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Pressure-driven valence change in ternary Eu pnictides

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Abstract. We observed a structural phase transition with extremely anisotropic changes of the lattice parameters as a function of pressure at 2.6 GPa in EuPdP, which crystallizes in the hexagonal layered Ni₂In structure type. On the basis of the results of pressure-dependent x-ray diffraction experiments on the isostructural series APdP and APdAs (A = Sr or a trivalent rare-earth element) we show that the phase transition in EuPdP is accompanied by a valence change of the Eu. Strong but continuous changes of the lattice parameters with increasing pressure, which are due to increase of the Eu valence, were observed in EuNiP, EuPtP and EuPdAs, too. An estimation of the average Eu valence in these compounds leads to preferred values of the order of $2\frac{n}{6}$.

1. Introduction

In several earlier publications [1–5] we have reported on the uncommon behaviour of the ternary Eu pnictides of EuTX stoichiometry (T = transition metal, X = pnictogen), which all crystallize in the hexagonal Ni₂In structure type (figure 1). It consists of layers of Eu and layers containing (T, X) atoms which alternate in the *c*-direction. It was shown by ¹⁵¹Eu Mössbauer and Eu L_{III} x-ray absorption measurements that the compounds EuTP (T = Ni, Pd, Pt) and EuPdAs contain a static mixture of Eu²⁺ and Eu³⁺. At one or two phase transitions of first (for $T_p < 300$ K) or second order (for $T_p > 300$ K), the average Eu valence in these compounds decreases with increasing temperature. Because the ionic radius of Eu³⁺ is smaller than that of Eu²⁺, the volume shrinks considerably at the phase transition. The reason for the characteristic anisotropic change of the lattice constants at the phase transition—i.e. a strong decrease of the *c*-axis parameter whereas *a* increases slightly—was phenomenologically explained by a model of electrostatically charged layers [2].

The Ni₂In structure allows a maximum of two inequivalent crystallographic Eu sites only, which result—according to x-ray single-crystal data [3]—from a slight shift of the (T, X) atoms from their ideal position towards one neighbouring Eu layer. Nevertheless, we found at ambient pressure Eu valences, ν , which are within the phases of the compounds EuTP (T = Ni, Pd, Pt) and EuPdAs in the vicinity of $\nu \simeq 2\frac{n}{6}$ ($n \in \{1, 2, 3, 4\}$) [2, 4, 5].

In order to compare the influence of pressure with that of temperature, we performed pressure-dependent measurements of the lattice parameter of EuTP (T = Ni, Pd, Pt), EuPdAs and—as reference samples—various compounds of APdP and APdAs stoichiometry containing divalent Sr or trivalent rare-earth elements.

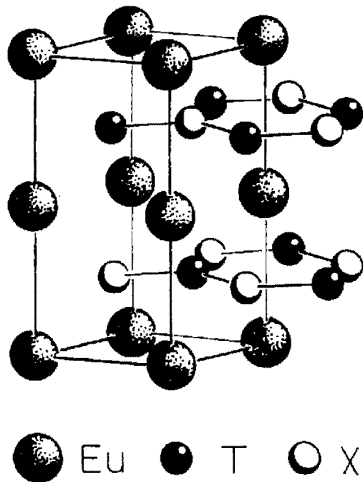


Figure 1. The hexagonal Ni_2In structure type of EuTX stoichiometry.

Table 1. Compressibilities of the Ni_2In -structure-type pnictides for which measurements were made. The compressibilities κ_I ($I = a, c, V$) were obtained by means of a linear fit to the data between the given pressure values p_1 and p_2 by using $\kappa_I = (1/I(p_1))\Delta I/\Delta p$.

Compound	Pressure range (GPa)	κ_a (10^{-3} GPa^{-1})	κ_c (10^{-3} GPa^{-1})	κ_V (10^{-3} GPa^{-1})	κ_c/κ_a
SrPdP	0–5	2.18(9)	7.0(2)	11.2(2)	3.2
LaPdP	0–5	2.76(7)	4.6(2)	10.0(2)	1.7
NdPdP	0–5	2.18(5)	3.4(2)	7.7(2)	1.6
EuPdP	0–2.6	1.94(9)	8.4(1)	12.2(3)	4.3
EuPdP	2.6–5	–1.4(2)	15.1(7)	12.5(5)	–12
SrPdAs	0–5	2.0(2)	6.7(3)	4.8(2)	3.4
LaPdAs	0–5	2.94(4)	5.00(6)	10.7(1)	1.7
CePdAs	0–5	3.26(7)	5.7(1)	12.1(1)	1.8
SmPdAs	0–2.6	2.49(5)	5.0(2)	9.8(1)	2.0
EuPdAs	0–5	–0.6(2)	23.8(4)	22.8(6)	–40
EuNiP	0–1.5	1.4(2)	6.3(5)	9.1(8)	6.4
EuNiP	1.5–3.3	1.6(2)	21.1(5)	24.2(4)	13
EuNiP	3.3–7	2.1(1)	5.7(2)	9.8(2)	2.7
EuPtP	0–2.5	1.6(1)	20.9(5)	23.8(4)	13
EuPtP	2.5–5	1.6(1)	9.8(7)	12.9(3)	6.3

2. Experimental details

The measurements of the lattice constants as functions of pressure at room temperature were—except for SrPdAs—performed with the Multi Anvil X-ray device (MAX 80) by using energy-dispersive x-ray diffraction on powdered samples at the Hamburger Synchrotron Strahlungslabor (HASYLAB), beamline F2/1. Those for SrPdAs were obtained by using the (‘Holzapfel-type’) diamond anvil cell at HASYLAB, beamline F3.

3. Results

First of all, we present the pressure-dependent lattice parameters of the APdP compounds containing $A = \text{Sr}, \text{La}, \text{Nd}$ and Eu , which are shown in figure 2. The most conspicuous

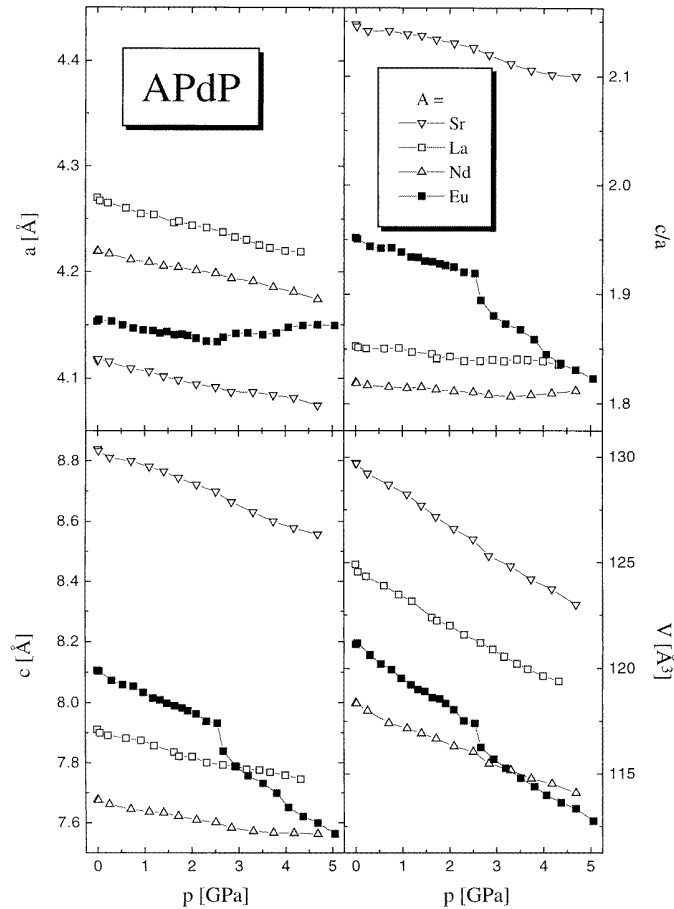


Figure 2. Lattice parameters of APdP ($A = \text{Sr, La, Nd, Eu}$) versus pressure.

result was found for EuPdP. While the lattice parameters decrease linearly with increasing pressure at low pressures, they change abruptly at 2.6 GPa and, when the pressure is increased above 2.6 GPa, they depend in a much more anisotropic way on pressure. The largest step of the lattice parameters was found between about 2.55 GPa and 2.65 GPa: while the c -axis parameter decreases strongly with increasing pressure ($\Delta c/c \simeq -1.2\%$), the a -axis parameter increases slightly ($\Delta a/a \simeq +0.1\%$). This reminds us of the lattice anomaly found at the continuous phase transition, which was observed in EuPdP as a function of temperature [2]: coming from high temperatures, the c -axis parameter decreases by about 1%, whereas a increases by about 0.1%.

Looking at the integer-valence compounds, we can—from the structural point of view—clearly distinguish divalent SrPdP from LaPdP and NdPdP containing trivalent rare-earth elements. The trivalent compounds are on one hand characterized by a rather large lattice constant a , which is somewhat more compressible than that of SrPdP, and on the other hand by a c -axis parameter which is significantly smaller and less compressible than that of SrPdP (all of the compressibilities determined are listed in table 1). EuPdP can be classified between divalent and trivalent compounds. Above 2.6 GPa the lattice parameters of EuPdP

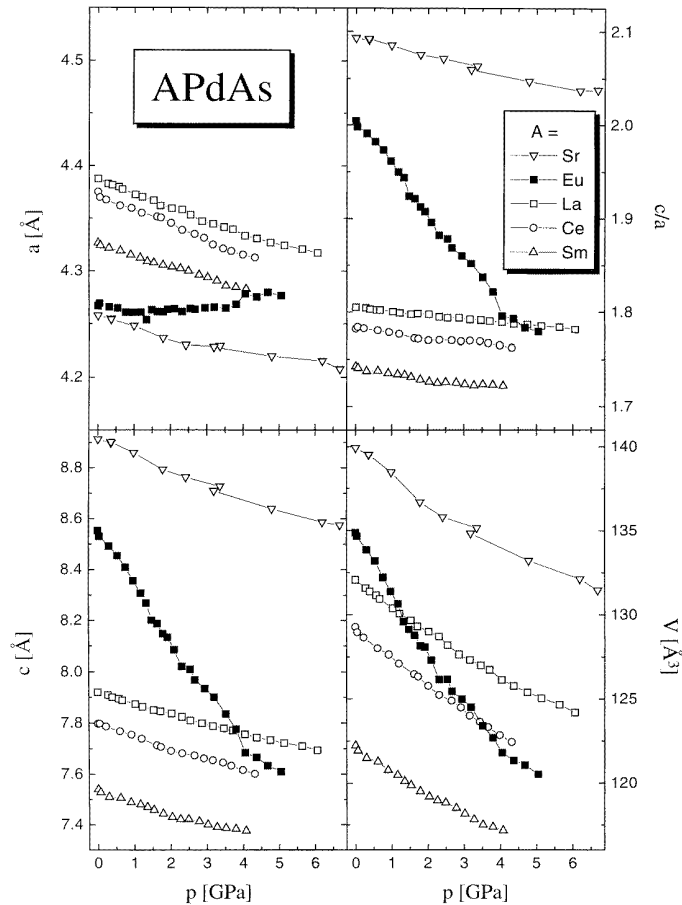


Figure 3. Lattice parameters of APdAs ($A = \text{Sr, La, Ce, Sm, Eu}$) versus pressure.

approach those of the trivalent compounds.

Similar results were found for the series APdAs ($A = \text{Sr, La, Ce, Sm, Eu}$). Looking at the pressure-dependent lattice parameters of these compounds (shown in figure 3), we see that SrPdAs also differs from the trivalent compounds of APdAs stoichiometry not only because of the larger ratio c/a , but also in having a considerably larger ratio κ_c/κ_a , i.e. a more anisotropic compression.

EuPdAs can be classified—in the same way as EuPdP—between the compounds containing a divalent A element and those containing a trivalent one (see table 1). With increasing pressure the lattice parameters of EuPdAs again approximate those of the trivalent reference compounds, but, unlike in the case for EuPdP, the extremely anisotropic pressure dependence of the lattice parameters has its onset at ambient pressure and persists until $p \simeq 4$ GPa (indicating a continuous phase transition below 4 GPa).

Strong continuous changes of the lattice parameters as functions of pressure also occur in a similar anisotropic way in the non-integer-valence compounds EuNiP and EuPtP (see figure 4). The compressibility in the c -direction is in EuNiP—in sharp contrast to that in the a -axis direction—very high between 1.5 GPa and 3.3 GPa (see table 1). A corresponding

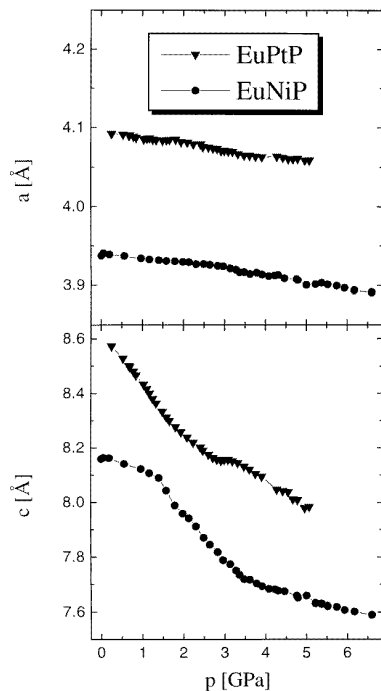


Figure 4. The lattice constants a and c of EuNiP and EuPtP versus pressure.

strong and anisotropic pressure dependence of the lattice parameters was found for EuPtP below 2.5 GPa.

4. Discussion

In earlier publications [2, 4] it was shown that the structural phase transitions occurring in the non-integer-valence EuTX compounds, i.e. EuTP (T = Ni, Pd, Pt) and EuPdAs, are connected with a characteristic change of the Eu valence of $\Delta v \simeq 0.16$, which was determined by means of Eu L_{III} and ^{151}Eu Mössbauer measurements. However, the determination of the valence change is not only possible via these measurements; the valence change can also be estimated from the lattice change itself. In the case of the temperature-dependent phase transitions, this was done according to Vegard's law, and it leads to consistent results. Hence, in order to estimate the dependence of the Eu valence on pressure from the present data, it seems promising to calculate the Eu valence in the same way, which we therefore want to describe briefly.

On plotting the unit-cell volumes of the APdP [6] and APdAs [7] compounds as functions of the ionic radii of the trivalent rare-earth atoms [8] (see figure 5), one clearly sees the linear dependencies of the volumes on the ionic radii, given by the straight lines—except for the Eu compounds. On the basis of the assumption that the volumes of EuPdP and EuPdAs should also depend in the same way on an average ionic radius of the Eu atoms (averaged between that for Eu^{3+} and that for Eu^{2+})—which should according to Vegard's law depend linearly on the Eu valence—we can easily calculate the average Eu valence by linear interpolation.

On applying pressure, however, the observed decrease of the volume of the Eu compounds is not only due to an increase of the Eu valence, but also due to that part of

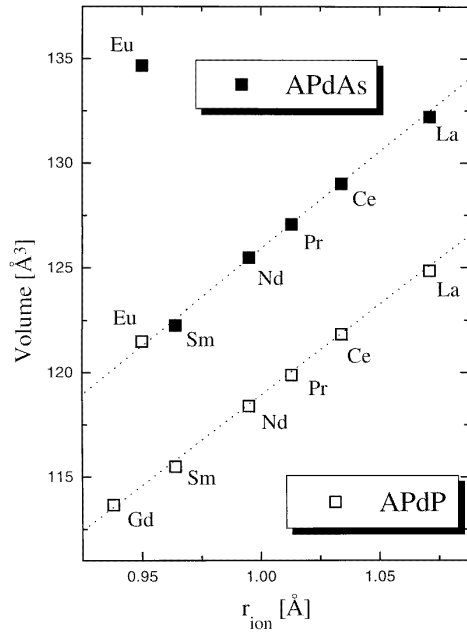


Figure 5. The unit-cell volumes of the APdP [6] and APdAs [7] compounds versus the ionic radii of the trivalent rare-earth atoms [8].

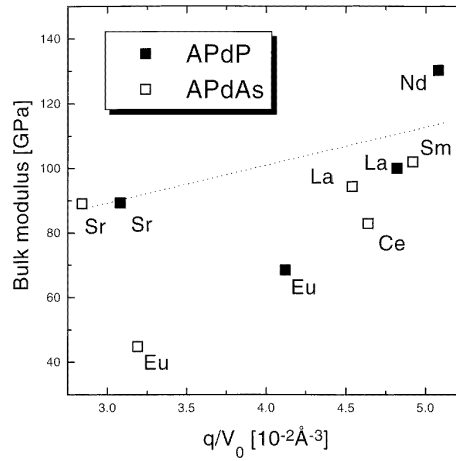


Figure 6. Bulk moduli of APdP and APdAs as functions of the valence electron density q/V_0 (see the text).

the volume compression which is not affected by the valence change. In order to estimate this part—we will call it $\Delta V_{ref} = V_0 B_{ref}^{-1} p$ ($V_0 = V(1 \text{ bar})$)—we plotted the bulk moduli B determined for APdP and APdAs as functions of their valence electron density q/V_0 , i.e. the number of valence electrons of the A atom per unit-cell volume (see figure 6).

The strong reduction of the bulk moduli of the Eu compounds results from the non-integer Eu valence, which increases with rising pressure towards the smaller trivalent state. The enhancement of the compressibility found for CePdAs is in our opinion also due to a valence instability of the Ce atom. For this compound a particularly anomalous high and anisotropic thermal expansion was observed [9], which also indicates a valence instability of the Ce atom.

Except for the compounds containing Ce or Eu, the bulk moduli of the APdP and APdAs compounds increase as functions of q/V_0 . This is a characteristic behaviour for integer-valence intermetallic compounds containing alkaline-earth or rare-earth elements. A linear increase of the bulk moduli was for instance found for AB_6 [10], ASe [11], ACu_2Si_2 [12] and—just recently—also for AT_2P_2 ($T = Co, Ni$) [13].

In order to estimate roughly the volume compressibilities of the Eu compounds, which are not affected by the valence change of the Eu—i.e. ΔV_{ref} (see above)—we assumed a linear dependence of B_{ref} for the Eu compounds on q/V_0 , which is given by the dotted line in figure 6.

Accordingly, the measured volume contraction $\Delta V(p)$ as a function of pressure for the Eu compounds is then given by

$$\Delta V(p) = V_0 - V(p) = \frac{\delta V}{\delta v} \Delta v - \Delta V_{ref} = \frac{\delta V}{\delta v} (v(p) - v_0) - V_0 B_{ref}^{-1} p$$

with the known parameter B_{ref} (see above), $\nu_0 = \nu(1 \text{ bar})$ (the Eu valence derived from Eu L_{III} and Mössbauer measurements [2, 4, 5]), and $\delta V/\delta \nu$ being the ratio of the volume and the valence change according to Vegard's law (see above).

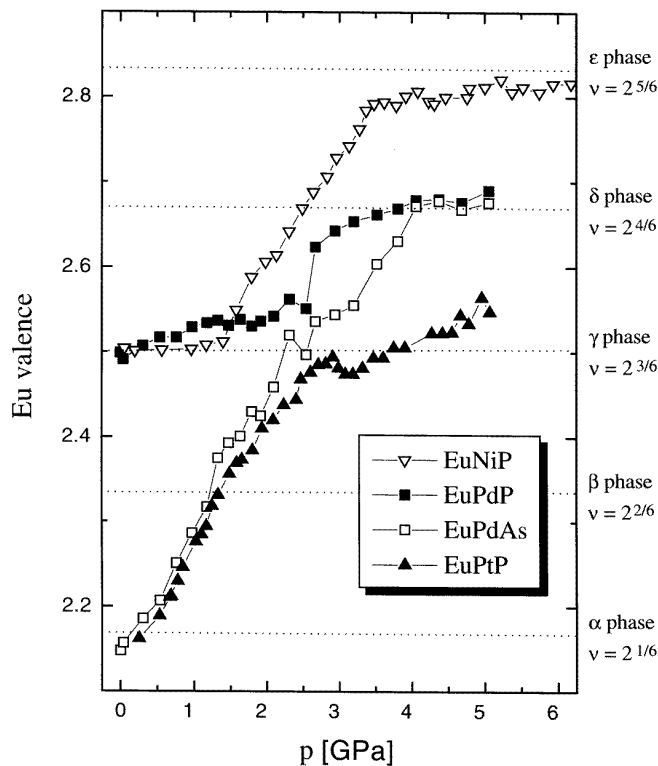


Figure 7. The estimated Eu valences of EuTP ($P = \text{Ni, Pd, Pt}$) and EuPdAs as functions of pressure.

The calculated pressure dependence of the Eu valence $\nu(p)$ is shown as a function of pressure in figure 7 for EuTP ($T = \text{Ni, Pd, Pt}$) and EuPdAs. In all of the cases we observe phase transitions towards higher Eu valences with increasing pressure. Like the observations made on the basis of the temperature-dependent measurements, the Eu valence within the different phases—i.e. the pressure ranges which are characterized by only a weak dependence of the Eu valence on pressure—is again preferably in the vicinity of $\nu \simeq 2\frac{n}{6}$ (in previous publications these phases were marked as α -, β -, γ - or δ -phases (for $n = 1, 2, 3, 4$, respectively)).

The origin of the preferred Eu valences being of the order of $\nu \simeq 2\frac{n}{6}$ has been unknown up to now, but we suppose it to be due the arrangement of Eu^{2+} and Eu^{3+} , which should be connected with the hexagonal lattice. If this arrangement is a periodic one with long-range order, it should be visible as additional superstructure peaks in the x-ray diffraction spectra. However, evidence for a periodic arrangement of divalent and trivalent Eu was found only for $\nu = 2\frac{3}{6}$: according to single-crystal data [3], in the γ -phase of EuPtP (4 K), layers consisting of Eu^{2+} and Eu^{3+} alternate in the c -direction. One of the reasons for no superstructure peaks being detected up to now for $n \neq 3$ may be that—due to the lack of single crystals—most of the data were obtained by means of x-ray powder diffraction.

Hence, we recommend the preparation of single crystals and their investigation via x-ray diffraction. In order to obtain information concerning the local arrangement of the atoms, EXAFS measurements at the Eu L_{III}x-ray absorption edge may be helpful, but—due to the non-integer Eu valence—it will probably be difficult to analyse these data.

5. Conclusions

In the non-integer-valence compounds EuTP (T = Ni, Pd, Pt) and EuPdAs, structural phase transitions occur with increasing pressure which are connected with an increase of the average Eu valence. The phase transitions are characterized by an extremely anisotropic change of the lattice: the compressibility in the *c*-direction is strongly enhanced, whereas in the *a*-direction it is reduced or even negative. This characteristic anisotropic change of the lattice constants is also visible at the phase transitions, which occur in these compounds as functions of temperature [2, 4, 5], and was—within a model of electrostatically charged layers [2]—phenomenologically explained in terms of a change of the Eu valence. By assuming a linear correlation between the volume and valence, the Eu valence can be roughly estimated also as a function of pressure: while the Eu valence increases strongly at the phase transitions, it depends only weakly on pressure within the phases at values near $\nu = 2\frac{n}{6}$ ($n = 1, 2, \dots, 5$). In our opinion the arrangement of Eu³⁺ and Eu²⁺ in the hexagonal lattice is responsible for the discrete changes of the Eu valence.

In order to study the change of the Eu valence at the phase transition occurring in EuPdP at 26 kbar, we plan to make high-pressure ¹⁵¹Eu Mössbauer measurements in the near future.

Acknowledgments

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