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Pressure-induced melting of charge order in Eu_4As_3 without structural change

Hisao Kobayashi^{1,4}, Yutaka Kazekami¹, Nobuhiko Sakai¹,
Yasuo Ohishi², Makoto Shirakawa³ and Aakira Ochiai³

¹ Graduate School of Material Science, University of Hyogo, 3-2-1 Koto Hyogo 678-1297, Japan

² Japan Synchrotron Radiation Institute, Hyogo 679-5198, Japan

³ Department of Physics, Tohoku University, Sendai, 980-8578, Japan

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

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Abstract

We have carried out high-pressure x-ray diffraction experiments on Eu_4As_3 at room temperature, and individual atomic coordinates as well as lattice parameters were derived precisely from the diffraction data. We have confirmed that a trigonal structure with the $R3c$ space group does not change up to 19 GPa. The results show that the volume of the EuAs_6 octahedron and the valence state of the Eu ion are closely correlated, and pure trivalent and divalent Eu ions occupy two nonequivalent Eu sites, respectively, in the charge-ordered state at ambient pressure. We present clear evidence on the basis of the pressure dependence of these volumes at two nonequivalent Eu sites that a melting of the static charge order occurs at about 10 GPa and Eu_4As_3 is in a mixed-valence state above 10 GPa.

1. Introduction

Valence fluctuation phenomena, which occur in certain rare earth compounds, have received much attention. A wide variety of such phenomena have been observed, depending on the configuration of $4f^n$ and the relative position of $4f$ levels in the electronic structure of the compound. Among these compounds, Yb_4As_3 with its cubic anti- Th_3P_4 structure ($I\bar{4}3d$) exhibits a charge-ordering phase transition at $T_1 = 290$ K and typical heavy-fermion behavior despite the low carrier density [1–3]. Thus, it has been the subject of intensive study [4–7]. Sm_4Bi_3 also shows charge ordering at $T_1 = 260$ K [8]. These charge orderings lead to a transformation from the cubic structure to a trigonal structure with the $R3c$ space group and to a shrinkage along the threefold direction. The resultant trigonal structure exhibits two crystallographically nonequivalent rare earth sites, one occupied by the trivalent rare earth ion, the other by the divalent rare earth ion [4, 9]. Thus, the trivalent rare earth ions align along the threefold direction. The shrinkage in the trigonal structure is thought to be caused by the chains with a smaller ionic radius of the trivalent rare earth ion. However, a

Madelung energy calculation indicated that the actual charge-ordered structure is not stable [10]. The mechanism of this charge ordering remains an open question despite considerable efforts.

In Eu_4As_3 , ^{151}Eu Mössbauer spectroscopy [11] has revealed that the Mössbauer absorption spectra consist of two subspectra at -10 and 0 mm s^{-1} below 340 K, which correspond to the Eu^{2+} and Eu^{3+} ions, respectively, with the intensity ratio 3:1 and of a single spectrum at -8.5 mm s^{-1} at higher temperatures, which shows the intermediate valence state of the Eu ion. Furthermore, it was confirmed using a high quality single-crystal sample that the trigonal structure of Eu_4As_3 with two nonequivalent rare earth sites at room temperature changes to a cubic anti- Th_3P_4 structure with one rare earth site around $T_1 = 340$ K [12]. Thus, these results indicate that a similar charge ordering occurs at T_1 in Eu_4As_3 .

The hybridization of a narrow $4f$ band with broad conduction bands is one of the important parameters in these charge-ordering compounds, which is possible to control by hydrostatic pressure. In Yb_4As_3 , the temperature dependence of resistivity under pressure shows that T_1 decreases with pressure and disappears around 9 GPa [13]. In Sm_4Bi_3 , a pressure-induced first-order structural transition was observed from trigonal to cubic at 2.3 GPa and 200 K, accompanied by a

⁴ Author to whom any correspondence should be addressed.

volume reduction of about 10% [14]. This is believed to be an occurrence of a valence change of the Sm^{2+} ion into the Sm^{3+} ion during the transition. Thus, the trigonal structure has been considered to be closely related to the charge order in Yb_4As_3 and Sm_4Bi_3 .

The pressure dependence of T_1 in Eu_4As_3 was determined recently by x-ray diffraction using synchrotron radiation [15]. The results show that T_1 increases linearly with pressure up to 5 GPa. Hydrostatic pressure typically changes the distortion of the polyhedron around a rare earth site as well as the hybridization. The distortion affects the electronic state of the rare earth ion through the crystalline electric field. This crystalline electric field effect is ignored in Eu compounds because the Eu^{2+} and Eu^{3+} ions have the $^8\text{S}_{7/2}$ and $^7\text{F}_0$ electronic states, respectively. Thus, Eu_4As_3 is a new and promising candidate for use in studying the mechanism of charge ordering under pressure in this family of compounds.

Detailed knowledge of the structure is important for understanding the mechanism of charge ordering. In this paper, we present the first evidence of pressure-induced melting of static charge order in Eu_4As_3 at 10 GPa without structural change. This result has been obtained by x-ray diffraction measurements using synchrotron radiation under good hydrostatic conditions. It clarifies that there is a substantial correlation between the volume of the EuAs_6 octahedron and the valence state of the Eu ion and that the volume ratio between two nonequivalent Eu sites is unity above 10 GPa.

2. Experimental details

Single-crystal samples of Eu_4As_3 were grown in a tungsten crucible by a usual Bridgman method [12]. The sample obtained was analyzed by x-ray diffraction and was confirmed to be a single phase having a trigonal structure with the $R3c$ space group at room temperature. The x-ray diffraction data under pressure up to 19 GPa were collected on the beamline BL10XU at SPring-8, Japan, with angle-dispersive techniques and an image-plate detector at room temperature. The incident x-ray wavelength was 0.4955 Å, which was calibrated using a measurement of the x-ray diffraction pattern of CeO_2 at ambient conditions. Finely ground samples were loaded into a diamond-anvil cell with ruby chips and nitrogen 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. The quasi-hydrostatic conditions in the present experiment were achieved up to 19 GPa and were better than those in our previous study where Fluorinert was used as the pressure-transmitting medium [15]. This is because the widths of the diffraction lines above 8 GPa under the present experimental conditions are about 1.5 times narrower than those under the previous conditions.

3. Experimental results

Figure 1 shows selected integrated x-ray diffraction patterns of Eu_4As_3 at high pressures and room temperature. The

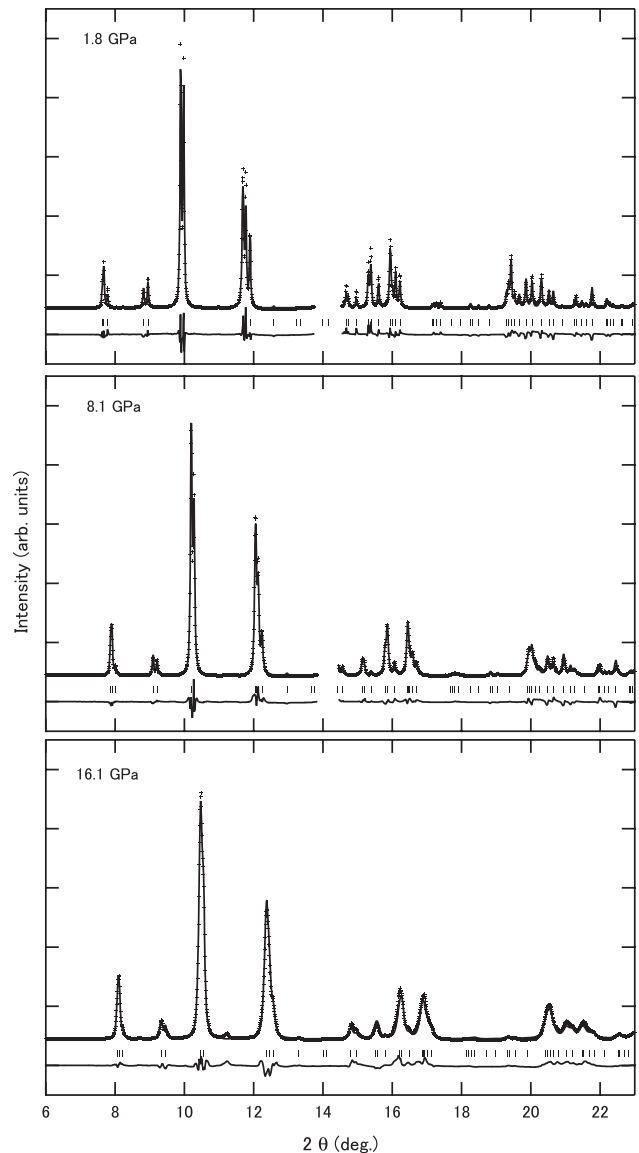


Figure 1. Selected integrated x-ray diffraction patterns of Eu_4As_3 at 1.8, 8.1 and 16.1 GPa, where the crosses show the observed diffraction intensities. The solid lines represent the results of Rietveld refinement fitting and the tick marks show the positions of all reflections allowed by the $R3c$ symmetries. The differences between the observed and calculated intensities are shown below the tick marks. The observed weak diffraction line around $2\theta \sim 11^\circ$ at 16.1 GPa comes from solid nitrogen.

diffraction patterns under lower pressure are very similar to those of Eu_4As_3 at ambient conditions and Yb_4As_3 below T_1 [7, 12], and split main peaks caused by the shrinkage in the trigonal structure were observed under higher pressures, as seen in figure 1. The observed x-ray diffraction patterns were analyzed with the Rietveld refinement program RIETAN-2000 [16] using the known trigonal structure ($R3c$) with two nonequivalent Eu sites, namely the 2a site with one free coordination parameter and the 6b site with three free coordination parameters in rhombohedral settings. The As has a single 6b site with three free coordination parameters. In each x-ray diffraction pattern, the region at $2\theta \sim 14^\circ$ was

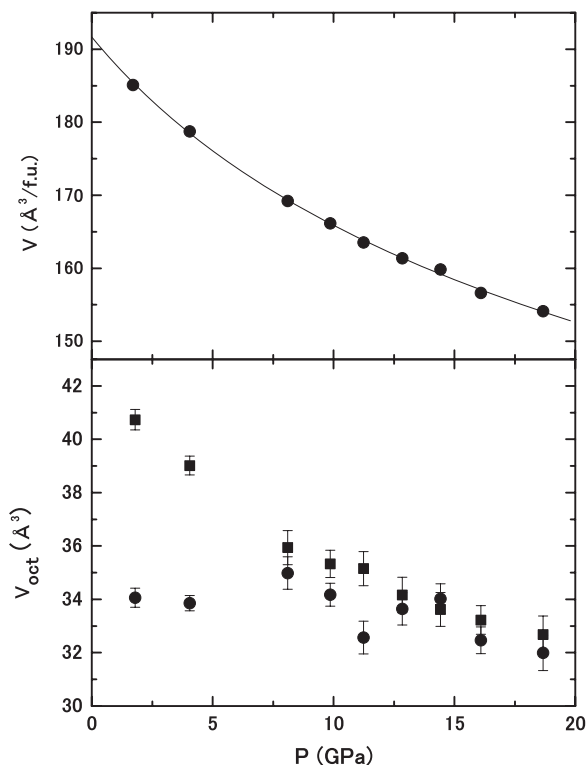


Figure 2. Pressure dependence of volume, V , of Eu_4As_3 and volume, V_{oct} , of the distorted EuAs_6 octahedra. These values were evaluated by the refined lattice and atomic coordination parameters under pressure. The solid line represents the fitting result based on the Birch–Murnaghan equation. The circle and square with error bars represent the 2a and 6b sites, respectively.

excluded from the refinement procedure below 13 GPa where a diffraction line from the gasket was observed. All observed x-ray diffraction lines in the patterns up to 19 GPa gave good fits as shown in figure 1. Thus, we have confirmed that the symmetry of the crystal structure of Eu_4As_3 does not change up to 19 GPa at room temperature. It should be noted that not only lattice parameters but also individual atomic coordination parameters were derived in these refinement procedures.

The compression behavior of Eu_4As_3 is shown in figure 2, where the pressure dependence of volume, V , exhibits no anomaly. The bulk modulus, B , was evaluated based on the Birch–Murnaghan equation, $P = \frac{B}{B'} \left(\left(\frac{V_0}{V} \right)^{B'} - 1 \right)$, where V_0 is the ambient-pressure volume and B' is the pressure derivative of B . The solid line in figure 2 represents the best fitting curve obtained and the refined B and B' values are 47(2) GPa and 4.95(7), respectively. However, as is shown in the discussion, we find an anomalous pressure-induced change of the local structure which is associated with the melting of the charge ordering above a pressure P_m of about 10 GPa [17, 18].

4. Discussion

The lattice parameters of rare earth compounds, where rare earth ions are in the same valence state, change smoothly as a function of the atomic number of the rare earth atom. Since the deviation of the lattice parameters between pure divalent

and trivalent rare earth ions is well known from systematics, the average valence of a rare earth ion in an intermediate valence system with a simple structure can be assigned by an empirical correlation between the valence and the lattice parameter. The trigonal structure has the two nonequivalent Eu sites, namely the 2a and 6b sites in rhombohedral settings, which are coordinated by six As ions forming the distorted EuAs_6 octahedra. Furthermore, these Eu sites are expected to be occupied by different valence ions in the charge-ordered state. In this case, the lattice parameters and volume of the unit cell assign a weighted mean valence of Eu ions at the two nonequivalent sites. Since there is one As site in the trigonal structure, local volume around each Eu site is thought to be correlated with a valence state of the Eu ion under pressure. Thus, the volume, V_{oct} , of a distorted EuAs_6 octahedron at each Eu site was evaluated by the refined lattice and atomic coordination parameters under pressure. The results are shown in figure 2 as a function of pressure. The $V_{\text{oct}}(6b)$ value is larger than $V_{\text{oct}}(2a)$ below P_m while it is the same as $V_{\text{oct}}(2a)$ above P_m within experimental accuracy. The $V_{\text{oct}}(2a)$ and $V_{\text{oct}}(6b)$ values at ambient pressure are extrapolated to be 34.5 and 42.0 \AA^3 , respectively.

We may interpolate the expected lattice parameter of Eu^{3+}As with a rock-salt structure to be 5.88 \AA by a series of other RE^{3+}As compounds where RE represents a rare earth atom [20]. In the rock-salt structure, RE ions are coordinated octahedrally by six As ions. Thus, the expected $V_{\text{oct}}(\text{Eu}^{3+})$ is evaluated to be 33.9 \AA^3 , which is in very good agreement with $V_{\text{oct}}(2a)$ at ambient conditions. We may evaluate $V_{\text{oct}}(\text{Eu}^{2+})$ from the Eu^{2+} ion in EuAs having a Na_2O_2 -type structure [19]. The Eu site, however, has trigonal prismatic coordination. We cannot evaluate $V_{\text{oct}}(\text{Eu}^{2+})$ from EuAs . Since Eu ions in Eu monochalcogenides are divalent with the rock-salt structure, $V_{\text{oct}}(\text{Eu}^{2+})$ values are obtained in these monochalcogenides. The expected $V_{\text{oct}}(\text{Eu}^{3+})$ values are estimated from the series of other RE^{3+} monochalcogenides [20]. The $V_{\text{oct}}(\text{Eu}^{2+})/V_{\text{oct}}(\text{Eu}^{3+})$ ratio is evaluated to be 1.21 in each Eu monochalcogenide, which agrees very well with the $V_{\text{oct}}(6b)/V_{\text{oct}}(2a)$ ratio at ambient conditions. Thus, the pure trivalent and divalent Eu ions occupy the 2a and 6b sites, respectively, in the charge-ordered state at ambient conditions. This result corresponds to previous results of ^{151}Eu Mössbauer spectroscopy [11] and the charge-ordered structure in Sm_4Bi_3 and Yb_4As_3 [4, 9].

As seen in figure 2, $V_{\text{oct}}(6b)$ decreases with increasing pressure, whereas $V_{\text{oct}}(2a)$ stays almost unchanged up to P_m . With increasing pressure, the $V_{\text{oct}}(6b)/V_{\text{oct}}(2a)$ ratio decreases from 1.22, reaching unity above P_m within experimental accuracy. The x-ray diffraction process probes the lattice on a timescale longer than the fluctuation time of the individual ion valence. Thus, the V_{oct} value is correlated with the average valence of Eu ions at each site. The present result reveals that the Eu ions have the same average valence at both the 2a and 6b sites above P_m . Consequently, the pressure-induced melting of charge order takes place at P_m without structural change. If the valence of the Eu ion at the 6b site changes from divalent to trivalent at P_m , a volume reduction of about 10% would presumably be observed, as is the case in Sm_4Bi_3 at

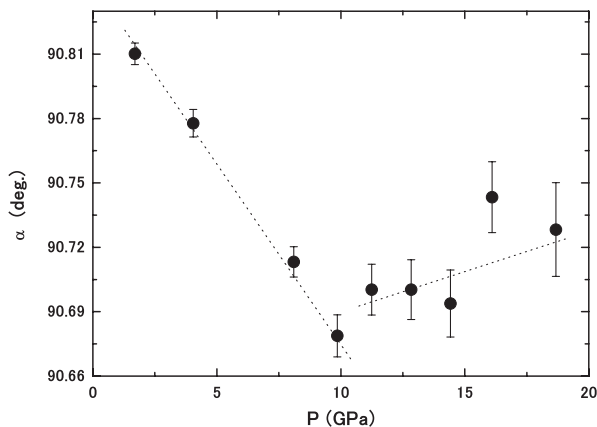


Figure 3. Pressure dependence of deviation from the orthogonal axes in the cubic phase by an angle, α , in Eu_4As_3 . The broken lines are guides to the eye.

2.3 GPa [14]. However, no discontinuity was observed at P_m in the pressure dependence of V . Furthermore, the compression behavior of Eu_4As_3 is well explained by the Birch–Murnaghan equation as seen in figure 2, and the refined B is comparable to those of EuAs [19] and Eu monochalcogenides [21]. Thus, above P_m , Eu_4As_3 is in a mixed-valence state with the trigonal structure. As seen in figure 3, the pressure dependence of the deviation from the orthogonal axes in the cubic phase by an angle, α , shows an anomaly at the same pressure at which the $V_{\text{oct}}(6b)/V_{\text{oct}}(2a)$ ratio becomes unity. This indicates that the change of V_{oct} and that of α is intimately connected, reflecting a change of the local electronic state of Eu ions in Eu_4As_3 .

5. Summary

We have carried out x-ray diffraction measurements of Eu_4As_3 up to 19 GPa at room temperature. The individual atomic coordinates as well as the lattice parameters were derived precisely under high pressure. The pressure dependence of α changes at about 10 GPa with the $R3c$ trigonal structure, where V shows no anomaly as a function of pressure. Since the $V_{\text{oct}}(6b)/V_{\text{oct}}(2a)$ ratio at ambient conditions is in very good agreement with the expected $V_{\text{oct}}(\text{Eu}^{2+})/V_{\text{oct}}(\text{Eu}^{3+})$ ratio, it is concluded that the pure trivalent and divalent Eu ions occupy the 2a and 6b sites, respectively. The $V_{\text{oct}}(6b)/V_{\text{oct}}(2a)$ ratio decreases with increasing pressure, and is equal to unity above 10 GPa. The anomaly in the pressure dependence of α corresponds to the pressure-induced melting of the static charge order and Eu_4As_3 is in the mixed-valence state above 10 GPa.

Acknowledgments

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