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Phase transitions of LnAs (Ln = Pr, Nd, Sm, Gd, Dy and Ho) with NaCl-type structure at high pressures

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Abstract

By use of synchrotron radiation the powder x-ray diffraction of lanthanide monoarsenides LnAs (Ln = Pr, Nd, Sm, Gd, Dy and Ho) with a NaCl-type structure has been studied up to 60 GPa at room temperature. First-order phase transitions with crystallographic change were found at around 27.1 GPa for PrAs, 24.2 GPa for NdAs and 32.1 GPa for SmAs. The high-pressure form of the lighter LnAs (Ln = Pr, Nd and Sm) is a tetragonal structure and can be viewed as a distorted CsCl-type structure. The atoms in the tetragonal structure are located at Ln: 0, 0, 0; As: 1/2, 1/2, 1/2. The space group is $P4/mmm$. Pressure-induced phase transitions of the heavier LnAs (Ln = Gd, Dy and Ho) with many f electrons occur at around 36 GPa for GdAs, 44 GPa for DyAs and 46 GPa for HoAs. The structure of these high-pressure phases is unknown. The high-pressure structural behaviour of LnAs (Ln = Pr, Nd, Sm, Gd, Dy and Ho) with the NaCl-type structure is discussed.

1. Introduction

The x-ray diffraction of lanthanide mononictides LnX (Ln = lanthanide, X = P, As and Sb) with a NaCl-type structure has been studied up to 60 GPa at room temperature [1–5]. First-order phase transitions of LnX with the crystallographic change occur at high pressures. The structure of CeP changes from the NaCl-type to the CsCl-type structure at around 19 GPa [1]. The high-pressure form of LnP (Ln = La, Pr and Nd) is a tetragonal structure which can be seen as the distorted CsCl-type one [2]. CeAs shows the typical NaCl–CsCl transition at around 14 GPa [3]. However, the x-ray diffraction of LnAs except for this arsenide has not been investigated at high pressure yet. LnSb (Ln = La, Ce, Pr and Nd) transform from the NaCl-type to the tetragonal structure (distorted CsCl type) at the pressure between 11 and 15 GPa [4, 5]. The high-pressure structural behaviour of actinide pnictides with the NaCl-type structure has been reported by Benedict *et al* [6, 7]. The electronic and structural phase transitions of cerium pnictides at high pressure are discussed by Svane *et al* [8, 9].

By use of synchrotron radiation we have studied the x-ray diffraction of LnAs (Ln = Pr, Nd, Sm, Gd, Dy and Ho) with the NaCl-type structure up to 60 GPa at room temperature. The pressure-induced phase transitions in LnAs are observed at room temperature. The structure of the high-pressure phase of the lighter LnAs (Ln = Pr, Nd and Sm) is determined. The high-pressure structural behaviour of LnAs (Ln = Pr, Nd, Sm, Gd, Dy and Ho) with the NaCl-type structure is discussed.

2. Experiment

Lanthanide monoarsenides LnAs (Ln = Pr, Nd, Sm, Gd, Dy and Ho) with the NaCl-type structure were prepared by reaction of stoichiometric amounts of each rare earth metal and arsenic in a sealed silica tube at around 900 °C. The compounds prepared by us were characterized by powder x-ray diffraction using Cu K α radiation and silicon as a standard.

By use of synchrotron radiation the powder x-ray diffraction pattern of LnAs was measured with the diamond-anvil cell and the imaging plate up to 60 GPa at room temperature [2, 5]. The incident beam was monochromatized by a Si(111) double crystal to a wavelength of 0.4959 Å or 0.6198 Å. The pressure in the diamond cell was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby [10]. A 4:1 methanol–ethanol solution was used as the pressure-transmitting fluid.

3. Results and discussion

The powder x-ray diffraction of SmAs was measured with wavelength of 0.4959 Å up to about 50 GPa at room temperature. Figure 1 shows powder x-ray diffraction patterns of SmAs at high pressures. The profile indicates only characteristic lines of the NaCl-type structure at 1.9 GPa and room temperature. The *d*-values of 111, 200, 220, 311, 222, 400, 331, 420, 422, 511, 440, 531, 600, 620 and 622 lines in SmAs decrease with increasing pressure up to 32 GPa. New diffraction lines appear above 32.1 GPa and grow with increasing pressure. Low- and high-pressure phases co-exist in a wide pressure range. The high-pressure phase in SmAs almost becomes a single phase at around 45 GPa. The 110 line of the CsCl-type structure expected as the high-pressure phase is split into two lines, 110 and 101. Thus, the structure of SmAs changes from the cubic to the tetragonal one. X-ray diffraction data for the high-pressure phase of SmAs are given in table 1. The diffraction lines of the high-pressure phase are assigned by the index of the tetragonal structure, which can be seen as the CsCl-type structure with a large tetragonal distortion. Crystal data of the high-pressure phase of SmAs are *a* = 3.445(7) Å, *c* = 2.847(7) Å and *V* = 33.8(2) Å³ at around 45 GPa. The atoms in the high-pressure form of SmAs are located at the following positions: Sm: 0, 0, 0 and As: 1/2, 1/2, 1/2. The space group is *P4/mmm*.

Figure 2 shows the relative volume (*V/V*₀)–pressure curve for SmAs. The cell volume with the NaCl-type structure decreases with increasing pressure up to 32 GPa. The structural change to the tetragonal structure occurs with a volume collapse of about 10%. When the pressure is decreased, the diffraction lines of the NaCl-type structure reappear at around 15 GPa.

Up to about 32 GPa, the volume of SmAs decreases smoothly with pressure and the experimental data can be fitted by a Birch equation of state [11]:

$$P = 3/2B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]\{1 - 3/4(4 - B'_0)[(V/V_0)^{-2/3} - 1]\}$$

where *B* is the bulk modulus, *B'* its first pressure derivative, *V* the volume and *P* the pressure; the subscript zero refers to values at normal pressure. A least-squares fit to the data of SmAs

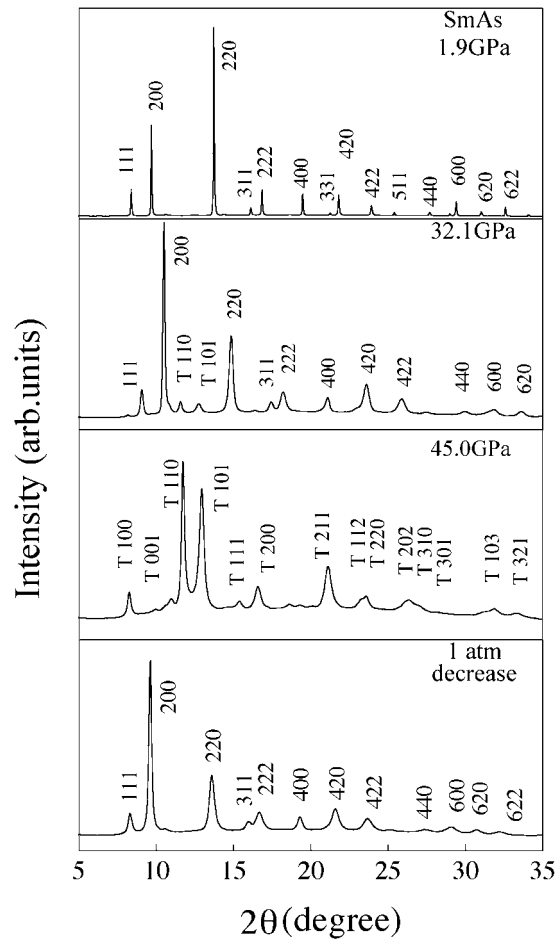


Figure 1. Powder x-ray diffraction patterns of SmAs at high pressures (wavelength of 0.4959 Å): (a) NaCl-type structure, (b) coexistence of NaCl and tetragonal (T) structures, (c) tetragonal structure, (d) NaCl-type structure (after the pressure is removed).

Table 1. X-ray diffraction data for the high-pressure phase of SmAs.

hkl	d_{obs} (Å)	d_{cal} (Å)	$(I/I_0)_{obs}$	$(I/I_0)_{cal}$
1 0 0	3.438	3.4447	17	14
0 0 1	2.8546	2.8471	3	5
1 1 0	2.4216	2.4358	100	66
1 0 1	2.1998	2.1945	79	100
1 1 1	1.852	1.8508	5	6
2 0 0	1.7181	1.7224	15	26
2 0 1	1.4824	1.4737	2	3
0 0 2	1.4217	1.4235	2	7
2 1 1	1.3518	1.3549	28	52

$$a = 3.445(7), c = 2.847(7), V = 33.8(2) \text{ at } 45.0 \text{ GPa.}$$

gives the following values: $B_0 = 84.2 \pm 3.5$ GPa and $B'_0 = 4.5 \pm 0.3$. The value of B_0 of SmAs almost agrees with the result shown in the previous paper [12].

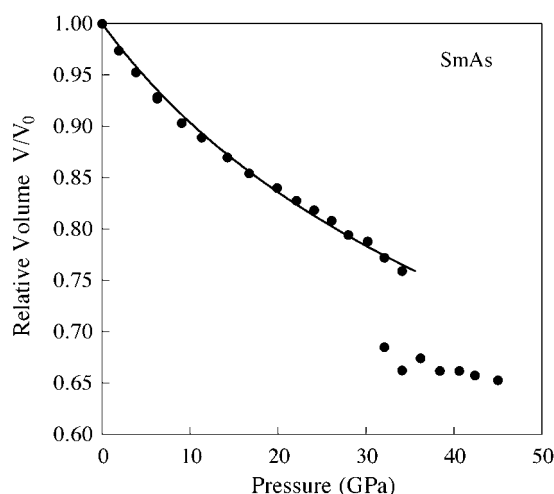


Figure 2. Relative volume (V/V_0)-pressure curve for SmAs at room temperature. The solid line is the fitted Birch equation of state.

The x-ray diffraction of SmP and SmSb with the NaCl-type structure has already been studied at high pressures [2, 5]. First-order phase transitions with the crystallographic change are observed at around 35 GPa for SmP [2] and 19 GPa for SmSb [5]. The transition pressure of SmAs is slightly lower than that of SmP, much higher than that of SmSb. The diffraction pattern of the high-pressure phase of both compounds is not similar to that of SmAs. Above the transition pressures the single phase of SmP is not obtained and the diffraction pattern of SmSb becomes broader. Thus, the structure of the high-pressure form of both compounds has not been determined yet.

We have investigated the powder x-ray diffraction of PrAs and NdAs with the NaCl-type structure at high pressures. The profiles of both arsenides indicate only characteristic lines of the NaCl-type structure at ambient pressure. The d -values of these diffraction lines monotonically decrease with increasing pressure. New diffraction lines of PrAs and NdAs appear at around 27 and 24 GPa, respectively and grow with increasing pressure. The x-ray diffraction pattern of the high-pressure phase in PrAs and NdAs is very similar to that of SmAs. X-ray diffraction data of the single phase of PrAs and NdAs are given in tables 2 and 3. The diffraction lines of the high-pressure phase can be indexed in the tetragonal structure. The high-pressure form of PrAs and NdAs is isostructural with that of SmAs. Crystal data of the single phase are $a = 3.524(1) \text{ \AA}$, $c = 2.961(3) \text{ \AA}$ and $V = 36.76(5) \text{ \AA}^3$ at around 40.6 GPa for PrAs, and $a = 3.536(8) \text{ \AA}$, $c = 2.890(7) \text{ \AA}$, $V = 36.1(2) \text{ \AA}^3$ at around 33.4 GPa for NdAs.

Figure 3 shows the relative volume (V/V_0)-pressure curve for NdAs. The volume decreases smoothly with pressure up to about 24 GPa. The structural change in NdAs suddenly occurs with a volume collapse of about 10% at around 24.1 GPa. The V/V_0 -pressure curve for NdAs with the NaCl-type structure can be fitted by the Birch equation of state up to 24 GPa. A least-squares fit to the experimental data of the arsenide gives the following values: $B_0 = 83.9 \pm 4.6$, $B'_0 = 4.3 \pm 0.5$. The results obtained by the fitting are $B_0 = 100 \pm 6.5$, $B'_0 = 4.5 \pm 0.6$ for PrAs. The bulk modulus, the lattice constant of the NaCl-type structure, the transition pressure and the structure of the high-pressure form for LnAs (Ln = Ce, Pr, Nd and Sm) are summarized in table 4. The values of B_0 and the transition pressure of CeAs are

Table 2. X-ray diffraction data for the high-pressure phase of PrAs.

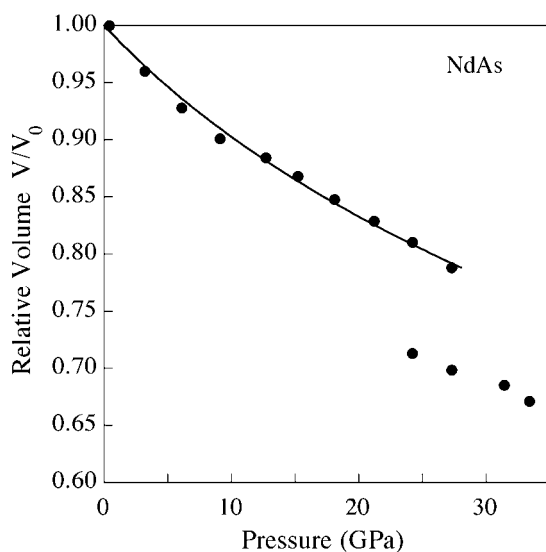
hkl	d_{obs} (Å)	d_{cal} (Å)	$(I/I_0)_{obs}$	$(I/I_0)_{cal}$
1 0 0	3.5316	3.5235	18	12
1 1 0	2.4882	2.4915	91	68
1 0 1	2.2669	2.2668	100	100
1 1 1	1.9068	1.9064	6	5
2 0 0	1.7623	1.7617	15	27
2 1 1	1.3909	1.391	31	53

$a = 3.524(1)$, $c = 2.961(3)$, $V = 36.76(5)$ at 40.6 GPa.

Table 3. X-ray diffraction data for the high-pressure phase of NdAs.

hkl	d_{obs} (Å)	d_{cal} (Å)	$(I/I_0)_{obs}$	$(I/I_0)_{cal}$
1 0 0	3.5402	3.5358	11	13
1 1 0	2.4839	2.5002	100	67
1 0 1	2.2599	2.2379	76	100
2 0 0	1.7676	1.7679	4	27
2 1 1	1.388	1.3873	11	53
1 1 2	1.2501	1.2512	27	19

$a = 3.536(8)$, $c = 2.890(7)$, $V = 36.1(2)$ at 33.4 GPa.

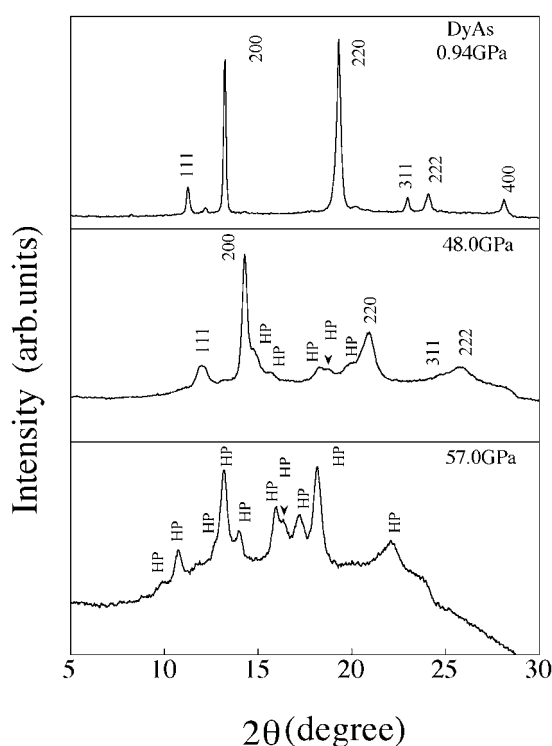
**Figure 3.** Relative volume (V/V_0)-pressure curve for NdAs at room temperature. The solid line is the fitted Birch equation of state.

considerably lower than those of other LnAs (Ln = Pr, Nd and Sm) [3].

The high-pressure form of PrAs, NdAs and SmAs agrees with the structure of the high-pressure phase of LnP (Ln = La, Pr and Nd) [2] and LnSb (Ln = La, Ce, Pr and Nd) [4, 5]. The volume collapse at around the pressure that shows the phase transition is about 10% for LnAs. Similar values are also found for corresponding LnP and LnSb [2, 5]. The c/a of the high-pressure form of LnAs (Ln = Pr, Nd and Sm) is 0.82–0.84. On the other hand, the value of c/a is 0.85–0.87 for LnP and 0.82 for LnSb [2, 5]. The tetragonal structure of LnX (X = P,

Table 4. Lattice constant of NaCl-type structure, bulk modulus, transition pressure and structure of the high-pressure phase for LnAs (Ln = Cs, Pr, Nd and Sm).

	NaCl-type structure a (Å)	B_0 (GPa)	Transition pressure (GPa)	Structure of high-pressure form
CeAs [3]	6.072	69 ± 1	14.0	Cubic (CsCl)
PrAs	6.009	100 ± 6.5	27.1	Tetragonal
NdAs	5.970	83.9 ± 4.6	24.2	Tetragonal
SmAs	5.921	84.2 ± 3.5	32.1	Tetragonal

**Figure 4.** Powder x-ray diffraction patterns of DyAs at high pressures (wavelength of 0.6198 Å): (a) NaCl-type structure, (b) coexistence of NaCl-type structure and high-pressure phase (HP), (c) high-pressure phase.

As and Sb) is highly anisotropic. LnSb has the most anisotropic structure in LnX.

The powder x-ray diffraction of GdAs, DyAs and HoAs with the heavier lanthanide has been studied at high pressures. The profiles of these arsenides indicate only characteristic lines of the NaCl-type structure at ambient pressure. The first-order phase transition in GdAs occurs at around 36 GPa. The profile of the high-pressure phase of GdAs does not resemble that of SmAs [13]. The structure of GdAs is not determined above the transition pressure. Figure 4 shows x-ray diffraction patterns of DyAs measured with a wavelength of 0.6198 Å at high pressures. New diffraction lines appear above 44 GPa and grow with increasing pressure. The single phase of this arsenide at high pressure is obtained at around 57 GPa. This x-ray diffraction pattern of DyAs is not similar to that of SmAs and GdAs. The profile above the transition pressure cannot be assigned by the index of CsCl-type and distorted CsCl-type structures.

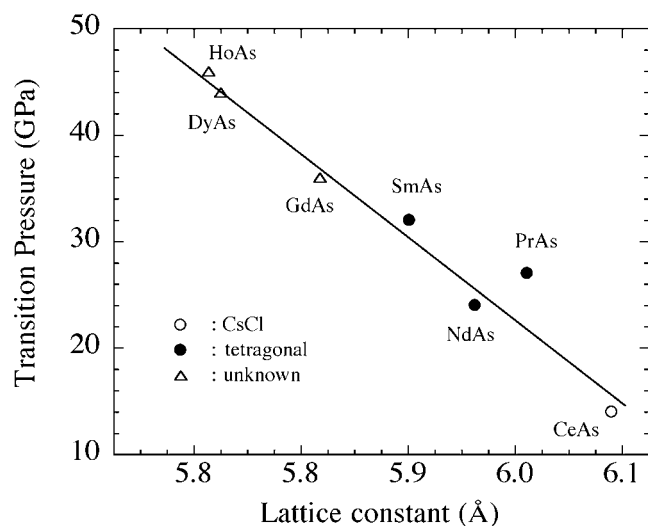


Figure 5. Transition pressures against lattice constants in the NaCl-type structure of LnAs (Ln = Ce, Pr, Nd, Sm, Gd, Dy and Ho). The structures of the high-pressure form are shown by the symbols.

The x-ray diffraction pattern of HoAs has been measured at high pressures. First-order phase transition of this arsenide with the crystallographic change occurs at around 46 GPa. The profile of the high-pressure phase of HoAs resembles that of DyAs.

Figure 5 shows the transition pressures against lattice constants in the NaCl-type structure for LnAs (Ln = Ce, Pr, Nd, Sm, Gd, Dy and Ho). The transition pressures of these arsenides increase with decreasing lattice constant, which decreases with increasing atomic number of lanthanide atoms. The transition pressures of LnAs do not depend on the structure of high-pressure phases. The similar results are also obtained for LnP and LnSb with the NaCl-type structure [2, 5]. The transition pressure of LnX (Ln = lanthanide; X = pnictogen) depends on the magnitude of the lattice constant of NaCl-type structure of LnX. The high-pressure forms of the lighter LnAs (Ln = Ce, Pr, Nd and Sm) show the CsCl-type or distorted CsCl-type structures. On the other hand, the structure of the high-pressure phases of the heavier LnAs (Ln = Gd, Dy and Ho) with many f-electrons is unknown. Thus, it is very interesting that the high-pressure structural behaviour of the heavier LnAs is not due to the ordinary NaCl–CsCl transition.

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