Diffusionless $\gamma \rightleftarrows \alpha$ Phase Transition in Polycrystalline and Single-Crystal Cerium

F. Decremps,[1] L. Belhadi,[1] D. L. Farber,[2] K. T. Moore,[2] F. Occelli,[3] M. Gauthier,[1] A. Polian,[1] D. Antonangeli,[1] C. M. Aracne-Ruddle,[2] and B. Amadon[3]

[1]*IMPMC, Université Pierre et Marie Curie, 75252 Paris, France*
[2]*LLNL, Livermore, California 94550, USA*
[3]*CEA, DAM, DIF, F-91297 Arpajon, France*

(Received 1 November 2010; revised manuscript received 8 December 2010; published 11 February 2011)

The cerium $\gamma \rightleftarrows \alpha$ transition was investigated using high-pressure, high-temperature angle-dispersive x-ray diffraction measurements on both poly- and single-crystalline samples, explicitly addressing symmetry change and transformation paths. The isomorphic hypothesis of the transition is confirmed, with a transition line ending at a solid-solid critical point. The critical exponent is determined, showing a universal behavior that can be pictured as a liquid-gas transition. We further report an isomorphic transition between two single crystals (with more than 14% of volume difference), an unparalleled observation in solid-state matter interpreted in terms of dislocation-induced diffusionless first-order phase transformation.

DOI: 10.1103/PhysRevLett.106.065701 PACS numbers: 64.60.F−, 64.30.Ef, 64.70.K−

In the most widely accepted picture, and in a unique manner among all the elements of the periodic table, Ce undergoes an isomorphic $\gamma \rightleftarrows \alpha$ first-order transition with a volume collapse of about 14%. Even more intriguing, the corresponding transition line seems to end at a solid-solid critical point (CP) around $p_c = 1.5$ GPa and $T_c = 480$ K [1,2]. Although there exists a common consensus that these features are tightly linked to the behavior of the single $4f$ electron, recent and thorough theoretical investigations still dispute over the electronic nature of the transition. Among them, the Mott transition scenario [3] and the Kondo volume collapse (KVC) model [4] have emerged, both being in good agreement with state-of-the-art photoemission experiments [5], x-ray [1,2] and neutron diffraction [6] and spectroscopic [7,8] studies. Mott transition and KVC models mainly differ on the role of the *spd* electrons in the transition, but they both assume that the $\gamma \rightleftarrows \alpha$ transformation is isostructural. According to Landau formalism, this is required to sustain the hypothesis of a CP. Alternatively, Eliashberg and Capellmann [9] proposed γ- and α-Ce to have different structures, and suggested the existence of a tricritical point. The experimental basis underlying this last hypothesis can be found in early x-ray diffraction work by Davis and Adams [10] where the compressibility was observed to diverge in the vicinity of the ending point, but only for the lower symmetry phase (i.e., α). In this case, the Landau theory of phase transformation imposes the symmetries of γ and α phases to be different and the second-order nature for the phase transition beyond the terminal point (here thus tricritical). This $\gamma \rightleftarrows \alpha$ transition scenario is in line with predictions by Nikolaev and Michel [11] based on a symmetry group change from $Fm\bar{3}m$ to $Pa\bar{3}$, a transformation mechanism recently confirmed by time-differential perturbed angular correlations measurements [12]. Interestingly, the same fcc to distorted fcc transition has been observed to occur in elements bordering Ce in the periodic table (La [13] and Pr [14]), as well as in cerium-based alloys [15] or δ-Pu [16].

In this Letter, we investigate the Ce structure across the $\gamma \rightleftarrows \alpha$ phase transition (Fig. 1) through high-pressure and high-temperature x-ray diffraction (XRD) experiments both on poly- and single-crystalline samples of pure Ce. The controversial question of the transformation mechanism is reappraised on the basis of crystallographical and thermodynamic arguments, showing a fair agreement with the isomorphic scenario and the existence of a CP. Further, the hysteresis region, so far not considered in depth, is here found to shrink to zero at $T = 460$ K, the temperature where both energetic terms and volume collapse at the transition vanish (see inset in Fig. 1). Remarkably, we will see that the equation of state of cerium at this critical temperature can be understood in the framework of the scaling theory of the liquid-gas transition of classical systems. Finally, the whole present data set (polycrystals and single crystals) supports the existence of an isostructural first-order diffusionless phase transformation with a large volume jump, an unparalleled picture of phase transition in solid-state matter.

Since the Ce physical properties are known to be affected by impurities even in very small concentration, high-purity samples were used as starting material. Polycrystalline samples were produced in a purpose-built crucible using a triarc furnace under argon atmosphere starting from material directly scraped from a cerium ingot (99.99%) with a diamond file in a glove box under a stream of dry nitrogen. Single crystals (discs with the surface normal parallel to the [001] direction, diameter $\simeq$ 100 μm, and thickness $\simeq$ 30 μm) were prepared by femtosecond laser cutting and mechanical polishing under a controlled atmosphere [17]. Samples were loaded in a

rhenium gasket hole of 400 μm diameter placed in a membrane diamond anvil cell (DAC), resistively heated and equipped with 800 μm culet size diamonds. Helium was used as the pressure transmitting medium. We used DACs able to independently control pressure and temperature without bringing the cell back to ambient conditions. It was placed in a vacuum housing designed to maintain stable high temperatures for periods of days. The temperature was regulated using an electronic module and measured with an accuracy better than 1 K by two K-type thermocouples with one glued on each anvil. Hysteresis was determined through the measurement of the lattice parameter at constant temperature during pressure sweeps at a continuous slow rate of the order of 0.04 bar/ min on the membrane DAC. Pressures were determined from the SrB_4O_7: Sm^{2+} fluorescence line before and after collection of each diffraction pattern. These two readings always provided identical pressure values (pressure uncertainty given by symbols sizes in all figures).

Figure 2(a) shows a typical XRD pattern, where no trace of oxidized cerium can be observed. Although we were unable to extract reliable intensities from the diffraction images, we carried out refinements testing both a perfect- and a distorted-fcc structure [11,13,14], without getting any evidence in favor of a possible distorted-fcc structure, irrespectively of the poly- or single-crystalline nature of the samples. In particular, the persisting absence of a new reflection peak on the whole set of XRD patterns clearly indicates no lowering of symmetry (down to, for example, a $Pa\bar{3}$ space group).

As shown in Fig. 2(b) for a typical case, several anomalies have been repeatedly observed on the isothermal pressure evolution of the volume. Besides the well known softening of the isothermal bulk modulus in the γ phase approaching the transition [1,2,6], the presence of metastability and hysteresis regions can be clearly identified. With increasing pressure, the γ phase is observed as the only phase up to 0.92 GPa. Above this pressure, the α phase appears (in coexistence with the γ phase over a large pressure range). As further discussed later in the Letter, the volume of the metastable γ phase is surprisingly shown to increase in the coexistence region (as already observed, but

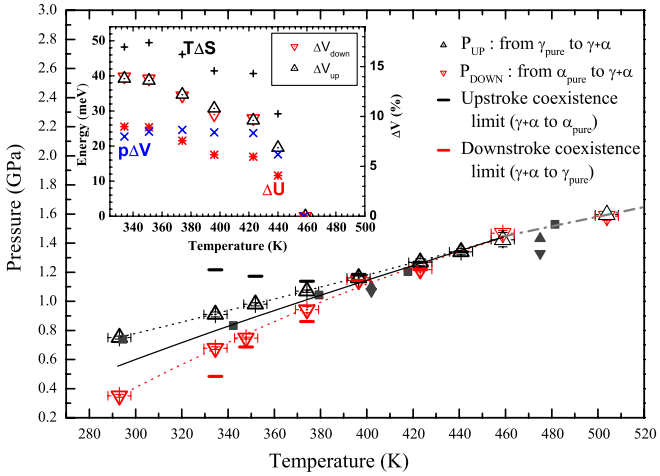

FIG. 1 (color online). (color online) Pressure vs temperature nonequilibrium phase diagram of cerium (dotted lines, as guides for the eyes). Up [black] (down [red]) open triangles denote the occurrence of the α (γ) phase increasing (decreasing) pressure along an isotherm. Black solid curve: thermodynamic transition line. Grey dash-dotted curve: Widom-like line behind the CP (determined from the FHWM pressure dependence of the diffraction peaks). Dark grey squares: data from Ref [2]. Dark grey triangles: data from Ref [1]. The domain of metastability for each phase is also shown as horizontal segments. Inset: Temperature dependence of the volume collapse (right scale, triangles) and energetic terms (left scale). Using both the continuity of the Gibbs free energy at the transition and the Clausius-Clapeyron relation, entropy term $T\Delta S$ (black plus signs), internal energy ΔU (red stars), and $p\Delta V$ (blue crosses) across the $\gamma \rightleftarrows \alpha$ thermodynamic transition line have been determined. In agreement with Refs. [23,26], our experimental results confirm the entropic stabilization of the γ phase (the $T\Delta S$ term is the predominant driving force of the transition below the CP). All values vanish at $T_c = 460$ K.

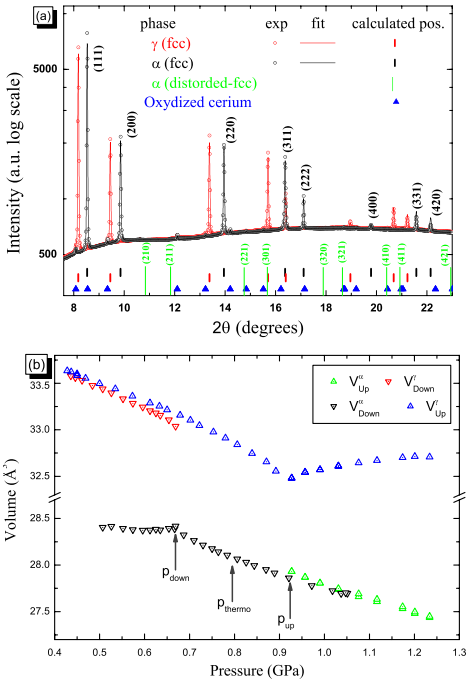

FIG. 2 (color online). (color online) (a) XRD patterns of polycrystalline cerium at 396 K: γ (open red circles, 1.18 GPa) and α (open black circles, 1.37 GPa) with corresponding Rietveld fits (solid lines). The use of a logarithmic scale highlights the absence of even a tiny contribution of impurities to the diffraction patters. The experiments were carried out at the ID09 beam line of the ESRF, using a monochromatic beam of 0.4138 Å and an image plate detector. The GSAS suite of programs with the EXPGUI graphical interface have then be used to fit all integrated diffraction patterns (using FIT2D). (b) Experimental synopsis of the V-p variation at 334 K. Up and down triangles denote increasing and decreasing pressure, respectively.

not recognized, by Lipp *et al.* [2]). Upon decompression, the pure α-Ce is retained down to 0.67 GPa, the pressure at which diffraction peaks from the γ phase begin to germinate. Another puzzling (but very important, as discussed later) aspect of our results is the noncompressibility observed in the metastable α-Ce down to 0.51 GPa, pressure at which the pure γ phase is recovered. Similar observations holds for all the isotherms below the CP. Thus, we can estimate the hysteresis loop and thereof the thermodynamic transition line [18].

The analogy between the experimental $p(V)$ curves given in Fig. 3 and the liquid-gas transition is obviously tempting. Although a finite-temperature Mott transition scenario, as for the instance proposed to explain the pressure and temperature dependence of conductivity of Cr-doped V_2O_3 [19], does not stand in our case, we point out that the $\gamma \rightleftarrows \alpha$ transformation in cerium may also by pictured in the framework of a KVC model, taking into account the valence histogram of the γ and α phases recently calculated by dynamical mean-field theory [20]. In this generic description, the most probable atomic configuration of the f electron in γ-Ce is a single occupied state, corresponding to a gaslike regime. Conversely, the α phase can be pictured as a "liquid" where the probability of double occupancy is calculated to be significant. Within this rough analogy, the properties of cerium in the vicinity of (p_c, T_c) are expected to follow a critical behavior $m \sim \pm|h|^{1/\delta}$, where the order parameter is the lattice parameter [21] and h the reduced pressure $(p - p_c)/p_c$. The pressure dependence of the lattice parameter at $T = T_c = 460$ K shows a vertical tangent at the critical pressure $p = p_c$

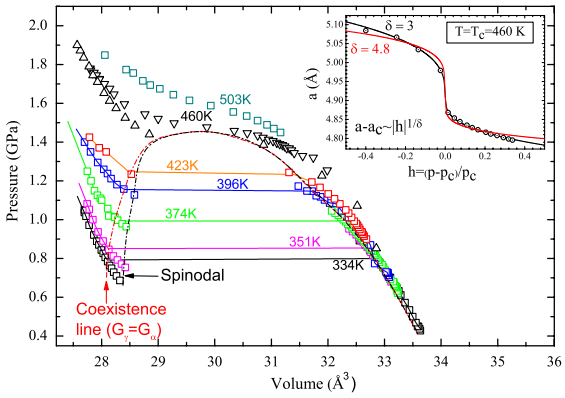

FIG. 3 (color online). (color online) Clapeyron diagram of Ce for a few representative isotherms (neglecting kinetics effects in the coexistence regions). Above $T = 460$ K, the volume jump at the transition is no longer observed, replaced by a continuous variation with pressure. The coexistence line (dash-dotted red line) delimits the region where the system stands in a biphasic configuration, whereas the spinodal line (dash-dotted black line) represents the boundary between metastable and unstable conditions. Inset: lattice parameter a as a function of pressure p at the critical temperature $T_c = 460$ K. The solid lines are fit according to critical behavior theories (mean-field in solid black line and 3D-Ising model in solid red line).

(inset Fig. 3). Consistent with the theoretical analysis by Dzero *et al* [22], the best fit value $\delta = 3$ reveals a mean-field regime for p close to $p_c = 1.44$ GPa, whereas the three-dimensional (3D) Ising value ($\delta = 4.814$) shows a poor match to the experimental observation.

All the so-far-presented results do not discriminate between powder and single crystal. On the other hand, the angular x-ray diffraction collected in the four runs using single-crystalline samples allowed us to address in detail the transformation mechanisms of the $\gamma \rightleftarrows \alpha$ transition. Indeed, as shown for the 318 K isotherm in Fig. 4, we clearly observe a transition path where, in spite of the large volume collapse (about 14%), both the single crystallinity and the orientation matrix are preserved. Even more stimulating, the image plate recorded in the metastable region demonstrates the occurrence of two single crystals in coexistence with the same structure and orientation. All these features clearly call for a compelling scenario of a diffusionless phase transformation induced by the strain energy. This scenario is consistent with the huge elastic softening of the longitudinal mode observed by ultrasonic studies [23], but contrasts to what is usually observed in a purely martensitic transformation: a path of homogenous collapse of the unit cell *without any* shearing can be proposed here to account for our observations. Whereas such phenomenological description has never been previously proposed for any kind of element, we emphasize that a dislocation based mechanism could sustain this conjecture. Since the α and γ crystals remain in crystallographic registry, but have a 14% volume change between phases, there must be a large number of edge dislocations at the α-γ interface to accommodate the atomic lattice strain. How many dislocations, or their exact nature is beyond the scope of this work. However, proof of their existence can be gleaned by the results of Zukas *et al* [24], where upon multiple transformations from γ to α by compression, deformation bands were observed in optical microscopy. Deformation bands are formed through the production and accumulation of edge dislocations [25]. The α-γ interface must act as the source for the edge dislocations due to the huge lattice mismatch, producing more dislocations with each subsequent transformation. After enough transformation cycles, the edge dislocations from the α-γ interface are appreciable enough to produce the deformation bands observed by Zukas *et al* [24]. Finally, this scenario also helps to reconcile the previously mentioned singular volume-pressure dependence of the metastable phases [i.e., the apparent negative value of the bulk modulus, see Fig. 2(b)] with the thermodynamic condition of a positive compressibility. Indeed, in the case of a γ-to-α transition (upstroke), the effect of the external pressure on the γ phase is, in the coexistence region, to increase the nucleation rate of the α phase. The negative volume difference between the two structures then induces stress relaxation at the γ-α interfaces. The pressure effect on the metastable phase is thus dual: (i) a classic "direct" volume reduction according to the thermodynamic expectations, and (ii) an

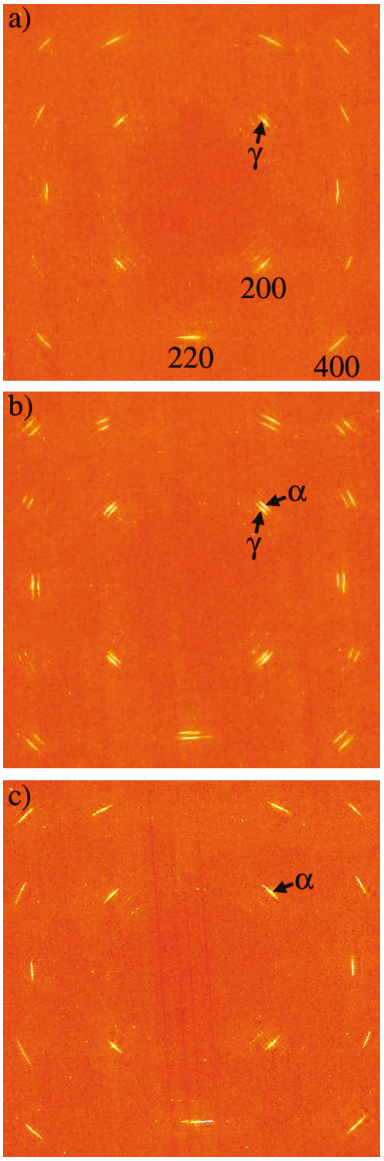

FIG. 4 (color online). 2D images of XRD diffraction patterns collected on single-crystalline cerium at 318 K across the phase transition. We observe a pure γ phase at $p = 0.32$ GPa (a) and a pure α phase at $p = 1.19$ GPa (c). At $p = 0.61$ GPa (b), two single crystals coexist with the same structure and the same orientation but with 14% of volume difference. According to these observations, a speculative synopsis of diffusionless phase transformation in Ce can be proposed: numerous small blocks of α phase could occur in the coexistence region as supported by diffraction patterns showing a mixture of both phases consistently observed as the 20 μm beam was scanned across the sample (diameter $\simeq$ 100 μm). Had there been one single region of α that nucleated, grew, and consumed the γ crystal, the pattern would change with beam location. Further, the nucleation and growth of a single site is flawed from simple energetic considerations. A single crystal of α remains—after the transformation with multiple nucleation sites—because each α crystallite is in crystallographic registry with the γ lattice. Thus, as the particles grow and impinge upon one another, their interfaces are in registry, allowing the crystallites to unite to form one larger crystal. This transformation is reversible, thus once the full transformation is complete, a single crystal of α (upon compression) or γ (upon release) remains.

opposite effect due to the nucleation of the stable α phase with a smaller volume. The issue of an apparent negative value of the bulk modulus for the metastable phase thus just signifies that the latter is more pronounced than the former. Identical arguments may be used to explain the behavior of the metastable α phase upon decreasing pressure.

We thank C. Denoual for fruitful discussion and M. Hanfland at ESRF for his help with the experiments. This work has been supported by ANR Contract No. ANR-08-BLAN-0109-01.

[1] R. I. Beecroft *et al.*, J. Phys. Chem. Solids **15**, 234 (1960).
[2] M. J. Lipp *et al.*, Phys. Rev. Lett. **101**, 165703 (2008).
[3] B. Johansson, Philos. Mag. **30**, 469 (1974).
[4] J. W. Allen and R. M. Martin, Phys. Rev. Lett. **49**, 1106 (1982); M. Lavagna *et al.*, Phys. Lett. A **90**, 210 (1982).
[5] E. Wuilloud *et al.*, Phys. Rev. B **28**, 7354 (1983); D. M. Wieliczka, C. G. Olson, and D. W. Lynch, Phys. Rev. B **29**, 3028 (1984).
[6] I.-K. Jeong *et al.*, Phys. Rev. Lett. **92**, 105702 (2004).
[7] J.-P. Rueff *et al.*, Phys. Rev. Lett. **96**, 237403 (2006).
[8] J. W. van der Eb, A. B. Kuzmenko, and D. van der Marel, Phys. Rev. Lett. **86**, 3407 (2001).
[9] G. Eliashberg *et al.*, JETP Lett. **67**, 125 (1998).
[10] B. L. Davis *et al.*, J. Phys. Chem. Solids **25**, 379 (1964).
[11] A. V. Nikolaev and K. H. Michel, Phys. Rev. B **66**, 054103 (2002).
[12] A. V. Tsvyashchenko *et al.*, Phys. Rev. B **82**, 092102 (2010).
[13] F. Porsch and W. B. Holzapfel, Phys. Rev. Lett. **70**, 4087 (1993).
[14] Y. C. Zhao, F. Porsch, and W. B. Holzapfel, Phys. Rev. B **52**, 134 (1995).
[15] J. C. Lashley *et al.*, Phys. Rev. Lett. **97**, 235701 (2006).
[16] K. T. Moore *et al.*, Phys. Rev. Lett. **96**, 206402 (2006).
[17] D. L. Farber *et al.*, High Press. Res. **26**, 1 (2006).
[18] Although the metastability region has also been observed to shape similarly as the hysteresis loop (shrinking around 460 K, see Fig. 1), we emphasize that any quantitative determination of the corresponding boundary is complicated by the interplay between thermal energy, kinetics, time nucleation/growth and time delay between two successivemeasurements.
[19] P. Limelette *et al.*, Science **302**, 89 (2003).
[20] K. Haule *et al.*, Phys. Rev. Lett. **94**, 036401 (2005); K. Haule, Phys. Rev. B **75**, 155113 (2007).
[21] L. Bartosch, M. de Souza, and M. Lang, Phys. Rev. Lett. **104**, 245701 (2010).
[22] M. Dzero *et al.*, Phys. Rev. Lett. **104**, 119901(E) (2010).
[23] F. Decremps *et al.*, Phys. Rev. B **80**, 132103 (2009).
[24] E. G. Zukas *et al.*, Metall. Trans. A **18**, 35 (1987).
[25] R. E. Hill *et al.*, *Physical Metallurgy Principles* (PWS Publishing, Boston, 1992), 3rd ed.
[26] B. Amadon *et al.*, Phys. Rev. Lett. **96**, 066402 (2006).