The 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, $\Delta S_{vib}^{\gamma \rightarrow \alpha} \approx (0.75 \pm 0.15) k_B$, is about half of the total entropy change. The bulk modulus follows a power-law pressure dependence which 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 to a complete description of their properties, including multiple phases and anomalous thermodynamics. This is particularly true in the 4$f$ and 5$f$ systems, where this boundary appears to occur in or near the elements Ce and Pu, respectively. In Pu, which possesses five allotropic phases at ambient pressure, a partial localization of some of the five 5$f$ electrons appears necessary to understand the higher temperature phases. Partial localization may also be present in U compounds. Ce metal is in principle simpler, possessing only a single 4$f$ 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 about 17% volume collapse at room temperature and pressure of roughly 0.8 GPa.

In the majority of theoretical models, the $\gamma \rightarrow \alpha$ transition has been attributed to an instability of the single 4$f^1$ electron. The earliest models focused on charge instability, while later models dealt with spin instability. The promotional model postulates a transition from $4f^1 5d^1 6s^2$ ($\gamma$-phase) to $4f^2 5d^2 6s^2$ ($\alpha$-phase), but is inconsistent with the 4f binding energy and the cohesive energies of other $5d^2 6s^2$ materials.

In the Mott transition (MT) model, the 4f electron in the $\gamma$ phase is localized and non-binding, but is itinerant and binding in the lower volume $\alpha$ phase. The energy for the phase transition is provided by the kinetic energy of the itinerant 4f electron. In the Kondo-volume-collapse (KVC) model, the 4f electron is assumed to be localized in both the $\gamma$ and $\alpha$ 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 altogether an explicit treatment of the lattice degrees of freedom; even the lattice entropy is not considered. More recent treatments include both the lattice and spin entropies, but still do not deal explicitly with the consequences of electron-lattice coupling despite the large volume collapse 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%. For example, the anomalous phonon properties in mixed-valent Sm$_{0.75}$Y$_{0.25}$S and YbInCu$_4$ have been ascribed to a strong coupling to its valence instability. 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 4f state. In $\gamma$-Ce, a comparison of phonon dispersion curves with those of thorium shows that the longitudinal branches of Ce are much softer than one would expect from the Lindemann rule, which accounts for the differences in interatomic distance, mass, and melting temperature of these elements. This relative softening, accompanied by a change in 4f localization (see conclusions), suggests an important role for electron-phonon coupling, as in Sm$_{0.75}$Y$_{0.25}$S, where the $[\xi\xi\xi]$ longitudinal phonon branch is also soft compared to transverse branches.

In this Letter, we further illuminate the role of the lattice in the $\gamma \rightarrow \alpha$ transition and present the first (remarkably) neutron diffraction experiment under pressure in elemental Ce. We measured thermal displacements of Ce in the $\gamma$ and $\alpha$ phases as a function of temperature at constant pressures ($P \sim 0.4$ and 0.5 GPa), and as a func-
tion of pressure at 300 K. The vibrational entropy change between the \( \gamma \) and \( \alpha \) phases, obtained from the thermal displacements using the Debye approximation, accounts for about half of the total entropy change and is thus non-trivial. Furthermore, the pressure dependences of the bulk modulus and thermal displacements are consistent with the explicit inclusion of electron-phonon coupling \[21, 22\]. 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 \( \gamma \to \alpha \) phase transition in elemental Ce.

A high-purity (99.99 \%) polycrystalline, cylindrical ingot of Ce was obtained from the Ames Laboratory. In order to stabilize the \( \gamma \) phase at room temperature, the Ce rod was sealed in a fused silica tube with low pressure (< 1 atm) Argon gas and placed in a furnace for 48 hours at 423 K, and then furnace cooled over 6 hours. Powder diffraction patterns of the \( \gamma \) and \( \alpha \) phases were collected at room temperature in the pressure range up to 0.85 GPa on NPD at the Los Alamos Neutron Science Center (LANSCE) and up to 3.5 GPa on the X-7A beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory \[23\]. Temperature dependent measurements at constant pressure \( (P \sim 0.4 \text{ and } 0.5 \text{ GPa}) \) were performed on SEPD at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. For the neutron powder diffraction measurements, high pressure Al cells were used for the pressure range up to 0.85 GPa. Contamination due to scattering from the cell was minimized using a Gd-based internal shielding, with spaces for the incoming, outgoing and \( \pm 90^\circ \) scattered beam. Details of the cell designs are described elsewhere \[24, 25\].

Fig. 1 shows the isotropic thermal displacements \( \langle u^2 \rangle_{\text{iso}} \) of Ce as a function of pressure (upper panel) and temperature (lower panel) obtained from the Rietveld refinement using GSAS \[26\] and EXPGUI \[27\]. The notable features in the upper panel are the very weak pressure dependence of \( \langle u^2 \rangle_{\text{iso}} \) below 0.7 GPa and the pronounced drop of \( \langle u^2 \rangle_{\text{iso}} \) \((\approx 30 - 40\%) \) at the phase transition, which indicates a significant stiffening of the lattice. The square symbol is the thermal displacement calculated from Born-von Kármán forces at ambient conditions \[28\]; the agreement with our measurement is quite good. One finds that these measurements yield essentially the same \( \Theta_B \) and \( \Theta_D \) in the \( \gamma \) and \( \alpha \) phases. Solid lines are fits using Eq. 1 with Debye temperatures \( \Theta_B = 133(3) \text{ K} \) and \( \Theta_D = 133(3) \text{ K} \),

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

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 constant offset. At high temperatures, \( T > \Theta_D \), the vibrational entropy can be approximated by \( S_{\text{vib}} \approx 3Nk_B\ln(1 + \ln(T/\Theta_D) + \ldots) \), where \( \Theta_0 \) is the logarithmic phonon moment \[31\].

Approximating \( \Theta_0 \) by \( \Theta_D \) \((\Theta_D \approx \Theta_0 e^{1/3}) \) yields the vibrational entropy change per atom, \( \Delta S_{\text{vib}} \approx \Delta S_{\text{vib}}^\gamma - \Delta S_{\text{vib}}^\alpha \), which can be expressed as

\[
\Delta S_{\text{vib}}^\gamma - \Delta S_{\text{vib}}^\alpha \approx 3k_B \ln \Theta_D^\alpha / \Theta_D^\gamma. \tag{2}
\]

Using Eq. 2 we obtain \( \Delta S_{\text{vib}}^\gamma - \Delta S_{\text{vib}}^\alpha \approx 3k_B \ln \left( \frac{133+3 \text{ K}}{104+3 \text{ K}} \right) \approx 0.75 \pm 0.15 \text{ kJ} \). This change is roughly half of the total entropy change, \( \Delta S_{\text{tot}}^\gamma - \Delta S_{\text{tot}}^\alpha \approx 1.54 \text{ kJ} \), which follows from the latent heat or the Clausius-Clapeyron relation, \( dP/dT = \Delta S_{\text{tot}}^\gamma / \Delta V^\gamma - \alpha \). This large change in vibrational entropy is qualitatively consistent with sound
speed measurements [32, 33] in pure Ce (\(\Theta_\gamma \approx 137\) K and \(\Theta_\alpha \approx 154\) K), but not with the measurements of the phonon density of states of the Ce0.9Th0.1 alloy at 150 K (\(\gamma\)-phase) and at 140 K (\(\alpha\)-phase) by Manley et al. [34], which showed little difference between \(\gamma\) and \(\alpha\) phases. We suspect that thorium atoms in Ce0.9Th0.1 alloys modify the elastic properties of Ce, as is observed in Mg-doped Ce alloys, where a few percent Mg significantly affect the Young’s modulus, particularly in the \(\alpha\) phase [35].

We now focus on the softening of the isothermal bulk modulus \(B_T\) with increasing pressure in the \(\gamma\) phase. The upper panel of Fig. 2 presents the measured \(P-V\) data. The closed circles in the lower panel of Fig. 2 were obtained by finite differences of the \(P-V\) data, \(B = -V dP/dV \approx -V \Delta P/\Delta V\). Here 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 \(\gamma\) phase \(P(V)\) data to a cubic polynomial for a more accurate description of \(B_T\), shown as solid line in the upper panel of Fig. 4. The \(B_T(P)\) derived from this fit is shown as solid line in the lower panel of Fig. 4. The dashed line in the \(\alpha\) phase is from Olsen et al. [36]. We note that our results are in good agreement with the adiabatic bulk modulus \(B_S\) obtained from ultrasound measurements by Voronov et al. [37, 38]. (The ratio between the isothermal and isentropic bulk modulus is \(B_T/B_S = C_P/C_V \approx 1\) for Ce at room temperature.) Fig. 2 shows that \(B_T\) decreases with increasing pressure below \(P < P_c\), and that its smooth extrapolation in the \(\gamma\) 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.

The softening of the bulk modulus with increasing pressure in the \(\gamma\) phase is directly related to the softening of the \(C_{11}\) elastic constant. In a cubic lattice the bulk modulus is \(B = [3C_{11} - 4C^\alpha + P]/3\), where \(P\) is the applied hydrostatic pressure and \(C^\alpha = (C_{11} - C_{12})/2\) is a shear modulus [39, 40]. \(C^\alpha\) is known to be pressure insensitive in the \(\gamma\) phase [21, 32, 33]. Therefore, the softening of the bulk modulus in the \(\gamma\) 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 \(\gamma\)-Ce [32, 33] and is related to the softening of longitudinal phonons [10] at 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., \(\lambda e Q^2\), where \(e\) is the strain, \(Q\) is a scalar order parameter, and \(\lambda\) 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 [21]. (In rare-earth compounds, the order parameter \(Q\) has been defined as a relative change of the lattice constant \(\Delta a/a\) [15, 18], which is proportional to the \(4f\) occupation number \(n_f\) [39, 10]. Because the strain couples to the square of the order parameter, it constitutes a “secondary” order parameter [22].) In this framework the thermal displacement behaves as \(a^\alpha \sim \sum_{p=1}^{2} E_1 + E_{2p} + E_3 p^{1-\alpha}\), where \(p \equiv |P - P_c|\), \(E_1 \) are constants and \(\alpha\) is the specific heat critical exponent [22]. The bulk modulus vanishes as \(B \sim p^\alpha\). In mean-field theory the exponent is \(\alpha = 0\), while for Gaussian fluctuations one expects \(\alpha = \frac{1}{3}\) [22].

As shown in Figs. 4 and 2 our experimental data exhibit the features of such a model. Our pressure-dependent measurements at 300 K show no divergence of the thermal displacement, instead, they exhibit a sharp drop across the first-order transition. In addition, we find a continuous decrease of the bulk modulus towards zero as the pressure approaches \(P_c\) with a simple scaling behavior, \(B_T \sim p^\alpha\) (see inset in lower panel of Fig. 2). Near the transition we extract the exponent \(\alpha \approx 0.46\) and the critical pressure \(P_c \approx 0.83\) GPa. Of course, \(\alpha\) is not a truly measured “critical exponent” because (1) we have only a few measured data points below the transition, and (2) the descent of \(B_T\) towards zero is clearly preempted by the first-order phase transition, as seen by the large volume collapse.

![Fig. 2: (Upper panel) \(P-V\) room temperature isotherm. The solid line is a cubic polynomial fit to the \(\gamma\) phase of Ce. (Lower panel) Bulk modulus vs pressure. The symbols are calculated from finite differences. The solid line is obtained from the polynomial fit to the \(\gamma\) phase \(P-V\) data in upper panel. The dashed line in the \(\alpha\) phase is from Olsen et al. [33]. Inset: The dashed line is a fit to the solid line near the transition (0.7 GPa \(\leq P \leq 0.837\) GPa), where \(B_T^0 \sim |P - P_c|^{0.46}\) with \(P_c \approx 0.83\) GPa and \(\alpha \approx 0.46\).](image-url)
In conclusion, these new experiments and analysis clearly demonstrate that vibrational entropy plays a significant role in stabilizing $\gamma$-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 of Ce also strongly suggest that electron-phonon coupling plays an important role in the $\gamma \rightarrow \alpha$ transition. Finally, we note that our results mean that a complete understanding of Ce and its fascinating $\gamma \rightarrow \alpha$ transition must take into account the important interactions between the spin, charge and lattice degrees of freedom, and that this relates closely to the competition between localization and itinerancy in f-electron materials.

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