Pressure-induced phase transitions in lanthanide monoantimonides with a NaCl-type structure

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By use of synchrotron radiation the powder x-ray diffraction of LnSb (Ln=lanthanide) with a NaCl-type structure has systematically been studied up to 40 GPa at room temperature. First-order phase transitions with the crystallographic change occur for LnSb at high pressures. The structure of the high-pressure phases of LnSb is classified into three groups. The lighter LnSb (Ln=La, Ce, Pr, and Nd) have the tetragonal structure (distorted CsCl-type) at high pressures. The high-pressure form of the middle LnSb (Ln=Sm, Gd, and Tb) is unknown. The heavier LnSb (Ln=Dy, Ho, Er, Tm, and Lu) show the typical NaCl-CsCl ($B1$-$B2$) transition at high pressures though the same transition is not observed in the heavier LnP and LnAs. The transition pressures of LnSb increase with decreasing lattice constant in the NaCl-type structure and do not depend on the structure of their high-pressure phases. The high-pressure structural behavior of LnSb is discussed.

INTRODUCTION

The high-pressure structural behavior of binary *AB* compounds with a NaCl-type structure has been a popular topic in condensed matter research. The majority of these compounds undergo the first-order structural phase transition from NaCl-type ($B1$) to CsCl-type ($B2$) structure at high pressures. The x-ray diffraction profiles of LnX (Ln=lanthanide; X=pnicogen) show the NaCl-type structure at ambient pressure. The powder x-ray diffraction of these compounds has been studied up to 60 GPa at room temperature. CeP and CeAs transform from the NaCl-type structure to a CsCl-type one at around 19 and 16 GPa.[1,2] On the other hand, CeSb transforms from NaCl-type to tetragonal structure, which can be seen as the distorted CsCl-type one.[3] The electronic and structural phase transitions of the cerium pnictides at high pressure are discussed by Svane *et al.*[4,5] The pressure-induced phase transitions for the lighter LnX (Ln=La, Pr, and Nd; X=P, As, and Sb) are also observed at room temperature.[6-8] These high-pressure forms are the tetragonal structure (distorted CsCl type). The structure of the high-pressure phases in the heavier LnP and LnAs is unknown though the phase transition of these compounds is observed at high pressures.[6,7]

By use of synchrotron radiation we have studied the powder x-ray diffraction of LnSb with the NaCl-type structure up to 40 GPa at room temperature. In this paper the structural phase transitions in LnSb at high pressures are discussed.

EXPERIMENTAL

LnSb was 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 char-

acterized by the powder x-ray diffraction using Cu$K\alpha$ radiation and silicon as a standard. The x-ray diffraction of Pm, Eu, and Yb compounds was not studied at high pressure because we cannot prepare these compounds with the fine pattern of the NaCl-type structure.

By use of synchrotron radiation the powder x-ray diffraction patterns of LnSb were measured with a diamond-anvil cell and an imaging plate up to 40 GPa at room temperature.[6-8] Incident beam was monochromatized by Si (111) crystals. The pressure in the diamond-cell was deter-
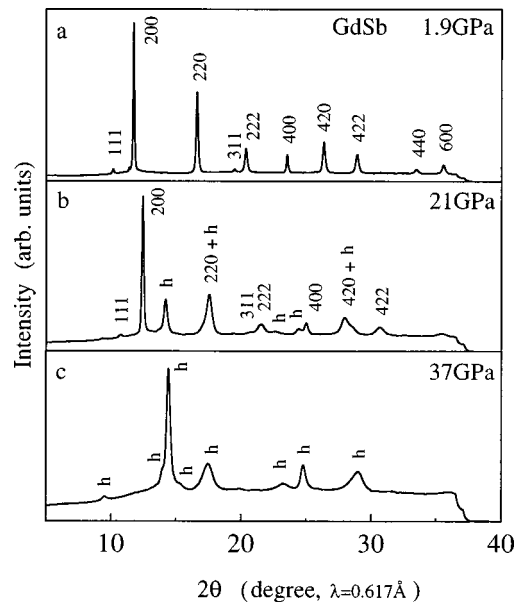

FIG. 1. Powder x-ray diffraction patterns of GdSb at high pressures. (a) NaCl-type structure, (b) coexistence of NaCl-type structure and high-pressure phase, (c) high-pressure phase (*h*).
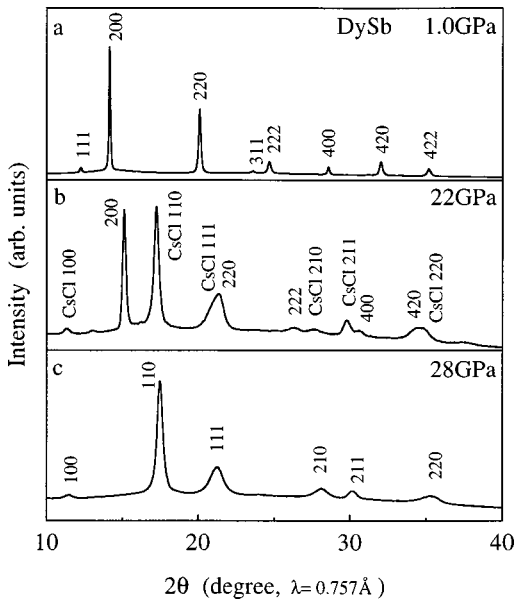
FIG. 2. Powder x-ray diffraction patterns of DySb at high pressures. (a) NaCl-type structure, (b) coexistence of NaCl and CsCl-type structures, (c) CsCl-type structure.

mined from a pressure shift in the sharp R-line fluorescence spectrum of ruby. A 4:1 methanol-ethanol solution was used as the pressure-transmitting fluid.

RESULTS AND DISCUSSION

Figure 1 shows the powder x-ray diffraction patterns of GdSb at high pressures. The profile of GdSb indicates only characteristic lines of the NaCl-type structure below 20 GPa. New diffraction lines appear at around 21 GPa. Low- and high-pressure phases coexist in a wide pressure range. The diffraction lines of the high-pressure form of GdSb cannot be assigned by the index of the cubic and tetragonal structures. The x-ray diffraction profiles of TbSb are similar to those of GdSb at high pressures. We have already reported that the high-pressure form of SmSb is unknown.[8] Thus, the structure of the high-pressure phase of the middle LnSb (Ln=Sm, Gd, and Tb) has not been determined.

Figure 2 shows the powder x-ray diffraction patterns of DySb 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, 311, 222, 400, 420, and 422 lines of DySb decrease with increasing pressure up to 21 GPa.

TABLE I. X-ray diffraction data for the high-pressure single phase of DySb.

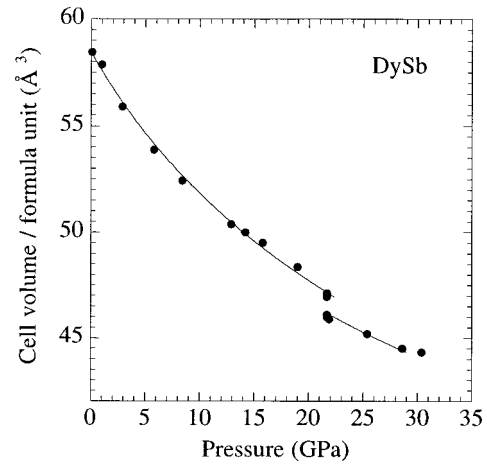|			DySb at 28 GPa			
h	k	l	d (obs.)	d (cal.)	I/I_0 (obs.)	I/I_0 (cal.)
1	1	0	2.492	2.506	100	100
1	1	1	2.055	2.046	25	1
2	1	0	1.559	1.585	6	2
2	1	1	1.456	1.447	9	36
2	2	0	1.252	1.253	8	11

FIG. 3. Cell volume/formula unit vs pressure curve for DySb at room temperature.

New diffraction lines appear above 22 GPa and grow with increasing pressure. The characteristic lines of the CsCl-type structure are observed in the new high-pressure phase. X-ray diffraction data of the high-pressure form of DySb are given in Table I. All lines of the high-pressure phase are indexed in the cubic CsCl-type structure. Crystal data of the single phase of DySb are $a=3.54(1)$ Å, $V=44.4(5)$ Å^3 at 28 GPa.

Figure 3 shows the cell volume/formula unit vs pressure curve for DySb. The cell volume with the NaCl-type structure monotonically decreases with increasing pressure up to 21 GPa. The structural change to the CsCl-type structure occurs with the volume collapse of about 3%. When the pressure is removed, the diffraction lines of the NaCl-type structure reappear at around 14 GPa.

Figure 4 shows the Dy-Dy and Dy-Sb distances in DySb at high pressures. The Dy-Sb distance in the NaCl-type structure is 3.08 Å at ambient pressure. This distance is much shorter than the sum of ionic radii of Dy^{3+}(0.99 Å) and Sb^{3-}(2.45 Å). The Dy-Sb distance is slightly shorter than
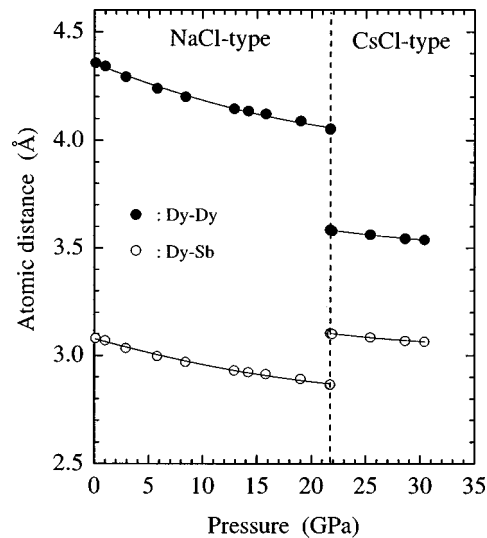

FIG. 4. Dy-Dy and Dy-Sb distances vs pressure curves for DySb at room temperature.
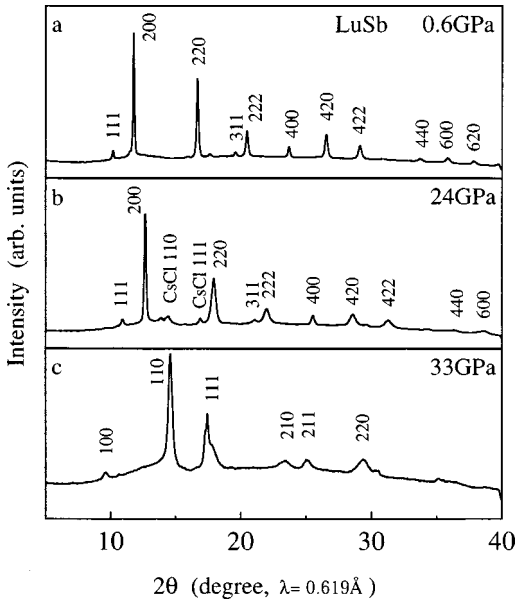
FIG. 5. Powder x-ray diffraction patterns of LuSb at high pressures. (a) NaCl-type structure, (b) coexistence of NaCl- and CsCl-type structures, (c) CsCl-type structure.

the sum of the atomic radius of Dy (1.77 Å) and the covalent radius of Sb (1.38 Å), longer than the sum of the covalent radii of Dy (1.59 Å) and Sb (1.38 Å). Thus, the chemical bond between Dy and Sb atoms has the covalent character. When the $B1$-$B2$ transition occurs at around 22 GPa, the Dy-Sb distance suddenly increases and becomes 3.07 Å in the CsCl-type structure. This almost agrees with the Dy-Sb distance (3.08 Å) in the NaCl-type structure at ambient pressure. On the other hand, the Dy-Dy distance in DySb abruptly decreases if the $B1$-$B2$ transition occurs. This distance (3.54 Å) in the CsCl-type structure agrees with the sum of atomic radius of Dy (1.77 Å).

Figure 5 shows the powder x-ray diffraction profiles of LuSb at high pressures. The pattern at around 0.6 GPa indicates only characteristic lines of the NaCl-type structure. New diffraction lines appear above 24 GPa and grow with increasing pressure. The single phase of the high-pressure form of LuSb is obtained at around 33 GPa. X-ray diffraction data of the high-pressure form of LuSb are given in Table II. All lines of the high-pressure phase are indexed in the cubic CsCl-type structure. Crystal data of the single phase of LuSb are $a = 3.46(2)$ Å, $V = 41.4(6)$ Å^3 at 33 GPa.

TABLE II. X-ray diffraction data for the high-pressure single phase of LuSb.

			LuSb at 33 GPa			
h	k	l	d (obs.)	d (cal.)	I/I_0 (obs.)	I/I_0 (cal.)
1	1	0	2.437	2.449	100	100
1	1	1	2.042	1.999	48	1
2	1	0	1.525	1.549	8	2
2	1	1	1.429	1.414	9	36
2	2	0	1.221	1.224	13	11

TABLE III. Crystal data of the single phase of high-pressure forms for LnSb (Ln=Dy, Ho, Er, Tm, and Lu).

compound	P (GPa)	structure	a (Å)	V (Å^3)
DySb	28	CsCl type	3.54	44.4
HoSb	31	CsCl type	3.57	45.5
ErSb	35	CsCl type	3.50	42.9
TmSb	31	CsCl type	3.46	41.4
LuSb	33	CsCl type	3.46	41.4

X-ray diffraction patterns of the heavier LnSb (Ln=Ho, Er, and Tm) are very similar to those of DySb and LuSb at high pressures. These antimonides show the $B1$-$B2$ transition at high pressures. The transition pressures of the heavier LnSb are about 22 GPa for HoSb, 25 GPa for ErSb, and 22 GPa for TmSb. The crystal data of the high-pressure form for the heavier LnSb (Ln=Dy, Ho, Er, Tm, and Lu) are summarized in Table III. It is well known that ionic crystals such as the alkali halide have the CsCl-type structure if the ratio of their ionic radii is above 0.732. The Ln-Sb distances in the CsCl-type structure almost agree with the sum of the atomic radius (R_{Ln}) of Ln and the covalent radius (R_{Sb}) of Sb. Thus, the structure of LnSb may be understood according to the rigid sphere model. The ratio of their radii (R_{Sb}/R_{Ln}) is above 0.78 for the heavier LnSb (Ln=Dy, Ho, Er, Tm, and Lu). These values suggest that the heavier LnSb have eight coordination (CsCl-type structure) at high pressures. On the contrary, the heavier LnP and LnAs does not show the $B1$-$B2$ transition at high pressures.[6,7] The ratio of their radii ($R_{P,As}/R_{Ln}$) for the heavier LnP and LnAs is considerably smaller than 0.78. Thus, the high-pressure form of these phosphides and arsenides cannot take the CsCl-type structure.

Figure 6 shows transition pressures vs lattice constants in the NaCl-type structure for LnSb (Ln=La, Ce, Pr, Nd, Sm,
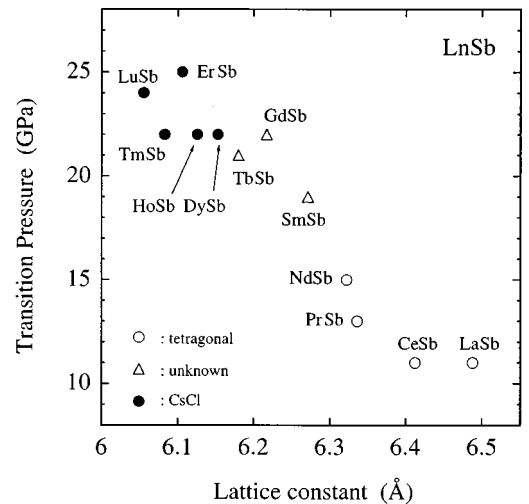

FIG. 6. Transition pressures vs lattice constants in the NaCl-type structure of LnSb (Ln=La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu). The structures of the high-pressure phases are shown by the symbol.

Gd, Tb, Dy, Ho, Er, Tm, and Lu). The transition pressures of these antimonides increase with decreasing lattice constant, which decreases with increasing atomic number of lanthanide atoms. The structure of the high-pressure phase of LnSb is classified into three groups. The lighter LnSb (Ln=La, Ce, Pr, and Nd) have the tetragonal structure (distorted CsCl type).[3,8] The high-pressure form of the middle LnSb (Ln=Sm, Gd, and Tb) is unknown. On the other hand, the heavier LnSb (Ln=Dy, Ho, Er, Tm, and Lu) show the typical NaCl-CsCl transition at high pressures. The transition pressure of LnSb does not depend on the structure of the high-pressure phase, but the magnitude of lattice constant in the NaCl-type structure.

The lighter LnP and LnAs with the NaCl-type structure have the CsCl-type or distorted CsCl-type structure at high pressures.[1,2,6,7] On the contrary, the high-pressure form of the heavier LnP and LnAs is unknown.[6,7] It is very interesting that the $B1$-$B2$ transition is not found for the heavier LnP and LnAs.

Middle rare-earth metals Sm, Gd, and Tb show consecutively the pressure-induced phase transitions. A Sm metal transforms successively from the Sm type to dhcp, to fcc, to trigonal, to monoclinic, and to tetragonal structures with increasing pressure.[9,10] The similar phase transitions are also observed for Gd and Tb metals at high pressures. The structure of the high-pressure phases of the middle LnSb (Ln=Sm, Gd, and Tb) may closely be related to the structural behavior of the corresponding metals at high pressure.

LuSb with the f orbital filled by electrons shows the $B1$-$B2$ transition at high pressures. The high-pressure structural behavior in the other heavier LnSb is similar to that of LuSb. Thus, the $B1$-$B2$ transition in the heavier LnSb is insensitive to the f electrons.

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