is accompanied by a 6.1% volume collapse. This sudden contraction in volume is often the sign of an electronic level change and 5*f* electron promotion in the conduction band. This is not the case here, and this tendency is not systematic for the actinide compounds, particularly as ThO_2 does not have any 5*f* electrons. This is a first order transition which starts at 88% relative volume and finishes when the volume reaches 85% of the initial fluorite-type phase volume (see Fig. 4). The transition zone extends by nearly 20 GPa before the pure cotunnitetype structure is obtained. The two phases cohabitation zone is in the same order of magnitude as the previous study³ made by Dancausse et al. in EDXRD where it existed over a range of nearly 15 GPa (from 40 to 55 GPa). This study shows the transition zone starting earlier at 33 GPa and is complete above 49 GPa. In spite of relaxation times shorter than in the EDXRD study (less than 30 min. between two pressure steps instead of several hours), the kinetics of the transformation appear unmodified.

B. Structural behavior of UO₂

As in the case of ThO₂, all 33 collected spectra were treated using Rietveld refinement. The initial cubic $Fm\bar{3}m$ lattice parameter was determined to be $a_0=5.4731(4)$ Å, in good agreement with the literature.^{1,2} Upon increasing pressure, the spectra show a similar evolution as observed for ThO₂ although there are some noticeable differences. For example, when the high-pressure phase appears at ~42 GPa, the transition zone is much larger, and the initial phase (fluorite-type structure) is still present at the maximum pressure reached, i.e., ~69 GPa. In the previous high-pressure study of UO₂ (Ref. 1) a much lower transition pressure of 29 GPa was found for the cubic ($Fm\bar{3}m$) to orthorhombic transition.

The possible orthorhombic *Cmcm* structure predicted by Benedict *et al.*¹ does not fit with the high-pressure spectra, only the cotunnite-type structure (*Pnma*) corresponds, by



FIG. 4. ThO₂ compressibility curve. The transition zone to a low symmetry structure covers 20 GPa and is accompanied by a 6.1% volume collapse.

peak refinement, to this phase. Figure 5 shows the Rietveld fit at 65 GPa for the fluorite-type plus cotunnite-type structures with good agreement factors: Bragg factors R_B are less than 4% for each of the two phases.

The absolute evolution of each of the high-pressure phase lattice parameters appears to be almost identical with those of the low-pressure phase but in relative $(\mathbf{a}/\mathbf{a}_0, \mathbf{b}/\mathbf{b}_0, \text{ and}$ \mathbf{c}/\mathbf{c}_0) the behavior is different (Fig. 6). These three relative parameters evolve uniformly with respect to each other in spite of very different compressibilities; the smallest axis **b** is most compressible whereas the **a** axis is most rigid. When one looks at the fluorite-cotunnite mixed phase zone the evolution of the initial cubic structure does not seem to be affected by the presence of the high-pressure phase.

1. Compressibility of UO₂

The structural phase transition from cubic to orthorhombic occurs around 40 GPa, and is accompanied by a 7% volume collapse, see Fig. 7. The transition begins at 87% of the initial volume and continues beyond 81%. The transition zone remains up to 69 GPa, the maximum pressure attained. From the compressibility curve (Fig. 7), by fitting the third order Birch-Murnaghan EOS up to 18 GPa, we have calculated a bulk modulus $B_0 = 207(2)$ GPa with a pressure derivative $B_0 = 4.5(4)$. This value falls in the expected value range¹ and it is in good agreement with the previous EDXRD experiment which gave 210(10) GPa.² Nevertheless our B'_0 is more realistic than the value of 7.2 previously found. Our B_0 value is also in total agreement with speed of sound measurements made on UO₂ single crystals at ambient temperature and pressure in 1965.¹⁵ These measurements found the elastic constants c_{11} =396 GPa and c_{12} =121 GPa giving B_0 $=(c_{11}+2c_{12})/3=212.7$ GPa.

The UO_2 compressibility curve evolves slower than for ThO_2 and the transition zone is much larger. UO_2 is more stable than ThO_2 , so that cohesion energies in UO_2 are stron-

ger. Even at the maximum pressure of 70 GPa reached during this study, a completely pure high-pressure phase was not observed, contrary to the EDXRD studies of Benedict *et al.* and Benjamin *et al.*,¹ which indicated the pure high-pressure phase at 40 GPa.

During the first UO₂ experiment, after having reached 54 GPa, we allowed the system to relax for 24 h, and then remeasured a data point. This point (corresponding to the white symbols in the fluorite and cotunnite-type structures in Fig. 7) lies perfectly on the compressibility curve. The cotunnite-type structure continued "to grow" during relaxation: at 54 GPa the orthorhombic phase was present at \sim 54% in volume compared to the initial phase and one day after its proportion increased to 68.6% showing that the rearrangement of atoms into different crystallographic positions is a slow process. During the same period, the pressure measured in the sample cavity, decreased from 54.3 to 52.5 GPa, due to mechanical relaxation of the DAC, and also, to a lesser degree, by the volume reduction in the sample due to the greater proportion of denser phase.

Another phenomenon which has previously been observed in ADXRD studies of actinide compounds and alloys^{16,17} is a change of slope in the compressibility curve (see Fig. 7) around 20-30 GPa for high-pressure studies using liquid nitrogen as the pressure transmitting medium. In UO2, the appearance of this "bump" starts just before the appearance of the first orthorhombic phase lines (102), (200) and (111) at 34 GPa. As with the study of ThO_2 at this stage, these lines are visible but still too weak in proportion to the initial structure to allow the determination of structural parameters with any accuracy. However the presence of this new phase would seem sufficient to create an effective pressure lower than the pressure determined by the ruby although this "bump" also coincides with the loss of liquid nitrogen hydrostaticity. This phenomenon, however, did not disturb the determination of the compressibility parameters calculated with data points taken before 20 GPa.

2. Interactinide distance in UO₂

In the cubic Fm3m structure, the atomic positions are very well defined in the primitive cell, and the interatomic distances can be easily calculated starting from the cell parameter. In the high-pressure orthorhombic structure, the atomic positions are not fixed, each atom has freedom degrees. They occupy the special 4c positions $(x, \frac{1}{4}, z), (-x, \frac{3}{4}, z)$ $(-z), (\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z), \text{ and } (\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z) \text{ with values of differ-}$ ent x and z according to the atom. Table I summarizes the interactinide distances in UO₂ determined by refinement at particular pressure points (ambient, critical, and maximum of this study and an intermediate point). In the cotunnite phase, each uranium atom is surrounded by 12 others at "nonequivalent" distances; shorter U-U distance corresponds, for a given atom, to its two first close neighbors. This distance decreases notably from one structure to another. At the beginning of the transition, the shortest U-U distance in the high-pressure phase is 3.33 Å and this goes down to 3.24 Å at the maximum pressure. The reduction with pressure in the interactinide minimum distance (short-range distance) between the fluorite-type and cotunnite-type structures is established to 10%. On the other hand, in average distance, this difference between the two phases is about 2% which can be explained by the practically constant distance of the longrange neighbors.

Average values between actinides are slightly higher than the Hill limit¹⁸ (equal to 3.5 ± 0.1 Å for uranium) below which 5*f* orbital overlap can occur in UO₂. The previous UO₂ XRD study¹ had also given U-U distances higher than the Hill limit, but a distance between nearest neighbors of about 3.5 Å (against 3.3 in our case). These distances were calculated not taking into account the degrees of freedom of the atoms around their ideal position. Our result indicates, on the assumption of Hill, that the present phase transition is not accompanied by a 5*f* electron delocalization. However, at 69 GPa, the average value of 3.536 Å is at the Hill limit, and a small additional pressure should be enough to exceed this limit.



FIG. 5. Rietveld fit of UO_2 at 65 GPa. The round symbols correspond to the observed pattern, the full line to the calculated one, the line above to the difference between the two spectra, and the ticks correspond to the reflection peak positions of the fluorite-type (top) and cotunnite-type (bottom) phases.

EXTENSION OF DISCUSSION TO AnO₂ COMPOUNDS

Nearly all the previous studies on actinide dioxides under pressure were undertaken in XRD by using silicone oil as the pressure transmitting medium, which in most cases leads to a B_0 bulk modulus value higher than the actual value. This was the case for all previous high-pressure studies on NpO₂, PuO₂, and AmO₂. Table II shows a summary of the compressibility parameters of all studies made up to the present: previous experiments, theoretical studies, current studies of ThO₂ and UO₂, and also redefined values for NpO₂, PuO₂, and AmO₂.

The bulk modulus values are all established at values of around 200 GPa whatever the actinide, and there is an agreement between the theoretical values calculated by Li *et al.*¹⁴ and experimental studies (see Table II). For UO₂ the B_0 value of 212.7 GPa obtained from ultrasound measurements¹⁹ is consistent with that obtained by our XRD



FIG. 6. Evolution of UO_2 relative lattice parameters vs pressure.



FIG. 7. Compressibility curve of UO_2 . The dark line in the low pressure phase corresponds to the Birch-Murnaghan fit. The beginning of the cotunnite phase is accompanied by a 7% volume collapse and the transition zone is very large. White symbols observed at 52 GPa correspond to a measured point after decreasing pressure for several hours of system relaxation. In spite of the maximum pressure high value ~69 GPa, the high-pressure phase is not pure; it cohabits with the cubic phase.

study. No studies have been made on PaO₂ due to the great difficulty of synthesizing this oxide and obtaining the right stoichiometric balance. Theory suggests, for PaO₂, a transition to a lower symmetry structure at much lower pressures than observed for other AnO₂ compounds.¹² PuO₂ and AmO₂ bulk moduli were largely overestimated in previous work.^{3,20} Recalculation of the bulk modulus was performed from this old data at low pressure and taking into account the overestimation of values caused by the pressure bump due to solidification of the silicone oil pressure transmitting medium. We redefined average values of around 180 GPa for PuO₂ and 200 GPa for AmO₂.

One point not shown in Table II is that the transition from cubic to cotunnite-type phase in AnO₂ compounds falls in the same range of pressure, 30-50 GPa, except for UO₂ where this occurs at higher pressures as mentioned previously (references are given in Table II). The degree of volume collapse at the transition for the dioxides also falls in the same range of values whatever the actinide. It would thus seem that the first order transition to cotunnite structure is not related to the "delocalization" of the 5*f* electrons.

TABLE I. Volume variation and U-U distances in UO_2 fluoritetype and cotunnite-tpe structures. "Min." means minimum distance, "Max." the maximum distance, and "Aver." the average distance from the first 12 uranium atoms which surround an atom of uranium.

Pressure	Space	Volume	U-U dist. (Å)			
(GPa)	(GPa) group		Min.	Aver.	Max.	
0	$Fm\overline{3}m$	163.95		3.869		
44	$Fm\overline{3}m$	141.73		3.687		
	Pnma	130.92	3.329	3.613	3.756	
58	$Fm\overline{3}m$	135.11		3.630		
	Pnma	125.82	3.285	3.567	3.753	
69	$Fm\overline{3}m$	131.27		3.594		
	Pnma	122.24	3.239	3.536	3.757	

Electronic structure. ThO₂ has a rather broad gap and is insulating. In contrast UO_2 is a semiconductor (5f electrons are not itinerant) whereas the majority of uranium compounds are metallic and thus have 5f states which hybridize with the conduction band. By applying pressure, it should be possible to "delocalize" 5f electrons by increasing bandwidth W_f of the 5f which consequently would become higher than the Coulomb correlation energy U_f (=4.5 eV). But it is more probable that this change of f electron state occurs by increasing the conduction bandwidth so that it overlaps the 5f states and becomes occupied. In this last case, Kelly et al.12 predicted a reduction in the cell parameter to 82% of the initial parameter \mathbf{a}_0 required to have the 5f states in the conduction band. In the present study, the critical pressure occurs at an approximate \mathbf{a}/\mathbf{a}_0 ratio of 95.5% and, at 93% the transition is not complete (see Fig. 6); these percentages are far from the theoretical predictions.

This theoretical model suffers from assumptions, which establish the completely ionic type of bonding whereas there is some covalent character in AnO₂, and this defect leads thus to a too drastic reduction in the lattice parameters. In the first assumption, 5f bandwidth becomes higher than the Coulomb correlation energy for the **a** parameter reduced to 89% of **a**₀. Even if this value corresponds to a pressure lower than the second model, it remains very far from our 45–70 GPa. By extrapolating the curve that presents the evolution of the relative lattice parameters against pressure (Fig. 6), pressures higher than 110 GPa are reached at the point $\mathbf{a}/\mathbf{a}_0=89\%$. It would therefore be necessary to reach much higher pressures to determine if a second transition to a lower symmetry structure occurs.

CONCLUSION

ThO₂ and UO₂ have an identical structural behavior under pressure. We observe a first-order phase transition from the cubic CaF₂-type structure to the orthorhombic PbCl₂-type structure at much higher pressures than found in previous studies.

	Previous study			ESRF-ADXRD Present study		Theory add-in		
	B_0 (GPa)	B'_0	Ref.	B_0 (GPa)	B'_0	B_0 (GPa)	B'_0	Ref.
ThO ₂	262(4) 193	6.7(5)	3 3	198(2)	4.6(3)	290 175 220(8)		12 13 14
PaO_2								
UO ₂	210(10) 192(20) 212.7	7(2) 9(4) 6.4(6)	2 1 19	207(2)	4.5(4)	222.7 230	3.5	14 12
NpO ₂	200	3.8	21	200 ^a				
PuO ₂	379(4)	2.4(4)	3	178 ^a		218.7 190	3.1	14 12
AmO_2	280(3)	2.6(6)	20	205 ^a		216.1	3.1	14
CmO_2	218(5)	7(1)	20			218.0	3.1	14

TABLE II. Summary of the bulk modulus values and its first pressure derivative for AnO_2 . PaO_2 was never studied under pressure.

^aThe compressibility parameters of NpO₂, PuO₂, and AmO₂ were reevaluated from the original experimental data of the former studies; these values are only indicative which is why B'_0 pressure derivatives are not given.

The UO₂ high-pressure phase has been clearly defined as being orthorhombic *Pnma* as do all AnO₂ compounds except NpO₂ which is quantitatively indexed in the orthorhombic *Cmcm* structure.²¹ Taking into consideration this result it would be interesting to restudy the structural behavior of NpO₂ under pressure because the space group *Cmcm* indexation in the orthorhombic structure had clearly been attached to 5*f* electrons delocalization.

Actinide dioxides behavior under pressure differs from that of pure actinides;²² one cannot define a systematic behavior starting from the dioxides compressibility parameters which is similar whatever the element An. It would thus seem that the participation or not of 5f electrons in the binding does not influence the compressibility parameters value. Therefore if one considers that electronic nature intervenes in a prevalent way in the bulk modulus value, all the AnO₂ compounds do not present any delocalization under pressure at the phase transition. For all, there is a transition to a lower symmetry orthorhombic structure accompanied by a volume

collapse, but this transition CaF_2 -type \rightarrow PbCl₂-type structure is also observed in many fluorite-type compounds whereas they do not have *f* electrons (for example, BaF₂, PbF₂, SrF₂, CdF₂, CaF₂, etc. and also ZrO₂, HfO₂, PrO₂, etc.^{23,24}).

It is probable that at very high pressure (beyond any experimental limit today), there must occur a transition to itinerant 5f states. Given the solid basis established by the present work, we urge theoretical calculations to explore this high-pressure regime. Present synchrotron advances promise the capability of multimegabar pressures within a decade, and predictions would thus spur new experiments in the future.

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