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Predictions of thermal expansion coefficients of rare-earth zirconate pyrochlores: A quasi-harmonic approximation based on stable phonon modes

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Rare-earth (RE) pyrochlores are considered as promising candidate materials for the thermal barrier coating. In this study, we performed first-principles calculations, augmented by quasi-harmonic phonon calculations, to investigate the thermal expansion behaviors of several RE₂Zr₂O₇ (RE = La, Nd, Sm, Gd) pyrochlores. Our findings show that RE₂Zr₂O₇ pyrochlores exhibit low-lying optical phonon frequencies that correspond to RE-cation rattling vibrational modes. These frequencies become imaginary upon volume expansion, preventing correct determination of the free energy versus volume relation and thereby quantification of thermal expansion using QH phonon calculations. To address this challenge, we proposed a QH approximation approach based on stable phonon modes where the RE-cation rattling modes were systematically eliminated. This approach is shown to provide accurate predictions of the coefficients of thermal expansion (CTEs) of RE₂Zr₂O₇ pyrochlores, in good agreement with experimental measurements and data from first-principles molecular dynamics simulations. In addition, we showed that the QH Debye model considerably overestimates the magnitudes and wrongly predicts the trend for the CTEs of RE₂Zr₂O₇ pyrochlores. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4954280]

I. INTRODUCTION

The efficient use of energy in turbine engines demands high combustion temperature, often much beyond the melting temperature of the superalloy used in the turbine blades.¹ This high-temperature operation is enabled by the application of a multilayer coating, i.e., thermal barrier coating $(TBC)^{2-4}$ on the turbine blades that shields the underlying superalloy from the hot combustion gas. The capacity of TBC in shielding heat is attributed to its outmost layer, i.e., the top coat, being a ceramic oxide of low thermal conductivity. Consequently the development of new top coat materials of lower thermal conductivities has always been central in the continuous pursuit of higher energy efficiency for turbine engines. Besides the apparent need for low thermal conductivity, one must also consider the strain compliance of the ceramic top coat with respect to the underlying metallic bond coat. Close coefficients of thermal expansion (CTEs) between the top coat and bond coat are thus required to minimize the mismatch strain during thermal cycling in order to ensure mechanical stability and prevent exacerbated coating failure.^{5,6}

Currently, the material commonly used for the top coat is ${\sim}7\,\text{wt}.\,\%\,\,Y_2O_3\text{-stabilized }ZrO_2$ (7YSZ) due to their lower inherent thermal conductivities^{7,8} and high CTEs⁹ that match the CTE of the metallic bond coat⁹ well to avoid top coat spallation.⁹ Nonetheless the performance of 7YSZ is discounted by accelerated sintering kinetics^{10,11} and phase destabilization^{12,13} at elevated temperatures, and susceptibility to calcium-magnesium aluminosilicate (CMAS) penetration,^{14,15}

and therefore alternative top coat materials are sought. In the search of alternatives for 7YSZ, rare-earth (RE) pyrochlores recently emerge as potential candidate materials, given their low intrinsic thermal conductivities (i.e., $1-2 \text{ W m}^{-1} \text{ K}^{-1}$), ^{16–18} and their sluggish sintering kinetics¹⁹ as well as their ability to moderate CMAS infiltration.²⁰ To assess the strain compliance of the RE pyrochlores, a series of experiments were carried out to measure their thermal expansions.^{21–25} In parallel to these experimental measurements, lately several theoretical studies^{26–28} were also performed, trying to predict the CTEs using computational methods to aid the experiments. For instance, Qun-bo et al.²⁶ studied the CTEs of several RE₂Zr₂O₇ systems using classical molecular dynamics (MD) simulations with a Buckingham-type pair-wise potential. Yet apparently, it is unlikely for such a simple potential that only accounts for the short-range interactions to be sufficient to accurately describe the interactions within the RE₂Zr₂O₇ system. In the studies by Feng et al.,^{27,28} a quasi-harmonic (QH) Debye model was used to examine heat capacities and CTEs of a few RE₂Zr₂O₇ and RE₂Sn₂O₇ systems. However in those studies, the phonon dispersion was simply assumed to be linear with the wave vector,²⁹ which may be enough to approximate some simple systems, but very much questionable for RE pyrochlores with complex phonon dispersions. As such, further work is necessary to explore the full phonon dispersions and improve our theoretical capacity to provide more accurate prediction of CTEs of RE pyrochlores in order to facilitate the material exploration.

In the present study, we utilize the quasi-harmonic (QH) phonon calculations, which have been proven to be a powerful tool for investigating thermal properties of many materials,^{30,31} to investigate thermal expansion of RE

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pyrochlores. The $RE_2Zr_2O_7$ (RE = La, Nd, Sm, Gd) pyrochlore group are chosen as the model systems for our study. The phonon dispersion spectra as the pyrochlore volume varies were computed employing the density-functional perturbation theory (DFPT).³² We found RE pyrochlores exhibit low-lying optical branches that correspond to REcation rattling vibrational modes. Lattice expansion was found to induce softening of these rattling modes, resulting in unphysical irregularities in the free energy versus volume relation determined from the QH phonon calculations. To address this challenge, we proposed a QH approximation approach based on stable phonon modes where the REcation rattling modes were eliminated. This approach was shown to correctly produce the free energy versus volume relation and accurately predict the CTEs of RE pyrochlores, verified by comparison with experimental measurements. Meanwhile, the QH Debye model and the first-principles molecular dynamics (FPMD) simulations were also employed to predict the thermal expansion behaviors of the RE pyrochlores. The predictions from FPMD simulations also show good agreement with experimental data, albeit being slightly higher than the ones predicted from our proposed QH approximation approach. On the other hand, the QH Debye model not only considerably overestimates the CTEs of RE pyrochlores, but also yields a different trend as the one observed in experiments.

II. METHODOLOGY

A. Free energy minimization and quasi-harmonic (QH) approximation

For an ensemble of a volume V, held at a fixed temperature T and without any applied pressure, the equilibrium volume can be obtained by minimizing the total free energy

$$F_{total}(V,T) = F_e(V,T) + F_{vib}(V,T), \tag{1}$$

where $F_e(V, T)$ is the free energy of electronic structure and $F_{vib}(V, T)$ is the vibrational Helmholtz free energy. With the electronic entropy contribution being negligible for insulators,³² $F_e(V, T) \approx F_e(V, 0)$, which can be readily obtained from first principles calculations. $F_{vib}(V, T)$, on the other hand, can be approximated by two methods, described as follows. One method is to perform QH phonon calculations,^{32,33} with $F_{vib}(V, T)$ expressed as

$$F_{vib}(V,T) = \frac{1}{2} \sum_{q,s} \hbar \omega_{q,s}(V) + k_B T \sum_{q,s} \ln \left[1 - \exp(-\hbar \omega_{q,s})(V) / k_B T \right], \quad (2)$$

where $\omega_{q,s}$ represents the phonon frequency at wave vector q and band index *s*. \hbar is the reduced Planck's constant and $k_{\rm B}$ is the Boltzmann's constant. $\omega_{q,s}$ can be deduced from atomic force constants computed by first-principles calculations.^{32,33}

The phonons dispersions can also be approached using the QH Debye model,³⁴ with $F_{vib}(V, T)$ expressed as

$$F_{vib}(V,T) = \frac{9}{8} k_B \Theta_D + k_B T \bigg\{ 3 \ln \bigg[1 - \exp \bigg(-\frac{\Theta_D}{T} \bigg) \bigg] - D \bigg(\frac{\Theta_D}{T} \bigg) \bigg\},$$
(3)

where $D(\Theta_D/T)$ is the Debye integral given by $D(y) = 3/y^3 \int_0^y x^3/(e^x - 1)dx$, with Θ_D being the Debye temperature defined as

$$\Theta_D = \frac{\hbar}{k_B} f(v) (6\pi^2 V^{1/2})^{1/3} \left(\frac{B}{M}\right)^{1/2}, \tag{4}$$

with *M* being the mass per cell, *B* being the adiabatic bulk modulus, ν being the Poisson ratio, and $f(\nu)$ given by³⁴

$$f(v) = \left\{ 3 \left[2 \left(\frac{2}{3} \frac{1+v}{1-2v} \right)^{3/2} + \left(\frac{1}{3} \frac{1+v}{1-v} \right)^{3/2} \right]^{-1} \right\}^{1/3}.$$
 (5)

To compute $F_{vib}(V, T)$ (using QH phonon calculations or QH Debye model), first-principles density functional theory (DFT) calculations using the Vienna ab initio simulation package (VASP)^{35,36} with Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)³⁷ approach based on plane-wave basis sets were performed on RE₂Zr₂O₇ (RE = La, Nd, Sm, Gd) pyrochlore group. The *f*-electrons for RE elements Nd, Sm, and Gd are not treated explicitly, but are kept frozen in the cores. The electron-core interaction was described by the Blöchl's projector augmented wave method (PAW) within the frozen-core approximation.³⁸ The pyrochlore crystal structure is of space group $Fm\bar{3}m$, consisting of RE^{3+} cations at 16d (1/2, 1/2, 1/2), Zr^{4+} cations at $16c(0, 0, 0), O^{2-}$ anions at 48f(x, 1/8, 1/8), and O^{2-} anions at 8b (3/8, 3/8, 3/8) in the primitive cell.³⁹ A pyrochlore cubic conventional cell of 88 atoms (see illustration later in Fig. 3(c)) was used in DFT calculations. A $2 \times 2 \times 2$ Monkhorst-Pack (MP) k-mesh for Brillouin-zone integrations and a cutoff energy of 450 eV for the plane-wave basis set were used, which gives an energy convergence of less than 10^{-3} eV/atom. The convergence criteria for total energy and force on each ion were set as 10^{-9} eV and 10^{-6} eV Å⁻¹, respectively. The optimized lattice constants were obtained to be 10.58 Å, 10.66, 10.74, and 10.83 Å for $Gd_2Zr_2O_7$, Sm₂Zr₂O₇, Nd₂Zr₂O₇, and La₂Zr₂O₇, respectively, all within <1% deviation from experimental values.⁴⁰ For the phonon calculations, the real-space force constants were obtained with the DFPT³² calculations using $2 \times 2 \times 2$ supercells (176) atoms) constructed from the pyrochlore primitive cell (22 atoms) with a $1 \times 1 \times 1$ MP k-mesh. The phonon properties were calculated using PHONOPY⁴¹ on $23 \times 23 \times 23$ g grid for all RE pyrochlores considered. In the QH phonon calculations, the crystal lattice parameter was varied by $\pm 5\%$ with respect to the equilibrium lattice parameter. With $F_{vib}(V, T)$ and subsequently $F_{total}(V, T)$ at different volumes determined, free energy minimization can be performed to obtain the equilibrium volume V(T) of the material system at

temperature *T*. The strain variation of $\pm 5\%$ is used to ensure sufficient precision in the fitting of $F_{total}(V, T)$ to determine V(T).

B. First-principles molecular dynamics simulations

Besides the afore-mentioned methods based on quasiharmonic approximation, the equilibrium volume of a RE pyrochlore can also be directly obtained via first-principles molecular dynamics (FPMD) simulations. A pyrochlore conventional cell of 88 atoms was constructed for the FPMD simulations. The canonical ensemble (NVT) with Langevin thermostat⁴²⁻⁴⁴ was employed to achieve the desired temperature in simulations. A $2 \times 2 \times 2$ MP k-mesh grid and a time step of 1 fs were used. Specifically, FPMD simulations were performed at T = 300, 600, 900, 1200, and 1500 K, on simulation cells of different cell volumes that correspond to isotropic lattice strains ranging from -5% to +3%. In each simulation, the system was equilibrated for 0.4-1.6 ps, and the pressure was monitored.⁴⁵ In general, more simulation time is required for the system to attain equilibrium as the temperature increases. From the above simulations, the evolution of average pressure (p) versus the cell volumes (V) at each temperature was obtained. By fitting the (p, V) data with respect to the Murnaghan equation of state (EOS),⁴⁶ the equilibrium cell volume V(T) corresponding to p = 0 at temperature T can then be determined.

C. Quantification of thermal expansion

With the equilibrium volumes at different temperatures known, the volumetric CTE α can be determined as

$$\alpha = \frac{1}{V(T)} \frac{dV(T)}{dT}.$$
(6)

Besides the volumetric CTE, another measure often conveniently adopted in experiments to quantify thermal expansion is the expansion ratio,^{21–25} denoted as R_{ex} and defined as

$$R_{ex} = \frac{\left[V(V)\right]^{1/3} - \left[V_{RT}\right]^{1/3}}{\left[V_{RT}\right]^{1/3}},$$
(7)

with V_{RT} being the value of V(T) at room temperature, 298 K. Below when we compare our model predictions with experimental measurements, this measure of expansion ratio is adopted to represent CTE.

III. RESULTS AND DISCUSSION

A. Predictions of thermal expansion from QH phonon calculations

1. Phonon dispersion spectrums and imaginary frequencies

To determine F_{vib} and F_{total} (cf. Eqs. (1) and (2)) from the QH phonon calculations, we examine the phonon properties of RE pyrochlores at different volumes. To avoid redundancy, below in our phonon and free energy analyses, we use the Gd₂Zr₂O₇ system as the representation (while the results of other RE₂Zr₂O₇ systems are presented in the supplementary material⁴⁷). The phonon dispersion spectra along high-symmetry directions in their Brillouin zones (BZ) and partial density of states (PDOS) of the $Gd_2Zr_2O_7$ system of different cell sizes are shown in Fig. 1. Here, the difference in the cell size is quantitatively represented by an isotropic lattice strain ε_L , defined with respect to the equilibrium lattice parameter at 0 K.

As seen in Fig. 1, we see all the phonon branches descend with the increasing in tensile strain, which is expected given that lattice expansion results in weaker interatomic bonding. Meanwhile, we note that certain frequencies become imaginary under tensile straining (i.e., $\varepsilon_L > 0$). The number of imaginary branches increases as ε_L increases and settles at eight under large ε_L values (see supplementary material⁴⁷).

2. Rattling modes and strain-induced softening

Those imaginary branches bring immediate challenge for QH phonon calculations. As seen in Eq. (2), the imaginary frequencies cannot be accounted for in the evaluation of $F_{vib}(V, T)$. Consequently, as the volume (and simultaneously the strain ε_L) varies, the set of phonon branches included in the evaluation of $F_{vib}(V, T)$ is not consistent, as more phonon branches are omitted⁴⁸ as ε_L increases (in the tensile regime) where we can see that more phonon branches are omitted as ε_L increases (in the tensile regime). This inconsistency leads to irregularities in the free energy evolution as illustrated in Fig. 2(a) (i.e., the F_{total} versus V curves in open symbols), preventing accurate determination of the equilibrium volumes at different temperatures and subsequently the prediction of CTE.⁴⁹

The above challenge necessitates a more refined approach towards the treatment of different phonon branches. In this regard, it is important to first understand the mechanistic origin underlying the imaginary frequencies. From the PDOS plot in Fig. 1, it is clear that the imaginary branches come from the localized low-lying rattling phonon modes attributed to vibration of the RE cation, which are softened under tensile straining. This softening suggests that the RE cation be not stable at its original location upon tensile straining. In this regard, we examine vibrational motions of atoms associated with these rattling phonon modes at high-symmetry points, Γ and L, as representatives. In the example case of $Gd_2Zr_2O_7$ (see Fig. 3(c) for the atomic configuration), we found that Gd atom exhibits dominant vibrational magnitude in the rattling phonon modes, while O' (8b) atom shows near zero vibration, and Zr and O (48f) atoms show very small amplitudes of vibration, mostly being lesser than 15% of that of the Gd atom. The above observation is consistent with the PDOS shown in Fig. 1. Hence, we further examined the corresponding vibrational patterns of Gd atoms in details. Fig. 3 shows two vibration patterns corresponding to the lowest bands at high-symmetry points Γ and L as representatives.⁵⁰ The directions and relative magnitudes of vibrational motions of Gd at Γ and L are schematically illustrated in Figs. 3(a) and 3(b) respectively. We can see that the motions are highly localized at RE atoms.

A close examination reveals that all these vibrational motions lay within the plane perpendicular to the Gd-O'



FIG. 1. Phonon dispersions and partial density of states (PDOS) for $Gd_2Zr_2O_7$ pyrochlores under strain values of ε_L being (a) -1%, (b) 0%, (c) +1%, and (d) +2% (positive and negative signs respectively indicate tension and compression), respectively. The eight rattling phonon branches that can become imaginary (i.e., negative frequencies) under tensile straining are indicated by red dashed line. For the PDOS, the blue solid, green dashed, yellow dashed-dotted, and red dotted curves denote those corresponding to Gd, Zr, O, and O' atoms (see Fig. 3(c)), respectively.

bond. This can be attributed to the fact that the Gd-O' bond is the strongest one among all bonds Gd forms with its neighbors. As a consequence, the resistance is less when the motion direction is perpendicular to the Gd-O' bond. Overall, we can treat these vibrational patterns as Gd-tetrahedral rotations around the O' atom. In particular, the vibrational positions corresponding to Γ and *L* can be categorized as 96g (in-plane displacement towards the adjacent O atom) and 96h (in-plane displacement toward the nearest Zr atom) sites in space group $Fm\bar{3}m$, respectively (see Fig. 4(a)).

Accompanying the vibration, atoms deviate from their original lattice positions. Consequently, the lattice potential is necessarily modified. In Fig. 4, we plotted the change in the lattice potential, i.e., ΔE , with respect to the phonon normal mode amplitude at different ε_L values for the two vibration patterns shown in Fig. 3. The normal mode amplitude



FIG. 2. Calculated free energy, (a) F_{vib} with full phonon braches and (b) F_{vib}^{SM} with stable modes only as a function of primitive cell volume of Gd₂Zr₂O₇ (from QH phonon calculations, see Eqs. (2) and (8)), for T = 0 K, 400 K, 800 K, 1200 K, and 1600 K.



FIG. 3. Vibrational patterns corresponding to one of the lowest rattling phonon branches at the (a) Γ and (b) *L* points, viewed from different projection directions of the pyrochlore primitive cell. Purple arrows attached to the RE³⁺ cations illustrate the directions and magnitudes of vibrational motions. (c) The atomic configuration of a conventional pyrochlore cell (with the space group being *F*m³m), consisting of larger RE³⁺ cations at 16*d*, smaller Zr⁴⁺ cations at 16*c*, O²⁻ anions at 48*f* and O^{*2-} anions at 8*b*.

essentially represents the magnitude of atomic motions in the corresponding phonon mode. We can see from Fig. 4 that for $\varepsilon_L \leq 0$ the ΔE curve shows a single potential well, like what one would expect from a harmonic oscillation, while for $\varepsilon_L > 0$ the ΔE curve exhibits two potential wells. The anharmonic double-well potential indicates that during vibration atoms will tend to displace to settle at the positions of local potential minimum rather than oscillate around their original positions, thereby leading to imaginary frequencies. In addition, we also note that the displacement of Gd, d_{Gd} , scales with the normal mode magnitude (cf. Fig. 3), which is well expected since Gd atoms exhibit the dominant vibrational magnitude in the rattling phonon modes. The d_{Gd} that corresponds to the local minimum of the potential well, denoted as d_{Gd}^E , gives an effective measure of the equilibrium displacement of the Gd cation in a strained lattice. We can see from Figs. 4(d) and 4(e) that the magnitudes of d_{Gd}^E and potential well depth (denoted as ΔE^m) increase monotonically as ε_L increases at both Γ and L points.

The results shown in Figs. 4(d) and 4(e) clearly indicate that the degree of anharmonicity elevates as ε_L rises. This is further elucidated in Fig. 5 where the lowest phonon frequencies of the RE-cation rattling modes at Γ and L are plotted versus the strain for different RE₂Zr₂O₇ pyrochlores. For all systems, the frequency monotonically decreases as the strain increases, and becomes imaginary beyond a threshold tensile strain. We can see from Fig. 5 that the imaginary frequency can appear for a tensile strain as low as 0.25% (i.e., for the case of Gd₂Zr₂O₇). This threshold strain increases as the radius of the RE-cation increases ($r_{Gd} < r_{Sm} < r_{Nd} < r_{La}^{52}$). In addition, we note that at the same strain, a pyrochlore with a larger RE-cation exhibits a higher frequency. Thus, the results in Fig. 5 indicate that less rattling exists for a $RE_2Zr_2O_7$ pyrochlore of a larger RE-cation. One important aspect to mention is that those rattling modes are associated with the localized vibrations of RE-cations (cf. Fig. 3), and do not correspond to global crystal structural or phase changes.

3. QH phonon calculations based on stable phonon modes

As previously illustrated by Fig. 2, the presence of imaginary frequency renders impossible to correctly evaluate $F_{vib}(V, T)$ by the QH phonon calculations, posting a serious obstacle for the determination of CTE. Given that imaginary frequencies come from RE-cation rattling modes, we rewrite $F_{vib}(V, T)$ as the following:

$$F_{vib}(V,T) = F_{vib}^{SM}(V,T) + F_{vib}^{RM}(V,T),$$
(8)

where $F_{vib}^{SM}(V,T)$ and $F_{vib}^{RM}(V,T)$, respectively denote the contributions of the stable phonon modes and the rattling phonon modes. Apparently the component $F_{vib}^{SM}(V,T)$ is not affected by the occurrence of imaginary frequencies. From the discussion in Section III A 2, we know that the rattling modes are associated with the vibration of RE-cations which is highly localized at the vicinity of RE sites and constrained within the plane perpendicular to the RE-O' bond. As such, we expect that the contribution of those rattling modes to overall lattice change is limited, and postulate that the lattice expansion behaviors are mainly prescribed by the stable phonon modes, i.e., by the $F_{vib}^{SM}(V,T)$ vs. V curves. In Fig. 2(b), the corresponding $F_{vib}^{SM}(V,T)$ vs. V curves (i.e., curves of solid symbols) are plotted, showing smooth U-shaped curves. From those curves the equilibrium volumes at different temperatures, and subsequently the volumetric CTE α and expansion ratio R_{ex} (defined in Eqs. (6) and (7), respectively), can be readily obtained.

In the above approach, a consistent set of phonon branches (i.e., the stable phonon branches) are ensured in the QH phonon calculations (in the evaluation of $F_{vib}^{SM}(V,T)$). For simplicity, below we refer to this approach as the QHSM approach. The volumetric CTE α and expansion ratio R_{ex} predicted by the QHSM approach is shown in Fig. 6. We see from Fig. 6(a) that the QHSM approach predicts $\alpha_{Gd_2Zr_2O_7} > \alpha_{Sm_2Zr_2O_7} > \alpha_{Nd_2Zr_2O_7} \approx \alpha_{La_2Zr_2O_7}$, consistent with trend observed in experimental studies,^{23,24} being $\alpha_{Gd_2Zr_2O_7} > \alpha_{Sm_2Zr_2O_7} > \alpha_{Nd_2Zr_2O_7}$. In Figs. 6(b)–6(e), the predicted R_{ex} data are compared with experimental data available in the literature (i.e., Shimamura,²⁴ Maloney,²⁵ Kutty,²³ Liu,²¹ and Qu²²), showing excellent agreement.

The agreement verifies the accuracy of the QHSM approach in predicting the lattice expansion behaviors of pyrochlores. Meanwhile, it also confirms the validity of the postulation that the rattling phonon branches yield ignorable contribution to thermal expansion.⁵³ As previously discussed, this can be attributed to the fact that the rattling modes are associated with the vibrations of RE cations which are weakly bonded with surrounding atoms. Consequently, such atomic vibrations become rather independent of the host lattice and thereby have little relevance or influence on



FIG. 4. (a) Schematic illustrating the bonding environment around the Gd (16d) atom, showing six O (48f), two O' (8b), and six Zr (16c) in the immediate vicinity of Gd. The cyan plane indicates the plane that cuts through Gd and is perpendicular to the O'-Gd bond. Summary of possible vibrational positions, (b) $96g(\Gamma)$ and (c) 96h(L), and their corresponding potential, ΔE , as a function of corresponding normal mode amplitude (and maximum displacement of Gd cations, d_{Gd}) for $\varepsilon_L = -1\%$, 0%, +1%, and +2%.⁵¹ The $d_{\rm Gd}$ and potential well depth ΔE that correspond to the local minimum of the potential are denoted as d_{Gd}^E and ΔE^m , respectively, and are shown for (d) Γ and (e) L points as functions of ε_L .

the overall expansion of the host lattice.^{54–56} It is however important to note that in the QHSM approach the free energy itself, i.e., $F_{vib}(V,T)$ is not predicted (which is certainly not possible with the imaginary frequencies). The above also hints a criterion regarding soft mode omission when examining thermal expansion, i.e., the soft modes to be omitted can only be associated with localized vibrations.

B. Predictions of thermal expansion from the QH Debye model and FPMD simulations

Besides QH phonon calculations, the volumetric CTE α and/or expansion ratio R_{ex} of RE₂Zr₂O₇ pyrochlores are also

calculated employing the QH Debye model³⁴ and FPMD simulations, with the results also presented in Fig. 6. We see the R_{ex} data from FPMD simulations generally agree well with experimental data, but are slightly higher than the ones predicted by the QHSM approach. This small discrepancy between FPMD and the QHSM approach predictions is expected as FPMD automatically includes contributions from the rattling modes which are omitted in the QHSM approach.

On the other hand, the QH Debye model significantly overestimates the thermal expansion. For instance, the R_{ex} data predicted by the QH Debye model are 15%–35% higher than the experimental data for the RE₂Zr₂O₇ pyrochlores considered. In addition, the QH Debye model predicts



FIG. 5. Calculated lowest frequencies of the rattling modes as a function of lattice strain ε_L at (a) Γ and (b) Lpoints for RE₂Zr₂O₇ (RE = La, Nd, Sm, Gd) pyrochlores.



FIG. 6. (a) Volumetric coefficient of thermal expansion α as a function of temperature for $RE_2Zr_2O_7$ (RE = La, Nd, Sm, Gd) pyrochlores predicted from the QH Debye model (unfilled symbols and dashed lines) and the QH approximation approach based on stable phonon modes, i.e., the QHSM approach (filled symbols and full lines). The expansion ratio R_{ex} versus temperature data predicted from the QH^{\$M} approach (solid black line), the QH Debye model (blue dashed line), and FPMD (solid purple symbol and dotted line) are compared with various experimental measurements (i.e., Shimamura,²⁴ Maloney,²⁵ Kutty,²³ Liu,²¹ and Qu^{22}) for (b) $Gd_2Zr_2O_7$, (c) $Sm_2Zr_2O_7$, (d) $Nd_2Zr_2O_7$, and (e) La₂Zr₂O₇.

 $\alpha_{Nd_2Zr_2O_7} > \alpha_{Gd_2Zr_2O_7} > \alpha_{Sm_2Zr_2O_7} \geq \alpha_{La_2Zr_2O_7}$, different from the experimental observation of $\alpha_{Gd_2Zr_2O_7} > \alpha_{Sm_2Zr_2O_7} > \alpha_{Nd_2Zr_2O_7} \geq \alpha_{La_2Zr_2O_7}$. The poor predictability of the QH Debye model indicates the QH Debye model fails to account for certain fundamental lattice vibration characteristics of RE₂Zr₂O₇ pyrochlores. This is not surprising, given that Θ_D and $F_{vib}(V,T)$ are prescribed by average materials properties, i.e., *B*, *M* and ν (see Eqs. (3)–(5)), and thus do not capture features of local lattice vibration.⁵⁷

IV. SUMMARY AND DISCUSSION

In summary, we studied the thermal expansion behaviors of the $RE_2Zr_2O_7$ (RE = La, Nd, Sm, Gd) pyrochlores using first-principles calculations. The corresponding phonon dispersion spectra as the lattice strain varies were computed, and QH phonon calculations were performed to evaluate the free energy of the system. Imaginary frequencies were observed when the system is subject to tensile straining. These frequencies were shown to come from the low-lying optical branches that correspond to RE-cation rattling vibrational modes, and induce unphysical irregularities in the free energy evaluation using the QH phonon calculations. To mitigate the difficulties associated with the imaginary frequencies, we proposed a QH approximation approach based on stable phonon modes. This approach enables accurate predictions of the CTEs of $RE_2Zr_2O_7$ pyrochlores, evidenced by good agreement with experimental measurements and data from FPMD simulations. Meanwhile, we found that the QH Debye model not only considerably overestimates the CTEs of $RE_2Zr_2O_7$ pyrochlores, but also fails to predict the relative trend among different $RE_2Zr_2O_7$ pyrochlores.

Albeit the success of the proposed approach in predicting the CTE, it is important to discuss possible consequences due to the omission of RE-cation rattling modes in the approach. One main consequence could be the underestimation of the CTE, which is hinted by the discrepancy, though very small, between predictions from the QHSM approach with data from FPMD simulations (cf. Fig. 6). In order to remedy the consequence, it is necessary to account for the contribution of the imaginary modes to the free energy. One possible route can be the independent anharmonic oscillator (IAO) approximation^{58–61} where the double-well anharmonic potential is fitted to a functional form (e.g., parabola-plus-Gaussian or 2–4 polynomial). Nonetheless, although the IAO method has been shown to be applicable in certain systems with few soft modes and simple crystal structures, it is rather challenging to directly apply it in complex systems like $RE_2Zr_2O_7$ pyrochlores, and thus necessitates further studies which will be pursued in our forthcoming research.⁶²

In addition, there are two methods based on FPMD, i.e., the temperature dependent effective potential approach (TPEP)⁶³ and the velocity-autocorrelation functions (VAF),⁶⁴ which were shown to provide avenues in mitigating the softmode issues. However, both methods suffer certain limitations when applying to complex oxides, such as pyrochlore oxides, elaborated in details as follows. In the TPEP approach, in order to minimize the computational cost, the variables in interatomic force constants (IFC) matrix were reduced using symmetry relations. To the best of our knowledge, only single-element systems with small number (10-40) of independent variables have been tested using this method in the literature. For complex oxides such as pyrochlore, the number of independent variables of harmonic IFC matrix is already rather large, e.g., ~ 400 for a $2 \times 2 \times 2$ pyrochlore supercell, not to mention the third order IFC matrix who has thousands of independent variables. Such a large number of variables in the IFC matrix render it is very challenging (or virtually impossible) to achieve a sound numerical fitting in the TPEP approach. For the VAF method, the phonon eigenvectors are assumed to be not altered by anharmonic effects. However, this assumption is not valid for certain complex systems containing many atoms in the primitive cell and with huge change of eigenvectors, such as pyrochlore oxides. Our preliminary results in applying VAF to the pyrochlore oxide shows that stable results cannot be obtained, especially at high temperatures. Therefore, although the TPEP and VAF methods based on FPMD may yield useful information about phonon properties, those constrains discussed above prevent their direct application to predict the thermal expansion coefficients for complex systems.

One may of course re-sorts to FPMD, which provides a *brute-force* approach to study the thermal expansion of materials. However, its application is bottlenecked by the heavy computational cost, which would grow exponentially to quickly become undesirable and even unbearable as the complexity and size of the system increases. The objective of our study is to identify an alternative based on the QHA approach, to provide a much more efficient route than FPMD. The QHSM approach we developed, though with certain aspects (e.g., the soft mode issue) that certainly necessitate further studies, has been demonstrated to have the capacity to obtain similar result as the ones yielded by FPMD, and can serve as a good utility for complex oxide systems.

SUPPLEMENTARY MATERIAL

See supplementary material⁴⁷ for additional phonon dispersions and potential wells at various strains for $Sm_2Zr_2O_7$, $Nd_2Zr_2O_7$, and $La_2Zr_2O_7$ pyrochlore oxides.

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