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ABSTRACT

Cubic cuprous oxide, Cu_2O , is characterized by a peculiar structural response to temperature: it shows a relatively large negative thermal expansion below 250 K, then followed by a positive thermal expansion at higher temperatures. The two branches of its thermal expansion (negative and positive) are almost perfectly symmetric at low temperatures, with the minimum of its lattice parameter at about 250 K and with the lattice parameter at 500 K almost coinciding with that at 0 K. We perform lattice-dynamical quantum-mechanical calculations to investigate the thermal expansion of Cu_2O . Phonon mode-specific Grüneisen parameters are computed, which allows us to identify different spectral regions of atomic vibrations responsible for the two distinct regimes of thermal expansion. Two different computational approaches are explored, their results compared, and their numerical aspects critically assessed: a well-established method based on the quasiharmonic approximation, where harmonic frequencies are computed at different lattice volumes, and an alternative approach, where quadratic and cubic interatomic force-constants are computed at a single volume. The latter scheme has only recently become computationally feasible in the context of lattice thermal conductivity simulations. When proper numerical parameters are used (phonon sampling, tolerances, etc.), the two approaches are here shown to provide a very consistent description, yet at a rather different computational cost. All of the experimentally observed features of the complex thermal expansion of Cu_2O are correctly reproduced up to 500 K, with a slight overall underestimation of the volume contraction.

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I. INTRODUCTION

Many important macroscopic properties of materials are governed by their atomic level vibrational motion, that is, phonons. Some technological applications have very distinct limits for the operating devices in terms of thermal conductivity and thermal expansion, for example.^{1–4} Because of this, while searching for possible new functional materials for, say, electronic applications, the range of properties that need to be studied and optimized extends further than the primary property at hand. The amount of chemical compositions and structures we know is vastly beyond the capabilities of extensive experimental testing. At the same time, with the increases in computational performance and methodological

advances, most, if not all, of the essential qualities of materials can nowadays be examined *in silico*.

Vibrational properties of materials can be studied computationally at different levels of complexity with additional information gained at each step. The computationally cheapest solution is to calculate the harmonic vibrational properties at the Γ -point alone (i.e., at the center of the Brillouin zone), which enables, for example, the simulation of IR and Raman spectra. The computational cost increases when the vibrational properties are investigated throughout the whole Brillouin zone, and even further, when some anharmonic contributions to phonon properties are included explicitly. Some key properties, such as lattice thermal conductivity, require computationally costly evaluation of the anharmonic

contributions.^{5–9} However, some of the anharmonic contributions to phonon properties (in particular, volume-dependent ones) can be retrieved at a much lower cost using the quasiharmonic approximation (QHA).^{10–13}

At the heart of the QHA is the assumption that the harmonic approximation still holds, even when the system is not at the equilibrium volume. The values of the second-order interatomic force-constants naturally vary if the lattice parameters of the unit cell change; in other words, phonon frequencies gain a volume dependence. The change of the phonon frequency with respect to the change in volume is one of the many equivalent definitions for the Grüneisen parameter, which, along with thermal expansion and thermoelasticity, is one of the most important quantities that can be calculated with the QHA.

Despite all the fundamental lattice-dynamical and thermodynamic relations among these quantities being known for a long time,^{10,11} their numerical evaluation still poses some severe computational challenges, particularly so for certain classes of materials characterized by soft phonon modes or by a peculiar thermal response. In this study, we compute the thermal expansion and mode Grüneisen parameters of Cu₂O with two distinct quantum-mechanical approaches: the quasiharmonic approximation, where harmonic frequencies are computed at several volumes, and a cubic force constant (CFC) method, where harmonic and cubic interatomic force-constants are evaluated at a single equilibrium volume. Computational and numerical aspects of both approaches are investigated, and their results critically compared to one another and to existing experimental data on both mode Grüneisen parameters and thermal expansion. Cuprous oxide, Cu₂O, provides a good testing platform as on the one hand it is a simple material with high symmetry (see Fig. 1 for a schematic representation of its structure) and on the other hand it exhibits a peculiar thermal behavior, such as negative thermal expansion below 250 K.^{14–20} Additionally, Cu₂O has a long history of studies for a

variety of applications.^{21–28} This provides a solid basis of experimental measurements against which the computational results can be compared.

II. THEORETICAL ASPECTS

A. Mode Grüneisen parameters

In the formal description of the microscopic origins of thermal expansion of solids, mode-specific Grüneisen parameters constitute a popular physical model, which embodies the information on the volume dependence of individual phonon frequencies. Because of Maxwell relations, Grüneisen parameters can be linked to several thermodynamic properties and can be computed in different ways in practical calculations.^{29,30}

Within the QHA, mode-specific Grüneisen parameters $\gamma_{\mathbf{q}j}$ are usually expressed as the change of the phonon frequency with respect to volume V , relative to the equilibrium volume V_0 ,

$$\gamma_{\mathbf{q}s} = -\frac{V_0}{\omega_{\mathbf{q}s}(V_0)} \left[\frac{\partial \omega_{\mathbf{q}s}(V)}{\partial V} \right]_{V=V_0}, \quad (1)$$

where $\omega_{\mathbf{q}s}$ is the harmonic frequency of phonon mode s with wave vector $\mathbf{q}$. In practice, the numerical evaluation of the derivatives within squared brackets in Eq. (1) requires the calculation of harmonic phonon frequencies at different volumes; two volumes are enough to get them from finite-differences,

$$\gamma_{\mathbf{q}s} = -\frac{V_0}{\omega_{\mathbf{q}s}(V_0)} \left[\frac{\omega_{\mathbf{q}s}(V_1) - \omega_{\mathbf{q}s}(V_0)}{V_1 - V_0} \right]. \quad (2)$$

An alternative working expression for mode-specific Grüneisen parameters can be derived from first-order perturbation theory by considering the dependence on strain of the phonon frequencies.^{31–33} For cubic lattices, this yields

$$\gamma_{\mathbf{q}s} = -\frac{1}{6\omega_{\mathbf{q}s}^2} \sum_{abcijklg} r_k^{cg} \frac{[e_{\mathbf{q}s}^{ia}]^* e_{\mathbf{q}s}^{jb}}{\sqrt{M_a M_b}} \Phi_{ij,k}^{a0,bl,cg} e^{i\mathbf{q} \cdot \mathbf{R}_l}, \quad (3)$$

where ijk are Cartesian indices labeling xyz components, abc represent atoms in the unit cell (M_a , M_b , and M_c being the corresponding masses), lg are indices labeling the lattice cells ($\mathbf{R}_l$ being the lattice vector which connects the origin of the Cartesian frame to the origin of the l th cell), $\mathbf{e}_{\mathbf{q}s}$ is the eigenvector of the phonon whose frequency is $\omega_{\mathbf{q}s}$, r_k^{cg} is the k th Cartesian component of the vector identifying the position of atom c in lattice cell g , and finally $\Phi_{ij,k}^{a0,bl,cg}$ are the anharmonic interatomic cubic force constants,

$$\Phi_{ij,k}^{a0,bl,cg} = \left[\frac{\partial^3 E}{\partial u_i^{a0} \partial u_j^{bl} \partial u_k^{cg}} \right]. \quad (4)$$

The cubic force constants in Eq. (4) are third-energy derivatives with respect to atomic Cartesian displacements. From a practical point of view, Eq. (3) now requires the evaluation of second- and third-order interatomic force constants at the equilibrium lattice volume. Typically, cubic force-constants are computed numerically from analytical forces evaluated at a large number of displaced

FIG. 1. Atomic structure of cuprous oxide, Cu₂O, in its $Pn\bar{3}m$ cubic space group. Red: oxygen and blue: copper.

nuclear configurations, which implies a larger computational cost compared to Eq. (2). However, we stress that the third-order force constants are often calculated to investigate the lattice thermal conductivity of a material^{5–9,34} and therefore mode Grüneisen parameters can be obtained as a side-product for no extra effort in that case.

B. Thermal expansion

Within the harmonic approximation to the lattice dynamics (i.e., if only second-order interatomic force constants are evaluated at a single volume), thermal expansion would be null,¹² as well as the thermal dependence of the elastic moduli.³⁵ The zero-pressure volumetric thermal expansion of a solid is often described in terms of a thermal expansion coefficient $\alpha_V(T)$, which is defined as

$$\alpha_V(T) = \frac{1}{V(T)} \left[\frac{\partial V(T)}{\partial T} \right]_{p=0}. \quad (5)$$

Mode Grüneisen parameters introduced in Sec. II A allow for the calculation of the thermal expansion coefficient as follows:¹³

$$\alpha_V^{\text{gru}}(T) = \frac{1}{K_0 V_0} \sum_{\mathbf{q}\mathbf{s}} \gamma_{\mathbf{q}\mathbf{s}} C_{V,\mathbf{q}\mathbf{s}}(T), \quad (6)$$

where K_0 is the static bulk modulus and $C_{V,\mathbf{q}\mathbf{s}}$ is the mode contribution to the constant-volume specific heat. Therefore, Eq. (6) enables the calculation of the thermal expansion of the system from the mode Grüneisen parameters obtained either from the QHA approach of Eq. (1) or from the CFC approach of Eq. (3). A drawback of Eq. (6) is that it does not take into account the temperature dependence of K and V . However, in many cases, this is a rather minor approximation because K typically decreases with increasing temperature, while V behaves in an opposite way, resulting in some cancellation of these effects.

Within the QHA, a more explicit way of determining the thermal expansion of the system relies on the minimization of the Helmholtz free energy with respect to volume at selected temperatures. When passing from the harmonic to the quasiharmonic approximation, thermodynamic functions gain a dependence on volume. The Helmholtz free energy under the QHA is written as³⁶

$$F^{\text{QHA}}(T, V) = U_0(V) + F_{\text{vib}}^{\text{QHA}}(T, V), \quad (7)$$

where $U_0(V)$ is the static internal energy of the crystal at 0 K. The vibrational part $F_{\text{vib}}^{\text{QHA}}(T, V)$ contains the volume-dependence on the phonon frequencies, which reads

$$F_{\text{vib}}^{\text{QHA}}(T, V) = E_0^{\text{ZP}}(V) + k_B T \sum_{\mathbf{q}\mathbf{s}} \ln \left[1 - e^{-\frac{\hbar \omega_{\mathbf{q}\mathbf{s}}(V)}{k_B T}} \right], \quad (8)$$

where $E_0^{\text{ZP}}(V)$ is the zero-point energy of the system. From a practical point of view, one has to compute harmonic phonons at several lattice volumes. It has recently been shown that four volumes are enough to guarantee stable numerical results for most systems.^{37–40} To obtain the equilibrium volume at a given temperature, one needs to minimize $F^{\text{QHA}}(V; T)$ with respect to the volume and keep T as a fixed parameter. By repeating the minimization at different temperatures, the $V(T)$ relation is obtained, which can then be derived

with respect to temperature as in Eq. (5) to get the thermal expansion coefficient.

III. COMPUTATIONAL DETAILS

All quantum-chemical calculations were performed with the CRYSTAL17 code using the hybrid functional PBE0 and triple- ζ valence (plus polarization) level Gaussian basis sets.^{41–44} The used basis sets are the same as in our previous paper on the lattice thermal conductivity of Cu_2O .³⁴ For the geometry optimization of the primitive cell, we used an $8 \times 8 \times 8$ grid for the reciprocal space sampling.⁴⁵ We used the default integration grid for the density functional theory (DFT) part and tight tolerances for the Coulomb and exchange sums of 8, 8, 8, and 16 (see user's manual for an exact definition of these thresholds). We used energy convergence criteria of 10^{-7} Hartree for geometry optimizations and of 10^{-10} Hartree for harmonic frequency calculations.

For the phonon calculations at the quasiharmonic level, we employed the QHA module of CRYSTAL17.^{13,37–39} The QHA calculations were performed by computing the harmonic frequencies at seven different volumes in a range from -3% to $+6\%$ at 1.5% intervals relative to the static equilibrium volume V_0 . A total of 100 temperatures were sampled between 10 and 500 K. Phonon dispersion is accounted for within a “direct space” approach. We performed the calculations with $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$ supercell expansions with an electronic reciprocal space sampling of $4 \times 4 \times 4$, $3 \times 3 \times 3$, and Γ -point only, respectively. We also checked the effect of using a denser sampling of $12 \times 12 \times 12$, $6 \times 6 \times 6$, and $4 \times 4 \times 4$ for the QHA calculations carried out with the primitive cell, $2 \times 2 \times 2$ supercell, and $3 \times 3 \times 3$ supercell, respectively. The denser sampling changes the QHA results by 1%, less than 3%, and 1% in the case of the primitive cell, $2 \times 2 \times 2$ supercell, and $3 \times 3 \times 3$ supercell, respectively, proving the convergence in terms of reciprocal space sampling.

Anharmonic phonon calculations were performed by combining analytical forces from CRYSTAL17 with PHONOPY and PHONO3PY codes.^{5,6} The same 10^{-10} Hartree value for the energy convergence threshold was used when calculating forces both for the second- and third-order force constants. Calculations were performed on both the $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells. The phonon dispersion relations obtained with the $3 \times 3 \times 3$ supercell are found in very good agreement with the phonon dispersions obtained using an even larger $4 \times 4 \times 4$ supercell.³⁴

Full sets of both second- and third-order force constants (without any further distance cutoff) were calculated within the applied supercells. This means that, in the evaluation of mode Grüneisen parameters from Eq. (3), the two sums over lattice cell indices l and g are truncated to include all and only those cubic force constants (4) where the three centers with respect to which the derivative is taken lie inside the supercell. The sensitivity of Eq. (3) to the truncation of these sums has already been noted.⁴⁶ The computed force constants were Fourier-interpolated to compute mode Grüneisen parameters on a richer $10 \times 10 \times 10$ $\mathbf{q}$ -mesh, similar to our previous study on Cu_2O as increasing the $\mathbf{q}$ -mesh further did not change the results numerically.

Finally, when calculating the thermal expansion coefficient with Eq. (6), we used a bulk modulus value of 107 GPa, as obtained at the DFT-PBE0/TZVP level of theory previously.³⁴

IV. RESULTS AND DISCUSSION

We used the experimental crystal structure of Kirfel and Eichhorn as the starting point for the full structural relaxation, the lattice parameter a being the only degree of freedom.⁴⁷ The optimized unit cell ($a = 4.318$ Å) was used for all subsequent supercell expansions. The performance of the used level of theory with respect to cell parameters and the electronic band structure of Cu_2O has been covered in more detail in a previous publication.³⁴ In particular, it was shown that the phonon dispersions obtained at the DFT-PBE0/TZVP level of theory are in very good agreement with the experimental phonon dispersions.

A. Mode Grüneisen parameters

Mode Grüneisen parameters γ_{qs} were computed by using the two approaches introduced in Sec. II A: the QHA scheme represented by Eq. (1) and the CFC scheme given in Eq. (3). Results are shown in Fig. 2 as obtained from the QHA (a) and from the CFC method (b). It is clearly seen that the lattice dynamics of Cu_2O is

characterized by phonons with very different behaviors on volumetric changes. Indeed, phonons with frequencies below approximately 60 cm^{-1} have large negative mode Grüneisen parameters (i.e., their frequency increases with volume), phonons with frequencies in the range of $60\text{--}100\text{ cm}^{-1}$ have large positive parameters (i.e., their frequency decreases with volume), phonons with frequencies in the range of $100\text{--}180\text{ cm}^{-1}$ have small negative parameters, and finally phonons with frequencies above 180 cm^{-1} have positive Grüneisen parameters. The peculiar thermal expansion behavior of Cu_2O is due to a subtle balance of these different phonon modes.

We investigated the phonon mode characteristics in Cu_2O with the help of the Phonon website⁴⁸ and found a good agreement with the previous analysis by Rimmer *et al.*²⁰ The only differences between our studies are found for the absolute values of γ_{qs} , which are smaller with hybrid DFT-PBE0 compared to DFT-PBE (Perdew-Burke-Ernzerhof functional), in line with our previous study comparing the performance of DFT-PBE and DFT-PBE0 for Cu_2O .³⁴ A visual inspection of the phonon modes corroborates the findings of Rimmer *et al.* By comparing the phonon dispersions of Cu_2O to model systems comprising different rigid Cu-O units, they were able to assign the phonon modes as follows: The transverse acoustic modes with the most negative Grüneisen parameters below 60 cm^{-1} correspond to vibrations of rigid O-Cu-O rods. Furthermore, the same modes are also responsible for the largest positive Grüneisen parameters in the range of $60\text{--}100\text{ cm}^{-1}$. This finding can be explained based on the crystal structure of Cu_2O , which contains two interpenetrating sublattices: the high symmetry point $R = (1/2, 1/2, 1/2)$ in the first Brillouin zone corresponds to the Γ -point for an individual sublattice and the acoustic modes at R point correspond to the sublattices vibrating in the antiphase. This delicate wave vector dependent behavior was also observed by Bohnen *et al.*, who showed the phonon modes at the R point to have positive contribution to the thermal expansion of Cu_2O .¹⁹ The phonon modes corresponding to the negative γ_{qs} values in the $80\text{--}200\text{ cm}^{-1}$ range can be characterized as rotations of rigid and near-rigid OCu_4 tetrahedra and the near-rigid O-Cu-O rod motion. The smaller band of positive γ_{qs} values around 100 cm^{-1} corresponds to rigid Cu-O motion, and finally, the higher-frequency optical modes are different Cu-O stretching modes contributing to positive thermal expansion.

We started the calculations using the CRYSTAL17 QHA procedure by exploring the effect of the size of the adopted supercell on the computed quantities. Here, no Fourier interpolation is performed for the second-order interatomic force constants. As a result, for each supercell, phonons are sampled only at those $\mathbf{q}$ -points in the grid commensurate to the supercell (i.e., phonons on a $2 \times 2 \times 2$ $\mathbf{q}$ -mesh are computed when a $2 \times 2 \times 2$ supercell is used, phonons on a $3 \times 3 \times 3$ $\mathbf{q}$ -mesh are computed when a $3 \times 3 \times 3$ supercell is used, etc.). Indeed, we see from Fig. 2(a) that the mode Grüneisen parameters obtained with different supercells are consistent, only the sampling of phonon dispersion being different. The $4 \times 4 \times 4$ supercell possesses additional sampling points compared to the $2 \times 2 \times 2$ supercell, but except for few data points at 47 and 340 cm^{-1} differing by less than 3%, the points from these two supercells lie on top of each other. This proves the numerical stability of the applied QHA algorithm. For symmetry reasons, the sampling from the $3 \times 3 \times 3$ cell results in a slightly different distribution of data points.

FIG. 2. Mode Grüneisen parameters of Cu_2O as a function of the size of the adopted supercell with (a) the QHA approach and (b) the CFC method. Dashed line at zero is for easier distinction between positive and negative values of γ_{qs} .

In particular, the $3 \times 3 \times 3$ grid does not sample those phonon modes characterized by the largest positive mode Grüneisen parameters with values >1.5 . We will show below how this affects the calculation of the thermal expansion of the system.

Next, we investigated the effect of the adopted supercell on the mode Grüneisen parameters obtained with the CFC approach of Eq. (3). Here, we explored two different supercells ($2 \times 2 \times 2$ and $3 \times 3 \times 3$). Results are given in Fig. 2(b). In this case, the different supercells do not result in a different sampling of phonon dispersion as a common Fourier interpolation on a denser $10 \times 10 \times 10$ $\mathbf{q}$ -mesh was used in both cases. With the CFC method, passing from a $2 \times 2 \times 2$ to a $3 \times 3 \times 3$ cell produces some changes in the computed mode Grüneisen parameters. In particular, when using a larger supercell, (i) mode Grüneisen parameters below 60 cm^{-1} become more negative and (ii) mode Grüneisen parameters are more positive in the range of $85\text{--}150 \text{ cm}^{-1}$. We will show below how these seemingly subtle differences affect the description of the thermal expansion of the system.

As per the origin of these differences, one has to keep in mind that the CFC method depends on the size of the adopted supercell in two respects: (i) the size of the cell determines the extent of second-order force constants used to build the dynamical matrices and therefore to sample the harmonic phonon dispersion and (ii) the size of the cell determines the extent of third-order force constants, that is the truncation of the lattice sums over l and g in Eq. (3). In this case, the factor affecting the results reported in Fig. 2(b) is the first one. Indeed, a $2 \times 2 \times 2$ supercell is not large enough to get converged second-order force constants, while it ensures a good description of third-order force constants, as we recently demonstrated on our study on the lattice thermal conductivity of Cu_2O .³⁴

B. Thermal expansion coefficient

Results on the thermal expansion coefficient $\alpha_V(T)$ of Cu_2O are reported in Fig. 3 from both the QHA and CFC approaches. Figure 3(a) shows the results from QHA calculations where the thermal expansion is determined by explicit minimization of the Helmholtz free energy, with the primitive cell and three supercells of different sizes. All supercells (i.e., all samplings of the phonon dispersion) provide a qualitatively consistent picture of a negative thermal expansion coefficient at low temperatures then followed by positive values at higher temperatures. However, the primitive cell (corresponding to the sampling of phonon dispersion only at the Brillouin zone center, Γ point) clearly provides results that quantitatively differ from those obtained with the larger supercells. The results obtained with the $4 \times 4 \times 4$ cell almost perfectly coincide with those from the $2 \times 2 \times 2$ cell so that the latter ensures full convergence of this thermal property. The results obtained with the $3 \times 3 \times 3$ supercell differ only slightly from the results obtained with the other two supercells. We have confirmed that our results are converged with respect to reciprocal space sampling (see Sec. III), so the slightly different results obtained with the $3 \times 3 \times 3$ supercell likely arise from the differences in the phonon sampling, as discussed above for mode Grüneisen parameters.

Figure 3(b) shows the thermal expansion coefficient $\alpha_V(T)$ calculated from Eq. (6) using the mode Grüneisen parameters obtained

FIG. 3. Thermal expansion coefficient $\alpha_V(T)$ of Cu_2O obtained with different supercells by (a) use of the QHA through the Helmholtz free energy minimization to get the $V(T)$ relation, which was then derived with respect to temperature as in Eq. (5), and (b) use of Eq. (6) from mode Grüneisen parameters obtained either with the CFC and the QHA approaches.

from the CFC and QHA schemes plotted in Fig. 2. We have discussed in Sec. IV A how the size of the adopted cell affected the computed mode Grüneisen parameters by the CFC method. Those differences that could seem small produce a significant effect on the corresponding thermal expansion coefficient. With the smaller supercell, the minimum of $\alpha_V(T)$ is found at a slightly higher temperature of 90 K as opposed to the minimum at 75 K with the larger supercell. Additionally, after the divergence of the minima of $\alpha_V(T)$, the absolute values are smaller with the $2 \times 2 \times 2$ supercell. The difference in the absolute value at the minimum is $1.4 \times 10^{-6} \text{ K}^{-1}$, and the gap between the results of the two supercell sizes slowly increases with temperature, up to $2 \times 10^{-6} \text{ K}^{-1}$ at 500 K. As discussed above for the mode Grüneisen parameters, these deviations

in the CFC method may arise from the fact that the second-order force constants are not fully converged with the $2 \times 2 \times 2$ phonon supercell, resulting in less accurate mode Grüneisen parameters and mode contributions to the specific heat.

Finally, we also calculated the thermal expansion coefficient from mode Grüneisen parameters obtained with the QHA approach of Eq. (1). Results are reported in Fig. 3(b) as a dashed line for the largest $4 \times 4 \times 4$ supercell and are found to almost perfectly match those obtained from the CFC approach on the largest $3 \times 3 \times 3$ supercell. This proves Eqs. (1) and (3) to be numerically equivalent when phonon dispersion is properly sampled in both approaches. However, from a practical point of view, the CFC method is computationally vastly more expensive in comparison to QHA. In the present case, the calculation of the thermal expansion coefficient with CFC required about 100 times more CPU hours in comparison to QHA, when using a similarly sized $3 \times 3 \times 3$ supercell. The difference in timings would be smaller if one could use different-sized supercells for the second- and third-order force constant calculations in the CFC method ($3 \times 3 \times 3$ for the second-order and $2 \times 2 \times 2$ for the third-order). In any case, it probably only makes sense to calculate α_V with the CFC method if the mode Grüneisen parameters can be obtained as a side product from a lattice thermal conductivity investigation.

The temperature range of the negative thermal expansion can be rationalized with the frequency distribution of mode Grüneisen parameters, considering that the relation between the phonon frequency and the temperature is $\hbar\omega = k_B T$. At low frequencies below 50 cm^{-1} (72 K), all mode Grüneisen parameters are negative, resulting in negative thermal expansion coefficient that decreases until the phonon modes with positive mode Grüneisen parameters start to become excited above 50 cm^{-1} . Above 150 cm^{-1} (216 K), there are enough populated phonon modes with positive Grüneisen parameter so that the overall thermal expansion coefficient becomes positive.

C. Comparison of QHA and CFC methods with experiments

Figure 4 compares the mode Grüneisen parameters obtained from the QHA and CFC methods. In both cases, the values obtained with the respective largest supercell are plotted. Apart from a couple of data points around 30 and 160 cm^{-1} , the obtained values lie exactly on top of each other for all phonon modes. At about 50 cm^{-1} , the CFC method shows larger negative mode Grüneisen parameters (the most negative one from QHA being -3.9 , while from CFC being -5.6), but this is only due to the denser $10 \times 10 \times 10$ sampling of the phonon dispersion in the CFC approach, which in this case is not really needed as it does not improve the description of the thermal expansion, which was shown to be already converged with a much smaller sampling above.

Agreement between mode Grüneisen parameters obtained with QHA and CFC was also obtained by Esfarjani and Stokes in a study on silicon⁴⁶ and Shao *et al.* in a previous study on Cu_2GeSe_3 .⁴⁹ However, in another study on BiCuOSe , larger differences between the two approaches were observed.⁵⁰ The γ_q for high-frequency optical modes were systematically larger in the case of CFC in comparison to QHA results, but the origin of the larger discrepancy remains unclear.

FIG. 4. Mode Grüneisen parameters of Cu_2O calculated using the QHA and the CFC methods on the two respective largest supercells. The experimental results for Γ -point phonons are from Reimann and Syassen.⁵¹

The calculated mode Grüneisen parameters compare well against the experimental results of Reimann and Syassen, who measured the zone-center phonon frequencies with Raman spectroscopy at 6 K under pressures up to 8.5 GPa.⁵¹ Starting from the lowest frequency measurements, a value of -3.4 was obtained for the mode with the zone-center frequency of 86 cm^{-1} . Our calculations show the largest negative values for the acoustic phonons around and below 50 cm^{-1} . The experimental γ_q between 110 and 350 cm^{-1} range from -0.6 to $+1.7$, much like in our calculations. The experimental parameters at 515 and 662 cm^{-1} are slightly lower than our computational results. Finally, the experimental frequency range of optical vibrations is blue shifted by about 25 cm^{-1} relative to the theoretical one. This shift might be due to the choice of the exchange-correlation functional, the quality of the basis set, as well as the lack of anharmonic corrections to the vibrational states.^{52,53}

The thermal expansion coefficients calculated with the QHA (from free energy minimization) and the CFC method are in very good agreement for the largest supercells, as shown from Fig. 5(a). Both QHA and CFC show a minimum for $\alpha_V(T)$ at 75 K with very small differences in the absolute value $-7.0 \times 10^{-6} \text{ K}^{-1}$ and $-6.8 \times 10^{-6} \text{ K}^{-1}$ for QHA and CFC, respectively. Use of a smaller $2 \times 2 \times 2$ supercell for the CFC method would result in a worse agreement with QHA, as already discussed in Fig. 3(b). Figure 5 also reports experimental data. The two experimental datasets on the thermal expansion of Cu_2O are in rather good mutual agreement for temperatures below 200 K, while they deviate from one another at higher temperatures, with the data by Schäfer *et al.*¹⁴ showing a more pronounced expansion than those by Dapiaggi *et al.*¹⁷ In a later study, the discrepancies between the experiments at high temperatures were attributed to the fact that different apparatus is needed to perform the experiments at low and high temperatures, the different temperature calibration procedures and strategies possibly affecting the true temperature estimation.⁵⁴ Similar to the theoretical results, the experimental data show a negative thermal expansion

FIG. 5. Thermal expansion of Cu_2O as computed from the QHA and CFC approaches and as measured experimentally: (a) thermal expansion coefficient $\alpha_V(T)$ calculated using the QHA (from free energy minimization on the largest $4 \times 4 \times 4$ supercell), calculated with the CFC method (with the largest $3 \times 3 \times 3$ supercell), and measured by Dapiaggi *et al.* and Schäfer *et al.*^{14,17} (b) Normalized percent variation in the lattice constant of Cu_2O in the 0–500 K range; theoretical results are from the QHA free energy minimization scheme on the largest supercell and experimental data are from Tiano *et al.*

below 220 K, but in the experiments, the minimum is found at a higher temperature, between 100 and 120 K with values at around $-8 \times 10^{-6} \text{ K}^{-1}$. Some of the differences between the theory and experiments can be attributed to our approach still relying on harmonic states. Temperature only affects the populations of the harmonic states, and we do not consider any anharmonic frequency shifts for our phonon frequencies.

In Fig. 5(b), we report the evolution of the lattice parameter of Cu_2O as a function of temperature in the temperature range of 0–500 K. Theoretical results are obtained from the QHA by

the explicit minimization of the Helmholtz free energy (and therefore correspond to the thermal expansion coefficient reported in the upper panel). Experimental data are from Tiano *et al.* Apart from a slight underestimation of the depth of the minimum, the theoretical description of the peculiar thermal behavior of Cu_2O matches the experimental one in the whole temperature range here explored. The lattice parameter initially decreases with temperature, reaches a minimum at about 250 K, and then increases in a symmetric way up to 500 K, where the value of the lattice parameter is almost equal to the value at 0 K. The thermal expansion of Cu_2O was also studied with the QHA by Bohnen *et al.*, where the correct type of behavior was observed, even though the used DFT-PBE method resulted in a slightly larger underestimation of the thermal contraction.¹⁹

V. CONCLUSIONS

We have studied the mode Grüneisen parameters and lattice thermal expansion of Cu_2O with the PBE0 hybrid density functional method, using both the quasiharmonic approximation and a cubic force constant method. Computational aspects of both approaches have been illustrated. The results from the two theoretical schemes are in excellent agreement with each other when large enough supercells are used in the sampling of phonon dispersion. Both methods provide a correct description of the peculiar thermal response of the Cu_2O lattice (apart from a slight underestimation of the contraction near the minimum), with a contraction of the lattice parameter at low temperatures, a minimum at about 250 K, followed by a symmetric increase in volume. Computationally, the QHA is clearly more affordable than the calculation of anharmonic third-order force constants that, for this system, is about 100 times more expensive than the former.

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