Anomalous compression behavior in a C15 Laves compound CeAl$_2$ under high pressure

Shota Tateno$^1$, Nobuya Kishii$^1$, Masashi Ohashi$^{1,2,3}$, Hidenori Miyagawa$^3$, Gendo Oomi$^{3,4}$, Isamu Satoh$^5$, Nobuyoshi Miyajima$^6$ and Takehiko Yagi$^{6,7}$

$^1$Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan
$^2$Institute of Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan
$^3$Department of Physics, Kyushu University, 6-10-1 Hakozaki, Fukuoka 812-8581, Japan
$^4$Kurume Institute of Technology, Kamitsu-machi, Kurume, Fukuoka 830-0052, Japan
$^5$Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577, Japan
$^6$Institute of Solid State Physics, the University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, 277-8581, Japan
$^7$Geochemical Research Center, the University of Tokyo, 7-3-1 Hongo, Tokyo, 113-0033, Japan

E-mail: ohashi@se.kanazawa-u.ac.jp

Abstract. Although there have been quite a number of discrepancies in the compression curves of CeAl$_2$, such results come from the lattice compression at non-hydrostatic condition by solidification of pressure transmitting medium. We have carried out the powder X-ray diffraction measurement of CeAl$_2$ under hydrostatic pressure with helium gas as pressure-transmitting medium which achieves the best hydrostatic conditions. Although no splitting of the peak is observed in the present diffraction pattern, it is found that a full width at half maximum is enhanced above 20 GPa for several Bragg reflections. Such behaviors suggest the existence of a new pressure-induced structural phase transition which is not observed in the previous reports under non-hydrostatic pressure.

1. Introduction

RAI$_2$ (R : rare earth) intermetallic compounds crystallize in the MgCu$_2$ type structure which belongs to the C15 Laves phase (space group $Fd\bar{3}m$, No. 227), where the rare earth ions have equivalent sites of cubic point symmetry[1, 2, 3]. Considering the Al$^{3+}$ ions as magnetically neutral, the configuration of the magnetic lattice consisting of rare earth ions is a diamond structure type, and the nearest neighbours of rare earth ions are Al atoms. The lattice constant of RAl$_2$ decreases with increasing $f$-electron number except for EuAl$_2$ and YbAl$_2$. This decrease is so-called lanthanoid contraction. Although the valence of rare earth ion is trivalent fundamentally, the valence of Eu and Yb ions in EuAl$_2$ and YbAl$_2$ is divalent.

CeAl$_2$ also crystallizes in the MgCu$_2$ type, and has been well known as a prototype of heavy fermion Kondo compound[4, 5, 6]. These characteristic properties are mainly originated from the existence of unstable 4$f$ electrons and the hybridization between local $f$ electrons and conduction band electrons. Since the magnitude of hybridization is affected strongly by an application of
external pressure and a lot of interesting phase transition is expected to induce, the investigation of these compounds under application of external forces like high pressure has been carried out extensively by many authors\[7, 8, 9\].

It is well known that some heavy-fermion compounds show a discontinuous volume change due to valence transition in compression curve\[10, 11\]. As for CeAl\(_2\), on the other hand, there have been quite a number of discrepancies in the compression curves. A discontinuous change in the pressure dependence of lattice constant at room temperature was reported around 6 GPa by some authors\[12, 13\]. But other authors did not find it below 20 GPa\[14, 15\]. Chandra et al. supported the latter group from their calculation about changes in electronic structure, but predicted that it could show transformation to either a MgNi\(_2\) or a MgZn\(_2\) type structure, which is hexagonal but again belongs to the Laves phase\[16\].

The origin of these discrepancies seems to be a complicated issue, but it may originate mainly from the lattice compression at non-hydrostatic condition by solidification of pressure transmitting medium. Takemura investigated in Zn that the anomaly on the compression curve is induced by the non-hydrostaticity associated with the solidification of the transmitting medium \[17\]. In this paper, we report the high-pressure powder X-ray diffraction measurement of CeAl\(_2\) with helium pressure-transmitting medium which achieves the best hydrostatic conditions, to discuss about the effect of the hydrostaticity from the compression curve and from the half width of each X-ray diffraction peak.

2. Experimental

A single crystal of CeAl\(_2\) was grown by using Czochralski pulling method with a tetra-arc furnace in argon gas atmosphere. The crystal axes were determined for all single crystals by X-ray back Laue method. For the X-ray diffraction measurements, the crystal was crushed and powdered using a mortar and pestle. The sample was found to be of single phase and the lattice parameter of cubic C\(_{15}\) Laves phase (space group \(Fd\bar{3}m\), No. 227) was determined to be \(a = 8.055 \pm 0.002\) Å at ambient pressure. It is in good agreement with a previous report \[4\].

Powder X-ray diffraction experiments were carried out under high pressure by means of diamond-anvil cell having a cut face of 0.45 mm in diameter. This diamond anvil type pressure apparatus is an improved Mao-Bell’s lever type. SUS 304 is used as the gasket which is the pressure transmitting disk. In order to prevent to blow out the transmitting medium, at first pre-press was carried out up to the half value of target pressure, and then drilled a hole (0.25mmϕ) in the center of the pattern. The powdered sample was put in the hole and a little piece of ruby to monitor the pressure. The helium gas was used as pressure transmitting medium, which has the advantage that hydrostatic pressure nature is very high also under high pressure comparing with liquid pressure transmitting medium. At first, powder sample and pressure marker put into the hole of gasket, and then the gasket was pressed by upper and lower-anvil. X-ray diffraction measurement was made at room temperature using Mo K\(_\alpha\) radiation from a 5.4 kW Rigaku rotating anode generator equipped with a 100 μm collimator. An image plate was used as the detector. The \(d\)-values were obtained by recording the diffraction.

3. Results

Figure 1 shows the diffraction patterns of CeAl\(_2\) at several pressures up to 23.3 GPa. Indices of some of the prominent peaks are also shown. A broad peak is observed at \(2\theta = 20 \sim 22^\circ\) the diffraction patterns at every pressures. Such behavior comes from the diffraction of the gasket of SUS 304. It is noted that all of the diffraction peaks are sharp compared with the previous results where a 4:1 methanol: ethanol mixture (ME) is used as the pressure-transmitting medium\[18\]. It means that good hydrostaticity is retained compared with that by using ME. The diffraction patterns does not change and all the diffraction peaks shifted to higher \(2\theta\) as
Figure 1. The powder X-ray diffraction patterns of CeAl$_2$ at room temperature under high pressures using helium gas as the pressure-transmitting medium. Indices of some of the prominent peaks are also shown.

increasing pressure. No splitting of the peak is observed within experimental error. The $d$-values of each Bragg reflections are obtained from the diffraction patterns.

4. Discussion
Assuming that the cubic structure is stable, the lattice constant $a$ is determined mainly from the $d$-values corresponding to the reflections (111), (200), (311), (331) and (422). Figure 2 shows the volume of CeAl$_2$ as a function of pressure, where the volume is obtained to be $V = a^3$. The figure compares two experimental runs, one with helium gas as the pressure-transmitting medium in the present study and the other with ME in the previous study [18]. It is found that $V$ decreases continuously with increasing pressure below 17 GPa in both compression curves, and that both compression curves are almost coincident with each other. It indicates that the non-hydrostaticity does not cause the uniaxial stress of the sample with keeping cubic symmetry within experimental error. Here, the bulk modulus was estimated by assuming the Murnaghan’s equation of state [19], which is described as follows,

$$
\frac{V}{V_0} = \left( \left( \frac{B_0'}{B_0} \right) \times P + 1 \right)^{-\frac{1}{B_0'}}
$$

, where $B_0$ and $B_0'$ are the bulk modulus and its pressure derivative at ambient pressure, respectively, and $V_0$ is the volume at high and ambient pressure. By least square fitting of
the experimental data in Figure 2 to Eq. (1) below 15 GPa, $B_0$ and $B'_0$ were obtained to be 62 GPa and 3.0 in the sample with helium gas as the pressure-transmitting medium, respectively. It is comparable to the values $B_0 = 63$ GPa and $B'_0 = 3.0$ in another results with ME.

On the other hand an anomaly exists in the compression curves under high pressure, where the slope of the compression curve changes above 20 GPa. Such anomaly is obviously observed not only in the compression curve by using ME as the pressure-transmitting medium, but also by using helium gas as the best hydrostatic conditions. It means that the anomaly does not come from the nonhydrostaticity but from physical origins such as the pressure induced phase transition. Furthermore, the compression curve tends to deviate from another one above 20 GPa. Taking account that crystals which has low structural symmetry are generally sensitive to uniaxial stress, such behavior may come from the reduction in the structural symmetry under pressure.

To make it clear, we estimated a full width at half maximum (FWHM) of Bragg peaks of each diffraction pattern of CeAl$_2$. Figure 3 shows the magnitude of FWHM as the function of pressure for several Bragg reflections taken from two experimental runs. For the one with ME as the pressure-transmitting medium shown in Fig. 3(a), FWHM is around 0.2° at low pressure but tend to increase at high pressure above 10 GPa. Such behavior is consistent with the previous report that the nonhydrostatify is induced by the solidification of ME pressure medium above 10 GPa[20].

With helium gas as the pressure-transmitting medium shown in Fig. 3(b), on the other hand, not only the magnitude of FWHM but also the dispersion of FWHM is much smaller than those with ME. Although helium solidifies at 11.5 GPa at room temperature[21], FWHM with helium gas remains nearly constant at least 20 GPa for all reflections in Fig. 3(b). Such behavior indicates that good hydrostaticity suppresses uniaxial strain of CeAl$_2$ crystal in helium gas as the pressure-transmitting medium.

Furthermore, it is found that FWHMs of (220) and (311) reflections are enhanced above 20 GPa in Fig. 3(b). It means that a precursory phenomenon of the splitting of (220) and (311) reflections, while that of (111) reflection is almost constant at all pressure region. Since such results indicate that (hhl) reflections of cubic structure at low pressure is split to (hlh) and (lhh) while (hhl) one is not, it is reasonable to assume that the pressure-induced structural phase transition from cubic to tetragonal structure occurs. However, it is difficult to estimate the
lattice parameters at high pressure phase because no splitting of the peak is observed in the X-ray powder diffraction pattern even at the highest pressure 23.3 GPa.

Figure 3. The pressure dependence on FWHM of several Bragg reflections of CeAl₂, in which (a) ME is used as the pressure-transmitting medium[18], and (b) helium gas is used as the pressure-transmitting medium. The arrow shows critical pressure where pressure-induced structural transition is suggested.

5. Conclusion
The compression behavior of C15 Laves compound CeAl₂ is interpreted through the powder X-ray diffraction measurement under hydrostatic pressure with helium gas pressure-transmitting medium. We support that no discontinuous change in the compression curve below 20 GPa as discussed by the latter group[14, 15]. However, we have suggested that the pressure-induced structural phase transition from cubic to tetragonal structure occurs at around 20 GPa. More precise experiments are needed to determine the space group and all other structural parameters accurately.

Acknowledgments
This work was performed under the Inter-University Cooperative Research Program of the Institute for Materials Research, Tohoku University, and the Visiting Researcher’s Program of the Institute for Solid State Physics, the University of Tokyo. This work was supported in part by Grants-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology of Japan, JGC-S Scholarship Foundation and Suzuki Foundation.

References
[1] Purwins H G and Leson A 1990 Adv. Phys. 39 309.
[2] Oishi T, Ohashi M, Suzuki and H, Satoh I 2010 Journal of Physics: Conference Series 200 082022.
[3] Ohashi M, Kishii and N, Tateno S 2016 accepted to Jpn. J. Appl. Phys.
[4] Onuki Y, Furukawa Y and Komatsubara T 1984 J. Phys. Soc. Jpn. 53 2734.
[5] Miyagawa H, Oomi G, Ohashi M, Satoh I, Komatsubara T, Hedo and M, Uwatoko Y 2008 Phys. Rev. B 78 064403.
[6] Ohashi M, Miyagawa H, Nakano T, Oomi G, Sechovsky V, Satoh I and Komatsubara T, 2014 J. Phys. Soc. Jpn. 83 024701.
[7] Ohashi M, Oomi G, Koiwai S, Hedo M and Uwatoko Y 2003 Phys. Rev. B 68 144428.
[8] Ohashi M, Oomi G and Satoh I 2007 J. Phys. Soc. Jpn. 76 114712.
[9] Ohashi M and Oomi G 2009 Jpn. J. Appl. Phys. 48 070221.
[10] Uwatoko Y, Suenaga K and Oomi G 1992 J. Magn. Magn. Mater. 104-107 645.
[11] Miyagawa H, Oomi G, Ohashi M, Maezawa K, and Kagayama T 2006 J. Alloys and Compounds 408-412 230.
[12] Croft M and Jayaraman A 1979 Solid State Commun. 29 9.
[13] Bartholin H, Waintal A, Parisot G, Kerrella F, Senatou J P 1980 Phys. Status Solidi A Appl. Res. 61 K87.
[14] Barbara B, Beille J, Cheiato B, Laurant J M, Rossignol M F, Waintal A, and Zemirli S 1986 Physics Letters 113 381.
[15] Vedel I, Redon A M, Léger J M, Mignot J M, Flouquet J 1986 J. Magn. Magn. Mater. 54-57 361.
[16] Chandra Shekar V N V, Sahu P C, Yousuf M, Rajan K G and Rajagopalan M 1999 Solid State Commun. 111 529.
[17] Takemura K 1999 Phys. Rev. B 60 6171.
[18] Miyagawa H, Ohashi M, Oomi G, Satoh I, Komatsubara T, Miyajima and N, Yagi T, 2006 Topology in Ordered Phases 203.
[19] Murnaghan F D 1951 Finite Deformation of an elastic solid (Dover Publication Inc., New York)
[20] Fujishiro I, Piermarini G J, Block S, and Munro R G 1982 in High Pressure in Research and Industry, Proceedings of the 8th AIRAPT Conference Upsala, edited by C. M. Backman, T. Johannisson, and L. Tegner (ISBN, Sweden), Vol. II, p. 608.
[21] Besson J M and Pinceaux J P 1979 Science 206 1073.