

X-ray study with synchrotron radiation for P- and Sb-based skutterudite compounds at high pressures

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 7853

(<http://iopscience.iop.org/0953-8984/16/43/024>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 18:24

Please note that [terms and conditions apply](#).

X-ray study with synchrotron radiation for P- and Sb-based skutterudite compounds at high pressures

Ichimin Shirotani¹, Takashi Noro¹, Junichi Hayashi¹, Chihiro Sekine¹,
Ram Giri¹ and Takumi Kikegawa²

¹ Muroran Institute of Technology, 27-1, Mizumoto, Muroran-shi 050-8585, Japan

² IMSS, KEK, 1-1, Oho, Tsukuba-shi, Ibaraki 305-0801, Japan

Received 15 April 2004

Published 15 October 2004

Online at stacks.iop.org/JPhysCM/16/7853

doi:10.1088/0953-8984/16/43/024

Abstract

Using synchrotron radiation, the x-ray diffraction of P- and Sb-based skutterudite compounds has systematically been studied at room temperature and high pressures. Bulk moduli of binary skutterudites CoX_3 ($X = \text{P}$ and Sb), filled skutterudites $\text{CeT}_4\text{X}_{12}$ ($T = \text{Fe}$, Ru and Os), $\text{LaRu}_4\text{X}_{12}$ and $\text{PrRu}_4\text{X}_{12}$ are obtained from the volume versus pressure curves fitted by a Birch equation of state. Bulk moduli are 150–225 GPa for P-based skutterudites and 80–115 GPa for Sb-based skutterudites. The bulk modulus of the phosphides is about two times that of the corresponding antimonides. The antimonides are very compressible compared with the phosphides. The Grüneisen constants (γ) for skutterudite compounds are estimated from the compressibility and its volume derivative in the Debye approximation. The bulk modulus of CoX_3 and $\text{CeT}_4\text{X}_{12}$ increases with increasing lattice constant, attaining a maximum for the Ru compounds. Bulk moduli for the Ru-based skutterudites are larger than those of the corresponding Fe and Os compounds. This may be closely related to the interesting physical properties in the Ru-based skutterudites. The bulk modulus of the binary skutterudites is smaller than that of the filled skutterudites. The cell volume for $\text{CeT}_4\text{X}_{12}$ ($T = \text{Fe}$, Ru and Os ; $X = \text{P}$ and Sb) decreases monotonically with increasing pressure. The valence state of Ce ion in these compounds does not change at high pressures.

1. Introduction

Filled skutterudites $\text{LnT}_4\text{X}_{12}$ ($\text{Ln} =$ lighter lanthanide; $T = \text{Fe}$, Ru and Os ; $X = \text{P}$, As and Sb) show interesting physical properties at low temperatures. Superconducting [1–3], semiconducting [4], metal–insulator transition [5, 6] and magnetic [7], heavy fermion [8], intermediate-valence [9] and non-Fermi liquid behaviour [10] have been observed in these materials. Furthermore, binary skutterudite compounds exhibit remarkable thermoelectric properties [11]. These materials crystallize in a filled skutterudite-type structure (cubic, space

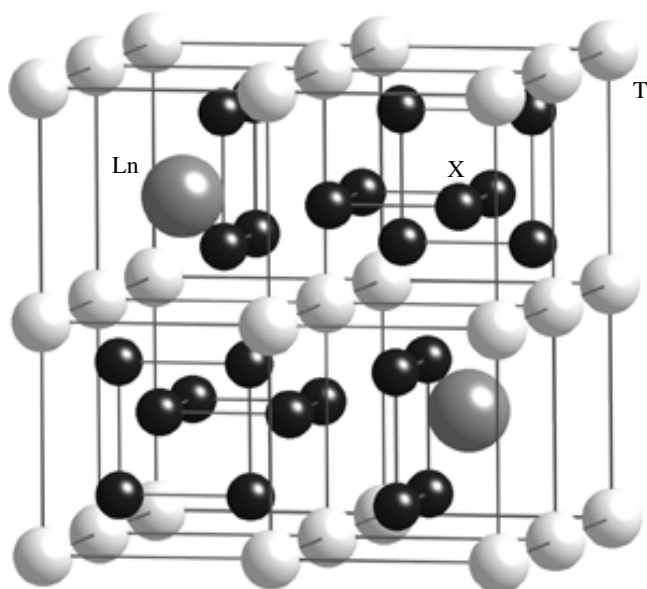


Figure 1. Crystal structure of $\text{LnT}_4\text{X}_{12}$ (Ln = lanthanide; T = transition metal; X = P, As and Sb) with a skutterudite-type structure. The T atoms are taken as the origin (000).

group: Im-3) [6, 12]. Figure 1 shows a crystal structure of the skutterudite compound. Ln atoms are located at (0 0 0) and $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ in the cubic structure. Transition metal atoms (T) are at the centre of a distorted octahedron of six pnictogen atoms (X). The skutterudite structure is characterized by the formation of well-defined X^4 groups. Ln atoms are unoccupied in binary skutterudite compounds.

Effects of the pressure on the resistivity of many filled skutterudites have been studied. The interesting electrical behaviour is found at high pressures. The superconducting transition temperature (T_c) of $\text{LaT}_4\text{P}_{12}$ (T = Fe, Ru and Os) has been measured at high pressures; the T_c of the Fe compound increases with increasing pressure. In contrast, the Ru and Os compounds exhibit a weak decrease in the T_c [13]. $\text{LaRu}_4\text{As}_{12}$ has the highest T_c (10.3 K) among the skutterudite superconductors [1]. T_c decreases at the rate of -0.4 K GPa^{-1} up to 8 GPa [14]. A metal-to-insulator transition for $\text{PrRu}_4\text{P}_{12}$ is found at around 62 K under ambient pressure [5]. The transition temperature rapidly increases up to 4.5 GPa [6]. The resistivity of the $\text{CeFe}_4\text{Sb}_{12}$ and $\text{YbFe}_4\text{Sb}_{12}$ has been studied at high pressure and low temperatures; the temperature of the maximum in resistivity (T_0) for the Ce compound increases with increasing pressure, while the opposite behaviour is observed for the Yb compound [8]. The effect of pressure on the electrical resistivity of the Kondo insulating compound $\text{CeOs}_4\text{Sb}_{12}$ has been studied at low temperatures [15, 16].

We have studied the powder x-ray diffraction of several filled skutterudites with synchrotron radiation at high pressures, the bulk modulus is also obtained from the volume versus pressure curve fitted by a Birch equation of state. The bulk moduli of $\text{LnRu}_4\text{P}_{12}$ for Ln = La, Ce and Pr are 172, 226 and 207 GPa, respectively [6, 17]. However, the x-ray diffraction of many binary and filled skutterudites has not been studied at high pressures yet.

Using synchrotron radiation, the powder x-ray diffraction for P- and Sb-based binary and filled skutterudites has systematically been investigated at room temperature and at high

pressures. In this paper, the pressure versus volume curve and the bulk modulus for binary and filled skutterudites are discussed.

2. Experimental procedure

Using a wedge-type cubic-anvil high-pressure apparatus, many ternary metal compounds have been prepared at high temperatures and high pressures. The upper and lower stages of the high-pressure apparatus consist of three anvils that slide on the wedge formed in shallow V-shaped grooves. The anvil's movement is completely synchronized by means of a wedge system. The sample assembly for the preparation of binary and filled skutterudites is similar to that used for the high-pressure synthesis of ternary metal compounds [18]. P- and Sb-based skutterudite compounds were prepared by reaction of stoichiometric amounts of each metal and red phosphorus or antimony powders at around 4 GPa. The reaction temperatures were between 800 and 1100 °C. The materials prepared by us were binary skutterudites CoX_3 ($X = \text{P}$ and Sb) and filled skutterudites $\text{CeT}_4\text{X}_{12}$ ($T = \text{Fe}$, Ru and Os ; $X = \text{P}$ and Sb), $\text{LaRu}_4\text{Sb}_{12}$ and $\text{PrRu}_4\text{Sb}_{12}$. These compounds were characterized by the powder x-ray diffraction using Cu K_α radiation and silicon as a standard at room temperature.

Using synchrotron radiation, powder x-ray diffraction patterns of binary and ternary skutterudites were systematically measured with a diamond-anvil cell and an imaging plate at room temperature and high pressures [6, 17]. The incident beam was monochromatized by $\text{Si}(111)$ double crystals. The x-ray beam was collimated to 40 nm in diameter. High-pressure diffraction experiments were performed at the beam line (BL-18 C) of the KEK Photon Factory in Tsukuba. We employed the diamond-anvil cell with diamond culet diameters of 500 μm . The sample was finely grounded and loaded in the 100 μm diameter hole drilled in a stainless-steel (T301) gasket. The pressure in the diamond cell was measured before and after each exposure based on the shifts of the ruby R_1 and R_2 fluorescence lines. A 4:1 methanol–ethanol solution was used as the pressure medium. The measurement of the x-ray diffraction was carried out under hydrostatic conditions because the 4:1 methanol–ethanol solution used as pressure medium was solidified at around 10 GPa.

3. Results

Figure 2 shows powder x-ray diffraction patterns of CoSb_3 ($\lambda = 0.6114 \text{ \AA}$) at room temperature and high pressures. The x-ray diffraction profiles indicate only characteristic lines of 130, 321, 330, 420, 332, 422, 510, 530, 600 and 611 with the skutterudite-type structure at high pressures. The d values of these lines decrease with increasing pressure up to 10.2 GPa. The lattice constant (a) of CoSb_3 decreases from 9.0366 \AA at 0.55 GPa to 8.7761 \AA at 10.2 GPa. New diffraction lines do not appear up to 10 GPa although the diffraction lines shift and the width broadens with increasing pressure. When pressure is reduced from 10 GPa to the ambient pressure, the d values of the diffraction lines return to those at ambient pressure. This behaviour is completely reversible. Similar results are also observed for CoP_3 .

Figure 3 shows the relative cell volume (V/V_0) versus pressure curves for CoSb_3 and CoP_3 . The cell volume of both binary skutterudites monotonically decreases with increasing pressure up to about 10 GPa. These experimental data can be fitted to a Birch equation of state [19]

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

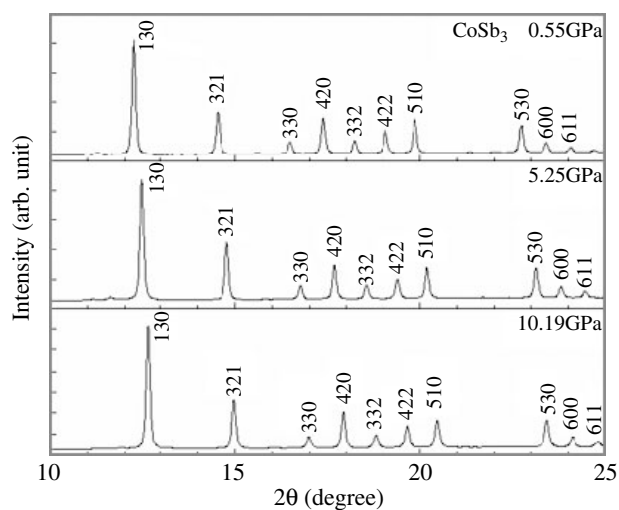


Figure 2. Powder x-ray diffraction patterns of CoSb_3 ($\lambda = 0.6114 \text{ \AA}$) at room temperature and high pressures.

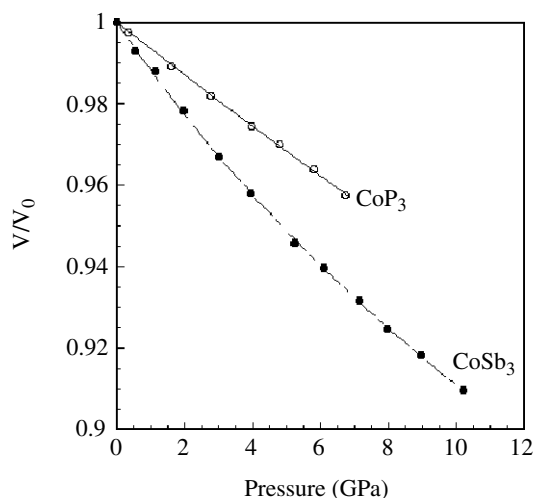


Figure 3. Relative cell volume (V/V_0) versus pressure curves for CoSb_3 and CoP_3 .

where B_0 is the bulk modulus, B'_0 its first pressure derivative, V the volume and P the pressure. A least-squares fit to the data of CoSb_3 gives the following values: $B_0 = 81 \pm 1 \text{ GPa}$ and $B'_0 = 6 \pm 1 \text{ GPa}$. CoSb_3 is isostructural with CoP_3 . The pressure versus volume curve for CoP_3 is also fitted by a Birch equation of state. B_0 and B'_0 of CoP_3 are 152 ± 4 and $1 \pm 1 \text{ GPa}$, respectively. The bulk modulus of CoP_3 is about two times that of CoSb_3 . This antimonide is more compressible than the phosphide.

The Grüneisen constant (γ) can be estimated from the compressibility and its volume derivative in the Debye approximation at a constant temperature:

$$\gamma = \frac{2}{3} - \left(\frac{1}{2}\right) V \left(\frac{\partial^2 P}{\partial V^2}\right)_T \left(\frac{\partial P}{\partial V}\right)_T^{-1}. \quad (2)$$

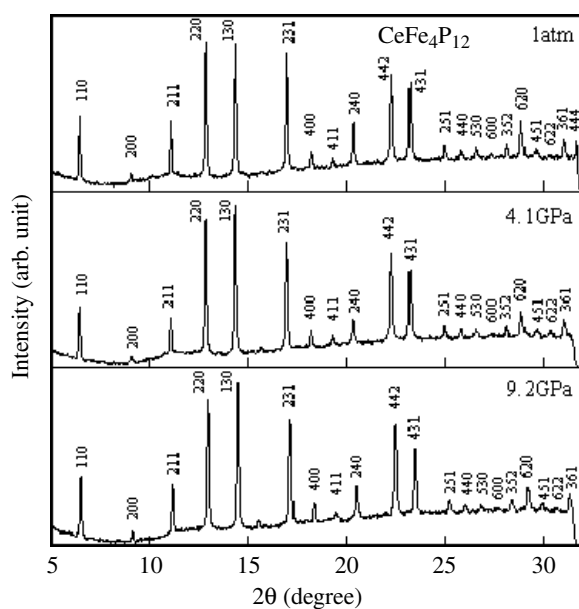


Figure 4. Powder x-ray diffraction patterns of $\text{CeFe}_4\text{P}_{12}$ ($\lambda = 0.6105 \text{ \AA}$) at room temperature and high pressures.

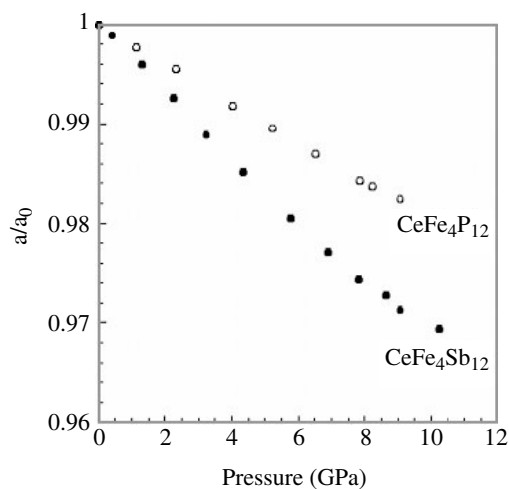


Figure 5. Ratio of the lattice constant (a/a_0) versus pressure curves for $\text{CeFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$.

We obtained the Grüneisen constants of 1.111 for CoSb_3 and 0.974 for CoP_3 . The Grüneisen constant obtained by Caillat *et al* was $\gamma = 0.952$ for CoSb_3 [20]. The value obtained by us for CoSb_3 is somewhat larger than their result.

Figure 4 shows x-ray diffraction profiles of filled skutterudites $\text{CeFe}_4\text{P}_{12}$ ($\lambda = 0.6105 \text{ \AA}$) at high pressures. The diffraction patterns of this compound do not change essentially although the diffraction lines shift to a high-angle region with increasing pressure. Figure 5 shows the ratio of the lattice constant (a/a_0) for $\text{CeFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$ at high pressures. The lattice constants of both compounds monotonically decrease with increasing pressure up to about 10 GPa. The pressure versus volume curve for both compounds is fitted by a Birch equation

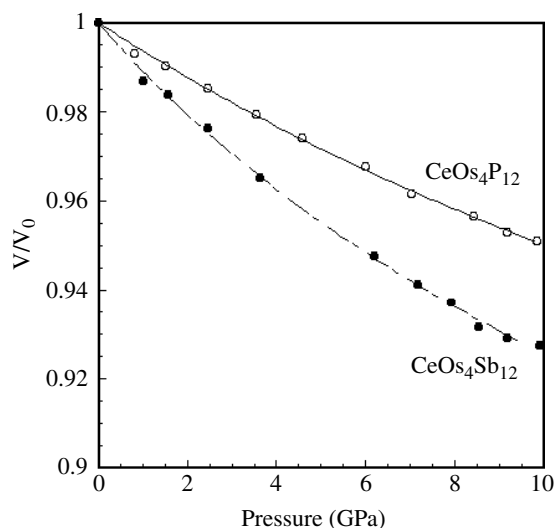


Figure 6. Relative cell volume (V/V_0) versus pressure curves for $\text{CeOs}_4\text{P}_{12}$ and $\text{CeOs}_4\text{Sb}_{12}$.

Table 1. Lattice constant, B_0 , B'_0 and Grüneisen constant γ for CoX_3 and $\text{LnT}_4\text{X}_{12}$ (Ln = La, Ce and Pr; T = Fe, Ru and Os; X = P and Sb).

	a (Å)	B_0 (GPa)	B'_0	γ
CoP_3	7.7064	152 ± 4	1 ± 1	0.974
$\text{CeFe}_4\text{P}_{12}$	7.7917	162 ± 4	1 ± 1	1.032
$\text{CeRu}_4\text{P}_{12}$	8.0497	226 ± 16	6 ± 2	1.135
$\text{CeOs}_4\text{P}_{12}$	8.0695	150 ± 5	11 ± 2	1.129
$\text{LaRu}_4\text{P}_{12}$	8.0608	172 ± 6	8 ± 1	1.15
$\text{PrRu}_4\text{P}_{12}$	8.0572	207 ± 12	6 ± 1	1.131
CoSb_3	9.0451	81 ± 1	6 ± 1	1.111
$\text{CeFe}_4\text{Sb}_{12}$	9.1391	88 ± 4	4 ± 1	1.113
$\text{CeRu}_4\text{Sb}_{12}$	9.2670	97 ± 5	8 ± 1	1.141
$\text{CeOs}_4\text{Sb}_{12}$	9.3018	85 ± 5	12 ± 2	1.139
$\text{LaRu}_4\text{Sb}_{12}$	9.2741	98 ± 4	8 ± 1	1.143
$\text{PrRu}_4\text{Sb}_{12}$	9.2622	111 ± 5	5 ± 1	1.123

of state. Bulk moduli of both skutterudites are 162 ± 4 GPa for $\text{CeFe}_4\text{P}_{12}$ and 88 ± 4 GPa for $\text{CeFe}_4\text{Sb}_{12}$. The bulk modulus of $\text{CeFe}_4\text{P}_{12}$ is about two times that of $\text{CeFe}_4\text{Sb}_{12}$.

Figure 6 shows the relative cell volume (V/V_0) versus pressure curves for $\text{CeOs}_4\text{P}_{12}$ and $\text{CeOs}_4\text{Sb}_{12}$. The cell volume with the skutterudite-type structure monotonically decreases with increasing pressure up to 10 GPa. The pressure versus volume curve for both compounds is fitted by a Birch equation of state. Bulk moduli of $\text{CeOs}_4\text{P}_{12}$ and $\text{CeOs}_4\text{Sb}_{12}$ are 150 ± 5 and 85 ± 5 GPa, respectively. The bulk modulus of the phosphide is about two times that of the antimonide. As mentioned in the Introduction section, the bulk moduli of $\text{LnRu}_4\text{P}_{12}$ (Ln = La, Ce and Pr) have already been obtained [17]. The x-ray diffraction of $\text{LnRu}_4\text{Sb}_{12}$ (Ln = La, Ce and Pr) has been investigated with synchrotron radiation at room temperature and high pressure. The bulk moduli of these compounds are 98 GPa for $\text{LaRu}_4\text{Sb}_{12}$, 97 GPa for $\text{CeRu}_4\text{Sb}_{12}$ and 111 GPa for $\text{PrRu}_4\text{Sb}_{12}$.

The values of the lattice constant, B_0 , B'_0 and the Grüneisen constant γ for many P- and Sb-based skutterudite compounds are summarized in table 1. The bulk modulus of the

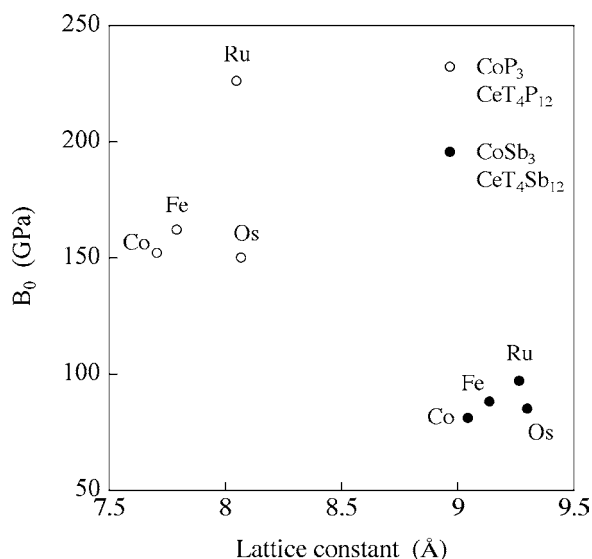


Figure 7. Bulk modulus versus lattice constant curves for CoX_3 and $\text{CeT}_4\text{X}_{12}$ ($T = \text{Fe, Ru and Os}$; $X = \text{P and Sb}$).

binary skutterudites is smaller than that of the filled skutterudites. The bulk moduli for P-based skutterudites are about two times those of Sb-based compounds. Since the compressibility is defined as the reciprocal of bulk modulus B_0 , the phosphides are less compressible compared with the antimonides. The lattice constant of the phosphides is about 15% lower than that of the antimonides. The large bulk modulus of the phosphides mainly arises from the small lattice constant. We have studied x-ray diffraction of LnX ($X = \text{P and Sb}$) with a NaCl-type structure at high pressures; the bulk moduli of PrX ($X = \text{P and Sb}$) are 74 and 44 GPa, respectively [21]. Thus, the metal phosphides are generally less compressible than the metal antimonides. The bulk modulus of $\text{PrRu}_4\text{X}_{12}$ is several times that of PrX . The P-based skutterudite compounds are very hard materials.

Figure 7 shows bulk modulus versus lattice constant curves for CoX_3 and $\text{CeT}_4\text{X}_{12}$ ($T = \text{Fe, Ru and Os}$; $X = \text{P and Sb}$). The bulk modulus of these compounds increases with increasing lattice constant, reaching a maximum for the Ru compounds. $\text{CeRu}_4\text{P}_{12}$ and $\text{CeRu}_4\text{Sb}_{12}$ have the largest bulk modulus among these corresponding skutterudites. It is of interest to note that the bulk modulus of $\text{CeRu}_4\text{X}_{12}$ is larger than that of $\text{CeFe}_4\text{X}_{12}$ with small lattice constants.

4. Discussion

We have systematically prepared new filled skutterudites with heavy lanthanide $\text{LnFe}_4\text{P}_{12}$ ($\text{Ln} = \text{lanthanide}$) at high pressures [22]. Figure 8 shows the relationship between the lattice constants and atomic numbers of lanthanide (including Y) in $\text{LnFe}_4\text{P}_{12}$ ($\text{Ln} = \text{lanthanide}$). The lattice constant of these compounds basically decreases with increasing atomic number. However, some anomalies in this curve are observed for the Ce, Eu and Yb compounds [22]. These may be closely related to the valence states in the materials. $\text{CeFe}_4\text{P}_{12}$ exhibits a small anomalous lattice constant compared to the otherwise smoothly decreasing lattice-parameter variation in going from an La to Lu-containing compound. The small lattice constant is also found for $\text{CeRu}_4\text{P}_{12}$ and $\text{CeOs}_4\text{P}_{12}$ [23, 24]. These compounds have lattice constants

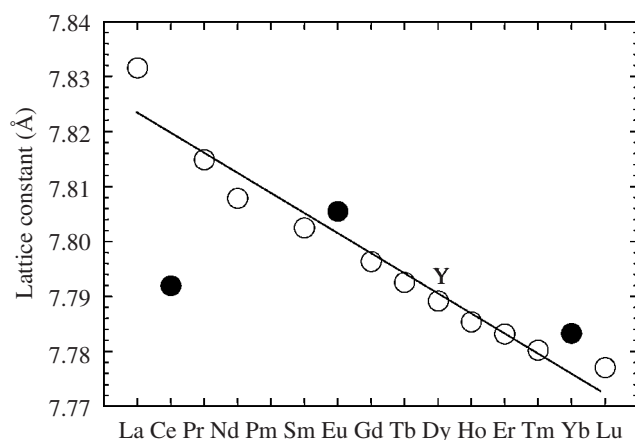


Figure 8. Relationship between the lattice constants and atomic numbers of lanthanide (including Y) in $\text{LnFe}_4\text{P}_{12}$ (Ln = lanthanide). The Ce, Eu and Yb compounds with an anomalous lattice constant are shown by a black circle. The lattice constant of $\text{YFe}_4\text{P}_{12}$ almost agrees with that of $\text{DyFe}_4\text{P}_{12}$. This is shown by the symbol Y in the figure.

smaller than those expected for the trivalent Ce ion. The reduced lattice constants of the Ce compounds suggest a valency of +4 for the Ce ion [23]. $\text{CeFe}_4\text{P}_{12}$, $\text{CeRu}_4\text{P}_{12}$ and $\text{CeOs}_4\text{P}_{12}$ show the semiconducting behaviour; the energy gaps ($\Delta E/k_B$) of these compounds are 1500, 1000 and 400 K, respectively [4]. Jung *et al* suggest that the oxidation state of Ce ion in these compounds is +4 [25].

On the other hand, Nordstrom and Singh [26] investigated the electronic structures of $\text{CeFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$, and pointed out that Ce ion in the Ce compounds are trivalent and Ce 4f states hybridize strongly with Fe 3d and P or Sb p states in the vicinity of the Fermi energy. The Sb-based compounds $\text{CeT}_4\text{Sb}_{12}$ (T = Fe, Ru and Os) show a metallic behaviour [8, 10, 15]. In these Sb-based compounds, there is no reduced lattice constant as in phosphides [23]. Bauer *et al* [15] suggested that the Ce ion in $\text{CeOs}_4\text{Sb}_{12}$ is trivalent from magnetic susceptibility measurements. The p-f hybridization in $\text{CeOs}_4\text{Sb}_{12}$ is discussed by Harima and Takegahara [27]. The electrical properties of $\text{La}_{1-x}\text{Ce}_x\text{Ru}_4\text{P}_{12}$ ($x = 0.6, 0.7, 0.8, 0.9, 1$) have been studied, and the semiconducting behaviour is observed even around $x = 0.7$ [4]. This cannot be explained by the oxidation state of Ce^{4+} [4]. Ce ion in $\text{CeFe}_4\text{P}_{12}$ is primarily trivalent from x-ray near-edge spectroscopy (XANES) measurements [28]. Thus, the valence state of the Ce-based P and Sb skutterudites are mainly trivalent.

As mentioned above, the cell volume of $\text{CeT}_4\text{X}_{12}$ (T = Fe, Ru and Os; X = P and Sb) decreases smoothly with increasing pressure up to 10 GPa. The monotonic P - V curve is observed up to 40 GPa for $\text{CeRu}_4\text{P}_{12}$ [17]. CeP with the NaCl-type structure shows an isomorphous transformation with a volume collapse of 3–8% around 10 GPa [29]. This is due to the electronic transition involving a charge in the valence state of Ce. Thus, the P - V curves for $\text{CeT}_4\text{X}_{12}$ suggest that the valence state in Ce ion does not change from +3 to +4 at high pressures.

As shown in figure 7, the bulk modulus of the P- and Sb-based skutterudites increases with increasing lattice constant, reaching a maximum for the Ru compounds. $\text{CeRu}_4\text{P}_{12}$ has the largest bulk modulus among these skutterudites. The bulk modulus of $\text{CeRu}_4\text{Sb}_{12}$ is larger than that of $\text{CeFe}_4\text{Sb}_{12}$ and $\text{CeOs}_4\text{Sb}_{12}$. $\text{LaRu}_4\text{X}_{12}$ and $\text{PrRu}_4\text{X}_{12}$ have large bulk modulus compared with Fe and Os compounds. The bulk modulus of $\text{LnRu}_4\text{P}_{12}$ for Ln = La, Ce and Pr is 172, 226

and 207 GPa, respectively. $\text{CeRu}_4\text{P}_{12}$ with the smallest lattice constant has the largest bulk modulus among the three Ru-based skutterudites. On the other hand, the lattice constant of $\text{CeFe}_4\text{P}_{12}$ is smaller than that of $\text{CeRu}_4\text{P}_{12}$, but the bulk modulus of the Fe compound is smaller than that of the Ru compound. This result suggests that the transition metal element plays an important role in the determination of the magnitude of the bulk modulus. The Ce 4f states in $\text{CeRu}_4\text{X}_{12}$ must hybridize more strongly with Ru 4d and P or Sb p states. The large bulk modulus in the Ru compounds may arise from the strong hybridization.

As shown in table 1, the Ru-based skutterudites, $\text{LnRu}_4\text{X}_{12}$ (Ln = La, Ce and Pr; X = P and Sb) have a large bulk modulus. The physical properties of the Ru compounds markedly differ compared with those of Fe and Os compounds. $\text{CeRu}_4\text{Sb}_{12}$ behaves like a non-Fermi liquid at low temperatures [10]. On the contrary, $\text{CeOs}_4\text{Sb}_{12}$ and $\text{CeFe}_4\text{P}_{12}$ indicate a different electrical behaviour [15, 16]. $\text{PrRu}_4\text{P}_{12}$ exhibits a metal–insulator (MI) transition at around 62 K [5]. However, the M–I transition is not observed in $\text{PrFe}_4\text{P}_{12}$ [30] and $\text{PrOs}_4\text{P}_{12}$ [5]. The superconductivity of $\text{LaT}_4\text{P}_{12}$ (T = Fe, Ru and Os) has been studied at low temperatures [2, 13]. The T_c of a Ru compound is the highest among these materials [1]. The magnetic susceptibility of $\text{GdT}_4\text{P}_{12}$ (T = Fe, Ru and Os) has been measured at low temperatures [24]. $\text{GdFe}_4\text{P}_{12}$ and $\text{GdOs}_4\text{P}_{12}$ show a ferromagnetic transition around 22 and 5 K, respectively. In contrast, $\text{GdRu}_4\text{P}_{12}$ behaves as an antiferromagnet below 22 K [31]. The interesting behaviour in the Ru-based skutterudites may closely be related to the large bulk modulus.

The bulk modulus of binary skutterudites is smaller than that of filled skutterudites although the lattice constant of binary compounds is smaller than that of filled skutterudites. The valence electrons in Ln atoms of filled skutterudites are transferred from Ln to $(\text{TX}_3)_4$ group. There is a bonding between Ln^{3+} and $(\text{TX}_3)_4^{3-}$ for filled skutterudites. This bonding must result in a larger bulk modulus compared with binary skutterudites.

Acknowledgments

This work was partly supported by a grant-in-aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (no. 14204032(IS)) and Priority Area ‘Skutterudite’ (no. 15072206).

References

- [1] Shirovani I, Uchiyumi T, Ohno T, Sekine C, Nakazawa Y, Kanoda K, Todo S and Yagi T 1997 *Phys. Rev. B* **56** 7866
- [2] Uchiyumi T, Shirovani I, Sekine C, Todo S, Yagi T, Nakazawa Y and Kanoda K 1999 *J. Phys. Chem. Solids* **60** 689
- [3] Bauer E D, Frederick N A, Ho P C, Zapf V S and Maple M B 2002 *Phys. Rev. B* **65** 100506
- [4] Shirovani I, Uchiyumi T, Sekine C, Kimura S and Hamaya N 1999 *J. Solid State Chem.* **142** 146
- [5] Sekine C, Uchiyumi T, Shirovani I and Yagi T 1997 *Phys. Rev. Lett.* **79** 3218
- [6] Shirovani I, Hayashi J, Adachi T, Sekine C, Kawakami T, Nakanishi T, Takahashi H, Tang J, Matsushita A and Matsumoto T 2002 *Physica B* **322** 408
- [7] Danebrock M E, Christoph B, Evers H and Jeitschko W 1996 *J. Phys. Chem. Solids* **57** 381
- [8] Bauer E D, Slebarski A, Freeman E J, Sirvent C and Maple M B 2001 *J. Phys.: Condens. Matter* **13** 4495
- [9] Dilley N R, Freeman E J, Bauer E D and Maple M B 1998 *Phys. Rev. B* **58** 6287
- [10] Takeda N and Ishikawa M 2001 *J. Phys.: Condens. Matter* **13** 5971
- [11] Sales B C, Mandrus D and Williams R K 1996 *Science* **272** 1325
- [12] Jeitschko W and Braun D 1977 *Acta Crystallogr. B* **33** 3401
- [13] DeLong L E and Meisner G P 1985 *Solid State Commun.* **53** 119
- [14] Shirovani I, Ohno K, Sekine C, Yagi T, Kawakami T, Nakanishi T, Takahashi H, Tang J, Matsushita A and Matsumoto T 2000 *Physica B* **281 & 282** 1021
- [15] Bauer E D, Chau R, Dilley N R, Maple M B, Mandrus D and Sales B C 2000 *J. Phys.: Condens. Matter* **12** 1261

- [16] Hedo M, Uwatoko Y, Sugawara H and Sato H 2003 *Physica B* **329** 456
- [17] Hayashi J, Shirotani I, Takeda K, Uchiumi T, Kimura S, Adachi T and Kikegawa T 2000 *Science and Technology of High Pressure* vol 2 (*Proc. AIRAPT-17, Hawaii, 1999*) ed M H Manghnani, W J Nellis and M F Nicol p 723
- [18] Shirotani I 2003 *Bull. Chem. Soc. Japan* **76** 1291
- [19] Birch F 1947 *Phys. Rev.* **71** 809
- [20] Caillat T, Kulleck J, Borshchevsky A and Fleurai J P 1996 *J. Appl. Phys.* **79** 8419
- [21] Shirotani I, Hayashi J, Adachi T, Sekine C, Kawakami T, Nakanishi T, Takahashi H, Tang J, Matsushita A and Matsumoto T 2002 *Physica B* **322** 408
- [22] Shirotani I, Shimaya Y, Kihou K, Sekine C and Yagi T 2003 *J. Solid State Chem.* **174** 32
- [23] Braun D J and Jeitschko W 1980 *J. Less-Common Met.* **72** 147
Braun D J and Jeitschko W 1980 *J. Solid State Chem.* **32** 357
- [24] Kihou K, Shirotani I, Shimaya Y, Sekine C and Yagi T 2004 *Mater. Res. Bull.* **39** 317
- [25] Jung D, Whangbo M-H and Alvarez S 1990 *Inorg. Chem.* **29** 2252
- [26] Nordstrom L and Singh D J 1996 *Phys. Rev. B* **53** 1103
- [27] Harima H and Takegahara K 2003 *J. Phys.: Condens. Matter* **15** S2081
- [28] Xue J S, Antonio M R, White W T and Soderholm L 1994 *J. Alloys Compounds* **207 & 208** 161
- [29] Jayaraman A, Lowe W, Longinotti L D and Bucher E 1976 *Phys. Rev. Lett.* **36** 366
- [30] Sato H, Abe Y, Okada H, Matsuda T D, Abe K, Sugawara H and Aoki Y 2000 *Phys. Rev. B* **62** 15125
- [31] Sekine C, Uchiumi T, Shirotani I, Matsuhira K, Sakakibara T, Goto T and Yagi T 2000 *Phys. Rev. B* **62** 11581