Different Results for the Equilibrium Phases of Cerium above 5 GPa

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The phases of cerium above 5 GPa have been studied using angle-dispersive powder diffraction techniques. The phase obtained between 5 and 12 GPa at room temperature with filings of Ce has a monoclinic, distorted-fcc structure with four atoms in a C-face-centered unit cell. Heating to 373 K for many hours yields the known α-U phase. With a single cut piece as a sample, the α-U phase is obtained at room temperature. [S0031-9007(97)03138-4]

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The richly varying behavior of cerium under different pressure and temperature conditions signals a subtly balanced electronic structure that makes it a key to the understanding of other lanthanide and actinide elements [1–5]. A particularly extensive literature has been generated by the unique phenomenon of the isostructural γ-Ce(fcc) $\rightarrow$ α-Ce(fcc) transition, accompanied by a large volume collapse at 0.7 GPa at room temperature, but terminating in a solid-solid critical point at 550 K [1]. Despite much effort, the precise mechanism of this transition has long remained uncertain [1]. Recent theoretical work argues for a Mott transition model, in which $4f$ electron delocalization in α-Ce is a central factor [4,5], and this view of α-Ce as a $4f$ metal also accounts for the higher pressure behavior [3,4]. However, the phase to which α-Ce transforms at 5 GPa was already a well-established subject of dispute in 1977 [2], had become "one of the most controversial subjects concerning high-pressure phases" a decade later [6], and still remains contested and unresolved up to the present time [7–9]. One body of literature claims that α-Ce transforms to the α-U structure, and the theoretical studies have taken this to be the case [3,4]. But another body of work concludes with equal certainty that the transition is to a different, monoclinic distorted-fcc structure. Remarkably little effort has been made to confront this oddly reproducible contradiction at the heart of a key system. There is a consensus that both forms transform to a body-centered tetragonal (bct) structure above 12 GPa [10].

In this Letter, we show that the true structure of the monoclinic form has four atoms in a unit cell with C-face-centered $C2/m$ symmetry [11]—a superstructure of the previously accepted body-centered $I2/m$ structure with two atoms per cell [1,12]. We report the first accurate determination of the variable coordinate in the α-U structure. And we demonstrate that the conflicting results obtained for the phases above 5 GPa arise from differing methods of sample preparation.

The existing nomenclature for cerium is itself rather confused and confusing. The transition at 5 GPa has generally been denoted $\alpha \rightarrow \alpha'$ [1]. The α' phase is then either α-U or the monoclinic form, and the latter is usually labeled α'' [12,13]. In addition, there have been thought to be two different monoclinic forms, α''-Ce(I) and α''-Ce(II) [11]. Since we conclude that they are identical, the transitions at room temperature simplify to fcc $\rightarrow$ fcc$'$ $\rightarrow$ $C2/m$ or α-U $\rightarrow$ bct. We will use these specific structural identifiers, except where it is necessary to revert to α', α'', etc., in referring to previous work.

Powder diffraction data were collected on station 9.1 at SRS, Daresbury, using angle-dispersive techniques, with an image-plate detector and an incident wavelength of 0.4447(1) Å [14]. We used Ce from two different ingots of 99.9% and 99.99% purity obtained from Rare Earth Products Ltd, UK; the higher purity sample was double vacuum remelted. Filings from these ingots were prepared and loaded into diamond-anvil cells under dry argon gas without any pressure medium, to minimize oxide and hydride phases. (In fact, test experiments with a methanol-ethanol medium showed no significantly different behavior.) The sample pressure was measured by the ruby fluorescence technique. Structural results were obtained by full Rietveld refinement using the program MPROF [15].

The onset of the transition from the fcc$'$ phase was first observed at 5.5(2) GPa. Figure 1 shows the powder pattern obtained at 8.3 GPa after complete transformation. The strong reflections are consistent with the body-centered monoclinic $I2/m$ structure first proposed by Ellinger and Zachariasen [12]. However, there are 17 detectable weak reflections that are not accounted for; 13 are strong enough to see in Fig. 1, as numbered. [Number "6" is not visible in the main profile, but can be seen in inset (b)]. Lines 1, 7, 12, and 13 are the four extra, superlattice reflections reported by Endo *et al.* [10], which Zachariasen [11] showed could be explained by the larger $C2/m$ unit cell. Figure 1 shows the fit obtained with the $C2/m$ structure, which accounts for all 17 of the detectable superlattice reflections. The refined lattice parameters are $a = 5.813(2)$ Å, $b = 3.145(1)$ Å, $c = 5.612(2)$ Å, and $\beta = 113.10(2)°$; the freely refined coordinates of Ce in the $4(i)$ positions of $C2/m$ [11] are $(0.2800(5), 0, 0.2516(6))$. This structure would be $I2/m$ if the coordinates were $(\frac{1}{4}, 0, \frac{1}{4})$. Constrained refinements show that z probably does not differ significantly from $\frac{1}{4}$.

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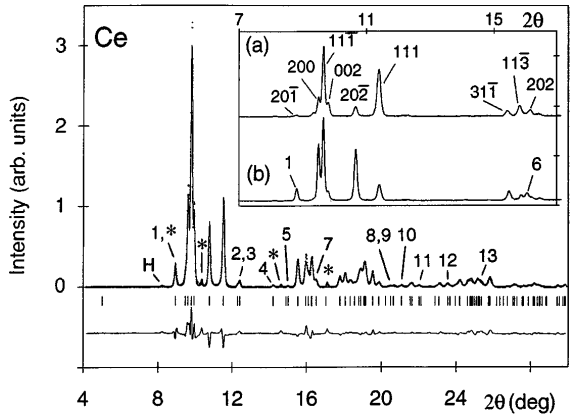

FIG. 1. Rietveld fit to an integrated profile from the $C2/m$ phase of Ce at 8.3 GPa. The tick marks show all the reflections allowed by the space group symmetry. The difference between the observed and calculated profiles is shown below the tick marks. The labeling of features in the profile is explained in the text. The inset shows profiles obtained by integrating two sectors, 90° apart around the powder rings, in another 2D image exhibiting pronounced preferred orientation effects. Reflections are indexed on the $C2/m$ unit cell in (a).

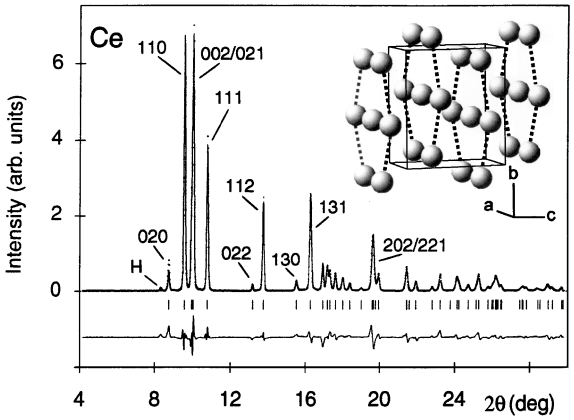

FIG. 2. Rietveld fit to an integrated profile from the α-U phase of Ce at 7.5 GPa. Reflection tick marks and a difference profile are shown as in Fig. 1. Some principal reflections are indexed on the α-U unit cell. The inset shows the α-U structure, with hcp-like planes indicated.

We have taken more than ten different filed samples through the 5.5 GPa transition, and in every case observe only the $C2/m$ phase—whether the sample was from the 99.9% or 99.99% pure ingot, and whether or not a methanol-ethanol pressure medium was used. No evidence of the α-U phase has been observed in any of these samples at room temperature. Five of the samples were taken above 12 GPa into the bct phase. On pressure decrease, they all returned to the $C2/m$ structure, again with no evidence of α-U.

However, 2D images recorded at room temperature after heating at 373 K for several hours in the range 6–8 GPa showed a mixture of smooth $C2/m$ powder rings and a few very intense spots at 2θ values expected for α-U. A single-phase α-U pattern with a much larger number of smaller spots was obtained (at room temperature) when a mixed $C2/m$-bct sample at 12 GPa was heated at 373 K for 27 hours—after which the pressure on return to room temperature had fallen to 7.5 GPa. The integrated profile of this pattern is shown in Fig. 2, together with a Rietveld fit. The refined lattice parameters are $a = 3.0143(2)$ Å, $b = 5.8935(3)$ Å, and $c = 5.1603(3)$ Å, in agreement with previous work [8,12]. The refined value of the single variable coordinate, y, for Ce in the $4(c)$ positions of *Cmcm* is 0.1014(2). This has not previously been determined, and differs significantly from the value of 0.1125 obtained in the most recent computational study [4].

All our patterns showed traces of two other phases. The weak low-angle peak labeled "*H*" in Figs. 1 and 2 is the strongest line from CeH_2. This line was reported but not identified by Olsen *et al.* [7]—at $d \sim 3.1$ Å in their Fig. 2. It can also be seen on the low-angle side of the α-U (020) peak in Gu *et al.*'s [8] pattern at 8 GPa, and persisting at 19 GPa (their Fig. 2). Asterisks in Fig. 1 mark some weak extra peaks—the lowest-angle one almost exactly coincides with superlattice reflection 1 of $C2/m$. These can be fitted to a fcc structure, with an extrapolated ambient-pressure lattice parameter close to that reported previously for a phase apparently intermediate between the fcc and fcc′ phases [16]. Reflections from this tentatively identified "int-fcc" phase have been seen before under pressure. Olsen *et al.* [7] report a line at ~2.9 Å which could be $(20\bar{1})$ from $C2/m$ (peak 1 in Fig. 1). However, indexing it as (111) of the int-fcc phase would explain why the ~2.9 Å line continues well beyond the pressure range of $C2/m$ in Ref. [7]. This interpretation is supported by the fact that the authors also detected (but could not identify) the (200) reflection of int-fcc at ~2.5 Å. In Gu *et al.* [8], a ~2.9 Å line can be seen just to the high-angle side of the α-U (020) peak at 8 GPa. Since its height relative to the CeH_2 line remains the same in their 19 GPa pattern, it is again mostly or all attributable to int-fcc rather than $C2/m$, in keeping with Gu *et al.*'s [8] finding that their sample contains very little monoclinic phase at 8 GPa [17].

When Zachariasen [11] first identified the $C2/m$ phase from the data of Endo *et al.* [10], he interpreted it as an additional phase. But the conclusion that there are two distinct monoclinic forms seems improbable. As discussed in some detail by Zachariasen and Ellinger (ZE), patterns from the monoclinic phase are strongly affected by preferred orientation [13]. We also observe this. The inset to Fig. 1 shows typical profiles obtained if a full 2D image is integrated over two narrow arcs 90° apart (around the powder rings). This simulates the more restricted data-recording range available in the earlier work, and the intensity differences are striking. Among other things, the strongest $C2/m$ superlattice reflection—$(20\bar{1})$, labeled "1"—is easily visible in (b) but not in (a). The intensities in (a) correspond quite closely to those observed by ZE at 9 GPa [18] and Schaufelberger and Merx at 10 GPa [19], while (b) is close to the pattern reported by Endo *et al.* [10]. ZE do report a profile more like (b) for one of their six samples, but in that case the sample

also contained the α-U phase, and an (unexpected) extra weak reflection at ~2.9 Å would almost certainly have gone un-noticed close to the (020) reflection from α-U at ~2.98 Å. Olsen *et al.* do not report peak intensities [7], but their group of three reflections around $d \sim 1.6$ Å corresponds to the $(31\bar{1})$, $(11\bar{3})$, and (202) peaks in (a) rather than the quite different profile around the same 2θ in (b). The literature thus contains no clear evidence to suggest there are two different monoclinic forms of Ce, and we conclude that the phase generally labeled α'' has the $C2/m$ structure in all cases.

Figure 3 shows how the $C2/m$ structure is related to the fcc′ phase (lattice parameter a_c). The body-centered cell previously identified for α'' is also outlined (lattice parameters a', b', c' and β'), and this cell provides the simplest means of describing the monoclinic distortion of the lattice. There is a small elongation along a' $[2a'/(b' + c') > \sqrt{2}]$; $\beta' \sim 92°$; and $\phi \sim 90.3°$, which makes c' slightly greater than b'. In the (true) $C2/m$ structure, alternate C-centered layers are displaced $\delta x \sim 0.35$ Å along **a** [20], as shown by the arrows, in a unit cell with $\mathbf{a} = \mathbf{c}' - \mathbf{a}'$, $\mathbf{b} = \mathbf{b}'$, and $\mathbf{c} = \mathbf{c}' + \mathbf{a}'$. The C-centered layers in this structure can be seen to correspond to the close-packed (111) planes of the fcc′ structure, and the δx displacements lie in these planes. The bct phase has the body-centered cell of Fig. 3 with $a_t =$

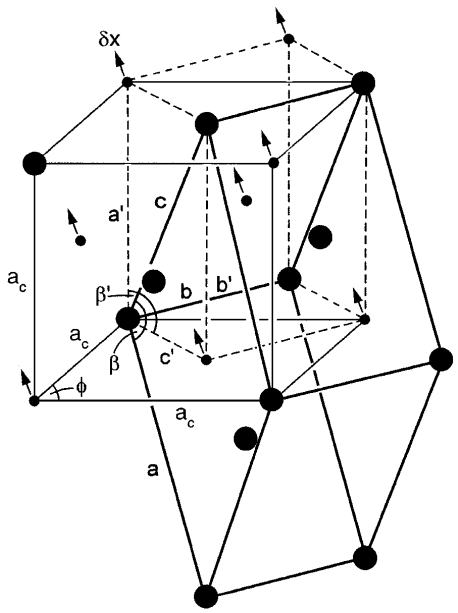

FIG. 3. The relationship of the cubic fcc′ unit cell (thin line; lattice parameter a_c), the $I2/m$ monoclinic cell (dashed line; lattice parameters a', b', c', and β'), and the $C2/m$ cell (heavy line; lattice parameters a, b, c, and β) of Ce. The large filled circles are $C2/m$ lattice points; the small filled circles are (additional) lattice points in the other cells. Arrows show the δx displacements of the $C2/m$ structure, treating all the filled circles as representing Ce atoms [with the standard origin shifted to put an atom at $(0, 0, 0)$]. The angle ϕ is referred to in the text. The $I2/m$ cell becomes that of the body-centered tetragonal phase when $b' = c'$ and $\beta' = 90°$. The small differences of a', $\sqrt{2}\,b'$, and $\sqrt{2}\,c'$ from a_c are not shown.

$b' = c'$, $c_t = a'$, and $\beta' = 90°$. Thus the structures in the sequence fcc → fcc′ → $C2/m$ → bct are all closely similar. By contrast, the α-U structure (shown in the inset of Fig. 2) can be described as distorted hcp, and thus the transitions fcc′ → α-U → bct involve relatively large structural rearrangements [9].

We now turn attention to the contradictory behaviors that have long been observed for the 5 GPa transition. They cannot be ascribed to stated sample purities or pressure conditions—samples of various nominal purities up to 99.99% have been used on both sides of the divide, with a similar range of techniques from large-anvil presses [10,19,21–23] to diamond-anvil cells [7–9,12,13], with [7–9] and without [12,13] pressure media. The commonly observed contaminant phase CeH_2 also makes no difference, as discussed above for Refs. [7,8]. However, there are *two* possible systematic differences to which we can find no clear exceptions: the α-U phase has been observed at room temperature in only, and all, studies performed on samples originating in the USA **(**[8,9], [13] (on six different samples), and [24] (as reinterpreted in Ref. [12])**)**—perhaps reflecting some small difference in impurities or microstructure—and the α-U phase has been absent at room temperature in only, and all, studies (including our own) that have used filed **(**[7], [10] (see Ref. [11]) or otherwise cold-worked samples [19] (see Ref. [13]) and [21,23,25]**)**. (α-U was obtained [26] from a cold-worked sample in Ref. [22], but with heating through the transition at 420 K.) It is a curious accident that all experiments appear to have been done with only non-cold-worked USA samples, and cold-worked non-USA samples.

We have therefore performed two further experiments. In the first, we used filings from the USA-originating sample from which "small chips" were cut in the recent diffraction study of Zhao and Holzapfel [9]. The filings transformed completely to the $C2/m$ phase at 5 GPa, with no evidence of any α-U phase. This is in direct contrast to the results of Zhao and Holzapfel on the same sample material [9], and excludes sample origin as a factor. As with our previous experiments on filed samples, heating for two hours at 373 K resulted in a partial transformation to an α-U phase characterized by spotty powder rings. We then cut small chips from the 99.9% ingot from Rare Earth Products used to provide filings for our main studies, reported above. These pieces gave only very weak powder rings from the $C2/m$ phase above 5 GPa, in a diffraction pattern dominated by several very intense spots from the α-U phase—in contrast to the behavior obtained (above) with filings from the same ingot. Over 20 years of dispute about the behavior in Ce above 5 GPa thus appears to have arisen simply from the sample preparation.

Since the $C2/m$ structure is fcc-like and α-U is hcp-like, it is interesting to compare their relationship with the transformation between fcc γ-Ce and dhcp β-Ce on cooling at ambient pressure [2]. This is known to be extremely sluggish, but to be assisted by impurities, large

grain size, and plastic deformation [2]. Our results would seem to rule out impurities as a factor in the 5 GPa transition. The fact that α-U tends to recrystallize from only a very few centers in the fcc′ phase [8] suggests a possible dependence on grain size—nucleation may require a minimum critical size that cold working breaks up. Though chips and filings alike give very sharp, smooth powder rings in the fcc′ phase, indicating a small grain size (≤ 1 μm) in both cases, it is possible that chips retain a few larger grains that are still too small to give discernible spots in our powder patterns, or happen not to be in strongly diffracting orientations. Otherwise, we speculate that dislocations introduced by cold working somehow favor the small shear distortion of the fcc′ $\rightarrow$ $C2/m$ transition over the larger structural rearrangements of the fcc′ $\rightarrow$ α-U transition [9]. However, this is counter to the effect on the $\gamma \rightarrow \beta$ transition where cold working assists rather than impedes fcc-like $\rightarrow$ hcp-like. Further studies will be needed to reach more definite conclusions.

There remains the matter of which is the true equilibrium phase. The general belief that it is the α-U form rests on ZE's finding that pressure cycling through the 5 GPa transition increases the proportion of α-U in the sample [13]. But it is possible that the pressure limits of the cycling favored α-U because of the much larger range of coexistence α-U and fcc′ [13,21], and so we have repeated this test on two samples. Starting from almost pure α-U at 7 GPa, we reduced the pressure to 2.5 GPa so that transformation to the fcc′ phase was complete, and then recompressed to 7 GPa. After only one cycle, the sample was almost entirely $C2/m$ in both cases. The case for α-U thus appears far from certain. Other considerations are that the densities of the two phases are almost the same [13]—we find the α-U phase only 0.11(8)% denser—and that, although the closest near-neighbor distance is 0.1 Å shorter in α-U, $C2/m$ has five near neighbors at ≤ 3.1 Å compared with four in α-U. Given the dependence on an as yet unknown factor in the microstructure, a computational comparison of the two phases may be the way to obtain a decisive answer.

In summary, we conclude that the $C2/m$ structure is the only monoclinic form of Ce in the range 5–12 GPa, and that the conflicting results previously obtained for the behavior above 5 GPa have arisen from differences in sample production and preparation. The sensitivity to this factor means it cannot be decided from existing experimental evidence whether $C2/m$ or α-U is the equilibrium phase at room temperature. But the balance of probabilities now requires conclusions about the role of $4f$ electron delocalization in the $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \alpha'$ transitions to be reconsidered for the case that α' is $C2/m$.

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