Structure phase transformation and equation of state of cerium metal under pressures up to 51 GPa*

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This study presents high pressure phase transitions and equation of states of cerium under pressures up to 51 GPa at room temperature. The angle-dispersive x-ray diffraction experiments are carried out using a high energy synchrotron x-ray source. The bulk moduli of high pressure phases of cerium are calculated using the Birch–Murnaghan equation. We discuss and correct several previous controversial conclusions, which are caused by the measurement accuracy or personal explanation. The c/a axial ratio of ε-Ce has a maximum value at about 29 GPa, i.e., $c/a \approx 1.690$.

Keywords: cerium, equation of state, high pressure, phase transition

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1. Introduction

Cerium (Ce) is a typical non-radioactive f-electron transition metal, being a research focus of high-pressure physics and strongly correlated electron fields due to its unique electronic structure and condensed matter phase polymorphism.[1] In addition, Ce is considered as an ideal module for studying the high pressure properties of heavy actinides because of their similar high pressure properties.[2] There are several controversies about Ce under high pressure, such as the phase transition route, phase transition mechanism, phase diagram, and phase boundary according to the experimental and theoretical reports (a recent review was given by NIkolaev and Tsvyashchenko[3]). The most distinguished characteristic of Ce is the isostructural phase transition of γ-Ce (fcc) to α-Ce (fcc) accompanied by about 14%–20% volume collapse at 0.6 GPa–1 GPa at room temperature,[4] which is considered to be related to the f electron properties,[5–9] as indicated in both the Hubbard-Mott transition (HM)[9] and the Kondo volume collapse (KVC)[7,8] models. In the HM scenario,[9] the 4f electron is localized and non-binding in the γ phase, but itinerant and band-like in the α phase. Thus the energy for the phase transition is provided by the kinetic energy of the itinerant f electron. Whereas in the KVC picture,[7,8] the 4f electron is assumed to be localized in both of the α and γ phases, and the phase transition is driven by the Kondo spin fluctuation energy and entropy. In addition, this phase diagram of Ce under 5 GPa is ambiguous, for the transformation product may be α'-Ce (α-U structure) or α''-Ce (C-face-centered monoclinic). These transition productions are recognized to be related to many factors, such as the initial size of grain,[10–12] the trajectory of pressure-temperature,[13] the initial heat treat state, even the sample primal preparation condition.[10,11] However, α'-Ce and α''-Ce both transform into the body-centered tetragonal phase (ε-Ce, bct) above 12 GPa.[10]

Up to now, the phase transformations have been controversial, meanwhile there is some argument about the equation of state of Ce. Both of the high pressure equation of state (Olsen[14]) and the ultrapressure equation of state(Yogesh[15]) were measured by the energy-dispersive x-ray diffraction (EDXD). As is well known, subject to the energy detect accuracy, the data measured by EDXD are less reliable than by the angle-dispersive x-ray diffraction (ADXD).[16] Therefore, we present high-accuracy experimental data under high pressure for the phase structure transition and equation of state by using synchrotron ADXD. Several previous controversial conclusions caused by the test accuracy or personal explanation are unambiguously indicated and corrected in this study.

2. Experiment

A Ce slice was cut from an ingot of 99.9% purity purchased from Alfa Aesar. During processing and transport, the Ce was immersed in silicon oil in order to avoid oxidizing. There is no other processing such as heat treatment or grinding before our experiments. The Mao–Bell type diamond anvil

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cells (DAC) with 300 μm anvil in diameter was used to provide the hydrostatic pressure. A T301 steel sheet served as the gasket with a chamber of 75 μm in diameter and 60 μm in thickness for packing the sample. The pressures were measured by the ruby fluorescence technique.[17] The high-purity silicon oil was selected as the pressure-transmitting medium. The synchrotron ADXD measurements were carried out at the Beam-line BL15U1 in the Shanghai Synchrotron Radiation Facility (SSRF) with the x-ray wavelength 0.6199 Å. An x-ray beam size of 1.8 μm×1.6 μm was employed in all the x-ray exposures. The Bragg diffraction rings were collected using a MAR165 CCD camera with a 79-μm pixel, and the XRD patterns were integrated from the images with FIT2D software.

3. Results and discussion

The representative diffraction spectra of Ce are shown in Fig. 1. The refine lattice parameter of γ-Ce is $a = 5.0970(4)$ Å (fcc) at 0.56 GPa. At 1.38 GPa, γ-Ce transmits to α-Ce (fcc, $a = 4.7722(9)$ Å), accompanied by a 16% volume collapse. The emergence of asterisked peaks shows the occurrence of the phase transition of α''-Ce at 5.39 GPa, which is in agreement with previous results.[10] We observed no signal of α'-Ce under pressures from 5 GPa to 12 GPa. The α''-Ce phase totally transforms into ε-Ce (bct) phase at 17.6 GPa. The high pressure ε-Ce (bct) phase is stable under pressures up to 51.9 GPa (shown in Fig. 1), the highest pressure in this study. The lattice parameters are $a = b = 2.7108(10)$ Å, $c = 4.5609(26)$ Å at 51.9 GPa. Upon pressure release to ambient conditions, the high pressure phase recovers to γ-Ce phase.

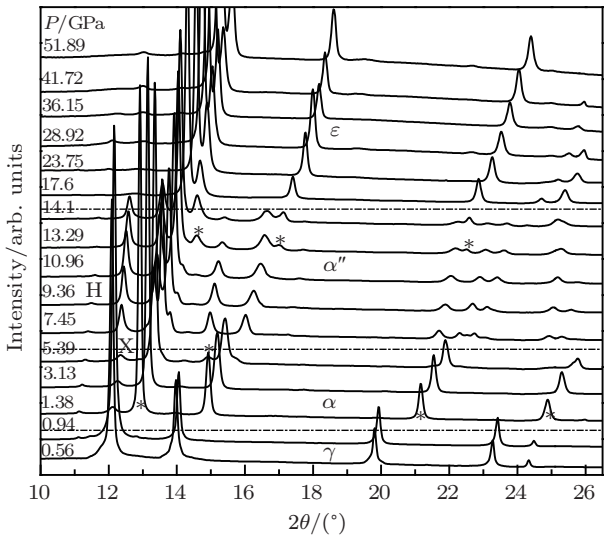


Fig. 1. Representative x-ray diffraction patterns of Ce. The γ-Ce, α-Ce, α''-Ce, and ε-Ce are shown in this figure respectively. The asterisk (*) denotes the occurrence of the new peaks upon phase transformation.

The α''-Ce has a low symmetry monoclinic structure, with a $C2/m$ space group. The structural of α''-Ce at 8.3 GPa was obtained by full Rietveld refinement in Refs. [4] and [10]. We indexed the diffraction peaks of Ce at 8.35 GPa in Fig. 2. The lattice parameters are $a = 5.789(2)$ Å, $b = 3.120(2)$ Å, $c = 5.559(4)$ Å, $\beta = 113.21(6)°$, and volume = 23.07(2) Å^3/atom, which are denser than the previous experiment data, i.e., $a = 5.813(2)$ Å, $b = 3.145(1)$ Å, $c = 5.612(2)$ Å, $\beta = 113.10(2)°$ at 8.3 GPa.[10]

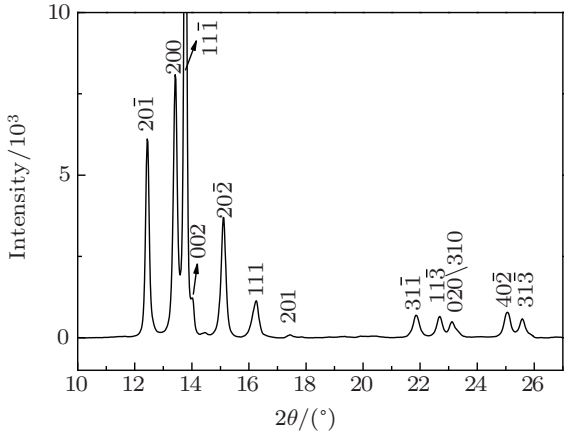


Fig. 2. The XRD of α''-Ce at 8.35 GPa.

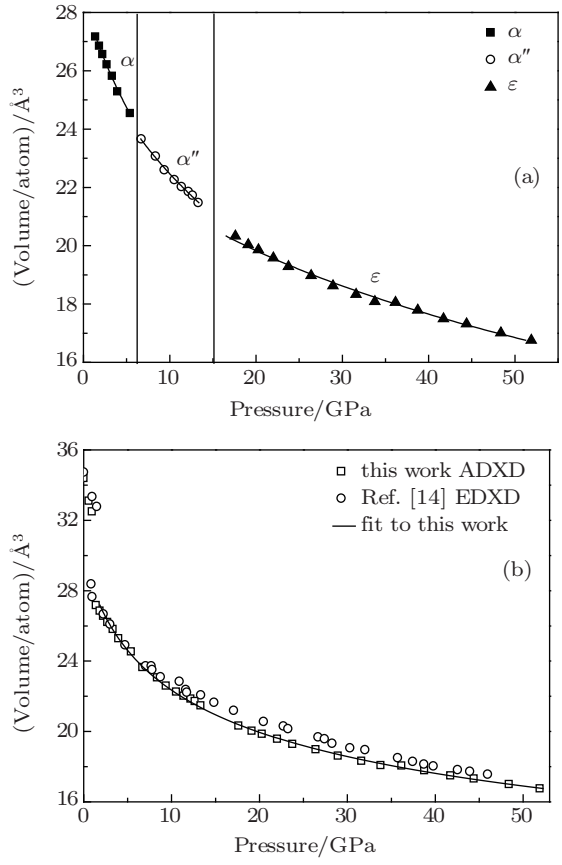


Fig. 3. (a) Pressure dependence of atomic volume of Ce (except γ-Ce). Each phase is fitted by Birch–Murnaghan equation of state fixing $B_0' = 4$. The square, circle, and triangle represent α-Ce, α''-Ce, and ε-Ce respectively. (b) The comparison between literature data and the results from this work. The results of experiment on polymorph are fitted to the Murnaghan equation (solid line).

Figure 3(a) shows the volume-pressure relationship of Ce. The data of each pure phase (without any two-phase coexisting regime) is fitted to the isothermal Birch-Murnaghan[18,19] equation of state:

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

where B_0 is the isothermal bulk modulus, B_0' is the bulk modulus first order derivative, and V_0 is the unit cell volume at ambient pressure.

Table 1. Comparison among equation-of-state parameters (B_0, B_0', V_0) of Ce.

Phase	B_0/GPa	V_0/Å^3	B_0'	Ref.
α-Ce	26.2±0.8	28.55±0.07	4.0	this work
	27.6	28.49	–	[20]
	24	29	–	[21]
	24.4	–	5.5	[14]
α''-Ce	33 .6±1.7	27.4±0.2	4.0	this work
	59	26.26	4.0	[21]
ε-Ce	65.9±2.8	24.3±0.2	4.0	this work
	89	–	5.5	[22]

The equation-of-state parameters of Ce are shown in Table 1. Our experimental data $B_0 = (26.2 \pm 0.8))$ GPa and $V_0 = (28.55 \pm 0.07)$ Å^3 of α-Ce are consistent with both experimental data in Refs. [14] and [21] and theoretical calculations in Ref. [20]. While for α''-Ce (monoclinic structure), the fitting results of $B_0 = (33.6 \pm 1.7)$ GPa and $V_0 = (27.4 \pm 0.2)$ Å^3 are different from the literature reported data of $B_0 = 59$ GPa and $V_0 = 26.26$ Å^3[21] which are obtained from the EDXD measurements. The difference may be ascribed to the experiment measurement method, for our data are calculated from ADXD instead of EDXD. Because ADXD has higher resolution, and advantages of resolving peaks in the complex monoclinic structure which usually suffers severe peak overlapping. As a consequence, the cell parameters calculated based on better resolved peaks are supposed to be more accurate than those calculated from EDXD data. Therefore the equation of state of α''-Ce measured by ADXD in our study should be more widely recognized than by EDXD. The bulk modulus of ε-Ce phase is $B_0 = (65.9 \pm 2.8)$ GPa, which is deviated from the reference result of $B_0 = 89$ GPa.[22] The difference is attributed to the accuracy of volume measurement of the previous study due to α'-Ce or α''-Ce and ε-Ce phase coexisting at pressures from 12 GPa to 17 GPa, the pressure range in which the previous studies were performed.

As shown in Fig. 3(b), the volumes of α-Ce, α''-Ce, ε slightly change (about 2.3% from $V_{\alpha-\mathrm{Ce}} = 24.45$ Å^3 to $V_{\alpha''-\mathrm{Ce}} = 23.87$ Å^3 at 5.71 GPa, about 0.2% from $V_{\alpha''-\mathrm{Ce}} = 21.48$ Å^3 to $V_\varepsilon = 21.44$ Å^3 at 13.29 GPa) during the phase transition. Therefore, the polymorph equation-of-state can be fitted to a unified equation. In this study we choose the first-order Murnaghan equation to describe the three high-pressure phases:

$$P(V) = \left(\frac{B_0}{B_0'}\right)\left[\left(\frac{V_0}{V}\right)^{B_0'} - 1\right], \quad (2)$$

with the parameters $B_0 = (15.4 \pm 1.9)$ GPa, $B_0' = 5.0 \pm 0.1$, $V_0 = (29.8 \pm 0.5)$ Å^3 (Fig. 3(b)).

Figure 4 shows the variations of lattice axial ratio of monoclinic and tetragonal with pressure. The $C2/m$ symmetry was demonstrated by McMahon who refined the diffraction of α''-Ce at 8.3 GPa by using the program MPROF.[10] The axial ratios of monoclinic phase are $c/b = 1.781$, $a/b = 1.855$ at 8.35 GPa, which coincide with the experiment results of $c/b = 1.784$, $a/b = 1.848$ at 8.3 GPa[10] and theory results of $c/b = 1.808$, $a/b = 1.815$.[23] For our data the $C2/m$ symmetry is adopted. Therefore, there is a large difference between our data and the data given by Olsen *et al.* who recognized α''-Ce as $I2/m$[14] in Fig. 4. Moreover, our axial ratio changing with pressure is similar to the axial ratio of α'-Ce (Gu[12]), which may be the reason why α'- and α''-Ce transform into the same ε-Ce at 12 GPa.

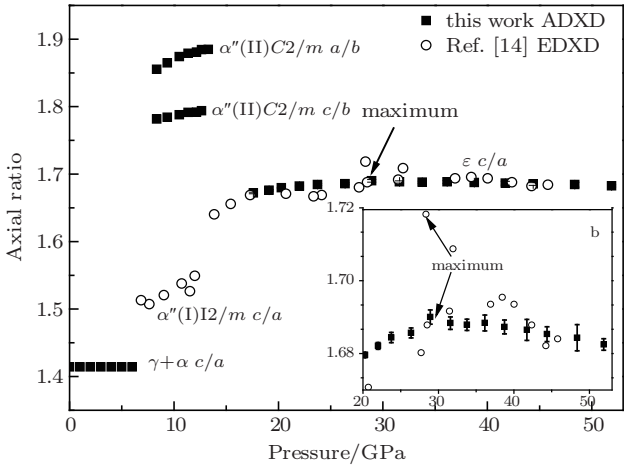


Fig. 4. Variations of axial ratio (long-axial/short-axial) for monoclinic (α''-Ce) and tetragonal (ε-Ce) descriptions with pressure. The fcc (γ-Ce and α-Ce) can be expressed as nonstandard bct structure ($a = b$, $c = \sqrt{2}a$).

The inset in Fig. 4 shows the inflection point of ε-Ce. It means that there is a maximum value of $c/a = 1.69$ at about 29 GPa, which is consistent with the value in Ref. [14] in which the maximum value of c/a is also about 29 GPa, which was reported but not identified directly, for the maximum value was recognized as 35 GPa by curve fitting. Moreover the ratio of $c/a = 1.680 \pm 0.006$ built by using the ultrapressure experiments from 90 GPa to 208 GPa[15] can be used in a lower pressure condition, e.g. the $c/a = 1.685$ at 44.4 GPa in Fig. 4 denoted as a black square, and the $c/a = 1.684$ at 44 GPa in Fig. 4 marked as a hollow circle.[14]

4. Conclusions

The ADXD experiments at high pressure with Ce metal loaded with silicon oil as a pressure-transmitting medium un-

der pressures up to 51 GPa result in an identical sequence of phase transitions with almost the same values of pressures for the phase transformations as in previous experimental conditions. The equation-of-state parameters of α''-Ce and ε-Ce are $B_0 = (33.6 \pm 1.7)$ GPa, $V_0 = (27.4 \pm 0.2)$ Å^3 and $B_0 = (65.9 \pm 2.8)$ GPa, $V_0 = (24.3 \pm 0.2)$ Å^3, respectively. The maximum value in the axial ratio at about 29 GPa is $c/a = 1.690$. Our experimental results will help to trigger more theoretical and experimental work about this mutation near 29 GPa.

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