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Charge ordering in Eu_4As_3 under pressure

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Abstract

The pressure versus temperature phase diagram of the mixed-valence Eu_4As_3 compound was determined by means of x-ray diffraction measurements using synchrotron radiation. The structural phase transition occurs at 343 K under ambient pressure with volume reduction and the transition temperature increases linearly with pressure up to about 5 GPa. The entropy change at this transition is estimated to be $41 \text{ J mol}^{-1} \text{ K}^{-1}$ from the Clausius–Clapeyron relation. The value is twice larger than the configuration entropy which is expected from a random arrangement of Eu^{3+} and Eu^{2+} ions in the thermally driven valence fluctuating state of Eu_4As_3 . Moreover, a new structural phase was observed above 20 GPa at room temperature.

1. Introduction

The valence fluctuating state in rare-earth compounds has received much attention because 4f electrons usually maintain a well-localized character. A wide variety of valence fluctuating states have been observed, depending on the configuration of $4f^n$ and the relative position of the 4f levels in the electronic structure of the compound. Charge ordering is a fundamental and important subject for valence fluctuating compounds because the mechanism of charge ordering is directly related to the features of the valence fluctuating state.

One typical thermal valence fluctuating compound is Eu_3S_4 with a Th_3P_4 structure in which the charge ordering occurs at about 186 K [1–4]. The constant activation energy of electron hopping from divalent to trivalent ions gives a description of the temperature dependence of the electrical resistivity and the features of the Mössbauer spectra. In particular, the observed centre shift, which is a scale for the valence state of the Eu ions, is consistent with the weighted mean value expected from the Eu_3S_4 chemical formula in the thermal valence fluctuating state. The long range Coulomb interaction plays an important role in this charge ordering.

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Sm_4Bi_3 and Yb_4As_3 with an anti- Th_3P_4 structure show charge ordering at 260 and 290 K, respectively, accompanied by a structural change. The mechanism of this charge ordering remains an open question despite considerable efforts. In mixed valence Eu_4As_3 , it was found by ^{151}Eu Mössbauer spectroscopy [5] that the Mössbauer spectra consist of two subspectra corresponding to the Eu^{2+} and Eu^{3+} ions below 340 K and of a single spectrum at high temperature. Recently, it has been confirmed using a high quality single-crystal sample [6] that charge ordering occurs in Eu_4As_3 . In Yb_4As_3 and Sm_4Bi_3 , the crystalline electric field is one of the most important interactions because the magnetic ions, the trivalent ones, have a large orbital angular momentum. Since the Eu^{2+} and Eu^{3+} ions have the $^8\text{S}_{7/2}$ and $^7\text{F}_0$ electronic states, respectively, these crystalline electric field effects are ignored. Thus Eu_4As_3 is a good candidate for use in studying the mechanism of charge ordering from the standpoint of the relative position of the 4f levels in the electronic structure.

Hydrostatic pressure provides an important experimental technique for studying the mechanisms of charge ordering. This is because pressure allows one to control the hybridization between the 4f state and the conduction bands. In this paper, we describe the results of our x-ray diffraction measurements on Eu_4As_3 under high pressures at high temperatures using synchrotron radiation.

2. Experimental details

Single-crystal samples of Eu_4As_3 were prepared using the following procedure [6]. Appropriate amounts of starting materials Eu (99.9% purity) and As (99.9999% purity) were sealed in an evacuated silica tube and then were heated to obtain a pre-reaction. Arsenic vapour reacted with the europium block completely during this process. The pre-reacted powder was melted at 1700 °C in a tungsten crucible sealed with an electron beam welder. The sample obtained was analysed by means of x-ray diffraction and was confirmed to be single phase with a trigonal structure at room temperature.

The x-ray diffraction data were collected on the beam line BL10XU at SPring-8 with angle-dispersive techniques and an image-plate detector under pressure up to 32 GPa at room temperature and up to about 5 GPa in the temperature range between 320 and 400 K. The incident x-ray wavelength was 0.495 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, DAC, with Fluorinert as the pressure-transmitting medium and ruby chips. 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 selected integrated x-ray diffraction patterns of Eu_4As_3 at high pressure and high temperature. Since the diffraction patterns show that the samples in the DAC at high temperature do not completely satisfy the powder conditions, we refined the symmetry of the crystal structure and the cell parameters only from the interplane spacings. All diffraction lines in the x-ray diffraction patterns below 19 GPa at room temperature are labelled with the indices of the trigonal structure which are the same as those for the charge ordered states of Sm_4Bi_3 and Yb_4As_3 . Several new diffraction peaks were observed in the x-ray diffraction patterns above 20 GPa. These new diffraction peaks grow in intensity with pressure but the diffraction peaks related to the trigonal structure, the low pressure phase, do not disappear even at 32 GPa as seen in figure 1(b). Accordingly, there is no structural phase transition of Eu_4As_3 below 19 GPa

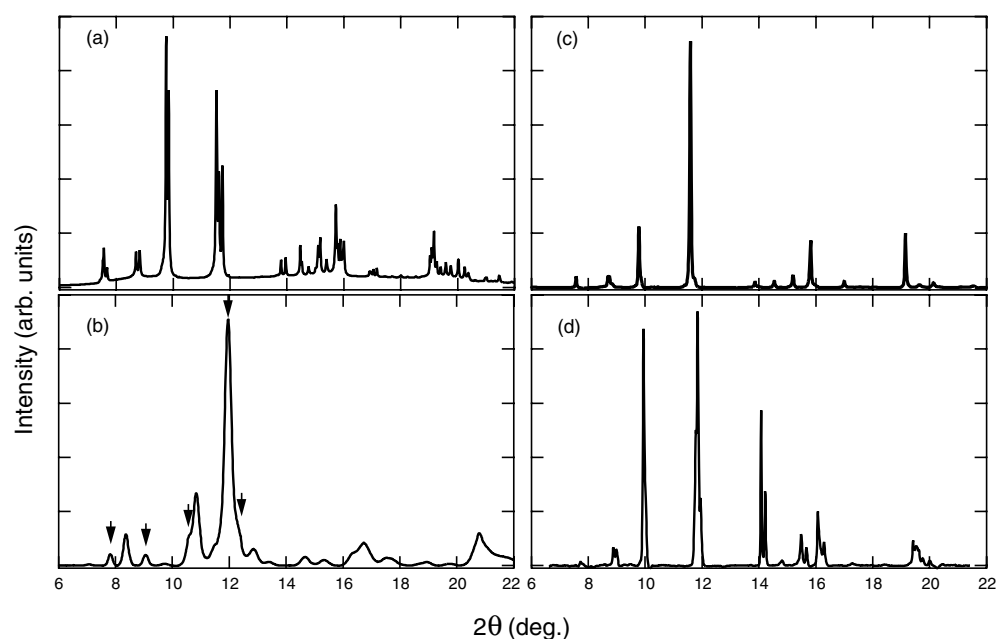


Figure 1. Integrated x-ray diffraction patterns of Eu_4As_3 at high pressure and high temperature: (a) 0.15 GPa and 300 K, (b) 32 GPa and 300 K, (c) 0.15 GPa and 348 K, and (d) 3.0 GPa and 358 K. The diffraction lines in (a) and (d) were indexed with the trigonal structure and the diffraction lines in (c) were indexed with the cubic anti- Th_3P_4 structure. The arrows in (b) indicate new diffraction lines below $2\theta = 12.5^\circ$.

and a new crystalline structural phase appears above 20 GPa at room temperature. The higher pressure phases were observed in Yb_4Bi_3 and Yb_4Sb_3 above 12 and 22 GPa, respectively [7]. These crystal structures were deduced as being deficient NaCl-type structures in which the lattice parameters at about 30 GPa were estimated to be 4.8 Å. Since five new diffraction peaks were observed below $2\theta = 12.5^\circ$ for Eu_4As_3 at 32 GPa, the crystal structure in this higher pressure phase has a more complex structure than the deficient NaCl-type one.

The splitting of the fundamental diffraction lines disappears above 345 K at almost ambient pressure and then all diffraction lines in the x-ray diffraction patterns are labelled with the indices of the cubic anti- Th_3P_4 structure. Thus the structural phase transition occurs at $T_c = 343(1)$ K, which is the same as those of Sm_4Bi_3 and Yb_4As_3 even though T_c is higher than those of Sm_4Bi_3 and Yb_4As_3 . This result is in good agreement with those of recent work [6] and previous ^{151}Eu Mössbauer spectroscopy [5]. We conclude that this structural phase transition occurs simultaneously with the charge ordering of the Eu ions. Figure 2 shows the temperature dependences of the volume, V , and of the deviation from the orthogonal axes of the cubic phase to an angle, α , in the trigonal phase. As seen in this figure, there is about 0.4% volume reduction at T_c with decreasing temperature. The magnitude of the volume reduction at T_c remains almost constant up to about 5 GPa. The temperature dependence of α shows a distinct step-like feature at T_c . Accordingly, the phase transition is of first order.

The pressure versus temperature phase diagram of Eu_4As_3 as determined from the x-ray diffraction patterns at high pressure and high temperature is shown in figure 3. The value of T_c increases linearly with pressure and dT_c/dp is estimated to be $10.08(5)$ K GPa^{-1} . Consequently, the charge ordered state is stabilized in Eu_4As_3 by pressure, which is consistent

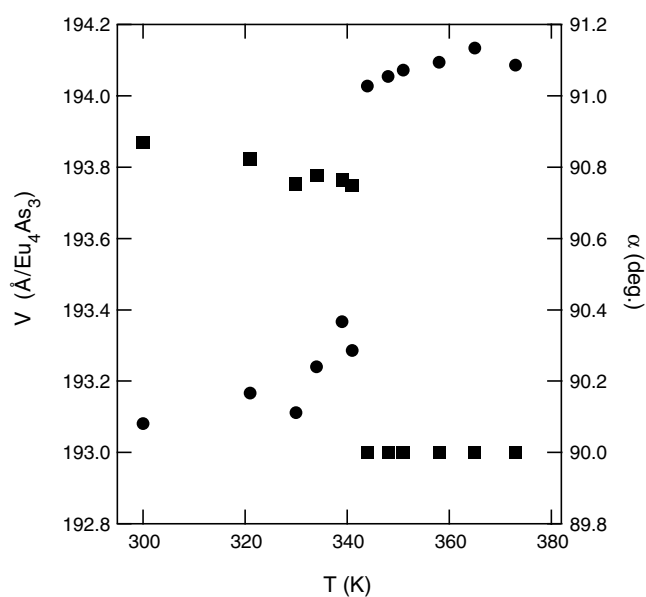


Figure 2. Temperature dependences of the volume, V , and angle, α , at about 0.1 GPa. The closed circle represents V per Eu_4As_3 and the closed square indicates α .

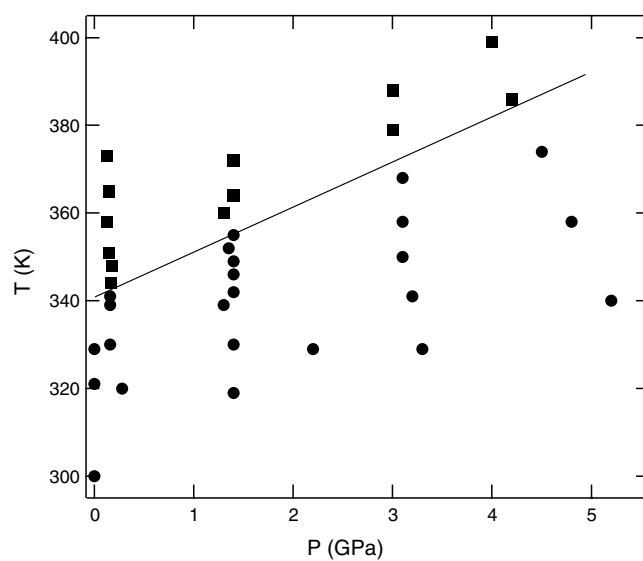


Figure 3. The pressure versus temperature phase diagram of Eu_4As_3 . The closed square and circle indicate the cubic anti- Th_3P_4 and trigonal structures, respectively. The solid line represents the phase boundary between these structures.

with the volume reduction at T_c . In Sm_4Bi_3 and Yb_4As_3 , however, T_c decreases with pressure and the charge ordered states disappear above 2 GPa for Sm_4Bi_3 and 9 GPa for Yb_4As_3 [8, 9].

The Clausius–Clapeyron relation, $dp/dT = \Delta S/\Delta V$, is applicable at the phase transition of Eu_4As_3 because the transition is of first order. The value of the entropy change, ΔS , is estimated to be $41(5) \text{ J mol}^{-1} \text{ K}^{-1}$ from $dT_c/dp = 10.08(5) \text{ K GPa}^{-1}$ and 0.4% volume

reduction, ΔV . This estimated ΔS value is about one order larger in magnitude than that evaluated from the specific heat measurements [6]. Usually, the entropy change at strongly first-order phase transitions is underestimated by specific heat measurements because of the huge change in specific heat of the sample. If Eu_4As_3 is a thermal valence fluctuating state in the cubic phase, random arrangement of the Eu^{2+} and Eu^{3+} ions is expected. The entropy of this randomness for Eu_4As_3 is simply evaluated to be $18.7 \text{ J mol}^{-1} \text{ K}^{-1}$, which is called the configuration entropy [8]. The ferromagnetic ordering temperature is 18 K for Eu_4As_3 [5, 6] which is much lower than T_c . The magnetic Eu^{2+} ion has the S state and the Eu^{3+} ion is nonmagnetic. Accordingly, contributions to ΔS from magnetic and crystalline electric field origins are negligible at the charge ordering transition of Eu_4As_3 . Recently we have measured ^{151}Eu nuclear resonant inelastic x-ray scattering of Eu_4As_3 at high temperature and estimated the specific heat at constant volume, C_v , for Eu from the phonon density of states [10]. The C_v values obtained are comparable with those expected in the high temperature limit of the Dulong–Petit law. Thus ΔS should be less than the configuration entropy for Eu_4As_3 , assuming the simple thermal valence fluctuation model in the cubic phase. Therefore, this discrepancy is most probably caused by the significant change in the electronic structure of Eu_4As_3 at the structural phase transition accompanied by the charge ordering of Eu ions.

In summary, we have measured the x-ray diffraction of Eu_4As_3 at high temperatures under high pressures using synchrotron radiation. A new crystallographic phase was observed above 20 GPa at room temperature which coexists with the low pressure phase. We further found that the phase transition from the cubic to the trigonal phase occurs (at $T_c = 343(1) \text{ K}$ at ambient pressure) with a volume reduction and T_c increases linearly with pressure. The ΔS estimated using the Clausius–Clapeyron relation is found to be twice larger than the configuration entropy. We, thus, suggest that the electronic structure of Eu_4As_3 significantly changes at this phase transition.

Acknowledgment

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