

Correlation-driven phonon renormalization and the equation of state of γ -cerium

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We investigate the thermodynamic properties of elemental cerium by assessing the crucial role of phonon free energy within the framework of dynamical mean-field theory (DMFT). While conventional density functional theory (DFT) often fails to capture the intricate energy landscape of f -electron materials, our approach integrates many-body electronic correlations with lattice dynamics to achieve a more rigorous description of the equation of state. We calculate the total energy as a function of the lattice constant at both the DFT and DFT + DMFT levels, subsequently incorporating the vibrational free energy derived from the phonon density of states. Our findings reveal that electronic renormalization of the force constants significantly alters the phonon spectra, particularly in the strongly correlated γ phase. By applying these phonon corrections to the energy profiles, we observe a substantial refinement in the predicted equilibrium volumes. Using principal component-based machine learning, we interpolate phonon dispersions continuously from a finite set of first-principles calculations and compare them with experiment, finding significantly closer agreement than conventional DFT and DFT + U calculations that neglect dynamical many-body correlations. This study underlines the necessity of accounting for both electronic and vibrational entropy when evaluating the phase stability and structural transitions of lanthanide systems under varying pressures and temperatures.

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I. INTRODUCTION

Elemental cerium exhibits a remarkable isostructural $\gamma \rightarrow \alpha$ phase transition with a volume collapse of approximately 15% [1,2]. Spectroscopic measurements reveal a pronounced change in the $4f$ electronic character across the transition, from incoherent, fluctuating local moments in the γ phase to a regime with coherent quasiparticles in the α phase [3,4]. Early theoretical proposals, therefore, centered on the nature of the $4f$ electrons, proposing a Mott-like localization transition driven by on-site Coulomb repulsion [5] and the Kondo volume collapse scenario, in which the quenching of local moments by conduction electrons generates the volume change [6,7]. A natural theoretical framework to understand the $\gamma \rightarrow \alpha$ transition is dynamical mean-field

theory (DMFT) [8,9]. In combination with density-functional theory, DFT + DMFT has demonstrated the volume collapse and the associated spectroscopic and magnetic properties in cerium from first principles [10–14].

Progress in the DFT + DMFT methodology to include correlated-electron force calculations [15–17] has further enabled increasingly quantitative thermodynamic and structural descriptions of the $\gamma \rightarrow \alpha$ transition. Recent studies have successively incorporated additional contributions to the free energy in cerium, moving from the electronic ground-state energy to the *electronic* entropy [16] and confirming previous suggestions [13,18] that the γ phase is stabilized by entropy.

A key remaining question is the quantitative role of *vibrational* free energy in determining the equilibrium lattice constants of both phases. Experimental evidence on this point is not yet settled: inelastic neutron scattering studies on cerium alloys find small differences in the phonon density of states across the transition [19], while high-pressure diffraction studies indicate a vibrational entropy change of about $0.75 k_B/\text{atom}$, roughly half the total entropy change [20]. Inelastic x-ray scattering measurements of the complete phonon dispersion of elemental cerium across the transition find an intermediate value of $\sim 0.33 k_B/\text{atom}$ [21], indicating a non-negligible but subdominant lattice contribution. Irrespective

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of its role in the transition itself, vibrational entropy is well known to expand equilibrium volumes through the Grüneisen mechanism, so that a fully predictive calculation of the lattice constants of both α - and γ -Ce requires its inclusion.

Crucially, lattice dynamics in cerium are not independent of the correlated electronic state. The strong renormalization of the $4f$ electrons modifies the interatomic force constants, so that phonon frequencies and vibrational entropies depend on whether the material is in the α or γ electronic state. Conventional density-functional treatments of lattice dynamics, which do not incorporate the feedback of $4f$ correlations on the interatomic forces, cannot capture this effect. Computational methods that combine DFT + DMFT with linear-response calculations of forces have been developed for correlated materials. The calculation of phonons in correlated materials within DFT + DMFT was pioneered in the context of paramagnetic iron, where the frozen-phonon method was employed to demonstrate that electronic correlations have a strong effect on the lattice stability and phonon spectra across phase transitions [22,23]. The observed phonon softening in iron was subsequently attributed to the melting of ferromagnetic order rather than the structural transition itself, as revealed by eDMFT calculations [24]. A framework for computing forces within DFT + DMFT that explicitly incorporates electronic entropy was established in Ref. [16], and an efficient scheme combining fixed self-energy calculations with nondiagonal supercells was developed and benchmarked on Fe, NiO, MnO, and SrVO₃ [25]. Correlation-driven phonon anomalies have further been reported in FeSe [26] and vanadium [27]. For cerium specifically, DMFT-renormalized forces and phonon spectra were computed in Ref. [17]. In all these cases, however, the focus was placed on the phonon spectrum itself, without the resulting phonon free energy being incorporated into the equation of state. In the present work, this gap is closed by systematically evaluating the DMFT-renormalized phonon free energy across the full volume range of the α - γ transition and demonstrating its quantitative role in determining the equilibrium lattice constant of γ -Ce.

In this work, we close this gap by combining DFT + DMFT with a treatment of phonons that incorporates the influence of correlated electrons. We focus specifically on the vibrational free energy of γ -cerium as renormalized by electronic correlations, and on its contribution to the equilibrium lattice constant. By treating electronic and vibrational degrees of freedom consistently within the correlated framework, we extend the thermodynamic description of cerium to include the full free energy at finite temperature.

II. METHODS

We carried out DFT combined with DMFT calculations at an inverse temperature of $\beta = 20 \text{ eV}^{-1}$, corresponding to $T \simeq 580 \text{ K}$, employing the embedded DMFT functional package EDMFT [28] interfaced with the all-electron WIEN2K code [29]. This framework enables a fully self-consistent treatment of both the electronic structure and the lattice dynamics in elemental cerium within the same theoretical formalism.

The DMFT impurity problem was solved using a continuous-time quantum Monte Carlo (CT-QMC) method

[30,31]. The statistical errors of the CT-QMC calculations, estimated from the fluctuations of the total energy over the final self-consistent DMFT iterations, are of order 1 meV per primitive cell, negligible on the energy scales discussed in this work. Following Ref. [32], which shows that the $4f$ occupancy of elemental cerium is robust with respect to the choice of double-counting scheme and remains close to its nominal value, we adopt the nominal double-counting correction [33]

$$V_{\text{dc}} = U \left(n_f - \frac{1}{2} \right) - J \left(\frac{n_f}{2} - \frac{1}{2} \right), \quad (1)$$

with fixed $n_f = 1$ throughout this work. The resulting $4f$ occupancy obtained from the fully converged DFT + DMFT calculations is discussed in Sec. S1 of Supplemental Material (SM) [34], where it is shown to remain close to unity over the entire range of lattice constants considered. For further technical details of the implementation, we refer to Ref. [28]. The Matsubara self-energy was analytically continued to the real-frequency axis using the maximum entropy method [35]. The quasiparticle weight was independently extracted from both Matsubara and real-frequency data and found to be mutually consistent, providing an internal validation of the calculations.

In the WIEN2K calculations, the basis set size was controlled by choosing RKmax = 7, which is commonly adopted for cerium and provides a well-converged description of total energies within the present setup [36]. DFT calculations were carried out within both the local density approximation (LDA) [37] and the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE) [38]. Within DFT + DMFT, the cerium f orbitals were described using an on-site Coulomb interaction of $U = 6.0 \text{ eV}$ and a Hund coupling of $J = 0.7 \text{ eV}$, consistent with values successfully employed in previous studies of elemental cerium [10,13,30,36] as well as related Ce-based compounds [39]. The dependence of the equilibrium lattice constant on the choice of U within DMFT is discussed in detail in Sec. S2 of SM [34]. The local Coulomb interaction, parametrized by U and J , is treated within the DMFT impurity solver in the density–density (Ising) form [33], consistent with Ref. [40].

For the lattice dynamics calculations, a finite-displacement approach is employed within an in-house framework that provides a flexible interface with both DFT and DFT + DMFT [25,41]. Since each displaced supercell in DFT + DMFT requires a full solution of the impurity problem and the computational cost increases with supercell size, the nondiagonal supercell technique [42] is adopted to sample a $4 \times 4 \times 4$ $\mathbf{q}$ -point grid efficiently. Phonon calculations are performed at fixed lattice constants rather than at fully relaxed equilibrium volumes. In elemental cerium, this procedure does not generate spurious forces within the finite-displacement framework. Owing to the single-atom basis of the fcc structure and the preservation of crystal symmetry, a uniform change of the lattice constant produces only a finite hydrostatic stress, while the internal atomic forces remain strictly zero. The equilibrium volume is therefore determined directly from the equation of state through a systematic scan of lattice constants. The harmonic phonon problem is well defined, and no imaginary modes are observed across the volume range considered. Throughout this work, the fixed-self-energy approximation [25] is employed for all

displaced configurations. Within this approach, the DMFT self-energy is computed once for the equilibrium structure and subsequently kept fixed when evaluating the forces for the displaced geometries, thereby neglecting the explicit displacement dependence of the local self-energy. This approximation reduces the computational cost by approximately one order of magnitude compared to a fully self-consistent variable-self-energy scheme, as the latter requires a complete DMFT self-consistency cycle for each displaced supercell configuration. The validity of this approximation is assessed in Sec. S3 of SM [34] through a comparison with phonon calculations performed using a variable-self-energy scheme. In elemental cerium, spin-orbit coupling (SOC) governs the fine multiplet structure and effective degeneracy of the $4f$ states, which are central to the electronic free-energy landscape associated with the α - γ transition [28,43]. For this reason, SOC is explicitly included in all calculations of the internal energy and electronic free energy presented in this work. We note that its quantitative effect on the electronic free energy as a function of lattice constant remains small, as discussed in the RESULTS section. Spin-orbit coupling (SOC) [44] was not included in the DMFT phonon calculations, as the current implementation lacks the interface to treat SOC within the finite-displacement phonon workflow. A similar approximation was adopted in Ref. [41]. The effect of neglecting SOC has been argued to be roughly equivalent to a renormalization of temperature [18], consistent with our finding that SOC exerts only a secondary influence on the lattice-dynamical contribution to the free energy. To quantify the impact of this approximation, we examine the effect of SOC on the DFT + DMFT spectral function, which is further discussed in Sec. S4 of SM ([34], see also Ref. [45] therein). While SOC substantially reshapes the low-energy electronic spectrum in the vicinity of the Fermi level, the corresponding correction to the phonon free energy is small on the relevant thermodynamic energy scale at the DFT level, as demonstrated in Sec. S5 of SM [34]. On the DFT + DMFT level, SOC slightly expands the equilibrium lattice constant, but restoring forces (and thus phonon frequencies) are largely unaffected, as shown in Sec. S6 of SM [34]. In all, these results indicate that, although SOC is essential for an accurate description of the electronic structure, its influence on the lattice-dynamical contribution to the total free energy remains secondary within the present framework. In this work, the DMFT electronic free energy is evaluated using the stationary implementation of the DFT + DMFT functional [28]. Crucially, this formalism goes beyond the internal energy E by explicitly evaluating the Luttinger–Ward functional, which inherently incorporates the electronic entropy S of the strongly correlated $4f$ shell, approximated by the impurity entropy obtained from the CT-QMC solver. The phonon free energy $F_{ph}(T)$ is calculated within the harmonic approximation by summing over all phonon modes in the Brillouin zone. For a given temperature T , the absolute phonon free energy is expressed as

$$F_{ph}(T) = \frac{1}{2} \sum_{\mathbf{q},\nu} \hbar \omega_{\mathbf{q},\nu} + k_B T \sum_{\mathbf{q},\nu} \ln \left[1 - \exp \left(-\frac{\hbar \omega_{\mathbf{q},\nu}}{k_B T} \right) \right], \quad (2)$$

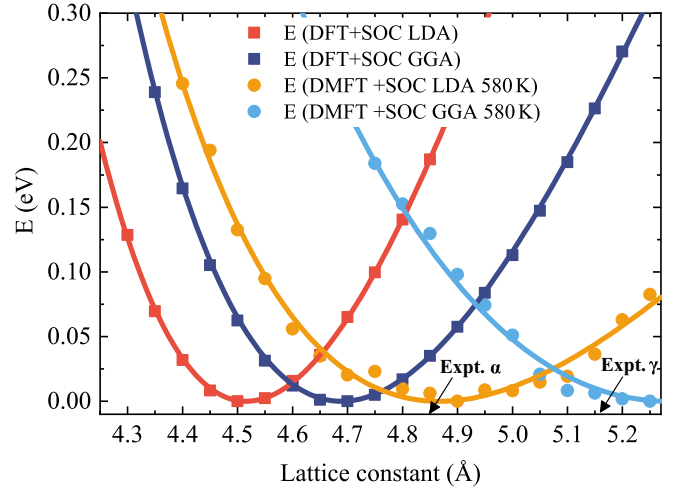


FIG. 1. Lattice-parameter dependence of the internal energy of cerium, calculated within DFT and DMFT. Experimental lattice constants at ambient pressure are indicated by arrows: Expt. α = 4.85 Å (low temperature) [1] and Expt. γ = 5.16 Å (room temperature) [47].

where $\omega_{\mathbf{q},\nu}$ denotes the DMFT-renormalized phonon frequency for wave vector $\mathbf{q}$ and branch index ν . The first term represents the zero-point energy contribution, while the second term captures the thermal effect through Bose–Einstein statistics [46].

III. RESULTS

A. Electronic internal and electronic free energy

The lattice-parameter dependence of the internal energy obtained within DFT and DFT + DMFT is shown in Fig. 1. The calculated curves span a broad range of lattice constants covering both the compressed-volume regime associated with the α -phase and the expanded-volume regime corresponding to the γ phase.

Within conventional DFT, including SOC, the equilibrium lattice constant at zero temperature is $a_0 = 4.52$ Å at the LDA + SOC level, in close agreement with Refs. [17,48], where SOC was not included. The corresponding GGA calculation yields a larger equilibrium lattice constant of $a_0 = 4.69$ Å, consistent with previous GGA results [48,49]. As expected, the GGA functional predicts a larger equilibrium volume than LDA owing to its reduced tendency to overbind [50]. From a fundamental perspective, density functional theory is a zero-temperature formalism and is therefore expected to describe the low-temperature α phase. Yet, both LDA and GGA severely underestimate its equilibrium lattice constant (4.52 Å and 4.69 Å, respectively, versus the experimental value of 4.85 Å [1]). This pronounced discrepancy reveals the inability of static mean-field approaches to capture the strongly correlated nature of the $4f$ electrons, leading to an overestimation of binding. Consequently, there is no rigorous physical basis for expecting standard DFT to reproduce the significantly larger lattice constant of the entropy-stabilized high-temperature γ phase (experimental $a \approx 5.16$ Å [47]). These limitations motivate the incorporation of dynamical

cal many-body correlations together with finite-temperature thermodynamic contributions to obtain a meaningful equation of state.

In addition, as shown in Sec. S6 of SM [34], the total-energy curves as a function of lattice constant obtained from LDA and LDA + SOC calculations are essentially identical. This indicates that SOC has a negligible effect on the equilibrium structural properties at the DFT level. Furthermore, the inclusion of SOC induces only minor modifications to the DMFT electronic free energy, as shown in Sec. S7 of SM [34], where the SOC and non-SOC free-energy curves nearly coincide over the entire lattice-parameter range at 580 K. Collectively, these findings demonstrate that SOC exerts a negligible influence on both the equilibrium lattice constants and the finite-temperature free-energy landscape within the present theoretical framework.

The inclusion of dynamical electronic correlations within DMFT leads to a pronounced lattice expansion. At $T = 580$ K, the LDA + DMFT + SOC minimum shifts to $a_0 = 4.88 \text{ \AA}$, substantially larger than the LDA + SOC value. The resulting lattice constant lies significantly closer to the experimental γ -phase value and reflects the reduction of the DFT overbinding tendency. The overall behavior of the total energy curves is in close agreement with previous LDA + DMFT studies of cerium [17,28,51], which reported comparable correlation-induced shifts of the equilibrium lattice constant at the level of the internal energy E . In those works, the local $4f$ correlations were treated using both the Hubbard I approximation and the CT-QMC impurity solver. The quantitative consistency of the internal energy minima obtained here with earlier results demonstrates the robustness of the LDA + DMFT description of cerium.

In contrast, the GGA + DMFT + SOC calculation yields a substantially larger equilibrium lattice constant of $a_0 = 5.28 \text{ \AA}$, which exceeds the experimental value, as noted previously [28]. Indeed, the largest uncertainty in DFT + DMFT predictions of lattice constants comes from the choice of the DFT exchange-correlation potential (for other f -electron materials, see [52]). Still, the temperature and correlation-induced lattice expansion within DFT + DMFT will also depend on the details of the many-body setting employed (interaction parameters, double-counting scheme and valency, temperature). The dependence of the GGA + DMFT + SOC equilibrium lattice constant on the choice of U is examined in Sec. S8 of SM [34], where we show that a reduced U can bring the internal-energy lattice constant into agreement with experiment. Alternatively, in an LDA + DMFT + SOC setting, a larger U will improve the volume. The semiempirical choice of U is, however, constrained by agreement with spectral properties, for which previous DMFT studies have found $U = 6$ eV to be accurate. The large variability for varying DFT potentials and Hubbard interactions significantly limits the predictiveness of the DFT + DMFT approach and calls for truly first principles approaches, such as GW + DMFT [53,54].

Here, instead, we take a physics-informed decision. Below, we take into account phonon contributions to the free energy. Phonon entropy generally favors larger equilibrium volumes [46]. Indeed, a larger lattice constant, conversely, leads to softer interatomic force constants. The resulting lower phonon

frequencies mean that these modes become more thermally accessible, yielding higher vibrational entropy. Since any DFT functional must yield an electronic equilibrium volume smaller than the experimental value, so that phonon entropy can account for the remaining expansion, we therefore proceed with LDA + DMFT, rather than GGA + DMFT.

B. Lattice dynamics and phonon free energy

We now extend the analysis by incorporating vibrational free-energy contributions into the energy landscape. Figure 2(a) shows the phonon dispersion relations calculated within the local density approximation (LDA) along the high-symmetry path Γ -X-K- Γ -L for a series of lattice constants ranging from $4.30 \text{ \AA}$ to $5.25 \text{ \AA}$.

For all lattice constants considered, the three acoustic phonon branches originate from zero frequency at the Γ point, consistent with translational invariance. No imaginary phonon frequencies are observed anywhere in the Brillouin zone for any of the lattice constants investigated. This establishes that the crystal structure remains dynamically stable within the LDA description over the entire volume range examined, with no indication of soft-mode-driven lattice instabilities.

A clear and systematic volume dependence of the phonon spectrum is observed. As the lattice constant increases, phonon modes exhibit a pronounced softening across the Brillouin zone. At smaller lattice constants, corresponding to compressed volumes, the phonon frequencies are uniformly higher, reflecting stronger interatomic force constants. Upon lattice expansion, the frequencies decrease smoothly and continuously, indicating a conventional weakening of bonding interactions rather than the emergence of anomalous lattice behavior.

The softening is most pronounced for phonon branches in the intermediate- and high-frequency range, which show substantial downward shifts with increasing lattice parameter. Despite this softening, all modes remain well separated from zero frequency, confirming the absence of incipient dynamical instabilities even at the largest lattice constants considered. The continuous evolution of these modes further confirms that the lattice response to volume expansion within the DFT description is governed by changes in the harmonic interatomic force constants, with no evidence of anharmonic or soft-mode-driven instabilities.

Figure 2(b) presents a detailed view of the phonon dispersion relations of cerium in the large-volume γ -phase regime ($a \geq 5.05 \text{ \AA}$), calculated within standard DFT (LDA; $T = 0$ K) along the high-symmetry path Γ -X-K- Γ -L. As the lattice constant increases from $5.05 \text{ \AA}$ to $5.25 \text{ \AA}$, as indicated by the color evolution from purple/red to cyan/green, a pronounced and highly nonuniform softening emerges in the low-frequency phonon branches. This effect is particularly evident in the low-energy modes and is most severe along the K- Γ segment, where the branches exhibit a clear downward bending and a substantial reduction in frequency. The softening is markedly stronger in the low-frequency sector than in the high-frequency branches, which instead display a more gradual and nearly rigid shift. This behavior, therefore, cannot be interpreted as a simple volume-induced rescaling of the phonon spectrum. Rather, it reflects a mode-selective

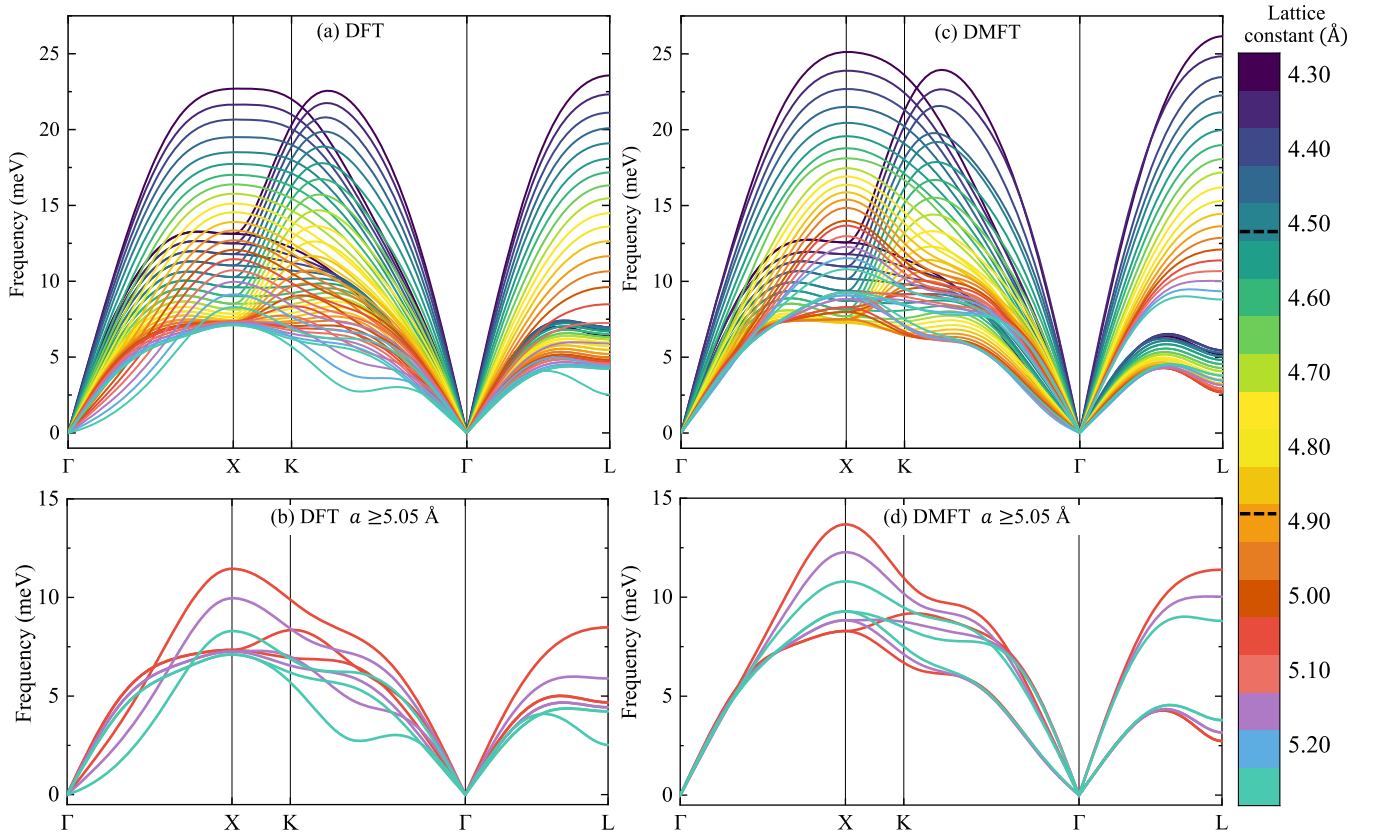


FIG. 2. *Ab initio* computation of correlation-driven phonon dispersions in cerium. (a), (c) Full phonon dispersion relations explicitly calculated from first principles within standard DFT (LDA, $T = 0$) and DFT + DMFT ($T = 580$ K), using a $4 \times 4 \times 4$ $\mathbf{q}$ -point mesh. The color bar indicates the lattice constant (in Å), with dashed lines marking the respective theoretical equilibrium constants ($a_0^{\text{DFT}} = 4.52$ Å; $a_0^{\text{DMFT}} = 4.88$ Å) from Fig. 1. (b), (d) Detailed views of the directly computed large-volume γ -phase regime ($a = 5.05, 5.15$, and 5.25 Å).

renormalization, with the low-energy vibrational modes showing enhanced sensitivity to lattice expansion. Such anomalous softening indicates that specific phonon modes, especially along the X–K– Γ path, are strongly affected by changes in the underlying bonding environment in the expanded lattice. This selective response highlights the non-trivial lattice-dynamical behavior in the γ -phase, where the low-frequency modes undergo a significantly stronger renormalization than the rest of the spectrum.

The absence of pronounced mode flattening or imaginary modes at the Brillouin-zone boundaries further excludes the presence of competing low-energy structural distortions within the explored parameter range. Instead, the phonon spectrum retains well-defined dispersions and finite mode separations throughout, underscoring the robustness of the lattice against symmetry-lowering distortions driven by harmonic phonon instabilities. While higher-order anharmonic effects [55] could quantitatively modify the high-temperature lattice dynamics, the complete absence of harmonic soft modes confirms the intrinsic mechanical stability of the fcc phase across the explored volume range.

Figure 2(c) presents the phonon dispersions calculated within the LDA + DMFT framework along the same high-symmetry path and for the same lattice constants as those shown in Fig. 2(a), enabling a direct, mode-resolved comparison between the uncorrelated and correlated descriptions. Again, the three acoustic branches emanate from

zero frequency at Γ , and all phonon frequencies remain positive throughout the Brillouin zone across the entire lattice-parameter range. The absence of imaginary modes in both approaches indicates that the structure is dynamically stable within the harmonic approximation and that the inclusion of local electronic correlations does not introduce symmetry-lowering lattice instabilities. Quite the opposite, a phonon minimum developing in DFT between K and Γ for the largest lattice constant, disappears in DMFT.

While the overall topology of the spectrum and its smooth volume evolution are preserved, LDA + DMFT induces a clear quantitative renormalization that is not uniform across branches. Most notably, the highest branches are systematically shifted upward in LDA + DMFT relative to LDA, reaching significantly larger peak frequencies, particularly near the Brillouin-zone boundary around X and along the approach to L. This correlation-induced hardening of the upper phonon manifold is clearly evident in Fig. 2(c) relative to Fig. 2(a), and this effect persists over the entire range of lattice constants investigated. At the same time, the lower-lying branches exhibit a more moderate and mode-dependent response. These branches show comparatively smaller shifts with respect to LDA and, in several q -space regions, a tendency toward reduced dispersion and enhanced clustering, indicating that correlations modify the relative separations of nearby modes rather than producing a simple rigid shift of the entire spectrum.

The volume dependence remains conventional in both methods: increasing the lattice constant leads to an overall softening trend. However, the magnitude and distribution of this softening differ once correlations are included. Within LDA + DMFT, changes in curvature and mode spacing are especially apparent along the X–K– Γ segment, where several branches become more closely packed, and their dispersions evolve differently from the LDA case. Along the Γ –L direction, the comparison highlights a particularly strong upward renormalization of the highest-frequency branches in LDA + DMFT, while the lower branches remain closer to their LDA counterparts.

Figure 2(d) presents a detailed, volume-resolved view of the phonon dispersion relations for cerium in the large-volume γ -phase regime ($a = 5.05, 5.15$, and 5.25 Å), extracted directly from the LDA + DMFT calculations. We focus specifically on this expanded lattice-parameter range because it corresponds to the physical state of the high-temperature γ phase, where the influence of electronic correlations on lattice dynamics is most pronounced and physically relevant. A central finding from our LDA + DMFT results is that the individual vibrational branches respond in a highly nonuniform and mode-selective manner to lattice expansion—a complex behavior that is completely absent in the standard DFT description. In typical DFT calculations [see Fig. 2(b)], phonon branches undergo a conventional volume-driven softening, with the low-frequency branches exhibiting a particularly anomalous and rapid decrease in frequency. In striking contrast, the LDA + DMFT dispersions in Fig. 2(d) reveal a remarkable inversion precisely in the low-frequency region. While the high-frequency branches still follow the expected trend and soften with increasing lattice parameter, the low-frequency branches at the X and L points actually move upwards. Most notably, at the X point, the frequency rises from 8.28 meV to 9.28 meV as the lattice constant expands from 5.00 Å to 5.25 Å—an increase of more than 1 meV over this volume range. This upward shift is carried specifically by the transverse acoustic (TA) branch at the X point, while the longitudinal acoustic (LA) branch continues to soften conventionally, decreasing from approximately 13.7 meV to 10.8 meV over the same volume range. The TA branch stiffens while the LA branch softens, and this mode-selective response reflects a correlation-driven renormalization of the transverse interatomic force constants by the localized $4f$ electrons. This renormalization counteracts the usual volume-induced softening specifically for shear-type atomic displacements in the γ phase. The anisotropic character of this effect confirms that $4f$ correlations modify the interatomic force constants in a way that cannot be captured by conventional DFT.

The physical origin of this correlation-induced hardening can be understood in terms of the renormalization of electronic screening by the localized $4f$ shell. Within DFT, the partially itinerant $4f$ electrons contribute to the screening of interatomic forces under transverse atomic displacements, effectively reducing the restoring force and softening the transverse force constants. The DMFT self-energy suppresses this itinerant contribution by dynamically transferring $4f$ spectral weight away from the Fermi level (see Sec. S4 of SM [34] for the corresponding spectral function), thereby reducing the capacity of the $4f$ electrons to screen shear-type

displacements. As a consequence, the transverse interatomic force constants are stiffened relative to their DFT counterparts, producing the observed hardening of the TA branches in the γ -phase volume regime. The methodological framework underlying such DMFT-renormalized forces has been developed in Refs. [15–17], and applied to a range of correlated systems including paramagnetic iron and cerium compounds; the mode-selective TA hardening identified here represents a specific manifestation of this many-body renormalization in the γ phase of elemental Ce.

The comparison between Figs. 2(b) and 2(d) is therefore particularly illuminating: the uncorrelated DFT picture shows an anomalously rapid downward plunge of the low-energy modes, whereas the inclusion of dynamical correlations in DMFT not only suppresses that softening but actively reverses it into an upward shift for the very same branches. This inversion confirms that the low-frequency vibrations in these regions of the Brillouin zone are extremely sensitive to correlation-driven modifications of the local bonding geometry. In the strongly correlated γ phase, the $4f$ electrons renormalize the force constants in a mode-specific way, leading to a nontrivial redistribution of phonon energies that cannot be captured by conventional DFT. Such correlation-induced lattice-dynamical effects are crucial for the thermodynamic stability of the expanded γ phase and highlight the necessity of treating electronic correlations and phonon renormalization on an equal footing.

To quantify global versus local changes in phonon renormalization, we map the phonon dispersion calculated at a given lattice constant onto a high-dimensional vector of phonon frequencies along the chosen high-symmetry path. A principal-component analysis then reveals that the dominant fraction of the variance is captured by only a few components, with the leading mode accounting for approximately 98% of the total variance and corresponding to an almost uniform hardening or softening of the spectrum. Therefore, the correlation-induced modification of the phonon spectrum exhibits a pronounced collective character, implying that its lattice-parameter dependence can be represented on a low-dimensional manifold.

Exploiting this reduced representation, we construct a continuous interpolation of the phonon dispersions as a function of lattice constant by modeling the projection coefficients of the leading principal components with a multilayer perceptron neural network. The interpolation is validated through leave-one-out tests, demonstrating excellent agreement with explicitly calculated phonon spectra and confirming that the smooth, collective evolution of the dispersions is faithfully captured. This compact description enables a numerically stable evaluation of the phonon free energy over the full lattice-parameter range considered. Further technical details of the interpolation procedure are provided in Sec. S9 of SM ([34], see also Refs. [56–58] therein).

To further validate the interpolation scheme, DMFT phonon dispersions were predicted at three lattice constants that were not included in the training dataset and compared with experimental measurements reported in Ref. [21]. As shown in Fig. 3, the spectra predicted by the model trained on LDA + DMFT calculations exhibit excellent agreement with the experimental phonon branches along the high-symmetry

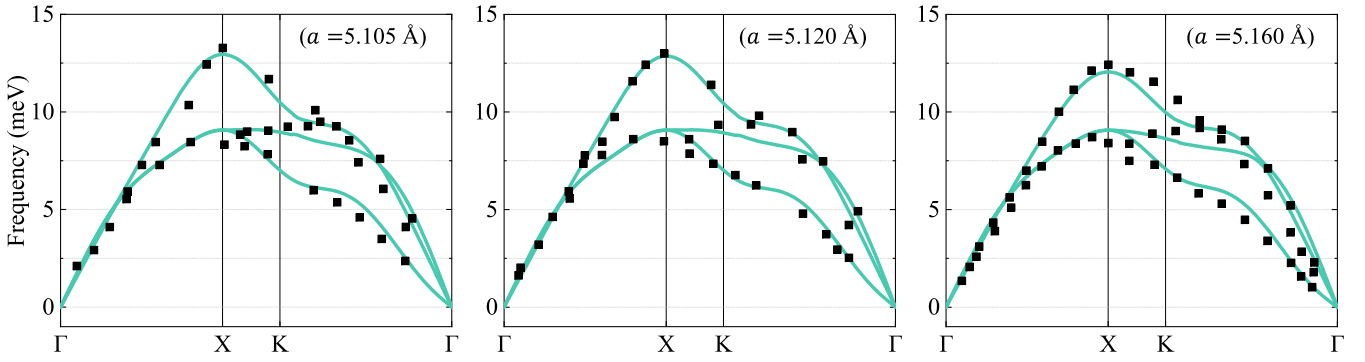


FIG. 3. Phonon dispersion relations obtained using principal component-based neural network interpolation trained on LDA + DMFT calculations, compared with experimental data from cerium under hydrostatic pressure at ambient temperature from Ref. [21]. Results are shown for lattice constants $a = 5.105, 5.120$, and 5.160 Å along the Γ -X-K- Γ high-symmetry path. The predicted dispersions (green lines) show very good agreement with the experimental phonon frequencies (black symbols).

path. This consistency demonstrates that the low-dimensional representation, combined with neural network interpolation, reliably captures the collective evolution of the phonon spectrum and provides predictive capability beyond the explicitly computed data.

Although a phonon spectrum formally comprises a large number of frequencies associated with different wave vectors and vibrational branches, the above principal-components analysis suggests that variations in volume primarily lead to shifts of groups of phonon branches, rather than independent changes of individual modes. It is then instructive to examine the lattice-parameter dependence of the overall phonon dispersion.

Figure 4 demonstrates a pronounced correlation-dependent modification of the lattice dynamics across the α - γ transition through the *average* phonon frequency. The average is obtained from the full phonon dispersions calculated within

LDA and LDA + DMFT, shown in Figs. 2(a) and 2(c), respectively, by averaging the phonon frequencies along the chosen high-symmetry path in the Brillouin zone. In the compressed volume regime corresponding to the α phase, the two approaches yield nearly identical average frequencies, such that $\Delta\omega_{\text{avg}}$ remains close to zero. This indicates that electronic correlations exert only a marginal influence on the lattice response at small volumes.

With increasing lattice parameter, a systematic deviation emerges. Whereas LDA predicts substantial, nearly linear phonon softening upon lattice expansion, the inclusion of dynamical electronic correlations within LDA + DMFT markedly reduces this softening, leading to a monotonically increasing frequency difference $\Delta\omega_{\text{avg}}$. This behavior demonstrates that electronic correlations qualitatively modify the lattice dynamics across the α - γ transition. The resulting nonlinear evolution of the phonon frequencies with lattice constant further suggests that simple interpolation between discrete lattice constants may be unreliable, motivating the use of the machine-learning interpolation scheme introduced above.

Figure 5 shows the temperature dependence of the absolute phonon free energy, $F_{\text{ph}}(T)$, of elemental cerium calculated within the LDA framework [panel (a)] and LDA + DMFT framework [panel (b)] for lattice constants between 4.30 and 5.25 Å. The free-energy values have been obtained from explicit evaluation of the harmonic free-energy expression at discrete temperature intervals of 50 K, with neighboring points connected, rather than from a global functional fit. In the LDA + DMFT case, the underlying phonon dispersions are computed at a fixed inverse temperature $\beta = 20$ (corresponding to $T \approx 580$ K), and are assumed to be temperature independent within the harmonic approximation. The temperature dependence of $F_{\text{ph}}(T)$ therefore arises solely from the Bose-Einstein occupation factors entering the harmonic free-energy expression. In both approaches, $F_{\text{ph}}(T)$ decreases smoothly and monotonically with increasing temperature from the low-temperature regime up to beyond 900 K. This behavior reflects the progressive increase of the vibrational entropy contribution and is consistent with a harmonically stable lattice over the entire lattice-parameter range.

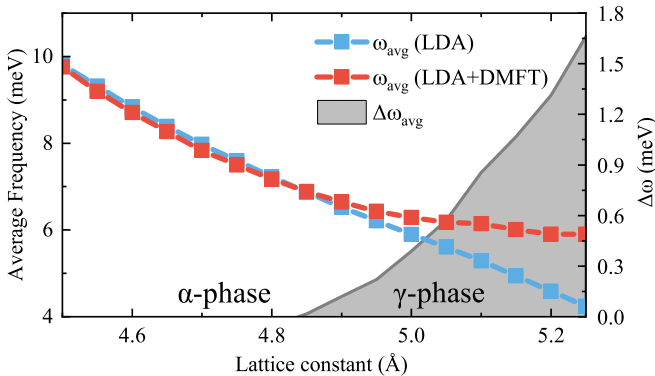


FIG. 4. Average phonon frequency as a function of lattice constant for elemental cerium, calculated within DFT (blue squares) and DFT + DMFT (red squares). The shaded region represents the difference in the average phonon frequency between the two approaches, defined as $\Delta\omega = \omega_{\text{avg}}^{\text{LDA+DMFT}} - \omega_{\text{avg}}^{\text{LDA}}$. In the compressed volume regime corresponding to the α phase, the two methods yield nearly identical average frequencies, indicating a minor influence of electronic correlations on lattice dynamics. Upon lattice expansion towards the γ phase, a systematic deviation develops, with LDA + DMFT suppressing the volume-induced phonon softening observed at the LDA level.

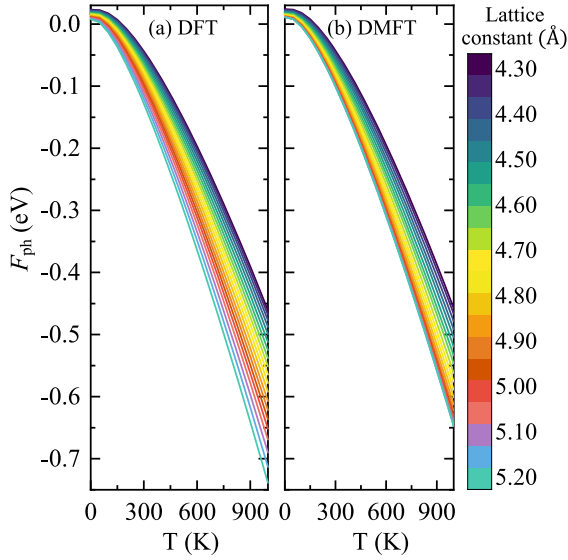


FIG. 5. Temperature dependence of the absolute phonon free energy F_{ph} of elemental cerium calculated within (a) LDA and (b) LDA + DMFT for lattice constants between 4.30 and 5.25 Å. The LDA + DMFT phonon dispersions are computed at $\beta = 20$ ($T \approx 580$ K) and used within the harmonic approximation.

In the LDA results shown in Fig. 5(a), the phonon free energy displays a pronounced dependence on the lattice parameter. At a given temperature, curves corresponding to larger lattice constants are systematically shifted to lower (more negative) values of F_{ph} , while smaller lattice constants yield higher free energies. This ordering is preserved across the entire temperature range and becomes progressively more pronounced at elevated temperatures. As temperature increases, the set of curves fans out, indicating that the volume dependence of the vibrational free energy is strongly enhanced by thermal effects. In particular, at temperatures above several hundred kelvin, the separation between curves associated with neighboring lattice parameters becomes substantial, signaling a sizable contribution of phonons to the relative thermodynamic stability of different volumes within the LDA description.

Figure 5(b) shows the corresponding phonon free energies obtained within LDA + DMFT. As in the LDA case, all curves decrease smoothly with temperature and remain well behaved throughout the entire temperature range, consistent with the absence of dynamical instabilities as inferred from the phonon spectra. The overall temperature dependence of $F_{\text{ph}}(T)$ is qualitatively similar to that found in LDA, indicating that the dominant entropic contribution associated with lattice vibrations is preserved when local electronic correlations are included.

A clear quantitative difference emerges, however, in the volume dependence of the phonon free energy. In contrast to the LDA results, the LDA + DMFT curves are significantly more closely spaced for different lattice constants at all temperatures. Although the monotonic ordering with lattice constant is maintained, the overall spread of $F_{\text{ph}}(T)$ is markedly reduced. This effect is particularly evident at high temperatures, where the LDA results show a strong fan-out of curves, while the LDA + DMFT curves remain comparatively

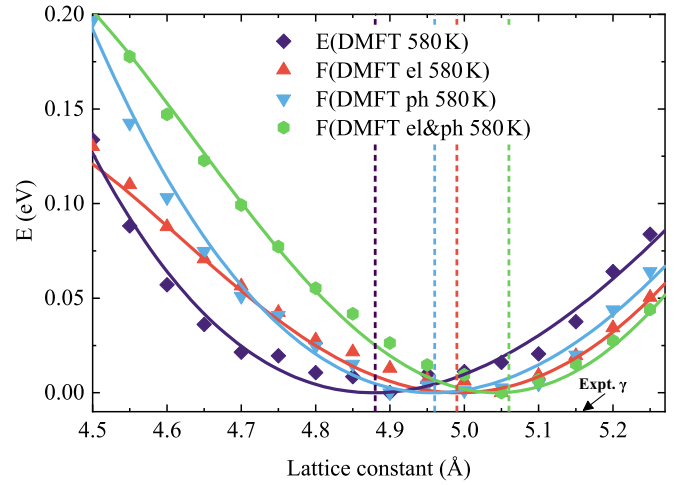


FIG. 6. Lattice-parameter dependence of the internal energy and free-energy contributions within DMFT at 580 K. Symbols denote the calculated data points for the internal energy E , the electronic free energy F_{el} , the phonon free energy F_{ph} , and the combined electronic plus phononic free energy $F_{\text{el+ph}}$. Solid lines represent third-order Birch–Murnaghan fits to the corresponding datasets. Vertical dashed lines indicate the lattice constants at which each fitted curve attains its minimum. All energies are given per primitive unit cell (one atom per fcc cell), and all curves have their minima aligned to zero.

clustered. The reduced separation between curves indicates that the sensitivity of the phonon free energy to changes in lattice constant is substantially suppressed once electronic correlations are taken into account. This behavior is fully consistent with the correlation-induced renormalization of the phonon spectrum discussed earlier, which redistributes vibrational frequencies in a nonuniform manner. Since the DFT equilibrium volume deviates substantially from the experimental value, the inclusion of vibrational contributions at this level does not restore agreement or alter the central conclusions of the present work. For clarity of presentation and to maintain focus on the correlation-driven effects captured within DFT + DMFT, the detailed temperature-dependent total free-energy analysis at the DFT level is therefore discussed in detail in Sec. S10 of SM [34].

Figure 6 illustrates the lattice-parameter dependence of the internal energy and the various free-energy contributions obtained within the DMFT framework at 580 K. In the absence of any entropic corrections, the internal-energy curve exhibits a minimum at a lattice constant of approximately 4.88 Å, which serves as a reference for assessing entropic effects. Upon including electronic entropy corrections, the equilibrium lattice constant increases to about 4.99 Å, indicating a moderate lattice expansion driven by local-moment entropy and highlighting the importance of finite-temperature electronic effects in the equation of state of cerium.

Instead, when only phonon free-energy contributions are incorporated (neglecting SOC), the minimum of the free-energy curve is located at a slightly smaller lattice constant of about 4.96 Å, showing that lattice vibrational effects alone do not stabilize the expanded structure either. By contrast, when both electronic and phononic contributions are taken into account simultaneously, the total free energy exhibits a

TABLE I. Calculated and experimental fcc lattice constants of γ -Ce obtained using different theoretical approaches and experimental conditions.

Method	U (eV)	J (eV)	T (K)	P (GPa)	a (Å)	Ref.
This work						
LDA+SOC					4.52	
GGA+SOC					4.69	
LDA+DMFT+SOC (internal E , CT-QMC)	6.0	0.70	580		4.88	
LDA+DMFT+SOC (electronic F , CT-QMC)	6.0	0.70	580		4.99	
LDA+DMFT+SOC (phononic F , CT-QMC)	6.0	0.70	580		4.96	
LDA+DMFT+SOC (electronic + phononic F , CT-QMC)	6.0	0.70	580		5.06	
GGA+DMFT+SOC (internal E , CT-QMC)	6.0	0.70	580		5.28	
Prior theoretical work						
LDA					4.49	[59]
LDA					4.50	[17]
LDA					4.52	[60]
LDA+DMFT non self-consistent ASA (Hubbard I)	6.0	0.46	0		4.91	[51]
LDA+DMFT self consistent ASA (Hubbard I)	6.0	0.46	0		4.93	[51]
LDA+DMFT (Hubbard I)	6.0	0.70	232		4.95	[17]
LDA+DMFT PAW (Hubbard I)	6.0	0.00	273		4.98	[61]
LDA+DMFT ASA (Hubbard I)	6.0	0.00	273		4.91	[61]
LDA+DMFT (internal E , Hirsch-Fye QMC)	6.0		400		4.88	[13]
LDA+DMFT (internal E , Hirsch-Fye QMC)	6.0		800		4.99	[13]
LDA+DMFT (internal E , Hirsch-Fye QMC)	6.0		1600		5.03	[13]
LDA+DMFT+SOC (internal E , CT-QMC)	6.0	0.70	400		4.96	[28]
LDA+DMFT+SOC (internal E , CT-QMC)	6.0	0.70	900		4.97	[28]
LDA+DMFT+SOC (electronic F , CT-QMC)	6.0	0.70	400		5.04	[28]
LDA+DMFT+SOC (electronic F , CT-QMC)	6.0	0.70	900		5.06	[28]
LDA + U (FLL, FM imposed)	6.1	0.70			5.04	[60]
LDA + U (AMF, FM imposed)	6.1	0.70			4.99	[60]
GGA					4.70	[59]
GGA + U (Dudarev, FM imposed)	5.4				5.05	[60]
GGA + U (FLL, FM imposed)	6.1	0.70			5.27	[60]
r ² SCAN					4.65	[62]
PBE0					5.22	[49]
SIC LSD					5.14	[63]
LAK meta-GGA					5.14	[62]
Experiment						
X-ray diffraction (γ -phase)			room temperature	0.00	5.16	[47]
X-ray diffraction (γ -phase)			room temperature	0.56	5.10	[64]
X-ray diffraction (γ -phase)			room temperature	1.30	5.06	[47]
X-ray diffraction (α -phase)			77	0.00	4.85	[1]
X-ray diffraction (α -phase)			298	0.81	4.82	[1]

minimum at approximately 5.06 Å, in good agreement with experiment.

This congruence underscores the crucial role of electronic correlations *and* vibrational entropy, both of which are captured within the current DMFT framework and are necessary to stabilize the high-temperature, large-volume γ phase of cerium. We note that the DMFT free energy evaluated at the experimental lattice constant, $a = 5.16$ Å [47], exceeds the theoretical minimum by only about 0.015 eV per primitive cell $\approx 150 \text{ K} \times k_B$, which is small compared to the temperature, $T = 580 \text{ K}$, considered here.

As shown in Table I, conventional LDA and GGA approaches significantly underestimate the lattice constant of γ -Ce. Earlier LDA + DMFT calculations based on

the Hubbard-I approximation already yield improved values around 4.9–5.0 Å. Given that these evaluations were effectively zero-temperature internal-energy minimizations, it is physically expected that they fall slightly short of the experimental high-temperature volume. Finite-temperature LDA + DMFT calculations using QMC found slightly larger lattice constants on the basis of the total internal energy but still fell short of the experimental value [28]. More recent CT-QMC-based LDA + DMFT + SOC studies computing *electronic* free energies (using the impurity entropy), predict equilibrium lattice constants of 5.04 Å (5.06 Å) at $T = 400 \text{ K}$ ($T = 900 \text{ K}$) [28], in notably better agreement with experiment. In the present results, the lattice constant in a purely electronic picture comes out slightly smaller, 4.99 Å, at

$T = 580$ K. We believe this discrepancy to arise mainly from a different treatment of the Coulomb interaction. While we use density-density interactions, Haule and Birol [28] used the full Coulomb interaction. Combining the electronic free energies with the renormalized phonon free energy, we find the equilibrium lattice constant of $5.06 \text{ \AA}$ at $T = 580$ K, in near-quantitative agreement with experiment. The phonon-driven $\sim 1.5\%$ increase in lattice constant underscores the importance of a fully finite-temperature treatment that accounts for both electronic correlations and lattice vibrations. Future work will assess whether the remaining 1% underestimation of the lattice constant can be accounted for by using the full Coulomb interaction along with SOC in our comprehensive electron-phonon workflow, or whether a step beyond density-functional based kinetics is required.

To assess the temperature robustness of the DMFT results, we have also examined the lattice-parameter dependence of the internal energy and the electronic free energy at 900 K. The corresponding data are presented in Sec. S11 of SM [34]. The positions of the free-energy minima remain very close to those obtained at 580 K, with only a marginal shift towards larger lattice parameters, confirming that the conclusions drawn in the main text are insensitive to the specific temperature chosen within the γ -phase regime.

It is also worth noting that the agreement obtained with SIC-LSD and the LAK meta-GGA [62,63] should be interpreted with caution, as neither approach includes an explicit treatment of dynamical correlations or finite-temperature entropy, both of which are essential for stabilizing the γ phase of cerium.

IV. CONCLUSIONS

In this work, we have presented a comprehensive finite-temperature investigation of the equilibrium lattice properties of elemental cerium by combining density-functional theory with dynamical mean-field theory and explicit phonon free-energy contributions. By treating electronic correlations and lattice vibrations on an equal footing, we construct a correlated-electron-lattice free-energy framework that enables a quantitative assessment of structural stability beyond static total-energy considerations.

While conventional density-functional approximations significantly underestimate the equilibrium volume of cerium, we find that the inclusion of dynamical electronic correlations within DMFT leads to a substantial expansion of the lattice. Importantly, electronic correlations also strongly renormalize

the lattice dynamics, modifying both the phonon spectrum and its volume dependence. As a consequence, the phonon free energy exhibits a markedly reduced sensitivity to the lattice constant once correlations are included, in sharp contrast to the pronounced volume dependence obtained at the DFT level.

The combined effect of electronic and vibrational entropy results in a pronounced restructuring and flattening of the finite-temperature free-energy surface in the expanded volume regime. This behavior stabilizes lattice constants that are in close quantitative agreement with experimental measurements of the high-temperature γ phase.

Specific to cerium, logical next steps are the inclusion of the full Coulomb interaction and spin-orbit coupling in all parts of the calculations, as well as simulations at lower temperatures to assess the emergence of a free-energy minimum associated with the α phase.

More broadly, our results demonstrate that correlation-induced renormalization of phonon free energies constitutes a key ingredient for a physically controlled description of finite-temperature phase stability in strongly correlated materials. The framework established here offers a systematic route for extending first-principles free-energy calculations to complex correlated solids, where the interplay between electronic correlations and lattice dynamics is crucial.

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DATA AVAILABILITY

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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