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X-ray diffraction study of elemental erbium to 70 GPa

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We have investigated phase transitions in elemental erbium in a diamond anvil cell (DAC) up to 70 GPa using angular-dispersive x-ray powder diffraction methods. We present evidence of a series of phase transitions that appear to follow the anticipated hcp→Sm-type→double hcp (dhcp)→distorted fcc sequence. In particular, we present evidence for the predicted dhcp→distorted fcc transition above 63 GPa. Equation of state data are also presented up to 70 GPa.

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INTRODUCTION

The lanthanide metals possess fascinating electrical, magnetic, thermal, and material properties that are frequently little-understood because of the complex interactions of 4f electrons within the lattice—especially when subjected to high pressures. The unfilled 4f electron shells are mostly localized in the atoms and, therefore, contribute only slightly to the bonding or crystal structure at atmospheric pressure. As a result, lanthanides have similar chemical properties and are often difficult to separate from one another.[1]

At ambient pressure, the pure metals from La through Lu have structures that vary consecutively from double hcp (dhcp)→Sm-type→hcp[1] with the exception of Ce, Eu, and Yb. With increasing pressure, the metals adopt structures in the scheme: hcp→Sm-type→dhcp→fcc→distorted fcc, reverting to the prior structure in the lanthanide series,[1] except that above Dy, the structures go directly from dhcp →distorted fcc, skipping the fcc phase.[2] The generally accepted, underlying driving force for these transitions involves reduction in the energies of the d states relative to the s and p states, which induces an s→d transfer of conduction electrons.[2,3] However, pressure can also induce delocalization and increase in hybridization in the 4f shell, further complicating any understanding of the high pressure behavior of lanthanides.[4,5]

Our interest in studying erbium [electronic configuration: $4f^{11}(5d6s)^3$ (Ref. 1)] stemmed from the lack of data in the literature about the element beyond about 30 GPa,[2,6] its interesting magnetic properties at high pressures[7] and in alloys,[8] and other optical properties, especially in transparent glass ceramics.[9] Our intention was to extend the experimental knowledge of this vital element to higher pressures in the interest of finding the predicted dhcp→distorted fcc transition somewhere above 60 GPa,[2] thereby filling a vital gap in high pressure lanthanide science.

EXPERIMENTAL METHOD

Elemental erbium with 99.9% purity was obtained in granular form (−40 mesh size) from Aldrich Chemical and was packed in argon. As erbium oxidizes slowly in air, we rapidly dropped the erbium (in the presence of flowing argon gas) into a mortar containing cyclohexane (99.9% purity, Aldrich Chemical) and gently ground the material with a pestle. The rhenium sample gasket was preindented to a thickness of 42 μm, and a hole of diameter ~130 μm was machined via electric discharge machining. The completed gasket was affixed to the base diamond of a Mao Bell cell, and the entire assembly was immersed in a beaker filled with cyclohexane. A few 10-μm ruby crystals were sprinkled inside the sample chamber to measure pressures.[10] After some erbium chips were introduced into the gasket by a hypodermic syringe, the other half of the Mao Bell cell was installed, and the sample was sealed in the beaker. Cyclohexane is normally transparent and served as our quasihydrostatic medium.[11] Because the hydrocarbon (C_6H_{12}) consists of atoms much lower in Z than erbium, we saw very little interference in the x-ray diffraction patterns from the pressure medium which remained transparent to the highest pressures studied. Cyclohexane scatters x-rays less than commonly-used silicon fluid[12] which makes it an attractive quasi-hydrostatic medium for x-ray studies. Angular-dispersive x-ray diffraction patterns were taken at room temperature at the 16 ID-B x-ray facility of the High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source in Argonne National Laboratory. The focused monochromatic x-ray beam was spatially collimated with a 30-μm pinhole. Pressure was measured using a diode-pumped 532-nm wavelength laser near the HPCAT beamline. Typical diffraction patterns were acquired with 15−30 s exposures. The patterns were recorded by a MAR345® image plate. For this experiment, the x-ray wavelength was 0.3857 Å. Figure 1 shows a picture of the sample taken at the highest pressure studied.

RESULTS

The low scattering power of the cyclohexane made it easy for us to locate and to center the sample in the x-ray beam. Material similarities between rhenium and erbium were apparent upon pressurizing the sample which made it vital to ensure that we took diffraction patterns "off sample" to distinguish rhenium patterns from erbium patterns and to ensure no rhenium contamination in our patterns. The low scattering cross section of the pressurizing medium provided a convenient method to easily "view" the sample as the DAC was

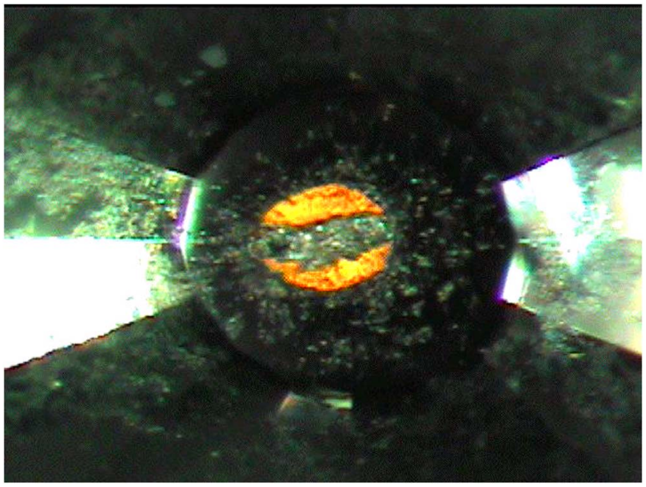

FIG. 1. (Color online) Transmission micrograph of erbium in cyclohexane at about 70 GPa. The pressure-transmitting medium appears orange (light gray) online due to low transmission lighting but is actually transparent.

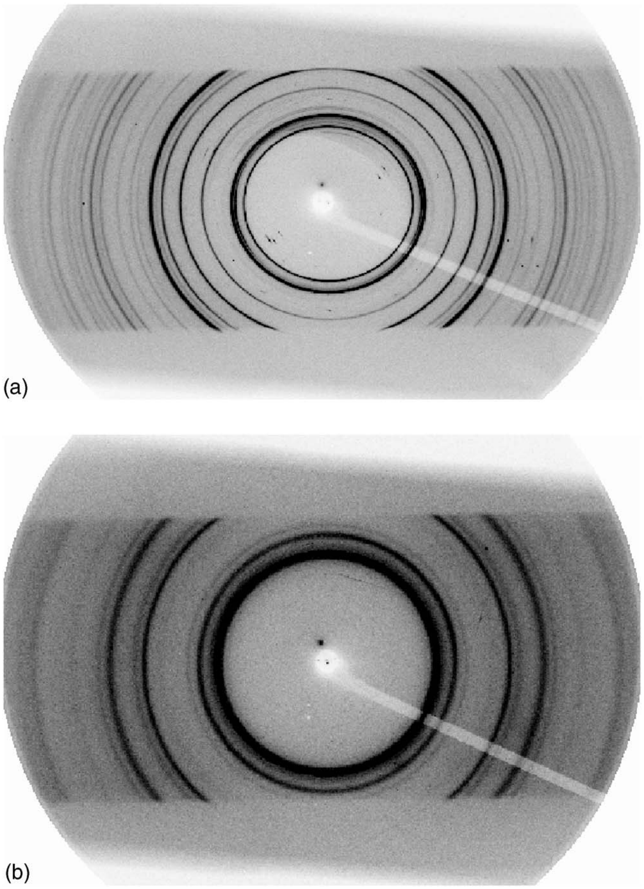

FIG. 2. (a) Erbium powder XRD pattern at 4.4 GPa illustrating the polycrystallinity of the sample; and (b) erbium powder XRD pattern at 70 GPa. Both patterns were collected at the Advanced Photon Source, Argonne National Laboratory (λ=0.3857 Å).

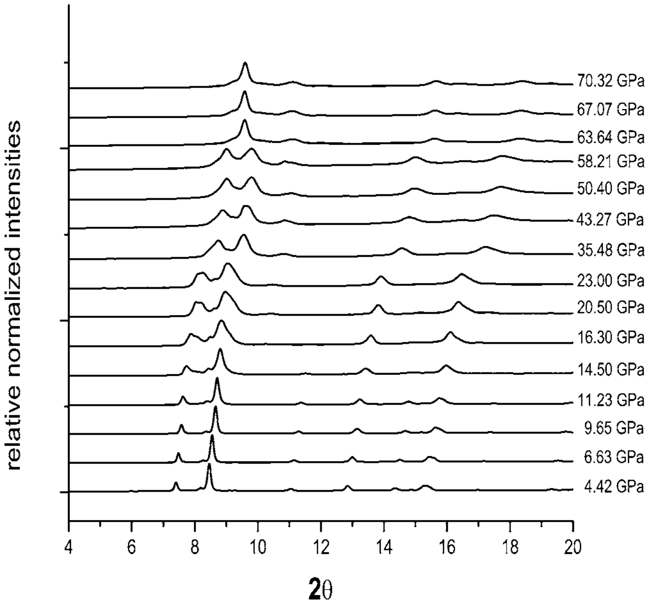

FIG. 3. Intensity vs 2θ plots of erbium in cyclohexane at the various pressures studied. λ=0.3888 Å.

scanned perpendicular to the beam. During the entire process of increasing pressure, there was no evidence of any sudden contraction of the sample.

Two-dimensional ring patterns from the charge coupled device were reduced to intensity versus 2θ plots using FIT2D®; then unit cell structure determinations were attempted using the JADE® data processing program. Figure 2 illustrates two x-ray diffraction (XRD) patterns at low and high pressures which illustrate the high powder pattern quality of the sample to the highest pressure studied. Figure 3 shows the intensity versus 2θ plots for erbium at various pressures studied.

At ambient pressure, the accepted structure for erbium is hcp (hP2) with $Z=2$, $a=b=3.5588(3)$ Å, $c=5.5874(3)$ Å, and a unit cell volume of 61.28 Å^3.[13] Table I contains data from our fits. The nearly ambient pressure patterns below 10 GPa were easily fit using the hcp (hP2, space group 194)[2] structure. At 4.42 GPa, $a=b=3.495\pm0.001$ Å; $c=5.486\pm0.003$ Å with unit cell volume=58.02 Å^3. From about 10 to about 23 GPa, the patterns were all easily fit using the Sm-type (hR9), $Z=9$, space group 166.[2] At 20.5 GPa, $a=b=3.244\pm0.004$ Å; $c=23.379\pm0.008$ Å with unit cell volume=213.02 Å^3. From 23 to 58 GPa, the patterns were easily fit using the dhcp structure (hP4, $Z=4$) which has the same space group (194, $P6_3/mmc$) as hcp.[13] At 50.4 GPa, $a=b=3.007\pm0.007$ Å; $c=9.573\pm0.007$ Å with unit cell volume=74.98 Å^3. Above 58 GPa to the highest pressure studied (70 GPa), the distorted fcc phase appears. We easily fit these lines to the C_{mmm} (space group 65, $Z=8$) orthorhombic cell.[2] At 70.32 GPa, $a=7.965\pm0.014$ Å, $b=5.751\pm0.006$ Å, $c=2.846\pm0.015$ Å and the unit cell volume $=130.39$ Å^3.

From our fits, we obtained the plot of the volume per atom (V) versus pressure in Fig. 4. We fit our data using the modified universal equation of state (MUEOS)[14,15]

TABLE I. Results from the JADE® fits for erbium.

Pressure	a (Å)	σ_a	b (Å)	σ_b	c (Å)	σ_c	Volume for atom (Å^3)	σ_v
4.4	3.4948	0.0012	3.4948	0.0012	5.4857	0.0027	29.010	0.025
6.6	3.4576	0.0011	3.4576	0.0011	5.4360	0.0024	28.140	0.022
9.7	3.4141	0.0014	3.4141	0.0014	5.3724	0.0014	27.115	0.023
11.2	3.3905	0.0019	3.3905	0.0019	5.3282	0.0045	26.520	0.037
14.5	3.3470	0.0052	3.3470	0.0052	5.287	0.014	25.65	0.10
16.3	3.3215	0.0052	3.3215	0.0052	23.603	0.045	25.058	0.092
20.5	3.2436	0.0039	3.2436	0.0039	23.379	0.083	23.67	0.10
23.0	3.2241	0.0044	3.2241	0.0044	23.325	0.097	23.33	0.12
35.5	3.0537	0.0020	3.0537	0.0020	10.137	0.026	20.468	0.064
43.3	3.0320	0.0160	3.0320	0.0160	9.84	0.12	19.55	0.32
50.4	3.0073	0.0088	3.0073	0.0088	9.573	0.028	18.75	0.11
58.2	2.9954	0.0058	2.9954	0.0058	9.332	0.025	18.130	0.080
63.6	8.0771	0.0085	5.7689	0.0073	2.9976	0.0053	17.459	0.042
67.1	8.0750	0.0190	5.7528	0.0072	2.982	0.033	17.32	0.20
70.3	8.0420	0.0170	5.748	0.014	2.989	0.011	17.269	0.085

$$\ln H = \ln B_0 + \eta(1-x) + \beta(1-x)^2,$$

where $H = Px^2/[3(1-x)]$, $x^3 = V/V_0$, $\eta = 1.5(B_0' - 1)$; and V_0, B_0, B_0' are the atomic volume, isothermal bulk modulus, and the pressure derivative of the bulk modulus at ambient pressure, respectively. The bulk modulus ($B_0 = 44$ GPa) and its derivative at ambient pressure were obtained from Ref. 16. Using these values ($B_0 = 44$ GPa) and constraining the bulk modulus, we obtained

$$V_0 = 32.6349 \pm 0.4581 \text{ Å}^3; \quad B_0' = 0.8332 \pm 0.7347;$$

$$\beta = 11.0626 \pm 4.7295.$$

As seen in a recent study of dysprosium[17] up to 86 GPa, the EOS appears continuous up to the highest pressures investigated. This is probably due to the fact that the phases hcp, Sm-type, dhcp, and distorted fcc represent different stacking sequences of hexagonal close packed layers and thus the present level of resolution, transition sluggishness, and/or quality of fits may preclude detection of any discontinuity in the transitions.[6] Errors in the volumes are included in the graph and were calculated by propagating the errors in unit cell parameters that were calculated from the JADE program fits.

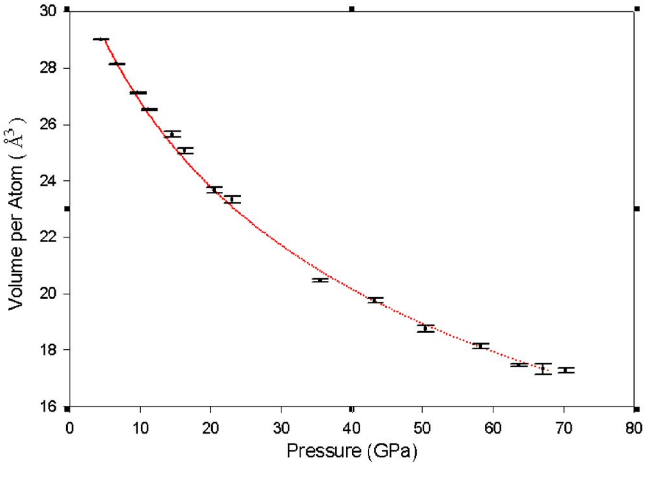

FIG. 4. (Color online) Measured volumes and fitted erbium equation of state.

SUMMARY

We have seen the anticipated dhcp → dfcc phase transition in erbium above 63 GPa. We have studied elemental erbium to 70 GPa, doubling the studied pressure range of this material and have seen the expected sequence of phase transitions as a function of pressure (hcp → Sm-type → dhcp → distorted fcc). We used cyclohexane as an easily loadable, chemically inert, and low-Z pressure-transmitting medium in studies of lanthanides, and it appears to be a promising quasihydrostatic medium. Further studies will extend the pressure range of study and further investigate dynamics of the dhcp → distorted fcc transition.[18]

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