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X-Ray Diffraction Study of Cerium, Zirconium, and Teflon at High Pressure

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Beamline(s):X17C

Three different samples were studied with energy dispersive x-ray diffraction. Two metals, cerium and zirconium, along with a polymer, teflon, were examined. The zirconium and teflon experiments were designed primarily as pilot experiments, and we did not go above room pressure. Zirconium is of interest, partially, due to the debate over static and dynamic equation of state results. Some of the explanation for this deals with sample purity. In this experiment we studied a highly pure zirconium sample with a large grain size. Teflon is a common material that is simply not well understood with respect to pressure. It has only been studied with rudimentary x-ray diffraction sources up to about 70 kilobars. This data so far suggest orthorhombic and monoclinic structures in this pressure regime. Between 70 and 100 kilobars a phase transition is expected. This is a challenging material to study since it contains mostly carbon atoms and exhibits complex polymeric structures. Most of this experimental time was focused on the study of cerium.

Cerium is a fascinating material to study because it exhibits so many unique properties. It has been examined to a greater extent than its neighboring lanthanides with respect to pressure and temperature. However, there are still many unresolved issues regarding its behavior with respect to pressure and temperature. It is clear that a large portion of the phase diagram up to 14 GPa and 1000 K is unknown and many of the known regions have poorly defined phase boundaries. For example, some of the publications admit that their pressure sensors are unreliable [1,2]. Some of the more recent publications estimate their pressures at elevated temperatures [2]. Also, much of the phase diagram has been determined primarily by resistance measurements. As one can see there is a vital need to examine the element cerium with direct measurements such as x-ray diffraction at pressure and temperature.

The focus of this discussion will be on the effects of pressure. At room temperature it is well known that cerium undergoes several phase transformations. At room temperature and room pressure cerium is stable in the γ -fcc phase [3]. This structure is stable to approximately 7 kilobars and possesses an unusual property. The derivative of the bulk modulus has been shown to be negative [4]. In other words, as you compress cerium it becomes more compressible in this pressure region. The first phase transformation, γ -fcc \rightarrow α -fcc, occurs below 10 kilobars with a volume collapse between 13% and 16%. This is the only iso-structural phase transformation observed in the lanthanide series. The most interesting aspect of this phase transition is that it occurs with such a large volume collapse. This is an indication that the 4f electrons are becoming delocalized with the application of pressure. The α -fcc phase has been shown to be stable to about 50 kilobars. At this point a phase transformation occurs to a low symmetry orthorhombic or monoclinic. There has been much discussion over these two structures. Some have suggested that sample purity is an issue [4]. The predominant belief is that the type of preparation of the sample is what determines which structure is stable [5]. Considering that the energy of the monoclinic structure is so close to that of the orthorhombic structure both of these factors may play a role. The ultra-high pressure phase is body centered tetragonal which has been observed between 13 GPa and 208 GPa [6].

A series of x-ray diffraction experiments were performed on cerium. We loaded several Merrill-Bassett diamond anvil cells (DAC) with polycrystalline cerium. The samples ranged from 50 to 100 microns in diameter. Ruby was used as a pressure marker and liquid argon as a pressure medium. It should be noted that some of the lower pressure samples were performed without a pressure medium. The samples were studied at beamline X17-C, the National Synchrotron Light Source at Brookhaven National Laboratory. Beamline X17-C is setup for energy dispersive x-ray diffraction (EDXD). The incoming radiation is polychromatic (white) with an energy range of approximately 5 to 80 KeV. The size of the beam was 50 x 60 microns and a germanium solid-state detector was used at $2\theta = 8$ and 15 degrees. The angle 2θ was calibrated with a gold foil, and the germanium detector was calibrated with common standards including: copper, rubidium, molybdenum, silver, barium, terbium, and americium.

Several x-ray diffraction spectra were taken at various pressures. The γ -fcc phase was observed between 0 and 7.3 kilobars with an initial volume (volume/atom) of $34.367 \text{ \AA}^3/\text{atom}$. At 7.3 kilobars a phase transition from γ -fcc to α -fcc was observed with a volume collapse of 14.6%. The value of the volume collapse is exceptionally reliable considering the fact that both γ -fcc and α -fcc are observed in the same x-ray diffraction spectrum. The γ -fcc phase remains stable up to approximately 50 kilobars. At this point it was possible that either the orthorhombic or monoclinic structure could be observed. At 51 kilobars the monoclinic C2/m structure (4 atoms/cell) was observed as shown in Figure 1a and 1b. The monoclinic structure remained stable to the highest pressure of 72 kilobars with a volume of $23.5 \text{ \AA}^3/\text{atom}$. The sample was downloaded to zero pressure at which all the phase transformations were reversible. However, the phase transitions exhibit a large hysteresis with respect

to pressure. For example, C2/m remained stable down to 43 kilobars. The pressure-volume data is shown in Figure 2. The equation of state has not been calculated for each structure because of the limited number of data points. Therefore, the bulk modulus, B, and the pressure derivatives of the bulk modulus are not calculated. These calculations could be made easily. However, it is in our best interest to collect more data to insure the accuracy of these values. The axial ratios, c/a and b/a , are calculated for C2/m and are found to be in good agreement with previous data [5]. The equation defining the axial ratios are given as follows:

$$c/a = -.0006 \times \text{Pressure} + 1.002$$

$$b/a = -.0004 \times \text{Pressure} + 0.567.$$

These experiments have provided several high quality data points in the P-T phase diagram. The γ -fcc, α -fcc, and C2/m structures were observed with energy dispersive x-ray diffraction up to a maximum pressure 72 kilobars.

This is the beginning of a series of experiments that will be performed over P-T space. More data will be collected at room temperature, as well as, elevated temperatures which may extend beyond the melting curve. Also, dynamic experiments will be made to ensure accuracy in the interpretation of the physical properties of cerium. It is clear from the amount of conflicting data and indirect measurements that the phase diagram for cerium is not well understood.

These experiments were carried out, in part, at the National Synchrotron Light Source, Brookhaven National Laboratory. Beamline scientist Jingzhu Hu assisted in the operation of beamline X17-C. Rachel Hixson and Rush Davidson assisted in the loading of the diamond anvil cells.

References:

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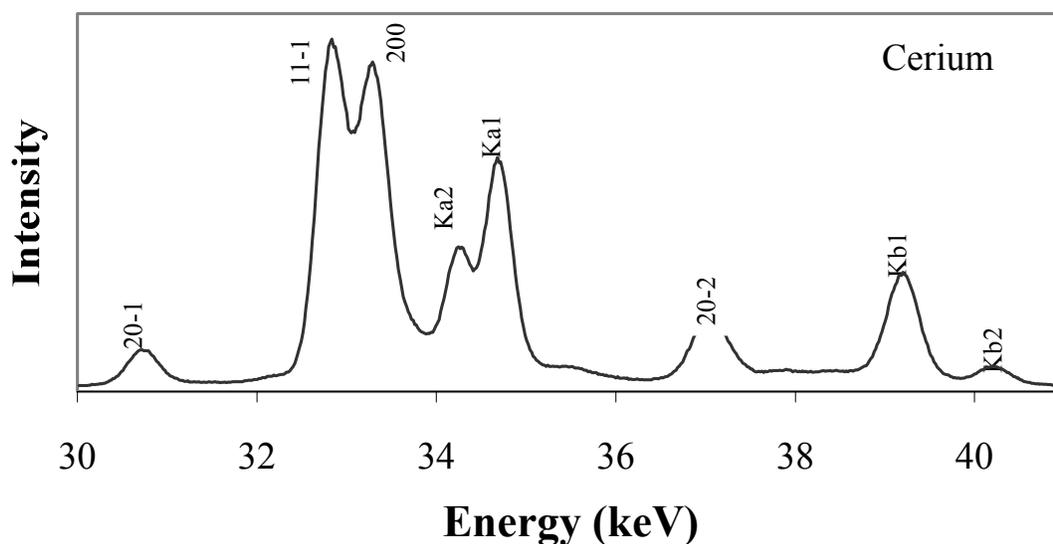


Figure 1a: EDXD spectra of Ce at 51 kilobars. Cerium is indexed as monoclinic C2/m. The lattice parameters are $a = 5.848 \text{ \AA}$, $b = 3.208 \text{ \AA}$, $c = 5.689 \text{ \AA}$, and $\beta = 112.4^\circ$. $E_d = 88.752 \pm 0.002$.

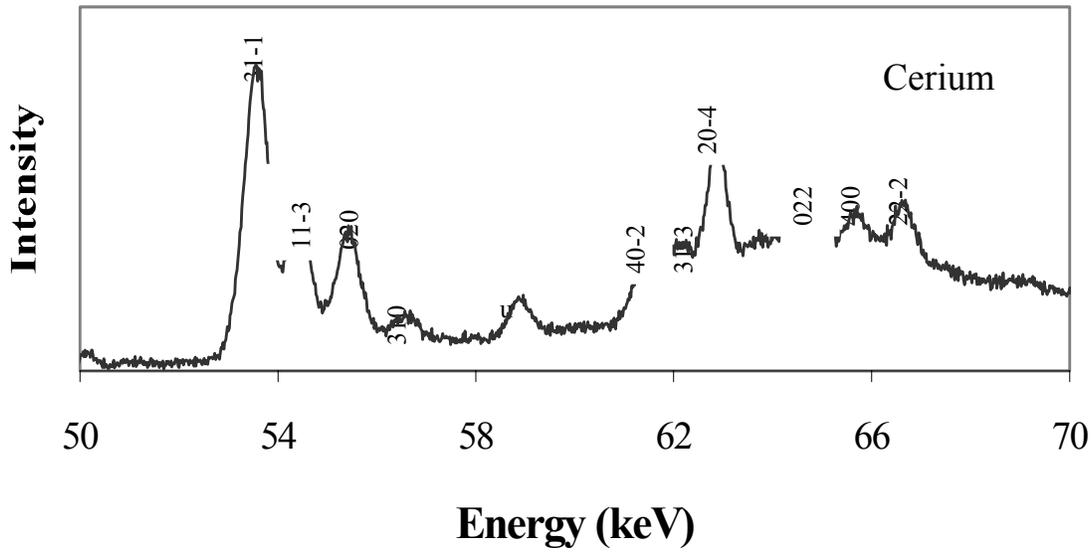


Figure 1b: EDXD spectra of Ce at 51 kilobars. Cerium is indexed as monoclinic C2/m. The weak peak labeled u corresponds to an unknown peak. The lattice parameters are $a = 5.848 \text{ \AA}$, $b = 3.208 \text{ \AA}$, $c = 5.689 \text{ \AA}$, and $\beta = 112.4^\circ$. $E_d = 88.752 \pm 0.002$.

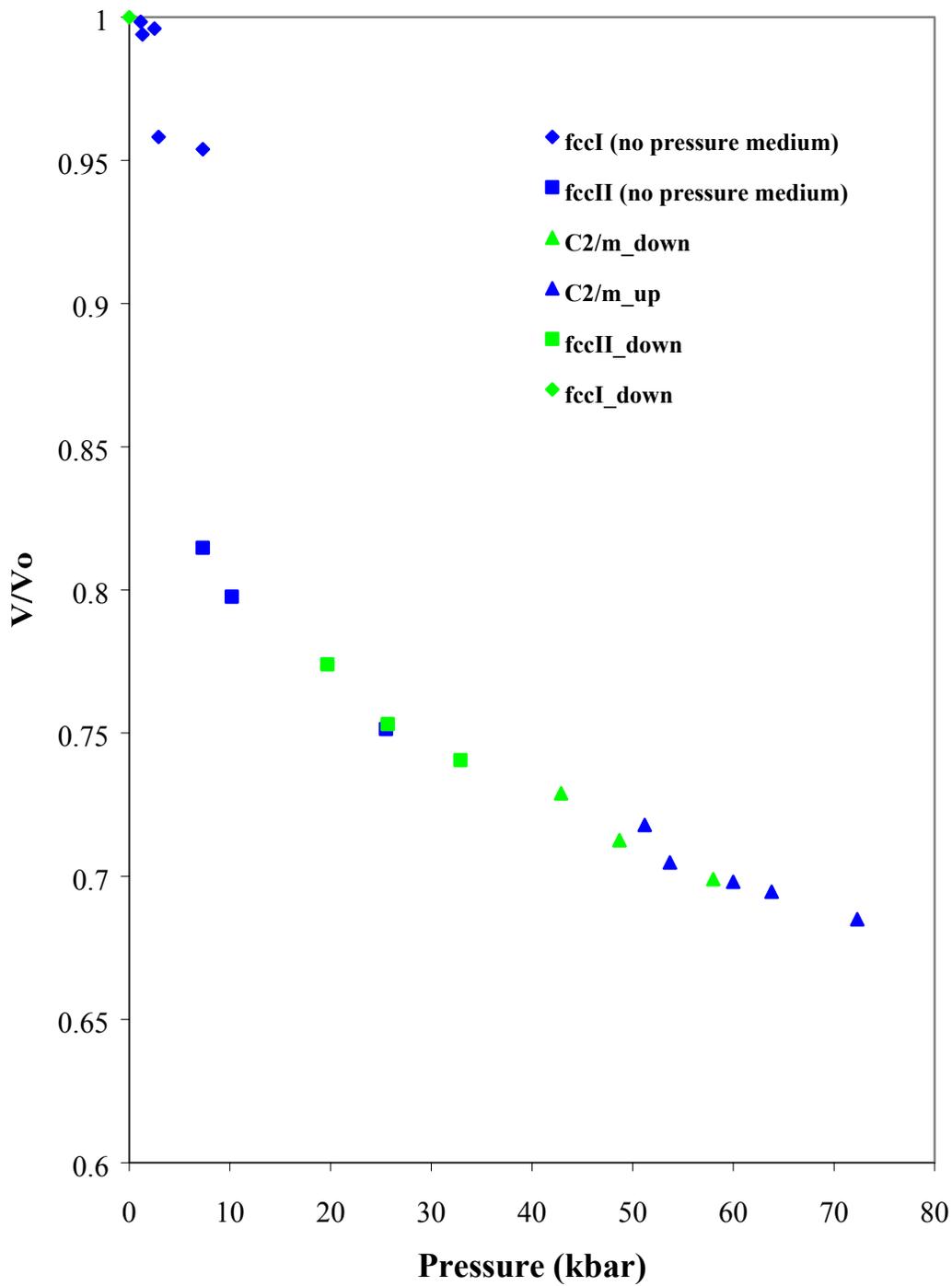


Figure 2: The pressure-volume curve of Cerium up to 72 kilobars. The blue data points represent uploading and the green data points represent downloading.