Charge ordering in Sm$_4$Bi$_3$ under pressure

H. Kobayashi$^1$, S. Yamaoka$^1$, S. Ikeda$^1$, N. Hirao$^2$, Y. Ohishi$^2$, Y. Yoda$^2$, and A. Ochiai$^3$

$^1$ Graduate School of Material Science, University of Hyogo, Hyogo 678-1297, JAPAN
$^2$ Japan Synchrotron Radiation Institute, Hyogo 679-5198, JAPAN
$^3$ Graduate School of Physics, Tohoku University, Sendai, 980-8578, JAPAN

E-mail: kobayash@sci.u-hyogo.ac.jp

Abstract. We have investigated the charge ordering in Sm$_4$Bi$_3$ under pressure by magnetic susceptibility and x-ray diffraction measurements. We observed discontinuous anomalies in the temperature dependences of magnetic susceptibility and volume at the charge ordering transition owing to the first-order transition and then the estimated charge ordering transition temperature decreases linearly with increasing pressure. The volume ratio between the SmBi$_6$ octahedra at two nonequivalent Sm sites indicates the partial charge ordering of Sm ions in the charge ordered phase. The evidence of the partial charge ordering in Sm$_4$Bi$_3$ is consistent with the smaller electronic component in the entropy change at the charge ordering transition.

1. Introduction

Sm$_4$Bi$_3$ and Yb$_4$As$_3$ are metals that crystallize into a cubic anti-Th$_3$P$_4$ structure with the $I43d$ space group at room temperature. Assuming a charge of -3 for the Bi and As ions, this indicates that the Sm and Yb ions have an averaged non-integral valence of +2.25. Thus, Sm$_4$Bi$_3$ and Yb$_4$As$_3$ are mixed valence systems and show charge ordering at $T_o = 260$ and 290 K, respectively, accompanied by a structural change from the cubic to a trigonal structure with the $R3c$ space group [1, 2]. In Yb$_4$As$_3$ with the trigonal structure, neutron and x-ray diffraction measurements [3, 4, 5] revealed that pure trivalent Yb ions order along one of the four chains along the ⟨111⟩ direction in the cubic structure.

Although Eu$_4$As$_3$ has the trigonal structure at room temperature, it was confirmed using single-crystal samples that Eu$_4$As$_3$ is the mixed valence compound and charge ordering occurs at $T_o = 343$ K [6]. It was demonstrated by high-pressure x-ray diffraction using synchrotron radiation that the local volume around the Eu site and the valence state of the Eu ion are closely correlated and pure trivalent and divalent Eu ions occupy two nonequivalent Eu sites in the charge-ordered state [7]. The charge ordering in mixed valence systems is one of important subjects since the mechanism of charge ordering is directly related to the feature of valence fluctuating state. However, the mechanism of these charge orderings in the rare-earth compounds with the cubic anti-Th$_3$P$_4$ structure remains open question despite considerable efforts.

2. Experimental

Single-crystalline samples of Sm$_4$Bi$_3$ were prepared by a self-flux method. The samples obtained were analyzed by x-ray diffraction and confirmed to be a single phase. Charge ordering occurs at $T_o = 261.8(3)$ K, which is in very good agreement with previous results [1, 6, 8].
The temperature dependences of the magnetic susceptibility under pressure were measured using a piston cylinder cell by a commercial SQUID magnetometer. Hydrostatic pressure was maintained using a Teflon cell filled with Fluorinert as a pressure transmitting medium. The pressure was calibrated by a measurement of the superconducting transition temperature of Sn metal. The magnetization of the sample under pressure was evaluated from the best fit of the obtained SQUID response curve of the sample in the pressure cell by using the idealized function of the SQUID response curve as described in the literature [9].

The powder x-ray diffraction data were collected at low temperatures under pressure on BL10XU at SPring-8 with an image-plate detector. The incident x-ray wavelength was 0.4114 Å, and finely ground samples were loaded into a diamond anvil cell with ruby chips and helium as a pressure-transmitting medium. Pressure was calibrated at each experimental condition by measuring the wavelength shift of the $R_1$ luminescence line of the ruby chips.

3. Experimental Results and Discussion

Figure 1 shows the temperature dependences of the inverse magnetic susceptibilities, $1/\chi$, under pressure. The $1/\chi$ values under pressure represent the Curie-Weiss behavior above 150 K with a discontinuous anomaly around 250 K. The anomaly corresponds to the charge ordering of Sm ions in Sm$_4$Bi$_3$. The obtained $T_o$ values decrease linearly with increasing pressure as shown in Fig. 2 and the pressure coefficient is found to be -12.2(3) K/GPa which agrees qualitatively with the previous result [10].

![Figure 1](image1.png)

**Figure 1.** Temperature dependences of the inverse magnetic susceptibilities, $1/\chi$, of Sm$_4$Bi$_3$ under pressure. The inset shows the anomalies in $1/\chi$ around the charge ordering transition temperature, $T_o$.

![Figure 2](image2.png)

**Figure 2.** Pressure dependence of the charge ordering transition temperature, $T_o$, of Sm$_4$Bi$_3$. The solid circles and squares with error bars represent $T_o$ estimated using magnetization and x-ray diffraction measurements, respectively. The solid line indicates the results of fitting.
Figure 3 shows selected integrated x-ray diffraction patterns of Sm$_4$Bi$_3$ at 1.1 GPa. All diffraction lines in the x-ray diffraction patterns above \( \sim 255 \) K are labeled with the indices of the cubic \( I\bar{4}3d \) structure and the splitting of the fundamental diffraction lines appears below \( \sim 240 \) K. The diffraction patterns below \( \sim 240 \) K are very similar to those of Eu$_4$As$_3$ and Yb$_4$As$_3$ observed below \( T_o \) at ambient pressure [5, 6, 7, 11]. The observed x-ray diffraction patterns were analyzed with the Rietveld refinement program RIETAN-2000 [12] using the cubic \( I\bar{4}3d \) and trigonal \( R3c \) structures above and below \( T_o \), respectively. All observed x-ray diffraction lines gave good fits at low temperatures up to 2.2 GPa. Figure 4(a) shows the temperature dependence of volume, \( V \), evaluated at 1.1 GPa. The change in \( V \) at \( T_o \), \( \Delta V \), decreases linearly with increasing pressure as shown in Fig. 4(b). The pressure dependence of \( T_o \) determined by x-ray diffraction measurements is shown in Fig. 2. The temperature of the structural change below 1.1 GPa corresponds to the anomaly in the temperature dependence of \( 1/\chi \) within experimental accuracy. These results indicate that the structural change from the cubic \( I\bar{4}3d \) to the trigonal \( R3c \) occurs simultaneously with the charge ordering of the Sm ions in Sm$_4$Bi$_3$. The negative value of \( \Delta V \) is consistent with the decrease in \( T_o \) with increasing pressure. Thus, the valence fluctuating phase is stabilized in Sm$_4$Bi$_3$ by applied pressure. This result is similar to that of Yb$_4$As$_3$, where \( T_o \) decreases with increasing pressure and the charge-ordered phase disappears above 9 GPa [13].

Figure 3. Selected integrated x-ray diffraction patterns of Sm$_4$Bi$_3$ at 1.1 GPa: (a) 255 and (b) 240 K, where the crosses show the observed diffraction intensities. The solid lines represent the results of Rietveld refinement fitting. The tick marks show the positions of all reflections allowed by the cubic \( I\bar{4}3d \) and trigonal \( R3c \) structures. The differences between the observed and calculated intensities are shown below the tick marks.

Figure 4. Temperature dependences of the volume of Sm$_4$Bi$_3$, \( V \), and the volume of the distorted SmBi$_6$ octahedron, \( V_{oct} \), at 1.1 GPa, (a) and the pressure dependence of volume change at the charge ordering transition temperature, \( \Delta V \), (b). In (a), the open and blue circles represent \( V \) and \( V_{oct} \), respectively. The black solid line in (b) represents the result of fitting.
In the charge-ordered phase with the trigonal $R3c$ structure, Sm ions are in two nonequivalent 2a and 6b sites, which are coordinated by six Bi ions forming distorted SmBi$_6$ octahedra and expected to be occupied by different valence Sm ions. Since there is one Bi site in both the structures, the local volume around the Sm site is correlated with the valence state of the Sm ion, as shown in the case of Eu$_4$As$_3$ [7]. Thus, the volume of a distorted SmBi$_6$ octahedron, $V_{\text{oct}}$, was calculated by the refined lattice and atomic coordination parameters. The temperature dependence of $V_{\text{oct}}$ at 1.1 GPa is shown in Fig. 4(a). The $V_{\text{oct}}$(6b) value is larger than $V_{\text{oct}}$(2a) below $T_o$ and the weighted mean volume of $V_{\text{oct}}$(6b) and $V_{\text{oct}}$(2a) is the same as $V_{\text{oct}}$(16c) in the cubic $I43d$ structure within our experimental accuracy. The $V_{\text{oct}}$(6b)/$V_{\text{oct}}$(2a) ratio was found to be $1.07(1)$ just below $T_o$ at 1.1 GPa and increases gradually with decreasing temperature, reaching $1.083(3)$ at 16 K.

In Sm$_{3+}$Bi with the rock-salt structure, Sm$_{3+}$ ions are coordinated octahedrally by six Bi ions. The expected $V_{\text{oct}}$(Sm$_{3+}$) was evaluated to be $42.8 \text{ Å}^3$ which is smaller than $V_{\text{oct}}$(2a) at 1.1 GPa. Since some Sm ions in Sm monochalcogenides with the rock-salt structure are divalent, the expected $V_{\text{oct}}$(Sm$_{2+}$)/$V_{\text{oct}}$(Sm$_{3+}$) ratio was evaluated to be 1.18 in each Sm monochalcogenide from the series of the rare earth monochalcogenides [14]. Thus, the evaluated $V_{\text{oct}}$(6b)/$V_{\text{oct}}$(2a) ratios are smaller than the expected $V_{\text{oct}}$(Sm$_{2+}$)/$V_{\text{oct}}$(Sm$_{3+}$) ratio. Since the weighted mean volume of $V_{\text{oct}}$(6b) and $V_{\text{oct}}$(2a) is the same as $V_{\text{oct}}$(16c), the weighted mean volume of Sm ions remains below $T_o$. The averaged valences of Sm ions at the 2a and 6b sites were evaluated to be around $+2.6$ and $+2.1$, respectively. Accordingly, these results reveal a roughly 50% partial charge ordering in the charge-ordered phase of Sm$_4$Bi$_3$. This partial charge ordering is inconsistent with the results for Eu$_4$As$_3$ and Yb$_4$As$_3$, where the almost pure trivalent and divalent Eu and Yb ions occupy the 2a and 6b sites, respectively, in the trigonal $R3c$ structure just below $T_o$ [4, 5, 7, 15].

The Clausius-Clapeyron relation, $dp/dT = \Delta S/\Delta V$, is applicable at the charge ordering transition of Sm$_4$Bi$_3$ because the transition is of first order. The entropy change, $\Delta S$, was estimated to be $3.93(1) \text{ J/molK}$ at ambient pressure from $dT_o/dp = -12.2(3)$ K/GPa and $\Delta V = -0.080(7) \text{ Å}^3$/f.u. The estimated $\Delta S$ of Sm$_4$Bi$_3$ at ambient pressure is about ten times smaller than that (40.6 J/mol K) of Eu$_4$As$_3$ [11, 16]. If Sm$_4$Bi$_3$ is a thermal valence fluctuating state in the cubic $I43d$ structure, a random arrangement of Sm$^{2+}$ and Sm$^{3+}$ ions would be expected. The entropy of this randomness is simply calculated to be $18.7 \text{ J/mol K}$ [8]. Because of the partial charge ordering in Sm$_4$Bi$_3$, the entropy change is expected to be approximately $10 \text{ J/molK}$, assuming the simple thermal valence fluctuation model in the cubic $I43d$ structure. This entropy change is 2.5 larger than $\Delta S$ estimated using the Clausius-Clapeyron relation.

The total $\Delta S$ includes electronic and vibrational components. On the basis of the specific heat and magnetization measurements, the antiferromagnetic magnetic ordering in Sm$_4$Bi$_3$ may occur at 2.7 K [17], which is much lower than $T_o$. Thus, the contribution of magnetic ordering to $\Delta S$ is negligible at $T_o$. In the case of Eu$_4$As$_3$, the change of the vibrational entropy of Eu$_4$As$_3$ was evaluated to be $13.4 \text{ J/molK}$ at $T_o = 343$ K by using $^{151}$Eu nuclear resonant inelastic scattering (NRIS) [16]. We have roughly estimated the change of the vibrational entropy of Sm$_4$Bi$_3$ to be $-8.0 \text{ J/molK}$ by using $^{149}$Sm NRIS. Consequently, the electronic contribution in the total $\Delta S$ is approximately $12 \text{ J/molK}$ at ambient pressure, which is comparable to the configuration entropy in the partial charge ordering.

In summary, we observed discontinuous anomalies in the temperature dependences of $1/\chi$ and $V$ at $T_o$ owing to the first-order transition and the estimated $T_o$ decreases linearly with increasing pressure. Since the $V_{\text{oct}}$(6b)/$V_{\text{oct}}$(2a) ratio was about 90% of the expected $V_{\text{oct}}$(Sm$_{2+}$)/$V_{\text{oct}}$(Sm$_{3+}$) ratio, it is concluded that partial charge ordering occurs in the charge-ordered phase. The evidence for partial charge ordering in Sm$_4$Bi$_3$ is consistent with the smaller electronic component in total $\Delta S$. 
Acknowledgments
The experiments using synchrotron radiation were performed at SPring-8 with approval of Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2004A0154, 2004B0726, 2008B1398, 2010B1517). H.K. acknowledges the partial support of the Japanese Ministry of Education, Culture, Sports, Science and Technology, and Grants-in-Aid for Scientific Research (B) 17340098.

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