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Phase transitions of LnSb (Ln = lanthanide) with NaCl-type structure at high pressures

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Abstract

Using synchrotron radiation, X-ray diffraction patterns of LnSb (Ln = Pr, Nd, Sm, Gd and Tb) with a NaCl-type structure have been measured up to 30 GPa at room temperature. First-order phase transitions with a crystallographic change occur at around 13 GPa for PrSb and 15 GPa for NdSb. The structure of the high-pressure phases of both antimonides is tetragonal (Ln: 0,0,0; Sb: 1/2, 1/2, 1/2; space group *P*4/*mmm*), and can be viewed as a distorted CsCl structure. The structure of the high-pressure phase of LnSb (Ln = La, Ce, Pr and Nd) is more anisotropic compared with that of corresponding LnP. Pressure-induced phase transitions of SmSb, GdSb and TbSb are observed at around 19, 22 and 21 GPa, respectively. © 2000 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

The pressure–volume relationship for CeP with a NaCl-type structure has been studied up to 23 GPa at room temperature [1,2]. The isomorphous transformation in CeP occurs at around 10 GPa accompanied by a volume collapse of 3–8%. This is due to the electronic transition involving a charge in the valence state of Ce [1]. Further, the compound transforms from the NaCl-type structure to the CsCl-type one at around 19 GPa [2]. Using synchrotron radiation, X-ray diffraction of LnP (Ln = La, Pr, Nd, Sm, Gd, Tb, Tm and Yb) has been studied up to 61 GPa at room temperature. First-order phase transitions of LnP with the crystallographic change occur at high pressures. The structure of the high-pressure phases of LnP (Ln = La, Pr and Nd) is a tetragonal structure which can be seen as the distorted CsCl-type structure [3]. The compression curves of CeSb and LaSb have been investigated up to 25 GPa. The phase transition in both antimonides occurs at around 11 GPa; the structure changes from the NaCl-type to the tetragonal structure [4]. The high-pressure tetragonal phase in CeBi appears at around 13 GPa with the volume collapse of 8% [5]. The high-pressure structural behavior of the 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].

Using synchrotron radiation we have studied X-ray diffraction of LnSb (Ln = Pr, Nd, Sm, Gd and Tb) with the NaCl-type structure up to 30 GPa at room temperature. The pressure-induced phase transitions for these compounds are observed above 13 GPa. In this report, the structure of the high-pressure phase of PrSb and NdSb is discussed.

2. Experimental

LnSb (Ln = Pr, Nd, Sm, Gd and Tb) were prepared by reaction of stoichiometric amounts of each rare earth metal and antimony in a sealed silica tube at around 800°C. The compounds prepared by us were characterized by powder X-ray diffraction using CuK_α radiation and silicon as a standard.

Using synchrotron radiation the powder X-ray diffraction

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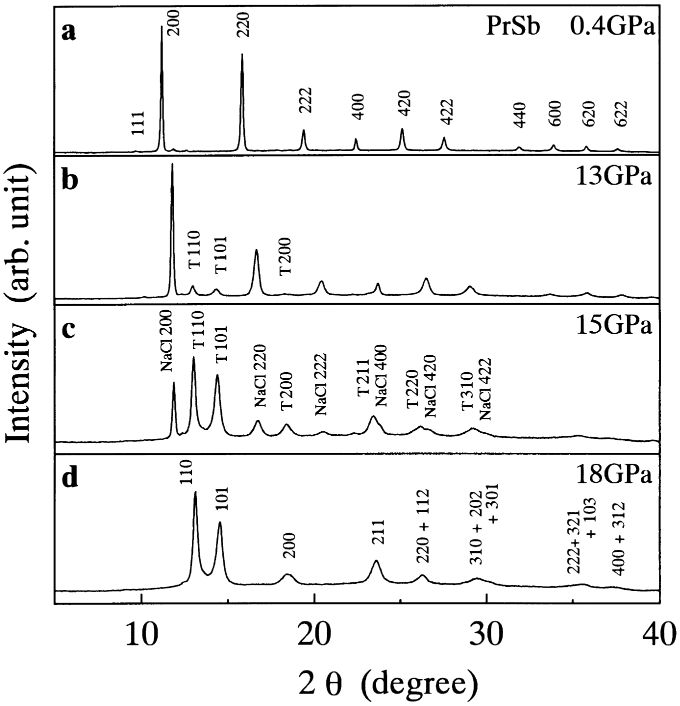

Fig. 1. X-ray diffraction patterns of PrSb at high pressures: (a) NaCl structure; (b) and (c) coexistence of NaCl and tetragonal (T) structures; and (d) tetragonal structure.

patterns of LnSb were measured with a diamond-anvil cell and a imaging plate up to 25 GPa at room temperature. Incident beam was monochromatized by Si(111) double crystal to a wavelength of 0.6196 Å [3]. The pressure in the diamond-cell was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby. A 4:1 methanol–ethanol solution was used as the hydrostatic pressure fluid.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns of PrSb at high pressures. The profile indicates only characteristic lines of the NaCl-type structure at around 0.4 GPa. The *d*-values of 111, 200, 220, 222, 400, 331, 420, 422, 600, 620 and 622 lines for PrSb decrease with increasing pressure up to 13 GPa. New diffraction lines appear above 13 GPa and grow with increasing pressure. The first-order phase transition in PrSb begins to occur at around 13 GPa. Low- and high-pressure phases coexist between 13 and 18 GPa. A single phase of the new high-pressure phase is obtained above 18 GPa. When the pressure is released, the diffraction lines of the NaCl-type structure are recovered at around

Table 1
X-ray diffraction data for the high-pressure phase (single phase) of PrSb

hkl	d_{obs}(Å)	d_{cal} (Å)	$(I/I_0)_{obs}$	$(I/I_0)_{cal}$
PrSb at 18 GPa				
110	2.720	2.729	100	66
101	2.457	2.458	71	100
200	1.935	1.930	29	27
211	1.518	1.518	40	54
220	1.364	1.365	15	10

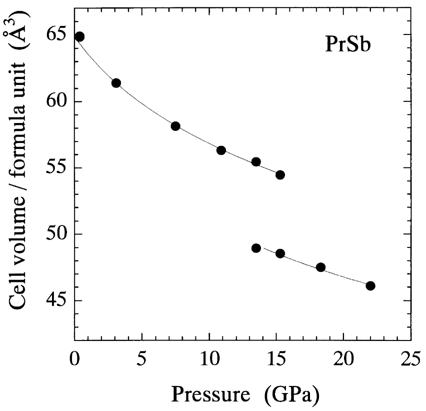

Fig. 2. Ratio of the cell volume/formula unit vs. pressure curve for PrSb at room temperature.

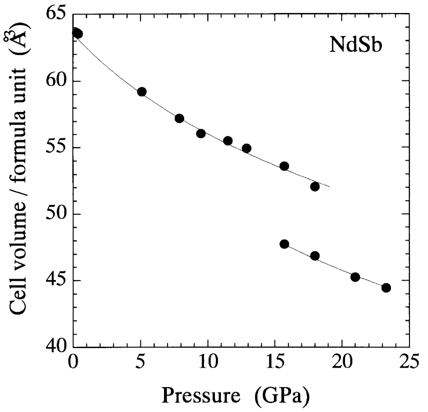

Fig. 3. Ratio of the cell volume/formula unit vs. pressure curve for NdSb at room temperature.

10 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 PrSb changes from the cubic to the tetragonal structure. X-ray diffraction data for the high-pressure phase of PrSb are given in Table 1. These 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 single phase of PrSb are $a = 3.860(3)$ Å, $c = 3.187(13)$ Å, $c/a = 0.83$ and $V = 47.5$ Å^3 at around 18 GPa. The high-pressure phase of PrSb is isostructural with that of PrP [3]. Fig. 2 shows ratio of the cell volume(V/V_0)/formula unit vs. pressure curve for PrSb. The cell volume with the NaCl-type structure decreases with increasing pressure up to 13 GPa.

Table 2
X-ray diffraction data for the high-pressure phase (single phase) of NdSb

hkl	d_{obs} (Å)	d_{cal} (Å)	$(I/I_0)_{obs}$	$(I/I_0)_{cal}$
NdSb at 21 GPa				
110	2.685	2.691	100	66
101	2.417	2.415	88	100
200	1.904	1.903	99	27
211	1.494	1.495	71	54
220	1.346	1.346	15	10

The structural change to the tetragonal structure occurs with the volume collapse of about 11%. Fig. 3 shows ratio of the cell volume (V/V_0) vs. pressure curve for NdSb. The profile of NdSb reveals only characteristic lines of the NaCl-type structure below 14 GPa. New diffraction lines appear at around 15 GPa. Low- and high-pressure phases coexist between 15 and 21 GPa. The single phase is obtained at around 21 GPa. The X-ray diffraction pattern of the high-pressure phase of NdSb is very similar to that of PrSb. The structure of NdSb changes from the cubic to the tetragonal structure at around 15 GPa. The X-ray diffraction data of the high-pressure phase for NdSb are given in Table 2. Crystal data of the single phase of NdSb are $a = 3.806(1)$ Å, $c = 3.123(6)$ Å, $c/a = 0.82$ and $V = 45.2$ Å^3 at around 21 GPa.

Crystallographic data of the high-pressure phases of LnSb (Ln = La, Ce, Pr and Nd) at various pressures are summarized in Table 3. The lattice constants of the high-pressure phase in the region at which the low- and high-pressure phases coexist are described in Table 3. The

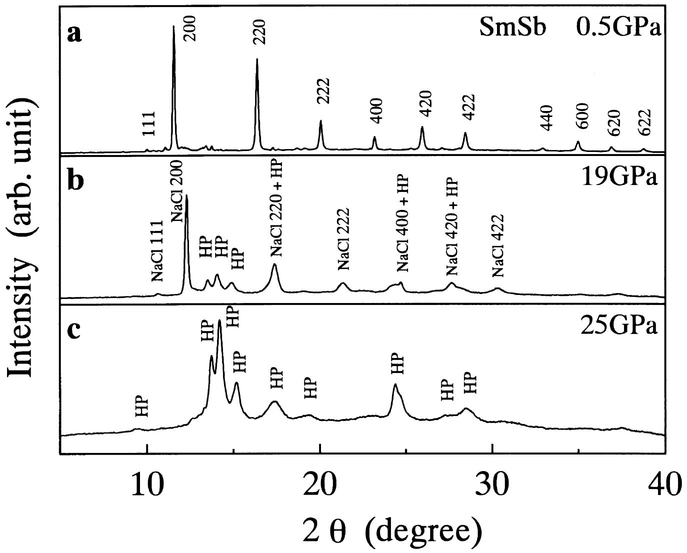

Fig. 4. X-ray diffraction patterns of SmSb at high pressures: (a) NaCl structure; (b) coexistence of NaCl structure and high-pressure phase (HP); (c) high-pressure phase.

Table 3
Crystal data of the high-pressure phases of LnSb (Ln = La, Ce, Pr, Nd) at various pressures

	P (GPa)	Structure	a (Å)	c (Å)	c/a	V (Å^3)	$\Delta V/V_0$ (%)
LaSb[a]	11	Tetragonal	4.019	3.279	0.82	50.8	10.1
CeSb[a]	11	Tetragonal	3.975	3.244	0.82	49.6	10.1
PrSb	15	Tetragonal	3.896	3.197	0.82	48.5	10.9
NdSb	18	Tetragonal	3.849	3.163	0.82	46.8	10.0

[a] Ref. [4].

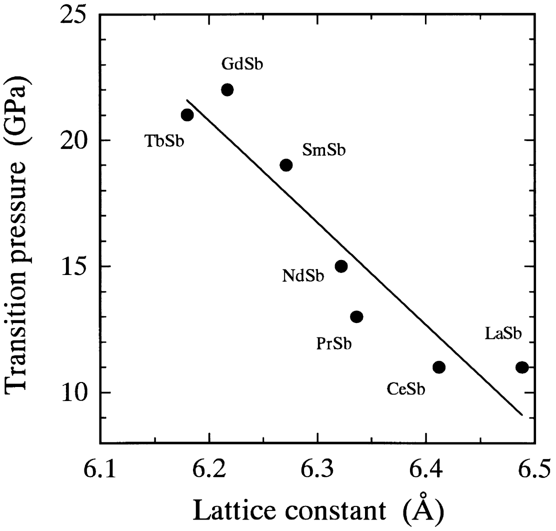

Fig. 5. Transition pressure vs. lattice constant in the NaCl structure of LnSb (Ln = La, Ce, Pr, Nd, Sm, Gd and Tb).

high-pressure phases in LnSb (Ln = La, Ce, Pr and Nd) appear at high pressures with the volume collapse of 10–11%. The structure of LnSb is tetragonal (space group, *P*4/*mmm*); the Ln and Sb atoms in the high-pressure form are located at the following positions: Ln: 0, 0, 0 and Sb: 1/2, 1/2, 1/2. The structure is highly anisotropic with $c/a = 0.82$. The c/a of LnP (Ln = La, Pr and Nd) with the tetragonal structure is 0.85–0.87 [3]. The high-pressure phase of CeP is the CsCl-type structure and on the other hand, CeSb is the tetragonal structure. Thus, the structure of LnSb is more anisotropic compared with that of corresponding LnP at high pressures.

The Pr–Sb distance in the high-pressure form of PrSb is 3.161 Å. This is shorter than the sum of the atomic radius of Pr (1.82 Å) and the covalent radius of Sb (1.38 Å). Thus, the Pr–Sb bond in the tetragonal structure may mainly be bound by the covalent character. The shortest Pr–Pr distance (3.187 Å) in the high-pressure phase of PrSb is considerably longer (2.868 Å) than that in PrP. The Pr–Pr bond in the high-pressure phase of PrSb becomes weaker compared with that in PrP. The similar behavior is also observed in the high-pressure phases of LaSb and NdSb. The anisotropic structure in LnSb may closely be related to the property of the metal–metal bond.

Fig. 4 shows the powder X-ray diffraction patterns of SmSb at high pressures. The profile of the compound indicates only characteristic lines of the NaCl-type structure below 18 GPa. New diffraction lines appear at around 19 GPa. The single phase of the high-pressure form is obtained above 25 GPa. However, the X-ray diffraction pattern of the high-pressure phase of SmSb cannot be assigned by the index of the tetragonal structure. The structure of the high-pressure phase of SmSb is not determined. The X-ray diffraction of GdSb and TbSb with the NaCl-type structure has been studied at high pressures. The first-order phase transitions for both compounds are observed at around 22 GPa for GdSb and 21 GPa for TbSb. The structure of the high-pressure phases of the compounds is not determined yet.

Fig. 5 shows transition pressures vs. lattice constants in the NaCl-type structure for LnSb (Ln = La, Ce, Pr, Nd, Sm, Gd and Tb). The transition pressures of these antimonides increase with decreasing lattice constant, which decreases with increasing atomic number of lanthanide atoms. This tendency has already been observed for LnP with the NaCl-type structure though the transition pressures of the phosphides are about 15 GPa higher than those of LnSb [3]. The high-pressure phases of LnSb (Ln = La, Ce, Pr and Nd) have the tetragonal structure. These do not show the typical NaCl–CsCl transition at high pressures. Further, the structure of the high-pressure phases of LnSb (Ln = Sm, Gd and Tb) with many f-electrons is unknown. Thus, the pressure-induced phase transitions of LnSb are very interest as the ordinary NaCl–CsCl transition is not the dominating mechanism in the high-pressure structural behavior.

References

[1] A. Jayaraman, W. Lowe, L.D. Longinotti, E. Bucher, Phys. Rev. Lett. 36 (1976) 366.
[2] I. Vedel, A.M. Redon, J. Rossar-Mignod, O. Vogt, J.M. Leger, J. Phys. C: Solid State Phys. 20 (1987) 3439.
[3] T. Adachi, I. Shirotani, J. Hayashi, O. Shimomura, Phys. Lett. A 250 (1998) 389.

[4] J.M. Leger, D. Ravot, J. Rossat-Mignod, J. Phys. C, Solid State Phys. 17 (1984) 4935.
[5] J.M. Leger, K. Oki, J. Rossat-Mignod, O. Vogot, J. de Physique 46 (1985) 889.
[6] U. Benedict, S. Dabos-Seignon, J.P. Dancausse, M. Gensini, E. Gering, S. Heathman, H. Luo, J. Staun Olsen, L. Gerward, R.G. Haire, J. Alloys Compd. 181 (1992) 1.
[7] U. Benedict, J. Alloys Compd. 223 (1995) 216.
[8] A. Svane, Z. Szotek, W.M. Temmerman, H. Winter, Solid State Commun. 102 (1997) 473.