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Journal of Alloys and Compounds 223 (1995) 216–225

Journal of ALLOYS AND COMPOUNDS

Comparative aspects of the high-pressure behaviour of lanthanide and actinide compounds

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Abstract

All lanthanide and actinide metals which are available as solids in sufficient quantity have undergone structural investigation at elevated pressure and can be systematically compared. Systematics is much less complete for the pressure behaviour of the compounds. We shall see that sufficient information is only available for some of the 1:1 compounds with elements from the fifth and sixth main groups of the periodic table, the monopnictides and the monochalcogenides. This is in part due to radioactivity and scarcity of some of the elements concerned, but also to lack of pressure studies on compounds of some of the more easily accessible lanthanides. The available information on high-pressure structures, transition pressures and compressibilities is presented in the form of graphs and tables. The paper centres on a comparison of the CeX compounds with ThX, on one hand, and with PuX, on the other, where the largest amount of data has been obtained.

Keywords: High-pressure behaviour; Transition pressures; Compressibility

1. Introduction

Pressure has been introduced as a parameter in solid-state studies much later than temperature. The pioneer in the area of high pressures was Percy W. Bridgman who, in the 1940s, was able to study a large variety of solids under pressures up to 10 GPa, mostly by piston-cylinder techniques which he devised.

The next thrust in high-pressure studies was brought about in the 1970s by the introduction of diamond anvil cells (DAC) [1,2] which allowed a major extension of the pressure range up to some tens of GPa, and which in their most recent versions have even been able to reach pressures of several hundred GPa. The highest pressures achieved up to now in a DAC seem to be 400–500 GPa (4–5 Mbar) [3], and thus these are the highest static pressure obtained in a laboratory in general.

Crystal structure and a number of physical properties can be and have been studied at these high pressures in situ. The transparency of single-crystal diamond to electromagnetic radiation in a wide range of energies favours X-ray and optical methods, but electrical resistance under pressure has been equally measured up to at least 30 GPa, and Mössbauer spectrometry has been carried out to pressures of about 40 GPa. Direct determination of magnetic properties under pressure has been initiated [4].

Application of pressure techniques to some actinide metals was favoured relatively early (in the 1940s) in the context of the Manhattan Project. The pressure study of actinide compounds started much later; most of the work on compounds was done after 1980. For the lanthanides and their compounds, a wave of interest arose in the 1970s, following the discovery of a pressure-induced isostructural collapse of 16% in volume in the 4f metal cerium [5]. However, as we shall see below, the large number of lanthanide compounds known has up to now been covered quite incompletely by high-pressure studies. Only 27 of the 121 known 1:1 lanthanide compounds with a non-metal have been studied up to now by X-ray diffraction under pressure [6]. In contrast, this method has been applied to nearly half of the 67 known AnX compounds. This leads to a situation where results for a corresponding 4f partner quite often cannot be found when we want to compare the observed pressure behaviour of a 5f compound. The reverse is also true in some cases. It turns out that at present the only compound class where some systematic 4f–5f comparison is possible is the B1 (NaCl) type compounds.

Previous attempts at 4f–5f comparison in the field of high-pressure structures and compressibilities are found in a Chapter in a handbook [6] and in a paper published in 1993 [7]. The present review will try to incorporate recent results and to advance towards a more complete picture.

0925-8388/95/$09.50
SSDI 0925-8388(94)09011-4

2. B1 type compounds, LnX and AnX

The X in these compounds is an element from either column VA (a "pnictogen" or maybe better "pnigogen") or column VIA (a chalcogen) of the periodic table. The compounds thus are the monopnictides and monochalcogenides.

We shall compare these compounds along several lines: (1) the occurrence and the crystal structure of high-pressure phases; (2) the pressures at which these phase transitions take place; (3) the extent of hysteretic phenomena, i.e. differences in transition pressure between pressure increase ("upstroke transition") and pressure decrease ("downstroke transition"); (4) the compressibilities (bulk moduli K_0 and their pressure derivatives K'_0); (5) the possible occurrence of isostructural phase transitions.

There is a basic question on how to establish this comparison. At first sight, one would like to compare the compound of a $4f^n$ element with the corresponding compound of its $5f^n$ homolog, i.e. compounds of Ce and Th, Pr and Pa, Nd and U, and so forth, would be the pairs to be compared. We shall attempt such comparisons, but we shall also attempt comparison between so-called "shifted homologs".

"Shifted homology" means comparing a $4f^n$ element with element $5f^{n+4}$ and was originally proposed [8,9] to explain similarities between $5f^{n+4}$ transplutonium elements and the $4f^n$ light lanthanides. We shall also try to apply this type of relationship to U, Np and particularly Pu, which in this picture should all have Ce as their 4f equivalent. In certain cases, we shall see that striking similarity is found when comparing element $4f^n$ with its "shifted homolog" $5f^{n+4}$.

Tables 1 and 2 show for which LnX and AnX pressure-induced structural transitions have been reported up to now. The compressibility data (bulk modulus K_0 and its pressure derivative K'_0) for these families of com-

Table 1
Pressure-induced structural transitions in lanthanide pnictides and chalcogenides LnX of the B1 structure type

X	Ln					
	La	Ce	Pr	Sm	Eu	Tm
P	–	B2 19 GPa 10.5 %	+	+	▨	+
As	+	B2 16 GPa 14 %	+	+	– (hexag.)	+
Sb	tetrag. 11 GPa ≈ 10 %	tetrag. 11 GPa ≈ 10 %	+	+	▨	+
Bi	–	tetr.+B2 13 GPa 5.5 %	+	+	▨	+
O	+	–	+	+	B2 ≈ 40 GPa ≈ 8 %	▨
S	+	–	+	–	B2 21.5 GPa ≈ 12 %	+
Se	+	B2 18 GPa ≈ 9 %	+	–	B2 14.5 GPa ≈ 13 %	–
Te	–	B2 8(1) GPa 8.5 %	B2 ≈9(1)GPa ≈ 11.5 %	B2 ≈11GPa 9 %	B2 11(1)GPa ≈ 13 %	hexag. 15 GPa ≈ 4 %

For each compound the table lists, from top to bottom: the structure of the high-pressure phase, the pressure (range) of transition (GPa), and the volume decrease on transition (%) (adapted from ref. [6]). Shaded area: compound unknown; –: studied under pressure, but no phase transition observed; +: compound exists, but no HPXRD study known.

Table 2
Pressure-induced structural transitions in actinide carbides, pnictides and chalcogenides AnX (An = Th, U, Np, Pu)

X	An			
	Th	U	Np	Pu
C	(B1 up to 65 GPa)	orthorhombic ≈ 27 GPa ≈ 6 %	+	+
N	(B1 up to 47 GPa)	rhombohedral ≈ 29 GPa ≈ 3 %	+	+
P	B2 ≈ 30 GPa ≈ 12 %	rhomboh. : orthorh. ≈ 10, : ≈ 28 GPa 0 % :	+	+
As	B2 18-26 GPa ≈ 10 %	B2 18-30 GPa ≈ 11 %	B2 25-40 GPa ≈ 9 %	B2 35-38 GPa ≈ 9 %
Sb	B2 9-12 GPa ≈ 9 %	B2 9-10 GPa ≈ 12 %	tetragonal 10-18 GPa ≈ 12 %	B2 : tetrag. ≈ 20, : ≈ 40 GPa ≈ 4, : ≈ 5 %
Bi	B2 ≤ 0 GPa +	B2 ≈ 5 GPa ≈ 11 %	tetragonal ≈ 8.5 GPa 12 %	+
S	hexagonal 23-33 GPa 0 %	rhombohedral ≈ 12 GPa 0 %	+	+
Se	B2 ≈ 15 GPa ≈ 9 %	B2 20-26 GPa ≈ 8 %	B2 ≈ 23 GPa ≈ 9 %	rhom. : B2 ≈ 20, : ≈ 35 GPa 0 % : ≈11 %
Te	B2 ≤ 0 GPa	B2 9-20 GPa ≈ 8 %	B2 12-20 GPa ≈ 7 %	B2 15-19 GPa ≈ 9 %

For each compound the table lists, from top to bottom: the structure of the high-pressure phase, the pressure (range) of upstroke transition (GPa), and the volume decrease on transition. (ThC, ThN: no transition in pressure range studied, ThBi, ThTe: B2 as ambient pressure phase; no transition, + means compound exists, but no HPXRD study known) (adapted from ref. [6]).

pounds are found in Tables 3 and 4. Finally, Table 5 shows for which LnX compounds isostructural phase transitions, accompanied by a volume collapse, have been reported. Table 6 lists data on the nitrides and bismuthides of Am, Cm and Cf.

No structural high-pressure data are known for the LnX compounds of Nd, Pm, Tb, Dy, Ho, Er and Lu. The data on the thulium and ytterbium compounds will in general not be discussed here because they should be compared to the heavy actinides for which no solids are available. In the actinide series, high-pressure data are missing for the AnX compounds of Ac, Pa, Bk and Es, and actinides heavier than Es are not available in sufficient amounts to form solids.

The lack of data has several causes. In the case of actinium, the intense $\alpha+\beta+\gamma$ activity of Ac and its daughters has up to now prohibited their study. This situation is not likely to change in the near future. Although large amounts of actinium are available, handling them to prepare compounds and to study these would require hot cells, which require quite an important investment, to protect workers from radiation. So the non-f references, La and Ac, of the two series cannot be directly compared on the basis of experimental high-pressure properties.

Table 3
Isothermal bulk moduli, K_0 (GPa), and pressure derivatives K'_0 determined from high-pressure X-ray diffraction for the lanthanide (Ln) pnictides and chalcogenides of the B1 structure type

X	Ln						
	La	Ce	Sm	Eu	Gd	Tm	Yb
N	+	+	+	+	192(35) 4(constr.)	+	+
P	(1 data point)	64(4) 3(1)	+	■	+	+	+
As	+	69(1) 2.6(2)	+	46 (hex.)	+	+	+
Sb	72(3) 2.5(5)	72(3) 2.5(5)	+	■	+	+	+
Bi	55	50 2	+	■	■	+	■
O	+	(≈ 30)	+	110(5)	■	■	130(19) 4(constr.)
S	+	82(3) 2.3(3)	42(3) 4(constr.)	61(5)	120(5)	+	72(5)
Se	+	76(4) 4.9(5)	40(5)	52(5)	+	38(1) 11(1)	61(5)
Te	55	53(4) 14(2)	40(5)	40(5)	■	46(5)	46(5)

For each compound the table lists, from to to bottom: the bulk modulus, in GPa, and the pressure derivative. Errors as indicated in the original publications (adapted from ref. [6]). Shaded area: compound unknown; –: studied under pressure, but no compressibility data known; +: compound exists, but no HPXRD study known; constr.: constrained.

Table 4
Isothermal bulk moduli K_0 (GPa) and pressure derivatives K'_0 for the actinide carbides, pnictides and chalcogenides AnX (An = Th, U, Np, Pu). For each compound the table lists, from top to bottom: the bulk modulus, and the pressure derivative. Errors as indicated in the original publications. (+ means compound exists, but no HPXRD study known; constr.: constrained.) (Adapted from ref. [6].)

X	An			
	Th	U	Np	Pu
C	109(4) 4.0(3)	160(4) 3.6(5)	+	+
N	175(15) 4.0(4)	203(6) 6.3(6)	+	+
P	137(7) 5(1)	102(4) 4(1)	+	+
As	118(4) 3.4(10)	100(4) 4.4(4)	70(1) 6.2(6)	69(3) 3.3(3)
Sb	84(8) 5(2)	62(3) 4(1)	55(2) 8(2)	68(2) 3.3(5)
S	145(6) 5(1)	105(8) 5(1)	+	+
Se	125(10) 4(constr.)	74(4) 5(1)	60(3) 2.5(2)	98(4) 2.6(5)
Te	102(4) B2! 3.8(4)	48(3) 4.9(3)	62(2) 1.8(4)	34(3) 12(4)

Table 5
Isostructural volume collapses observed under pressure in lanthanide pnictides and chalcogenides LnX

X	Ln				
	Ce	Sm	Eu	Tm	Yb
P	10 GPa	+	■	+	+
Bi	–	+	■	+	■
O	0-3 GPa ≈ 8 %	+	30 GPa ≈ 5 %	■	8-? GPa
S	12.5 GPa 4.5 %	0.65 GPa 13.5 %	–	+	11-16 GPa 2.5 %
Se	+	≈ 4 GPa ≈ 8 %	–	–	15-17 GPa ≈ 7 %
Te	–	2-8 GPa ≈ 17 %	≈ 1.5 GPa ≈ 5 %	1.5-3 GPa ≈ 9 %	13-18 GPa ≈ 10 %

For each compound the table lists, from top to bottom: the pressure (range) of collapse (GPa), and the volume decrease on collapse (%) (adapted from ref. [6]). Shaded area: compound unknown; –: studied under pressure, but no isostructural transition observed; +: compound exists, but no HPXRD study known.

Protactinium compounds have not been studied under pressure up to now because protactinium is scarce and

Table 6
High-pressure data for the mononitrides and monobismuthides of americium, curium and californium

		Am	Cm		Cf
N		B1 up to ~ 50 GPa			
	K_0	88(5)GPa	n.d.		n.d.
	K_0'	11(2)	n.d.		n.d.
	reference	[6]	[21]		[21]
Bi	h.p. phase	tetragonal	B2	tetragonal	B2
	ptrans	~ 15 GPa	~ 12	~ 20 GPa	11-12 GPa
	ΔV_{trans}	~ 12 %	~ 16 %	0	~ 7 %
	K_0	75(2) GPa	53(3) GPa		105(5) GPa
	K_0'	5(1)	8(2)		-2(2)
	reference	[22]	[23]		[24]

For each compound, the table lists, from top to bottom: the structure of the high-pressure phase, the pressure (range) of upstroke transition (GPa), the volume decrease on transition, the isothermal bulk modulus K_0 (GPa), its pressure derivative K_0', and the reference. n.d.: not determined.

expensive. Also the radioactive hazard is not negligible because ^{231}Pa forms ^{227}Ac by α-decay and thus enters the same hazard category as Ac, see above. It still would be useful for advancing systematic knowledge of the lighter AnX if the gap existing at Pa could be filled by some study of Pa compounds.

Promethium compounds were not studied because of their radioactivity (^{147}Pm emits β) and relatively fast decay.

Considering this situation, only a limited number of f-count or shifted homolog pairs can be found for a comparison. These are listed in paragraphs 2.1 and 2.2. Final comparison will concentrate on 4f–5f homologs with the same non-f partner, to eliminate possible effects of a difference in the latter partner.

2.1. Pairs of equal f-count

(1) Ce–Th: This is the pair where comparison is easiest. High-pressure structural and/or compressibility data for the mono-phosphides, -arsenides, -antimonides, -bismuthides, -sulphides, -selenides and -tellurides of both these elements have been obtained.
(2) Sm–Pu: these two elements can be compared with respect to their monoselenides and monotellurides.
(3) Eu–Am: Although a limited amount of data is available for both EuX and AmX, direct comparison of these two elements is not advisable because of the divalency of Eu (while Am is trivalent in the AmX compounds).
(4) Gd–Cm: The few isolated data available on the high-pressure behaviour of GdX and CmX do not allow comparison.

2.2. Shifted homolog pairs

(1) La–Np: These two elements could in principle be compared for the high-pressure properties of their mono-antimonides, -tellurides and -bismuthides, but comparison of non-f La with the f-element Np is subject to precaution.
(2) Ce–Pu: Data for the monoarsenides, -selenides, -antimonides and -tellurides are available for both elements.
(3) Pr–Am: Only PrTe has been studied among the PrX, while on the Am side, data are available only for AmN and AmBi: comparison of homologs with the same anion is not yet possible here.
(4) Sm–Cf: CfN and CfBi on the actinide side, and SmS, SmSe and SmTe on the lanthanide side, are the only compounds investigated: as for Pr–Am, comparison of homologs with the same anion is not yet possible.

2.3. Comparison of pressure-induced structural phase transitions

Our comparison will thus concentrate on the only pairs where sufficient data are available: Ce–Th on one side, and the shifted homologs Ce–Pu on the other. Since the three light actinides U, Np and Pu resemble each other in several respects, uranium and neptunium compounds will be included in the comparison with cerium.

Fig. 1 compares the high-pressure phases and upstroke phase transition pressures observed up to now in CeX compounds, on one side, and in Th, U, Np and Pu monopnictides and monochalcogenides on the other. To facilitate comparison according to f-count homologs as well as for shifted homologs, Pu and Th compounds are presented on either side of the Ce compounds (Pu compounds appear a second time in the increasing-Z sequence after Np).

The following restriction applies to this comparison: while the actinide compounds have been studied to pressures between 45 and 60 GPa, the upper pressure limit was 23–25 GPa (32 GPa in the case of CeAs) for the cerium compounds. This means that structural evolution at 25 GPa and higher is in general not known for CeX, and that, for example, phase transitions that might occur at higher pressure remain undetected. In particular, no structural phase transition was detected to 25 GPa in CeS; the transformation to a hexagonal phase observed at 23–33 GPa in the f-count homolog ThS might suggest that CeS also transforms somewhere below 60 GPa.

2.3.1. Ce–Th

For Ce as well as for Th compounds, B2 is the preferred structure type for the high-pressure phases. There are two exceptions among the 13 known compounds of these two elements:

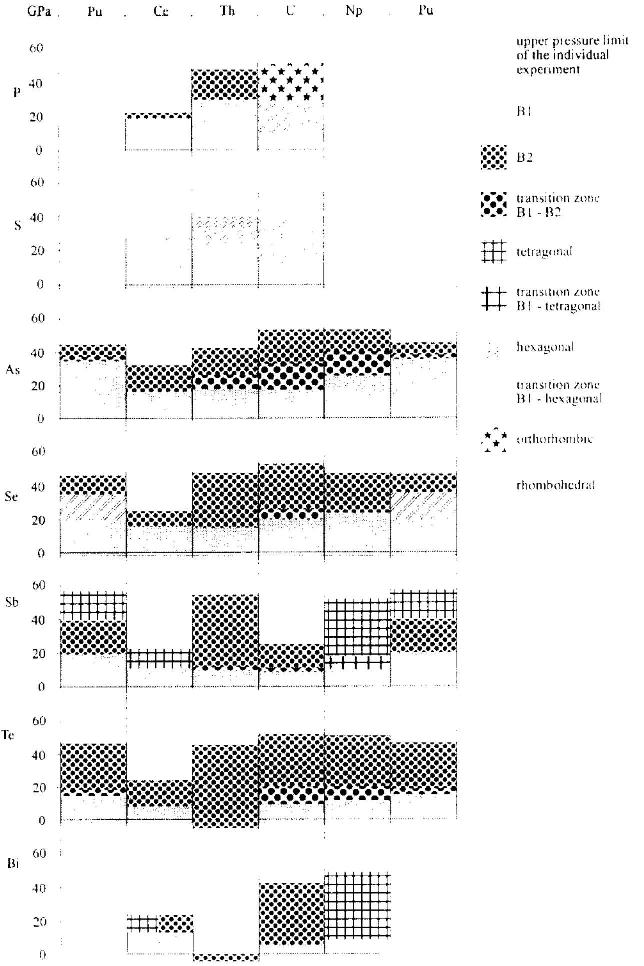

Fig. 1. Graphical comparison of high-pressure phases and upstroke phase transition pressures for monopnictides and monochalcogenides of Ce with those of the light actinides Th, U, Np and Pu. Data are taken from a recent review [6].

(1) CeSb has no B2 type phase, but instead goes tetragonal under pressure.
(2) ThS has a hexagonal high-pressure phase.

The general tendency in transition pressures is: for the light anion P, ThX transforms at higher pressure than CeX; for the medium–heavy anions As, Se and Sb, transformation of CeX starts at about the same pressure as for ThX; for the heaviest anions implied, Te and Bi, the pressure for transition to the high-pressure phase is much lower, (i.e. at ambient, or if one prefers, even "negative" pressure) for ThX than for CeX. These relationships are shown in Fig. 2.

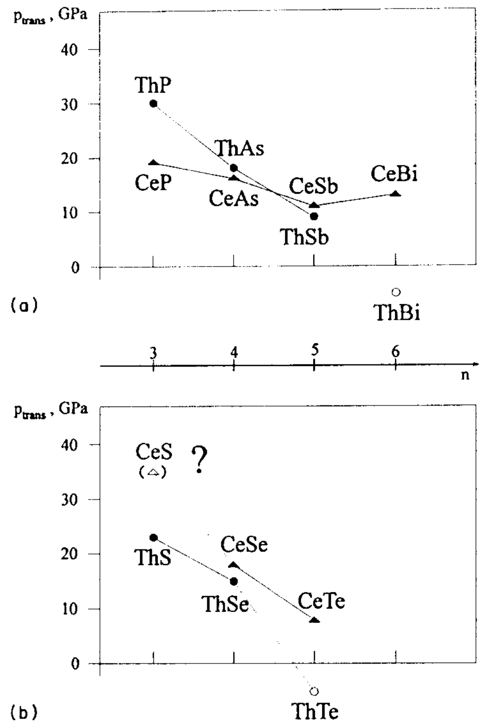

Fig. 2. Start of transformation on upstroke for the monopnictides (a) and monochalcogenides (b) of thorium as compared with those of cerium. *n*: Principal quantum number of the s and p subshells of the anion.

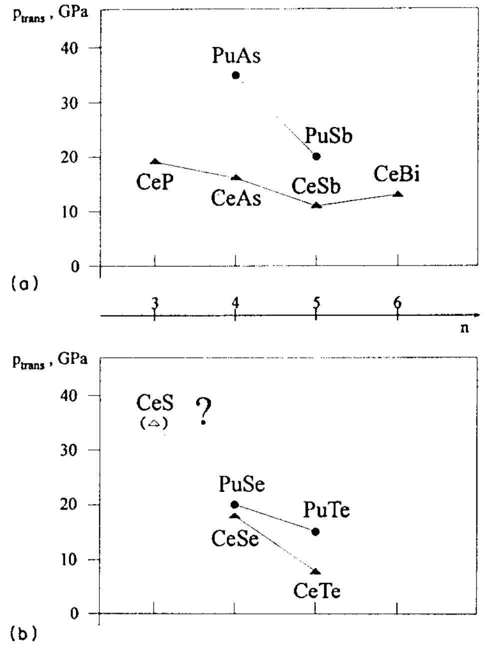

Fig. 3. Start of transformation on upstroke for the monopnictides (a) and monochalcogenides (b) of plutonium as compared with those of cerium. *n*: Principal quantum number of the s and p subshells of the anion.

2.3.2. Ce–Pu

This comparison is limited to the arsenides, selenides, antimonides and tellurides.

Upstroke transition pressures:

It is obvious from the two leftmost columns of Fig. 1 and from Fig. 3 that the plutonium compounds need higher pressure to destabilize the B1 type structure than the cerium compounds. The latter, in contrast, were seen to transform at about the same pressure as the corresponding thorium compounds, with the exception of ThTe which is already B2 type at ambient pressure.

High-pressure structures:

The B2 type appears as a high-pressure structure in seven of these eight compounds. CeSb has a tetragonal high-pressure structure which also appears in the homolog PuSb as the second high-pressure phase. The latter is formed when pressure is further increased on the first appearing (B2 type) high-pressure phase.

2.4. Hysteresis to phase transformation

The pressure-induced LnX and AnX phase transitions have to date only been studied at room temperature. Under these conditions, the back transformation on

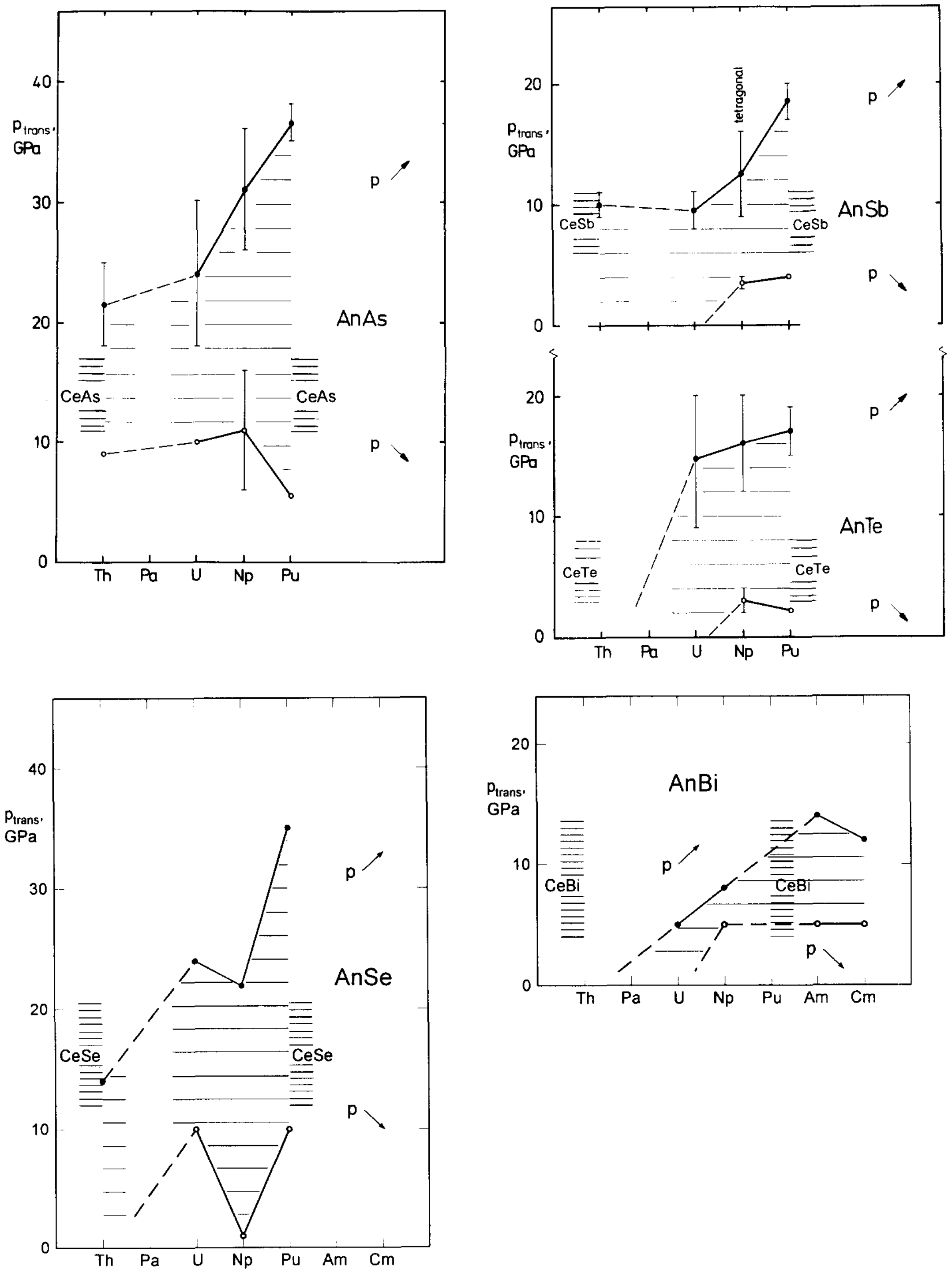

Fig. 4. Hysteresis zones for actinide and cerium compounds. Upper curve in each graph (●): transition on pressure increase; lower curve (○): transition on pressure decrease.

pressure release occurs at a much lower pressure than the transformation on pressure increase: this is probably due to kinetic factors, as is shown by the study of pressure-induced phase transitions at elevated temperature in lanthanide metals [10]. The true ("equilibrium") transition pressure is intermediate between the upstroke and downstroke transitions, but could only be determined by extrapolation of transition pressures at high temperature, which are not known for these compounds.

Fig. 4 shows the hysteresis zones, i.e. the pressure range between upstroke and downstroke transitions, for the arsenides, selenides, antimonides, tellurides and bismuthides of actinides and, for comparison, of cerium. Hysteresis zones are not known for the other LnX where pressure-induced phase transitions were observed. It seems that these early studies have only been made at increasing pressure and no measurements were taken on pressure release.

Although the actinide results and the cerium results were obtained by different groups, their techniques were quite similar, such that a comparison of the hysteresis zones seems possible. As seen from Fig. 4, the hysteresis zones reported for the cerium compounds are smaller than those of the actinide compounds, except for the bismuthides;' the actinide bismuthides show particularly narrow hysteresis zones. A physical reason for these differences is not apparent.

2.5. *Compressibility*

Fig. 5 shows the bulk moduli determined for LnX and AnX compounds, in this case compared only for equal f counts since few data for heavier actinides are available. The general trend for the actinide compounds is a decrease of the bulk modulus with increasing Z of the actinide from Th to Np or Pu, with an upturn for PuSe and PuSb (which is also found in the dioxides). In contrast, the lanthanides show practically no variation to the bulk modulus with Z of the lanthanide; most of the LnX bulk moduli are in the range 50–70 GPa, while values over 100 GPa are usual for ThX, and values near 100 GPa are observed for some UX.

2.6. *Isostructural transitions*

Table 5 shows for which LnX isostructural transitions were reported. Although indications for bulk modulus softening under pressure were reported for UBi, NpBi and CfBi [6], there is no clear proof that this is linked

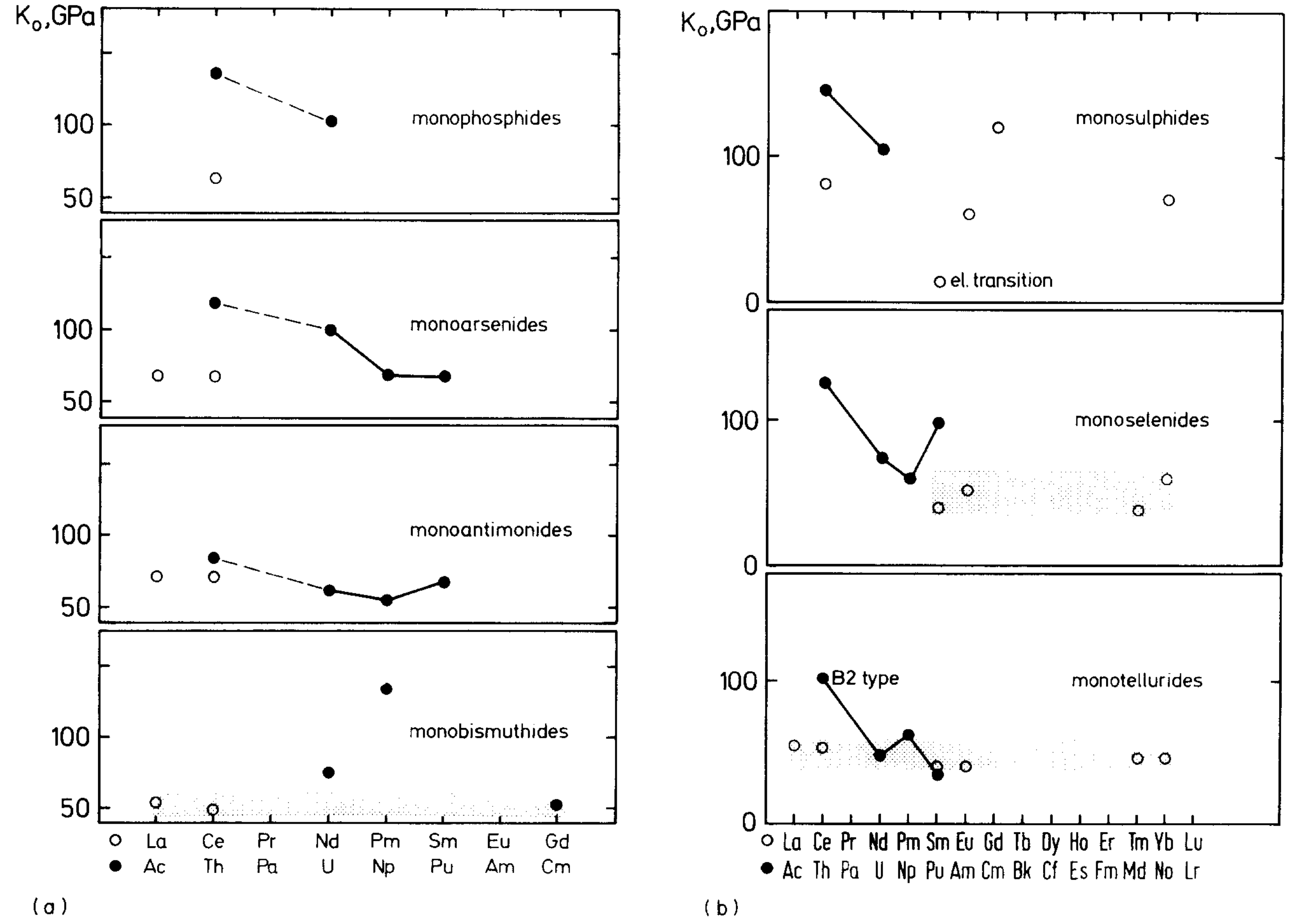

Fig. 5. Isothermal bulk moduli of B1-type compounds of the lanthanides and actinides. (a) Monopnictides with P, As, Sb and Bi; (b) monochalcogenides with S, Se and Te.

to an isostructural transition, such that this type of transition cannot be assumed up to now to occur in AnX.

2.7. Comparison of physical properties

Comparison of pressure effects on optical, electrical and magnetic properties between the two f series promises to complement and deepen the information obtained from the above described structural results. For the lanthanides, pressure effects on electrical resistance and optical reflectivity were studied for the samarium monochalcogenides (see, for example, Refs. [11,12]) and for a few other LnX compounds. In the actinide series, variation of electrical resistance and magnetic ordering temperatures with pressure was recently investigated for a number of monopnictides and monochalcogenides of uranium, neptunium and plutonium. Resistance study of PuSb under pressure is a typical example [13]. A quite comprehensive study was recently made on variation of optical reflectivity with pressure for monopnictides and monochalcogenides of thorium, uranium, neptunium and plutonium [14]. Some of these results will be used in a separate publication for comparison with results for appropriate lanthanide compounds. In the present paper, only the specific case of optical reflectivity in the f count homologs SmTe and PuTe will be briefly discussed.

2.7.1. Optical reflectivity of SmTe and PuTe

SmTe was reported [11] to undergo a valence transition under pressure where the valence of Sm increases from +2 to some value between +2 and +3. This transition has been studied by optical reflection under pressure [12]. While the near-infrared reflectivity of SmTe is only 1–4% at ambient and up to pressures of about 5 GPa, it increases to values up to 60% at higher pressures where the valence has increased. Recently, Abraham et al. [15] have determined the variation of the reflectivity of the f-count homolog of SmTe, PuTe, with pressure. Fig. 6 compares the reflectivities of SmTe and PuTe. PuTe is seen to exhibit 50–60% near-infrared reflectivity already at ambient and slightly elevated pressure, indicating high carrier concentration, a level of reflectivity that SmTe only reaches at much higher pressure after the valence transition. This confirms earlier observations, derived from a comparison of the compressibilities of PuTe [16] and SmTe [17], which interpret PuTe as intermediate-valent and assimilate its properties to those of the collapsed high-pressure phase of SmTe [18].

3. Dioxides

Dioxides of the cubic CaF_2 (fluorite) structure type are formed by Th, U, Np, Pu, Am and Cm. Their

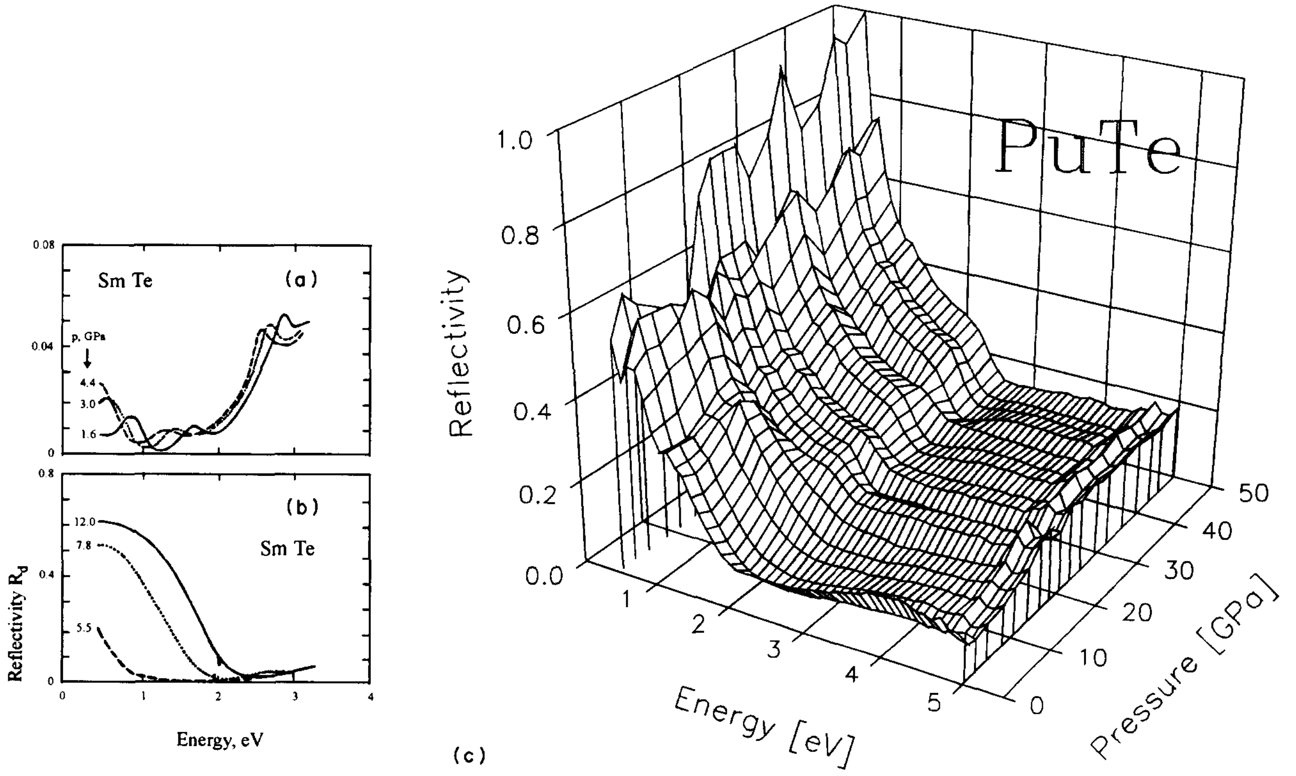

Fig. 6. Effect of pressure on the reflectivity of SmTe (Syassen [12]) and of PuTe (Abraham et al. [15]). (a) Semiconducting SmTe below 5 GPa; (b) intermediate valent SmTe above 5 GPa; (c) PuTe.

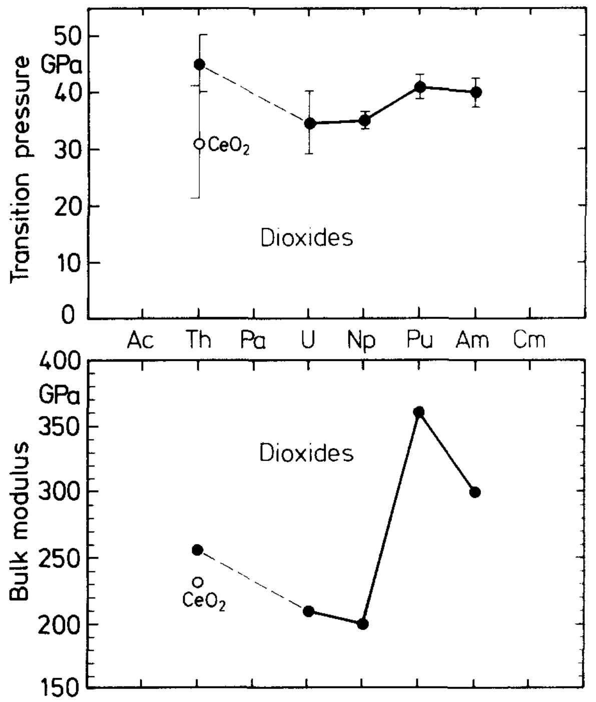

Fig. 7. Upstroke transition pressures (a) and bulk moduli (b) for the actinide dioxides and for CeO_2.

structural behaviour under pressure has been studied [6]. All of them transform to an orthorhombic high-pressure phase. In the lanthanide series, dioxides are stable only for Ce, Pr and Tb, and only CeO_2 has been studied under pressure. It forms the same type of high-pressure phase [19]. Fig. 7 compares the transition pressure and bulk modulus of CeO_2 with those of the actinide dioxides.

4. Anomalies in compression

In a recent compression study of UGa_3, UIn_3, UGe_3 and USn_3, a quite characteristic and unexpected anomaly in their compression curves $V/V_0=f(p)$ was detected (Fig. 8) for all four of these compounds of $AuCu_3$ structure type. The hump in the curve appearing above 10 GPa in these curves is not connected with a structural phase transition; the sample remains $AuCu_3$ type in the whole pressure range studied [20]. A definite explanation for this anomaly cannot yet be given, but the anomaly is very similar to that found in YbTe [17] which was explained by a valence change from Yb^{2+} to Yb^{3+} involving a 4f→5d electron transfer.

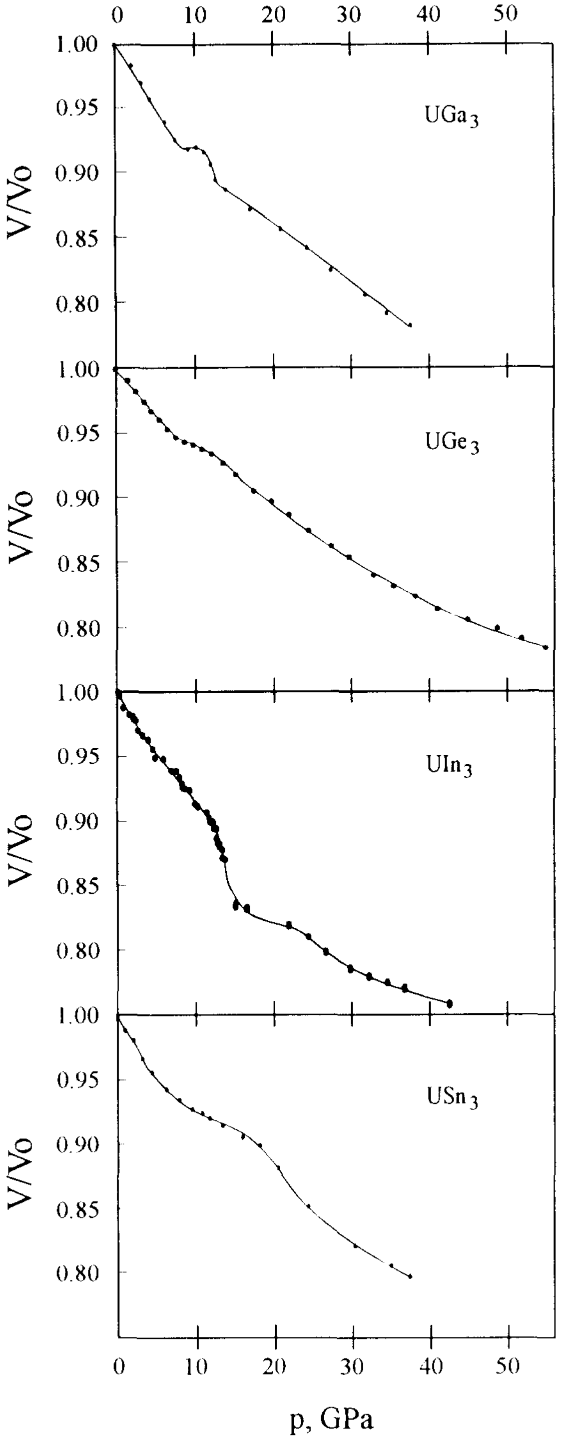

Fig. 8. Experimental $V(p)$ curves for UGa_3, UGe_3, UIn_3 and USn_3 [20].

5. Conclusions

The data presented do not show clearly whether there is more similarity between f-count homologs or between shifted homologs. More experimental and theoretical work will be needed to approach this question, and possibly to find a theoretical basis for the similarities observed in some cases between “shifted homologs”. Much more work on the pressure behaviour of lanthanide compounds will be necessary for a satisfactory 4f–5f comparison in this field. The compounds that would be particularly interesting to study are those of structure type B1 because they are relatively simple and a considerable amount of data on corresponding actinide compounds is available. Structural study should first be undertaken, then effects of pressure on the physical properties (electrical, optical and magnetic, if possible) should be investigated to refine and complete the knowledge about these compounds. Also for the actinide compounds under pressure there remains a wide field of physical studies to be done; such studies have just started for a few compounds, but seem to promise very interesting information.

In the actinide field, it would be scientifically rewarding to prepare and study PaX compounds which are something like the "missing link" in the series of the lighter actinides, in general, but also in particular with respect to high-pressure behaviour.

Shifted homology exists between the two divalent elements europium and einsteinium. While high-pressure data have been reported for a number of EuX compounds, no information is available for EsX. It would be extremely interesting to compare divalent behaviour between the two series on the basis of EsX results. One should consider attempts to prepare, and high-pressure experiments on, compounds such as EsTe and EsSe.

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