Dynamical response and instability in ceria under lattice expansion

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We present results of density functional theory calculations on the phonon dispersion and elastic constants of bulk ceria (CeO2) as a function of positive and negative isotropic strain, which could be induced thermally or by cationic doping. We find that, as the lattice is expanded, there is a significant softening of the B_{1u} mode at the X point. This mode consists of motions of oxygens in the [001] direction. At a strain of 1.6%, corresponding to a temperature of 1600 K, the B_{1u} and E_u modes at the X point cross, with an associated high, narrow peak in the phonon density of states appearing. We infer that this crossing indicates a coupling of the modes, leading to a transition to a superionic phase, where conductivity occurs in the [001] direction, mediated by anion interstitial site occupation. As the lattice is expanded further, the B_{1u} mode continues to soften, becoming imaginary at a strain of 3.4%, corresponding to a temperature of 2500 K. Following the imaginary mode would result in a cubic to tetragonal phase transition, similar to those known to occur with reducing temperature in zirconia (ZrO2) and hafnia (HfO2). Our calculated elastic constants, however, indicate that the structure remains mechanically stable, even at this level of expansion. As confirmed by our semiclassical free energy calculations, the cubic phase of ceria remains the most stable, while the imaginary mode indicates a change to a thermally disordered cubic phase, with the majority of disorder occurring on the anion sublattice. Our results explain the high temperature ionic conductivity in ceria and other fluorite-structured materials in terms of the intrinsic lattice dynamics, and give insight to the stability and anionic disorder at elevated temperatures.

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I. INTRODUCTION

Cerium dioxide (CeO2, or ceria) is an insulating rare earth metal oxide with a wide band gap and high thermal stability. It is used for a wide range of applications including glass polishing,1–3 ceramics,4,5 nanomedicine,6,7 solid state electrochemistry,8–10 and as a high-κ dielectric replacement for SiO2 in metal-oxide-semiconductor field effect transistors (MOSFETs).11–15 It is also of technological interest to the field of catalysis, where it can be used as a catalyst itself16–18 or as vacancies.8,26,27 How the material remains stable at high conductivity, related to the low energy of formation of oxygen vacancies, which allows the material to absorb oxygen under oxidizing conditions and release oxygen under reducing conditions.

Ceria stabilizes in the cubic fluorite phase (space group Fm3m) at ambient conditions and remains stable in this phase over a remarkably wide range of temperature,22,23 doping concentration,8,24,25 and level of nonstoichiometry.22,23 Coupled with this large stability range is a high ionic conductivity, related to the low energy of formation of oxygen vacancies.8,26,27 How the material remains stable at high temperatures, however, with a large degree of disorder in the anion sublattice, is not well understood.

The observed high ionic conductivity opens the possibility of using ceria as a solid electrolyte in solid oxide fuel cells (SOFCs)8–10 operating in the medium temperature range (600–900 K), where problems associated with start-up times and sealing are reduced.28 In this temperature range, ionic conduction is mediated by the presence of oxygen vacancies, which form both under the reducing conditions present in the cell and due to the presence of impurities. In order to avoid short circuiting the fuel cell, an ideal electrolyte will have high ionic and negligibly low electronic conductivity. In ceria, however, the formation of small polarons associated with oxygen vacancy formation (i.e., the reduction of CeIV to CeIII) has been proposed; these dopants are charge compensated by the formation of oxygen vacancies, without the associated rate for samples with higher Gd concentrations, which is as one would expect; the oxygen vacancy concentration depends on the concentration of Gd impurities, and greater oxygen vacancy concentrations will mean a greater anionic conductivity as temperature is increased. At temperatures above ~1600 K, however, the same conductivity was approached regardless of the doping concentration in the sample. The trend in ion...
conductivity versus temperature for the different samples also converged above this temperature. The author attributed this to a possible saturation in the concentration of oxygen vacancies in the samples. The level of nonstoichiometry of pure ceria ($x$ in CeO$_2$)$_{1-x}$ at this temperature in air is $x \approx 0.001$, which is at least an order of magnitude lower than that which would be present due to the Gd doping (up to 20% in the work of Hohnke). The reduction of ceria, therefore, is unlikely to lead to the concentrations of vacancies required to account for the convergence in conductivity versus temperature trends observed by Hohnke; it is possible that these results indicate a change in the mechanism of ionic conduction at elevated temperatures, from one purely mediated by oxygen vacancies.

The structural disorder of ceria at elevated temperatures (up to 1770 K) was studied experimentally by Yashima et al. They used neutron diffraction followed by a combination of Rietveld analysis, the maximum-entropy method (MEM), and MEM-based pattern fitting to determine the nuclear density distribution of ceria at various temperatures. The cubic fluorite structure can be pictured as consisting of a face-centered-cubic (fcc) lattice of cations, with all tetrahedral holes occupied by anions, so that the anions form a simple cubic sublattice. The octahedral hole in the fcc cation sublattice provides an interstitial site for the anions. The analysis of Yashima et al. demonstrated that oxygen in ceria has a complicated disorder, spreading over a much wider region than that of cerium. They found evidence for anisotropic thermal motions of oxygen about their ideal site, with increased motions along the [111] direction towards the interstitial site, which increased with increasing temperature. This suggests a diffusion mechanism mediated by anion Frenkel pairs, which form when oxygens move from their ideal lattice site to the interstitial site. This mechanism becomes more favorable when the lattice is thermally expanded. Their data were also consistent with a change to a thermally disordered phase, where the material remains on average cubic, with the majority of the thermal disorder occurring in the anion sublattice.

At temperatures close to, but below, their melting points cubic fluorite structured materials are known to undergo a transition to the “superionic” regime, characterized by a dramatic increase in ionic conductivity while electronic conductivity remains low. This transition is associated with a large dynamic disorder of the anion sublattice, where transport of anions occurs via a hopping mechanism though the details are still not completely understood. This mechanism of conduction may play a role in ceria at elevated temperatures; superionic conductivity has been observed in ultrathin Gd-doped ceria and Sm-doped ceria nanocomposites at relatively low temperatures (under 900 K), but in these cases was attributed to grain-boundary and size effects.

In this paper we study the static and dynamic stability of ceria over a range of values of isotropic strain, $\varepsilon$, defined as

$$\varepsilon = \frac{a - a_0}{a_0}$$

(where $a_0$ is the equilibrium lattice constant and $a$ is the strained lattice constant). We use density functional theory (DFT) in the generalized gradient approximation to exchange and correlation, with a Hubbard $U$ parameter applied to $f$ electrons of Ce (GGA + $U$), to calculate the force constants and derive the elastic constants and dynamical matrix. Calculations are further validated for certain values of strain and reciprocal lattice vector using a hybrid density functional, which provides a more accurate and unbiased description of the electronic structure, but is substantially more computationally intense than standard DFT. We find good agreement between the two approaches. At the $X$ point in the reciprocal lattice, the $B_{1u}$ mode, consisting of oxygen motions in the [001] direction, softens considerably as the lattice is expanded. At $\varepsilon = 0.016$, the $B_{1u}$ mode crosses the $E_u$ doublet (which involves oxygen motion perpendicular to [001]). A maximum in the density of phonon states occurs at the crossing point. We propose that the modes couple, resulting in an increased probability of anion interstitial site occupation. We infer that this leads to a transition to an ionic conductivity regime dominated by a mechanism mediated by anions occupying, or moving close to, the interstitial site. Given the experimentally determined relationship between temperature and lattice expansion in ceria, a strain of 1.6% corresponds to a temperature $T = 1600$ K, which is the value of $T$ at which Hohnke observed the convergence in ionic conductivity for samples with different Gd concentrations. As the lattice is expanded further, the $B_{1u}$ mode continues to soften, becoming imaginary at $\varepsilon = 0.034$, which corresponds to $T = 2500$ K (close to, but below, the melting point of $\sim 2800$ K$^5$). Following the imaginary mode results in a transition from the cubic to a tetragonal phase, similar to what is observed in zirconia and hafnia. From our calculated values of the elastic constants, however, we find that the structure remains mechanically stable at this level of expansion. Using a shell interatomic potential model, which describes the lattice dynamics of the expanded cell in reasonable agreement with our DFT approach, we calculate the free energies of the two phases in the quasiharmonic approximation, finding the cubic phase to remain the more stable as the mode becomes imaginary. We therefore attribute the appearance of the imaginary mode to a change to a thermally disordered phase, where the material remains on average cubic, with the majority of the thermal disorder occurring in the anion sublattice.

The rest of the paper is as follows: in Sec. II details of our calculations are given, in Sec. III we present and discuss our results, and in Sec. IV we summarize the main findings of our study.

II. CALCULATIONS

We have used DFT to calculate the equilibrium structure of bulk ceria and the force constants at a range of positive and negative isotropic linear strains. All our DFT calculations were carried out using the VASP code, utilizing the solids-corrected Perdew-Burke-Ernzerhof (PBEsol) GGA exchange-correlation (XC) functional with the projector augmented wave (PAW) method. To correct the self-interaction error present in DFT, we have taken two approaches. The first was to apply a Hubbard $U$ parameter ($U = 5$ eV) on the Ce$_{4f}$ (GGA + $U$), which has been shown to give accurate descriptions of the localized nature of $n$-type defects in ceria. The second was to use hybrid exchange correlation functionals (hybrid-DFT), where a percentage of exact exchange is included. For this we used the screened...
We have used a modified version of the shell-polarizable interatomic potential model developed previously,72,73 which gives accurate results on lattice dynamics at zero strain while maintaining good qualitative agreement with our DFT approaches at large strains, to calculate the vibrational contribution to the free energy of the relevant phases of CeO₂, under the quasiharmonic approximation. Our aim here is to test the stability of the phases at temperatures above 2000 K at a significantly reduced computational cost. We have used GULP74 to perform these calculations.

### III. RESULTS

#### A. Equilibrium properties of ceria

We present our calculated values of lattice constant ($a₀$), bulk modulus ($B₀$) and its pressure derivative ($B'₀$), elastic constants ($C_{11}$, $C_{12}$, and $C_{44}$), high-frequency dielectric constant ($\epsilon_∞$), and Born effective charges ($Z^*$) of CeO₂ in the cubic fluorite phase, compared with previous experimental and theoretical results from the literature. We find good agreement within our calculated $a₀$ and the low temperature experimental value of Gupta et al.,78 with our GGA + $U$ approach differing by 0.5% and our HSE06 hybrid-DFT approach differing by less than 0.05%. In the GGA + $U$ approach, using the PBEsol functional gives an improvement of 0.7% in $a₀$, when compared to experiment, over using the PBE functional.61-65 Our values of $B₀$ and $B'_₀$ also agree well with experiments.80,81,83 We have calculated the elastic constants, $\epsilon_∞$, and $Z^*$ using GGA + $U$. We find good agreement with experiment in our values of $C_{11}$, $C_{12}$, and $C_{44}$, with the largest discrepancy (7.7%) occurring for $C_{11}$. This latter discrepancy could be attributed to an overestimation of the lattice constant by our GGA + $U$ approach. Our results agree well with the calculations of Shi et al.75 at the LDA + $U$ level of theory and are in excellent agreement with previous calculations at the LDA level.76,77 Our calculated value of $\epsilon_∞$ is higher than experiment84,85 but agrees well with previous calculations at a similar level of theory,75,76,86 as do our calculated Born effective charges.

#### B. Dynamical properties of ceria

Our calculated phonon dispersion using GGA + $U$ is shown in Fig. 1, compared with the Raman scattering measurements of Nakajima et al.83 and Kouroklis et al.,87 the infrared
symmetry representations at the squares; Ref. 90) methods. The modes are labeled according to their green diamonds; Ref. 89), and inelastic neutron scattering (purple arrows; Refs. 88, 87, and 83), infrared spectroscopy (sideways-pointing brown triangles; Ref. 88), reflectivity-derived (purple squares; Ref. 90) methods. The modes are labeled according to their symmetry representations at the \( \Gamma \), X, and L points.

spectroscopy measurements of Ohura,\(^\text{88}\) the results of Marabelli \textit{et al.} derived from reflectivity measurements,\(^\text{89}\) and the inelastic neutron scattering measurements of Clausen \textit{et al.}\(^\text{90}\) These experimental measurements were carried out at room temperature (RT); in principle, a more accurate comparison between the data sets may be achieved by performing the GGA + \( U \) dispersion calculation with the lattice expanded by an amount corresponding to the thermal expansion at RT. The experimentally determined thermal expansion coefficient at RT, however, is \( \sim 10^{-6} \) K\(^{-1}\).\(^\text{78,91}\) The change in the calculated frequencies when the lattice is expanded by an amount corresponding to this thermal expansion is within the overall error in the results. For this reason we have chosen to perform the calculations at the athermal limit.

A comparison of the phonon frequencies in Fig. 1 shows that our GGA + \( U \) approach agrees well with experiment, in particular in reproducing the acoustic mode dispersion. Our calculated acoustic mode frequencies agree with the measurements of Clausen \textit{et al.}\(^\text{90}\) within \( \sim 1\%\), apart from the longitudinal acoustic (LA) mode at the \( L \) point, which we find is 4\% lower than the value they report. We find less good agreement, however, between our calculated infrared-active \( F_{1u} \) LO-TO mode splitting and experiment. We calculate the \( F_{1u} \) LO phonon mode at the \( \Gamma \) point to be \( \omega_{LO} = \) 552 cm\(^{-1}\), which is \( \sim 7.5\% \) lower than the experimental results of Marabelli \textit{et al.}\(^\text{89}\) and Ohura.\(^\text{88}\) We note that our calculation of the LO-TO mode splitting is determined using a nonanalytical correction term,\(^\text{69-71}\) which depends on \( \epsilon^{-\infty} \) and the Born effective charges \( Z^* \). We have used our calculated values for \( \epsilon^{-\infty} \) and \( Z^* \) (see Table I) when determining the splitting. If we instead use the experimental value of \( \epsilon^{-\infty} = 5.31 \)\(^\text{84}\) we find that \( \omega_{LO} = 596 \) cm\(^{-1}\), which is within 0.2\% of experiment.\(^\text{87,88}\) Our calculated dispersion is in excellent agreement with previous calculations at a DFT-LDA level of theory.\(^\text{75,76}\) One detail evident from our results but not observed in the calculations of Gürel \textit{et al.}\(^\text{76}\) and Shi \textit{et al.}\(^\text{75}\) is the crossing of the longitudinal and transverse branches of the Raman active (\( F_{2g} \) at the \( \Gamma \) point) mode at \( \sim 420 \) cm\(^{-1}\) in the \( \Gamma \rightarrow L \) direction (\( \{\zeta \zeta \zeta \} \) in Fig. 1). Along this direction the triply degenerate (at the \( \Gamma \) point) \( F_{2g} \) mode splits into a doublet and singlet (transverse and longitudinal, respectively). This branch crossing, which was not reproduced by Clausen \textit{et al.}\(^\text{90}\) in their shell model, explains their labeling of the modes along these branches. They predicted a singlet mode frequency lower than that of the doublet at the \( L \) point. From our results we see that the longitudinal branch does fall below the transverse branch at the point \( (0,0,0,0,0) \) along the \( [\zeta \zeta \zeta \zeta \zeta] \) direction (measured in units of \( 2\pi/a_0 \)), but the branches cross once more at the point \( (0,0,0,0,0) \), resulting in a higher singlet mode frequency than the doublet at the \( L \) point, as would be expected.

C. Dynamical properties as a function of isotropic strain

Our results for the effect of applying positive and negative \( \epsilon \) to the lattice, i.e., expansion and contraction, on the calculated phonon dispersion using GGA + \( U \) are shown in Fig. 2, along

![FIG. 2. (Color online) Phonon dispersion curves and densities of states for CeO\(_2\) determined using GGA + \( U \) at different values of linear strain \( \epsilon \). The horizontal axis is labeled according to the convention of Fig. 1. At the \( X \) point, the \( B_{1u} \) singlet is indicated by the downward-pointing (green) triangle, while the \( E_g \) doublet is indicated by the upwards-pointing (blue) triangle. The unshaded region highlights the softening of the \( B_{1u} \) mode at the \( X \) point.](image-url)
with the calculated phonon density of states (PDOS). Changing the value of \( \varepsilon \) is equivalent to applying a pressure \( p \) to the lattice. From our GGA + \( U \) approach we can determine this pressure. We found that \( p \) as a function of \( \varepsilon \) was fitted well (with a \( \chi \)-squared value under 10^{-3}) by the following polynomial:

\[
p = 3806e^2 - 607.7e(GPa),\]

(2)

where \( e \) is a strain of \( \varepsilon = -0.02 \) gives a pressure \( p = 13.7 \) GPa.

We first consider the case of negative \( \varepsilon \) (contraction). Negative \( \varepsilon \) results in a softening of the lattice and a corresponding increase in phonon frequencies. The \( F_{2g} \) mode determined at 449 cm\(^{-1}\) shifts to 489 cm\(^{-1}\) at \( \varepsilon = -0.02 \), i.e., at \( p = 13.7 \) GPa. Kourotkis et al.\(^{87}\) measured this mode to be 464 cm\(^{-1}\) at ambient pressure, increasing to 507 cm\(^{-1}\) at \( p = 13.4 \) GPa. Xiao et al.,\(^{79}\) using Raman measurements, found that this mode increased to 501 cm\(^{-1}\) at \( p = 12.0 \) GPa. Our results are in good agreement with these experimental results.

We now turn to the case of positive \( \varepsilon \) (expansion). From Fig. 2 we note that increasing \( \varepsilon \) leads to an overall softening of the phonon modes, as the material itself becomes softer. The crossing of the \( B_{1u} \) and \( E_u \) modes at the \( X \) point is shown more clearly in Fig. 3, where we have plotted their frequencies as a function of \( \varepsilon \). We have also determined a temperature scale that corresponds to the level of strain studied, which we have shown in Fig. 3, for which we have combined the data of Sameshima et al.\(^{31}\) (valid for the temperature range 298–1473 K), and the data of Yashima et al.\(^{41}\) (valid for temperatures up to 1770 K). The two experimental data sets are in good agreement in the temperature range common to both. For temperatures above 1770 K, we have applied a quadratic fit to the data of Yashima et al. (with a \( \chi \)-squared value of \( \sim 10^{-3} \)).

### D. \( B_{1u} \) mode softening at the \( X \) point

To study the effect of strain on the \( B_{1u} \) mode in particular, we have performed hybrid-DFT calculations of the phonon modes. Hybrid functionals (such as HSE06) provide a marked improvement in description of the electronic structure,\(^{66,92-94}\) resulting in more accurate structural properties (see Table I) and descriptions of the potential energy landscape. We therefore expect hybrid DFT to provide an improved description of the phonon dispersion in comparison with GGA + \( U \). As hybrid DFT is significantly more computationally intense in comparison to GGA + \( U \), we limit our application of this approach. We have performed force constant calculations using a \( 2 \times 2 \times 2 \) expansion of the primitive unit cell for \( \varepsilon = 0 \) and \( \varepsilon = 0.035 \). This supercell size provides phonon frequencies at the \( \Gamma \), \( X \), and \( L \) points. We present our results for all calculated frequencies at these reciprocal lattice points in Table II, shown in comparison to our GGA + \( U \) calculated values and experimental results,\(^{83,87-90}\) where available. For our hybrid-DFT calculations we have used the experimental value of \( \varepsilon^{\infty} = 5.31 \)\(^{84}\) when determining the nonanalytical correction term to account for \( F_{1u} \) TO-LO splitting at \( \Gamma \). Hybrid DFT gives us an improved description of the optical modes at the \( \Gamma \) point, and the high frequency \( E_u \) mode at the \( X \) point, but no significant improvement over GGA + \( U \) for the low frequency acoustic modes at the \( X \) and \( L \) points. To study the softening of the \( B_{1u} \) mode at the \( X \) point using hybrid DFT, we performed further calculations of the force constants using a cubic (12 atom) cell (this cell provides phonon frequencies at the \( \Gamma \) and \( X \) points only). We plot our results for the \( B_{1u} \) and \( E_u \) modes at the \( X \) point as a function of \( \varepsilon \) and \( T \) in Fig. 3.

Using our hybrid-DFT (GGA + \( U \)) approach, we find that the two modes cross at \( \varepsilon = 0.016 \) (\( \varepsilon = 0.02 \), corresponding to \( T = 1600 \) K (\( T = 1770 \) K), and that the \( B_{1u} \) mode becomes imaginary at \( \varepsilon = 0.034 \) (\( \varepsilon = 0.038 \), corresponding to \( T = 2500 \) K (\( T = 2700 \) K). Schematics of the two modes (singlet and doublet) are shown in Fig. 4. The \( B_{1u} \) mode is a singlet [Fig. 4(a)], consisting of motions of the \( O \) ions in the [001] direction, with no motion of the \( Ce \) ions. If we consider the \( O \) sublattice to contain chains of \( O \) ions in the [001] direction, we observe that, along the chains, the \( O \) atoms move in phase, with adjacent chains moving opposite in phase. The \( E_u \) mode is a doublet [Figs. 4(b) and 4(c)], consisting of both \( Ce \) and \( O \) motion. All motion occurs perpendicular to the [001] direction. Alternating layers of \( Ce \) along the [001] direction move in opposite phases. The \( O \) motion is at right angles to that of \( Ce \). Adjacent \( O \) ions move in opposite phases, so that the motion consists of a series of alternating oxygen-oxygen stretch modes. In this mode, the amplitude of motion of the...
TABLE II. Calculated phonon mode frequencies of CeO₂ at the high symmetry points of the Brillouin zone, \( \Gamma \), \( X \), and \( L \) determined using GGA + \( U \) and hybrid DFT using the HSE06 functional, shown in comparison to experimental results where available. The results are shown for different values of strain, \( \varepsilon \). Negative frequency indicates an imaginary mode (unit: cm⁻¹).

\[ \varepsilon = 0 \]

<table>
<thead>
<tr>
<th>Mode</th>
<th>GGA + ( U )</th>
<th>HSE06</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{1u} ) (LO)</td>
<td>552</td>
<td>591</td>
<td>585, 597, 598, 599</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>449</td>
<td>451</td>
<td>460, 465, 468, 473</td>
</tr>
<tr>
<td>( F_{1u} ) (TO)</td>
<td>290</td>
<td>269</td>
<td>218, 273, 274, 275</td>
</tr>
</tbody>
</table>

\[ \varepsilon = 0.035 \]

<table>
<thead>
<tr>
<th>Mode</th>
<th>GGA + ( U )</th>
<th>HSE06</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1g} )</td>
<td>583</td>
<td>611</td>
<td></td>
</tr>
<tr>
<td>( E_{u} )</td>
<td>453</td>
<td>460</td>
<td>464, 465</td>
</tr>
<tr>
<td>( A_{2u} )</td>
<td>264</td>
<td>275</td>
<td></td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>254</td>
<td>224</td>
<td>249</td>
</tr>
<tr>
<td>( B_{1u} )</td>
<td>179</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td>( E_{u} )</td>
<td>138</td>
<td>129</td>
<td>138, 139</td>
</tr>
</tbody>
</table>

Ce ions is a factor of \( \sim 10 \) times that of O at \( \varepsilon = 0 \), but this factor reduces as the cell is expanded, so that at \( \varepsilon = 0.04 \) the Ce amplitude is three times the amplitude of O.

### E. Coupling of the \( B_{1u} \) and \( E_{u} \) modes

When the \( B_{1u} \) and \( E_{u} \) modes cross at the \( X \) point, there is an associated large, narrow peak in the PDOS (indicated by an arrow in Fig. 2). This implies that the occupation of these modes will be high at high temperatures. If there is a large amount of (in-phase) atomic motion consisting of these modes, with relatively large amplitudes at higher temperatures, there will be an increased probability of a coupling, or combination, of the modes. We illustrate the resulting motion when the \( B_{1u} \) and \( E_{u} \) modes combine at the \( X \) point in Fig. 5. For clarity we only show the motion of a single oxygen chain in the [001] direction, with the adjacent chains not shown. We also show the relevant Ce motion in the vicinity of the oxygen chain. The interstitial site is in the center of the cube formed by the Ce ions (indicated by a black cross). When the modes combine, there is an alternating effect along the [001] oxygen chain. One oxygen ion (O1 in Fig. 5) moves towards the interstitial site, with a Ce (Ce1 in Fig. 5) moving closer to this site, providing a possible further stabilization for the oxygen. The next oxygen ion (O2 in Fig. 5) along [001] moves towards a Ce site, with the Ce ion (Ce2 in Fig. 5) moving away from this site. There is an equivalent Ce ion (Ce3 in Fig. 5) moving towards the Ce site along [110], which, as the Ce motion is greater than the oxygen motion perpendicular to [001], may lead to a “straightening” of the motion of this O ion in [001] direction. The pattern is repeated on moving along the [001] direction. The pattern is also repeated for different chains of oxygen ions along [001], but for each chain, a different interstitial site is involved in the motion.

### 1. Implications for ionic conductivity

The overall effect of this combined motion will be an increased probability of occupation of the interstitial site by

![FIG. 4. (Color online) Schematic of the eigenvectors associated with (a) the \( B_{1u} \) singlet mode and (b),(c) the \( E_{u} \) doublet mode at the \( X \) point. O (dark-gray/red spheres) atomic motion is indicated by dark-gray (green) arrows. Ce (light-gray/blue spheres) atomic motion is indicated by light-gray (orange) arrows. The eigenvectors are shown in the cubic unit cell with the simple cubic anion sublattice highlighted. The lengths of the arrows indicate the relative proportion of the magnitude of the O and Ce atomic motions, which reduces as the lattice is expanded (see text).](214304-6)
B1u motions associated with the vibrations of the cube formed by the Ce ions (light-gray/blue spheres). The gray/red spheres) in the [001] direction (adjacent O chains not shown). X at the point.

FIG. 5. (Color online) Combination of the B1u and E_u modes at the X point, shown for clarity acting on a single O chain (dark-gray/red spheres) in the [001] direction (adjacent O chains not shown). The interstitial site is represented by a black cross in the center of the cube formed by the Ce ions (light-gray/blue spheres). The motions associated with the B1u and E_u modes are indicated by thinner, darker-colored/shaded arrows, while the resulting motion from the combination of the modes is indicated by thicker, lighter-colored/shaded arrows.

an oxygen ion. From our calculated eigenvectors, we estimate that the amplitude of O motion in the B1u mode is \( \sim 0.5 \) Å at \( T = 1600 \) K. In the harmonic approximation, the amplitude of vibration is inversely proportional to the square root of the frequency. As \( \varepsilon \) is increased, the mode frequency reduces, leading to an increase in the amplitude. The motion of the oxygens in the [001] direction is greater than their motion perpendicular to it, but as \( \varepsilon \) is increased, the oxygen motion perpendicular to [001] increases. This, combined with the overall increase in amplitude as the frequency reduces, will lead to an increase in the probability of the anion approaching the interstitial site, facilitating ionic transport in the [001] direction in a caterpillarlike mechanism, where each oxygen ion moves to the site vacated by its nearest-neighbor (as a result of an oxygen occupying the interstitial site), i.e., the conductivity is mediated by Frenkel-like disorder. When the B1u and E_u modes combine, there will be a switch to this mechanism of ionic conduction, which will be independent of the number of oxygen vacancies present due to reduction or the presence of impurities. Since we predict the mode coupling to occur at \( \varepsilon = 0.016 \), or \( T = 1600 \) K, this provides an explanation for the observations of Hohnke. As the temperature rises above 1600 K, the predominant ionic conductivity mechanism switches from that mediated by the oxygen vacancies present in the samples due to the Gd impurities and/or reduction to that mediated by the anion interstitial site occupation resulting from the coupling of the B1u and E_u modes at the X point. There is therefore a convergence in ionic conductivity for the samples containing different Gd concentrations, and also a convergence in the rate of increase in ionic conductivity as the temperature is increased further. Our results are also consistent with the observation of Yashima et al. Their nuclear density distribution measurements indicated increased motion of oxygen in the [111] direction (i.e., towards the interstitial site), which suggested a curved diffusion path along [001], similar to the diffusion mechanism we are proposing (we note that Yashima et al. concluded that their data was also consistent with a diffusion path along the [111] direction).

Similar mechanisms of ionic conductivity in fluorite-structured materials have been proposed previously for UO_2, PbF_2, CaF_2, BaF_2, and SrF_2. When studying the effect of expansion on the antifluorite Li_3O, Gupta et al. and Fracchia et al. observed a similar softening of the B1u mode at the X point as we have calculated for ceria. In the case of Li_3O, however, the B1u mode is the lowest in frequency at the X point at equilibrium. As the lattice is expanded, the B1u mode softens and becomes imaginary at \( T = 1200 \) K, close to, but below, the melting point. In both studies the authors attributed the imaginary mode to a change to a superionic conductivity regime, mediated by cation hopping (as Li_3O is an antifluorite) along [001]. This conclusion does not necessarily follow, however, as the imaginary mode may indicate either a structural phase change or a change to a thermally disordered phase (see below). A more convincing argument was made by Garvartin et al., who calculated a crossing of the transverse and LO modes at temperatures above 1000 K in Li_3O. They attributed this to a change to a conductivity regime mediated by a caterpillarlike mechanism, similar to what we propose for ceria. They further validated their results using molecular dynamics (MD) simulations. Guglielmetti et al. have performed an MD study on defect formation and stability in ceria using empirical potentials. They found that anion Frenkel recombination became more favorable at higher temperatures, and that, for anions, interstitial migration was faster than vacancy migration at temperatures above 1700 K. Their results are consistent with our proposed conductivity mechanism at elevated temperatures. Our work, however, demonstrates the basis of the effect in the temperature dependent lattice dynamics of the material. Further calculations of defect formation and migration, which will complement our present study, are underway and will be reported elsewhere.

2. Implications for nanoclusters

Tsunekawa et al. and Wu et al. reported that below a certain size, ceria experiences an anomalous lattice expansion, where average bond length within particles increases significantly. This phenomenon has been rationalized as an effect of reduction, with ceria nanoparticles rapidly losing oxygen as the surface area to volume ratio of the particle increases. Concomitantly, Weber et al. observed a broadening of the Raman peak as the ceria particle size decreased. Our findings provide a direct link between the two effects: Expansion of the lattice as the particle size decreases will lead to a coupling of modes, providing favorable conditions for phonon-phonon scattering, which will result in the observed broadening. Moreover, this expansion also provides grounds for the low-temperature disorder or phase transitions reported to occur in ceria at the nanoscale.

F. Stability of ceria at elevated temperatures

From our hybrid-DFT (GGA + U) calculations, we determine that the B1u mode becomes imaginary at the X point at \( \varepsilon = 0.034 \) (\( \varepsilon = 0.038 \)), corresponding to \( T = 2500 \) K.
found that anion sublattice “melting” occurred in the range 2300–2700 K. Such anion disorder at temperatures below the melting point in cubic fluorite structures has been studied extensively using neutron scattering techniques.\textsuperscript{42,43,96–98,112} Moreover, the high ionic conductivity has been associated with the thermal disorder in yttrium-doped zirconia, in particular in its cubic form, stabilized by lattice-mismatched induced strain when interfaced with SrTiO\textsubscript{3}.\textsuperscript{113,114}

IV. CONCLUSIONS

In summary, we have studied the static and dynamic stability of ceria by determining the phonon dispersion for a range of isotropic strains using GGA + \( U \) and hybrid DFT. Our calculated properties of the equilibrium structure agree well with experiment and previous calculations. Under expansion, we find a substantial softening of the \( B_{1u} \) mode at the \( X \) point. Using hybrid-DFT (GGA + \( U \)), we determine that, at \( \varepsilon = 0.016 \) (\( \varepsilon = 0.02 \)), corresponding to \( T = 1600 \) K (\( T = 1770 \) K), the \( B_{1u} \) and \( E_u \) modes cross at the \( X \)-point. A large maximum in the PDOS occurs at the frequency at which they cross. By studying the atomic motions involved in the two modes, we infer that they couple, resulting in a significant increase in probability of O atoms occupying, or moving close to, an interstitial site. This provides a mechanism for ionic conductivity, where anions move in the [001] direction. Our proposed temperature at which this occurs is in excellent agreement with measurements of ionic conductivity of Gd-doped ceria samples performed at high temperatures, where it was observed that above 1600 K all samples, regardless of Gd content, approached the same conductivity. As the lattice was expanded further, the \( B_{1u} \) mode continued to soften. Using hybrid-DFT (GGA + \( U \)), we determined that it became imaginary at \( \varepsilon = 0.034 \) (\( \varepsilon = 0.038 \)), corresponding to \( T = 2500 \) K (\( T = 2700 \) K). We found that the imaginary mode corresponded to a cubic to tetragonal phase transition. Our calculated elastic constants, however, indicated that the cubic structure remains mechanically stable at all values of \( \varepsilon \) studied.

Free energy calculations in the quasiharmonic approximation, performed using an interatomic potential model, indicated that the cubic phase remained the most stable configuration when the \( B_{1u} \) mode became imaginary. We therefore attribute the imaginary mode to a transition to a thermally disordered phase which remains cubic on average, with the majority of the disorder occurring in the anion sublattice.

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As the frequency approaches zero when the strain is increased further, anharmonic effects will become dominant. These will dampen the atomic motion and redistribute the thermal energy via phonon-phonon interactions, meaning that the amplitude will not become infinite. Interestingly, this result is counterintuitive in the context of symmetry based predictions of phase stability. Typically, one observes an increase in symmetry with temperature, or equally a decrease with pressure. With ceria, the opposite occurs according to our calculations, when vibrational free energy is not taken into account.