

Role of the Lattice in the $\gamma \rightarrow \alpha$ Phase Transition of Ce: A High-Pressure Neutron and X-Ray Diffraction Study

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The temperature and pressure dependence of the thermal displacements and lattice parameters were obtained across the $\gamma \rightarrow \alpha$ phase transition of Ce using high-pressure, high-resolution neutron and synchrotron x-ray powder diffraction. The estimated vibrational entropy change per atom in the $\gamma \rightarrow \alpha$ phase transition, $\Delta S_{\text{vib}}^{\gamma \rightarrow \alpha} \approx (0.75 \pm 0.15)k_B$, is about half of the total entropy change. The bulk modulus follows a power-law pressure dependence that is well described using the framework of electron-phonon coupling. These results clearly demonstrate the importance of lattice vibrations, in addition to the spin and charge degrees of freedom, for a complete description of the $\gamma \rightarrow \alpha$ phase transition in elemental Ce.

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Materials with electrons near the boundary between itinerant and localized behavior continue to present a major theoretical challenge. This is particularly true in the $4f$ and $5f$ systems, where this boundary appears to occur in or near the elements Ce and Pu, respectively [1]. In Pu, which possesses five allotropic phases at ambient pressure, a partial localization of some of the $5f^5$ electrons appears necessary to understand the higher temperature phases [2]. Partial localization may also be present in U compounds [3]. Ce metal is, in principle, simpler, possessing only a single $4f^1$ electron, but still displays four different phases at ambient pressure. One of the most interesting and still not completely understood phenomena in Ce is the isostructural (fcc) $\gamma \rightarrow \alpha$ phase transition, which involves a volume collapse of $\sim 17\%$ at room temperature and pressure ~ 0.8 GPa [4].

In the majority of theoretical models [4–10] the $\gamma \rightarrow \alpha$ transition has been attributed to an instability of the single $4f^1$ electron. The earliest models focused on charge instability, while later models dealt with spin instability. The promotional model postulates a transition from $4f^1 5d^1 6s^2$ (γ phase) to $4f^0 5d^2 6s^2$ (α phase), but is inconsistent with the $4f$ binding energy and the cohesive energies of other $5d^2 6s^2$ materials [5]. In the Mott transition model [5] the $4f^1$ electron in the γ phase is localized and nonbinding, but is itinerant and binding in the lower volume α phase. The energy for the phase transition is provided by the kinetic energy of the itinerant f electron. In the Kondo-volume-collapse (KVC) model [7] the $4f^1$ electron is assumed to be localized in both γ and α phases, and the phase transition is driven by the Kondo spin fluctuation energy and entropy within the context of the single-impurity Anderson model. These early models

ignored the lattice degrees of freedom; even the lattice entropy was not considered. More recent treatments [6,8,9] include both lattice and spin entropies, but still do not deal explicitly with the consequences of electron-lattice coupling despite the large volume collapse accompanying a valence change at the transition.

In rare-earth compounds the electron-phonon coupling can be important because the ionic radii of different valences often differ by over 10% [11]. In addition, it has been shown that lattice vibrational contributions renormalize the two essential parameters of the Anderson model: the hybridization energy and energy of the $4f$ state [12]. In γ -Ce, a comparison [13] of phonon dispersion curves with those of Th shows that the longitudinal branches of Ce are much softer than one would expect from the Lindemann rule [14], which accounts for the differences in interatomic distance, mass, and melting temperature of these elements. This relative softening of the longitudinal branches and the vanishing of bulk modulus as $B \sim p^\alpha$ at the transition (as discussed below) suggest an important role for electron-phonon coupling, as in $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$, where the $[\xi\xi\xi]$ longitudinal phonon branch is also soft compared to the transverse branches [15].

In this Letter, we further illuminate the role of the lattice in the Ce $\gamma \rightarrow \alpha$ transition and present the first (remarkably) neutron diffraction experiment under pressure in elemental Ce. We measured thermal displacements of Ce in the γ and α phases as a function of temperature at constant pressures 0.412 and 0.527 GPa, and as a function of pressure at 300 K. The vibrational entropy change between the γ and α phases, obtained from the thermal displacements using the Debye approximation, accounts

for about *half* of the total entropy. Furthermore, the pressure dependence of the bulk modulus and thermal displacements are consistent with the explicit inclusion of electron-phonon coupling [16,17]. These results suggest that lattice dynamics and electron-phonon coupling, in addition to electronic and spin instabilities, are essential ingredients for a complete understanding of the $\gamma \rightarrow \alpha$ phase transition in elemental Ce.

A high-purity (99.99%) polycrystalline, cylindrical solid rod of Ce (diameter ≈ 5.96 mm, length ≈ 40 mm) obtained from the Ames Laboratory was used for the measurements. Neutron powder diffraction patterns of the γ and α phases were collected at room temperature in the pressure range up to 0.85 GPa using an Al pressure cell on NPD at the Los Alamos Neutron Science Center (LANSCE) and at constant pressures 0.412 and 0.527 GPa from room temperature to 145 K on SEPD at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. As a pressure medium, a 4:1 mixture by volume of deuterated methanol and ethanol was used for the pressure-dependent measurements, and helium gas was used for the temperature-dependent measurements. Details of the cell designs are described elsewhere [18,19]. Synchrotron x-ray powder diffraction measurements were performed at room temperature in the pressure range up to 3.2 GPa using $\sim 170 \mu\text{m}^3$ sample in a diamond anvil cell (DAC) on the X-7A beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. A mixture of finely ground NaCl and silicon oil was used as a pressure medium. The pressure in the DAC was determined by measuring the shift of the $R1$ emission line of ruby [20] and calibrated using the lattice parameter of NaCl.

Figures 1(a) and 1(b) show neutron powder diffraction patterns of γ - and α -Ce with the corresponding Rietveld fits for a $Fm\bar{3}m$ structure obtained using GSAS [21] and EXPGUI [22]. Lattice, thermal, and peak profile parameters were refined, and absorption and background corrections were applied. Neither contamination from the Al pressure cell nor noticeable texture effects were observed.

Recently, there have been arguments [23,24] that α -Ce should have a different symmetry from that of γ -Ce. We find no evidence for distorted-fcc structures in the α phase. We performed model calculations assuming distortion similar to that observed in distorted-fcc Pr [25], and found that any static displacement of Ce, if it exists, is less than 0.5% of the fcc lattice parameter, given the uncertainties in our data.

Figures 2(a) and 2(b) show the isotropic thermal displacements $\langle u_{\text{iso}}^2 \rangle$ as a function of pressure and temperature. A very weak pressure dependence of $\langle u_{\text{iso}}^2 \rangle$ below 0.7 GPa, as well as a pronounced drop of $\langle u_{\text{iso}}^2 \rangle$ ($\approx 30\%$ – 40%) at the phase transition, is observed. The square symbol is the thermal displacement calculated from measured phonon dispersion curves [13] using the Born–von Kármán force model at ambient conditions [26]; the agreement with our measurement is reasonable.

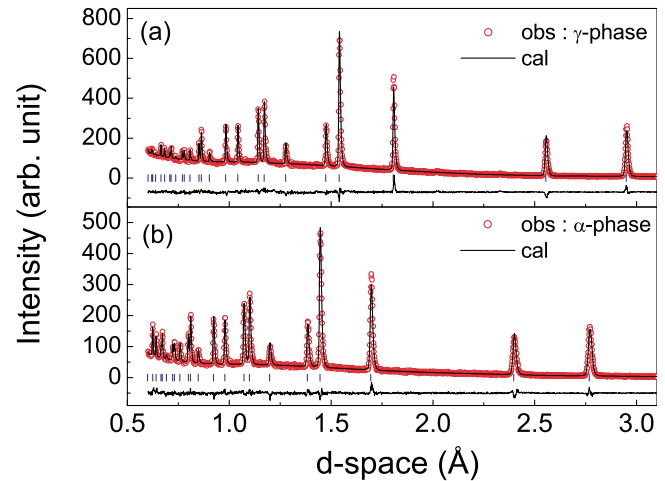


FIG. 1 (color online). Neutron powder diffraction patterns of Ce at $P = 0.527$ GPa for (a) γ phase ($T = 295$ K) and (b) α phase ($T = 149$ K) with corresponding Rietveld fits (solid line). Tick marks indicate positions of the Bragg reflections. Also shown are difference curves.

In Fig. 2(b) the closed squares represent measurements performed at 0.527 GPa with decreasing temperature and open circles at 0.412 GPa with increasing temperature. At $T = 260$ K (open circle) we had mixed γ and α phases and were able to obtain the thermal displacements of both phases simultaneously. The slight offset in the magnitudes of $\langle u^2 \rangle$ between the constant pressure and constant temperature measurements is typical of diffraction experiments [27] and is likely due to differences in backgrounds, absorption corrections, and uncertainties of the incident neutron spectra at the two facilities. Because of

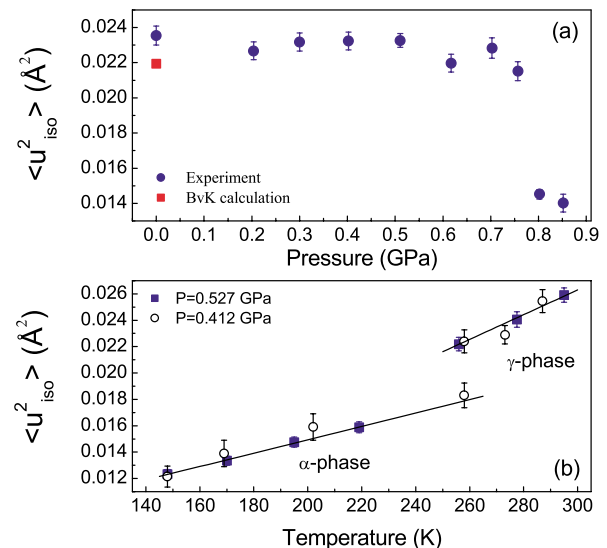


FIG. 2 (color online). (a) Isotropic thermal displacements of Ce (circles) vs pressure at 300 K. The square is calculated from Born–von Kármán force model at ambient conditions [13,26]. (b) Thermal displacements vs temperature. Data at $T = 260$ K have mixed γ and α phases. Solid lines are fits to Eq. (1) with Debye temperatures $\Theta_D^\gamma = 104(3)$ K and $\Theta_D^\alpha = 133(3)$ K.

this, the Debye temperatures are determined [28] from the slopes of the thermal displacements vs temperature curves assuming a temperature-independent offset, as in Eq. (1) below. The solid lines are fits using Eq. (1) [28] with Debye temperatures $\Theta_D^\gamma = 104(3)$ K and $\Theta_D^\alpha = 133(3)$ K,

$$\langle u^2 \rangle_{\text{measured}} = \langle u^2 \rangle_{\text{offset}} + \frac{3\hbar}{M\omega_D} \left[\frac{1}{4} + \left(\frac{T}{\Theta_D} \right)^2 \Phi_1 \right], \quad (1)$$

where $\Phi_1 = \int_0^{\Theta_D/T} x(e^x - 1)^{-1} dx$, $\Theta_D (= \hbar\omega_D/k_B)$ is the Debye temperature, and $\langle u^2 \rangle_{\text{offset}}$ is a temperature-independent constant.

At high temperatures, $T > \Theta_D$, the vibrational entropy can be approximated by $S_{\text{vib}} \approx 3Nk_B[1 + \ln(T/\Theta_0) + \dots]$, where Θ_0 is the logarithmic phonon moment [29]. Approximating Θ_0 by Θ_D ($\Theta_D \propto \Theta_0$) [30] yields the vibrational entropy change per atom, $\Delta S_{\text{vib}}^{\gamma-\alpha} \equiv S_{\text{vib}}^\gamma - S_{\text{vib}}^\alpha$, which can be expressed as

$$\Delta S_{\text{vib}}^{\gamma-\alpha} \approx 3k_B \ln \Theta_D^\alpha / \Theta_D^\gamma. \quad (2)$$

Using Eq. (2) we obtain $\Delta S_{\text{vib}}^{\gamma-\alpha} \approx 3k_B \ln \left(\frac{133 \pm 3 \text{ K}}{104 \pm 3 \text{ K}} \right) \approx (0.75 \pm 0.15)k_B$ which is consistent with $\Delta S_{\text{vib}}^{\gamma-\alpha} \approx \frac{3}{2}k_B \ln \left(\frac{u^\gamma}{u^\alpha} \right) \approx 0.7k_B$ from the pressure-dependent measurement [Fig. 2(a)]. This change is roughly half of the total entropy change, $\Delta S_{\text{tot}}^{\gamma-\alpha} \approx 1.5k_B$ [4], which follows from the latent heat or the Clausius-Clapeyron relation, $dP/dT = \Delta S_{\text{tot}}^{\gamma-\alpha} / \Delta V^{\gamma-\alpha}$. This large change in vibrational entropy is qualitatively consistent with sound speed measurements [31] of pure Ce ($\Theta_\gamma \approx 137$ K and $\Theta_\alpha \approx 154$ K), but not with the phonon density of states of the $\text{Ce}_{0.9}\text{Th}_{0.1}$ alloy obtained by Manley *et al.* [32] or the vibrational entropy calculations for Ce by Johansson *et al.* [6]. We suspect that the Th atoms in the $\text{Ce}_{0.9}\text{Th}_{0.1}$ alloy modify the elastic properties of Ce, as is observed in Ce alloyed with Mg, where a few percent Mg significantly affects the Young's modulus, particularly in the α phase [33]. We point out that the assumption of the Debye-Grüneisen model [34] used by Johansson *et al.* [6] fails for γ -Ce since the Poisson ratio is not volume independent [31]. Therefore, it is not justifiable to use this model to estimate vibrational entropy changes in Ce.

We now discuss the softening of the isothermal bulk modulus B_T with increasing pressure in the γ phase. The closed circles in Fig. 3(b) were obtained by finite differences of the P - V data in Fig. 3(a), $B = -VdP/dV \approx -V\Delta P/\Delta V$. The errors are estimated using the errors in applied pressures and lattice parameters. Lacking an equation of state that spans the $\gamma \rightarrow \alpha$ transition, we fit the γ phase $P(V)$ data to a cubic polynomial [solid line in Fig. 3(a)] for a more accurate description of B_T . The $B_T(P)$ derived from this fit is shown as a solid line in Fig. 3(b). The dashed line in the α phase is from Olsen *et al.* [35]. We note that our results are in good agreement with the adiabatic bulk modulus B_S obtained from ultrasound measurements by Voronov *et al.* [31]. (The ratio between the isothermal and isentropic bulk modulus is

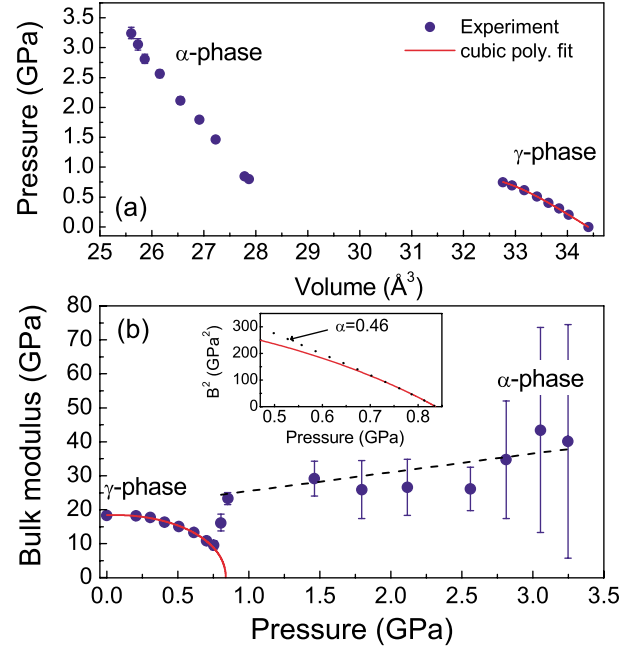


FIG. 3 (color online). (a) P - V room temperature isotherm. The solid line is a cubic polynomial fit to the γ phase of Ce. (b) Bulk modulus vs pressure. The symbols are calculated from finite differences. The solid line is obtained from the polynomial fit to the γ phase P - V data in (a). The dashed line in the α phase is from Olsen *et al.* [35]. Inset: The dashed line is a fit to the solid line near the transition ($0.7 \leq P \leq 0.83$ GPa), where $B_T^2 \sim |P - P_c|^{2\alpha}$ with $P_c \approx 0.83$ GPa and $\alpha \approx 0.46$.

$B_T/B_S = C_p/C_v \approx 1$ for Ce at room temperature.) Figure 3(b) shows that B_T decreases with increasing pressure below $P < P_c$, and that its smooth extrapolation in the γ phase vanishes at P_c , indicating an elastic instability of the lattice. The discontinuity of B_T in the region $P \approx P_c$ reflects the phase instability and the first-order nature of the transition.

In a cubic lattice the bulk modulus is given as $B = [3C_{11} - 4C^* + P]/3$, where P is the applied hydrostatic pressure and $C^* = (C_{11} - C_{12})/2$ is a shear modulus [29]. C^* is known to be pressure insensitive in the γ phase [16,31]. Therefore, the softening of the bulk modulus in the γ phase is a direct consequence of the softening of C_{11} . This result is consistent with the softening of the measured longitudinal sound speed with increasing pressure in γ -Ce [31] and is related to the softening of longitudinal phonons [13] at the ambient pressure mentioned above.

The pressure dependence of the thermal displacement and B_T of Ce can be described within the model of order-parameter-strain field coupling, e.g., λeQ^2 , where e is the strain, Q is a scalar order parameter, and λ is the coupling constant. Bergman and Halperin showed that in this model a continuous phase transition is preempted by an elastic instability, causing a renormalization of the bulk modulus [16]. [In rare-earth compounds, the order parameter has been defined as a relative change of the lattice

constant ($\Delta a/a$) [12], which is proportional to the $4f$ occupation number n_f [36–38]. Because the strain couples to the square of the order parameter, it constitutes a “secondary” order parameter [17.] In this framework the thermal displacement is pressure insensitive and behaves as $\langle u^2 \rangle \sim E_1 + E_2 p + E_3 p^{1-\alpha}$, where $p \equiv |P - P_c|$, E_i are constants and α is a specific heat critical exponent [39], and the bulk modulus vanishes as $B \sim p^\alpha$. In mean-field theory the exponent is $\alpha = 0$, while for Gaussian fluctuations one expects $\alpha = \frac{1}{2}$ [16,17].

As shown in Figs. 2(a) and 3(b) our experimental data exhibit the features of such a model. We observe no divergence of the thermal displacements; instead, they exhibit a sharp drop across the first-order transition. In addition, we find a continuous decrease of the bulk modulus which follows a simple scaling behavior $B_T \sim p^\alpha$ as the pressure approaches P_c [see inset of Fig. 3(b)]. Near the transition we extract the exponent $\alpha \approx 0.46$ and the critical pressure $P_c \approx 0.83$ GPa. Note that α is not a true “critical” exponent because we have measured only a few points below the transition and the descent of B_T towards zero is clearly preempted by the first-order phase transition.

In conclusion, these new experiments and analysis clearly demonstrate that vibrational entropy plays a significant role in stabilizing elemental γ -Ce, accounting for about half of the total change in entropy at the $\gamma \rightarrow \alpha$ transition. The pressure dependence of the thermal displacement and bulk modulus also strongly suggest that electron-phonon coupling plays an important role in the $\gamma \rightarrow \alpha$ transition. In particular, in view of the large ratio $\Delta S_{\text{vib}}^{\gamma-\alpha} / \Delta S_{\text{tot}}^{\gamma-\alpha}$, the agreement between the total entropy change and $k_B \ln(2J + 1)$ ($J = 5/2$) predicted by the KVC model is likely to be accidental, and may call for a reevaluation of the appropriateness of the single-impurity Kondo model for elemental Ce. [Note that $k_B \ln(2J + 1)$ actually overestimates $\Delta S_{\text{tot}}^{\gamma-\alpha}$ by at least 15%.] Thus, a complete understanding of Ce and the competition between localization and itinerancy in f -electron materials must take into account the important interactions between the spin, charge, and lattice degrees of freedom.

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