



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Linnera, J.; Karttunen, A. J.

Ab initio study of the lattice thermal conductivity of Cu2 O using the generalized gradient approximation and hybrid density functional methods

Published in: Physical Review B

DOI: 10.1103/PhysRevB.96.014304

Published: 18/07/2017

Document Version Publisher's PDF, also known as Version of record

Published under the following license: CC BY

Please cite the original version:

Linnera, J., & Karttunen, A. J. (2017). Ab initio study of the lattice thermal conductivity of Cu2 O using the generalized gradient approximation and hybrid density functional methods. *Physical Review B*, *96*(1), Article 014304. https://doi.org/10.1103/PhysRevB.96.014304

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

Ab initio study of the lattice thermal conductivity of Cu₂O using the generalized gradient approximation and hybrid density functional methods

J. Linnera and A. J. Karttunen*

Department of Chemistry and Materials Science, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland (Received 12 May 2017; revised manuscript received 28 June 2017; published 18 July 2017)

The lattice thermal conductivity of Cu_2O was studied using *ab initio* density functional methods. The performance of generalized gradient approximation (GGA), GGA-PBE, and PBE0 exchange-correlation functionals was compared for various electronic and phonon-related properties. The *3d* transition metal oxides such as Cu_2O are known to be a challenging case for pure GGA functionals, and in comparison to the GGA-PBE the PBE0 hybrid functional clearly improves the description of both electronic and phonon-related properties. The most striking difference is found in the lattice thermal conductivity, where the GGA underestimates it as much as 40% in comparison to experiments, while the difference between the experiment and the PBE0 hybrid functional is only a few percent.

DOI: 10.1103/PhysRevB.96.014304

I. INTRODUCTION

Copper(I) oxide Cu₂O (Fig. 1) is one of the first semiconductors known to man and has a history of being the first example of different phenomena and devices, such as the first *p*-*n* junction [1,2]. Copper oxides have been shown to have potential in a plethora of applications such as the *p*-type material in heterojunction photovoltaic cells [3,4], CO₂ reduction [5,6], methanol production catalysis [7], and, lately, also as a *p*-type thermoelectric material [8–10]. One of the biggest advantages of using copper oxides is the relatively high abundance of Cu and the proficiency of recycling it. For substituting the currently best-performing thermoelectric materials such as PbTe and Bi₂Te₃, the nontoxicity of copper makes it even more attractive for everyday use. In order to use copper oxides as thermoelectric materials, a lot of work is still required to boost the material performance to a useful level.

The heat-to-electricity conversion efficiency of a thermoelectric material is defined by a single, dimensionless figure of merit, $ZT = \sigma S^2 T / \kappa$, where σ is the electrical conductivity, S the Seebeck coefficient, and κ the thermal conductivity of the material. The problem of rationally optimizing materials towards a high thermoelectric efficiency is that σ , S, and κ are very difficult to decouple and systematically improve in a one-at-a-time fashion. One of the most promising techniques has been to consider κ as the sum of the electronic thermal conductivity κ_e and the lattice thermal conductivity κ_l and then reduce the latter by increasing phonon-phonon scattering via nanostructuring or doping [11,12]. This not only improves ZT by shrinking the denominator while keeping the electrical properties roughly the same but, in the best case, can even enhance them through increased carrier concentrations at appropriate doping levels. Although the procedure is simple on paper, finding the right material compositions and eventually synthesizing them in a controlled fashion is not as straightforward

With the recent advancements in atomistic materials modeling and the ever-increasing computational capacity, it is possible to predict many physical properties with an accuracy that is useful for rational materials design. Especially, the calculation of lattice thermal conductivities has evolved vastly over the last 10 years, from the use of empirical potentials for silicon to the full *ab initio* treatment of complex materials, several software packages having been developed for this purpose [13–21]. Although these methods and software provide a robust and parameter-free way to gain access to theoretical lattice thermal conductivities, they use density functional theory (DFT) to calculate interatomic force constants and, thus, are prone to the common pitfalls of DFT. One of these is the inability of the local density approximation (LDA) or generalized gradient approximation (GGA) to correctly describe relatively localized electronic states such as the *d* states of transition metals.

There are two common methods for handling the troublesome self-interaction error with localized d states: (i) introducing an on-site Coulomb repulsion to the LDA or GGA using the Hubbard U term, as popularized by Liechtenstein [22] and Dudarev [23] and (ii) using a so-called hybrid density functional, where a part of the exchange energy of the system is taken from the exact exchange of Hartree-Fock theory, as introduced by Becke [24,25]. For three-dimensional periodic systems, the first approach has gained much popularity due to its much lower computational cost when plane-wave basis sets are used. Hybrid functionals are more typically applied in molecular calculations based on local basis functions, where the computational cost of exact exchange is much lower in comparison to that of plane waves. However, it is also possible to apply local basis sets for solid-state systems with periodic boundary conditions, enabling the more cost-effective inclusion of hybrid functionals.

As DFT studies on the lattice thermal conductivity of complex materials become more and more common, it is also interesting to see how the DFT-GGA performs in comparison with hybrid functionals in the case of phonon-related properties. We have interfaced the CRYSTAL14 materials modeling package based on Gaussian-type basis sets with the Phono3py program package and we report, to our knowledge, the first full hybrid DFT calculations of lattice thermal conductivity [19,26,27]. The outline of the paper is as follows: In Sec. II we discuss the most important aspects of the theory of lattice

^{*}antti.j.karttunen@iki.fi



FIG. 1. Unit cell of Cu₂O. Red, O; brown, Cu.

dynamics related to our calculations. Then we report the results on the basic electronic and structural properties of Cu_2O in Sec. III A, followed by the phonon-related results such as the phonon dispersion, Grüneisen parameters, and lattice thermal conductivity in Sec. III B. Next, we discuss the origins of the performance difference between the GGA and the hybrid density functional in the case of Cu_2O in Sec. III C. Finally, we report our conclusions in Sec. IV.

II. THEORETICAL BACKGROUND

A. Lattice dynamics

Lattice dynamics theory has been thoroughly discussed in many textbooks [28–30]. Here we outline the theoretical framework for our computational work, introducing the key concepts that are required for a comprehensive analysis of the calculated lattice thermal conductivities. We begin by assuming that the crystal potential energy is an analytical function of the atomic displacements from their equilibrium positions. This potential contains all but the kinetic energy of the crystal. Then, with small enough displacements, the potential energy Φ can be expanded as a power series,

$$\Phi = \Phi_0 + \Phi_1 + \Phi_2 + \Phi_3 + \dots, \tag{1}$$

where Φ_0 is the constant potential and other components are

$$\Phi_1 = \frac{1}{1!} \sum_{lk\alpha} \Phi_\alpha(lk) u_\alpha(lk), \qquad (2)$$

$$\Phi_2 = \frac{1}{2!} \sum_{lk\alpha} \sum_{l'k'\beta} \Phi_{\alpha\beta}(lk, l'k') u_{\alpha}(lk) u_{\beta}(l'k'), \qquad (3)$$

$$\Phi_{3} = \frac{1}{3!} \sum_{lk\alpha} \sum_{l'k'\beta} \sum_{l''k''\gamma} \Phi_{\alpha\beta\gamma}(lk, l'k', l''k'')$$
$$\times u_{\alpha}(lk)u_{\beta}(l'k')u_{\gamma}(l''k''), \qquad (4)$$

where $\mathbf{u}(lk)$ is the displacement of the *k*th atom in the *l*th unit cell from its equilibrium position $\mathbf{r}(lk)$, m_k is the atomic mass of atom *k*, and Cartesian coordinates are denoted by Greek letters. $\Phi_{\alpha\beta}$ and $\Phi_{\alpha\beta\gamma}$ are the second- and third-order force constants, often called the harmonic and anharmonic force

constants, respectively. They are simply the *n*th derivatives of the potential with respect to the Cartesian coordinates, e.g.,

$$\Phi_{\alpha\beta}(lk,l'k') = \frac{\partial^2 \Phi}{\partial u_{\alpha}(lk)\partial u_{\beta}(l'k')}|_{0}$$
(5)

If we were to consider only the quadratic term in Eq. (1) and the kinetic energy of the system *T*, defined with the displacement derivative as

$$T = \frac{1}{2} \sum_{lk\alpha} m_k [\dot{u}_\alpha(lk)]^2, \qquad (6)$$

this would constitute the so-called harmonic Hamiltonian $H_H = \Phi_2 + T$. In practice, the first term Φ_1 is omitted by the assumption that forces on atoms at equilibrium vanish. That is enough to resolve the lattice dynamics from the dynamical matrix eigenvalue problem

$$\sum_{k'\beta} D_{kk'}^{\alpha\beta}(\mathbf{q}) W_{\mathbf{q}j}^{\beta k'} = \omega_{\mathbf{q}j}^2 W_{\mathbf{q}j}^{\alpha k}, \tag{7}$$

where **q** is the wave vector, *j* is the band index, $\omega_{\mathbf{q}j}$ and $W_{\mathbf{q}j}$ are the frequency and polarization vector of a phonon mode for a set {**q**, *j*}, respectively, and the elements of the dynamical matrix are

$$D_{kk'}^{\alpha\beta}(\mathbf{q}) = \sum_{l'} \frac{\Phi_{\alpha\beta}(0k, l'k')}{\sqrt{m_k m_{k'}}} e^{i\mathbf{q} \cdot [\mathbf{r}(l'k') - \mathbf{r}(0k)]}.$$
 (8)

Here and in Eq. (12) we have used the translational invariance condition, which states that the force constants depend on l, l', and l'' only through their difference, allowing us to drop the sum over l.

A more convenient way to write the terms of the potential expansion is to express the displacements with the use of the phonon creation and annihilation operators \hat{a}_{qj}^{\dagger} and \hat{a}_{qj} , respectively, resulting in

$$u_{\alpha}(lk) = \left(\frac{\hbar}{2Nm_k}\right)^{\frac{1}{2}} \sum_{\mathbf{q}j} \omega_{\mathbf{q}j}^{-\frac{1}{2}} (\hat{a}_{\mathbf{q}j} + \hat{a}_{-\mathbf{q}j}^{\dagger}) e^{i\mathbf{q}\cdot\mathbf{r}(lk)} W_{\mathbf{q}j}^{\alpha k}, \quad (9)$$

where N is the number of unit cells (for the full derivation, see, e.g., [29], pp. 93–95). This simplifies the expression for the harmonic Hamiltonian, allowing us to write it as a sum of harmonic oscillators,

$$H_H = \sum_{\mathbf{q}j} \hbar \omega_{\mathbf{q}j} \left(\frac{1}{2} + \hat{a}^{\dagger}_{\mathbf{q}j} \hat{a}_{\mathbf{q}j} \right).$$
(10)

Furthermore, we obtain the third-order potential Φ_3 from Eq. (4) as a sum of three-phonon collisions,

$$\Phi_{3} = \sum_{\mathbf{q}j} \sum_{\mathbf{q}'j'} \sum_{\mathbf{q}''j''} F_{\mathbf{q}j,\mathbf{q}'j''}(\hat{a}_{\mathbf{q}j} + \hat{a}_{-\mathbf{q}j}^{\dagger}) \\ \times (\hat{a}_{\mathbf{q}'j'} + \hat{a}_{-\mathbf{q}'j'}^{\dagger})(\hat{a}_{\mathbf{q}''j''} + \hat{a}_{-\mathbf{q}''j''}^{\dagger}), \qquad (11)$$

where the interaction strength is described by the term $F_{\mathbf{q}j,\mathbf{q}'j',\mathbf{q}''j''}$, written explicitly with phonon modes $\{\mathbf{q}, j\}$ as

$$F_{\mathbf{q}j,\mathbf{q}'j',\mathbf{q}''j''} = \frac{1}{3!\sqrt{N}} \sum_{kk'k''} \sum_{\alpha\beta\gamma} W_{\mathbf{q}j}^{\alpha k} W_{\mathbf{q}'j'}^{\beta k'} W_{\mathbf{q}''j''}^{\gamma k''}$$

$$\times \sqrt{\frac{\hbar}{2m_k \omega_{\mathbf{q}j}}} \sqrt{\frac{\hbar}{2m_{k'} \omega_{\mathbf{q}'j'}}} \sqrt{\frac{\hbar}{2m_{k''} \omega_{\mathbf{q}''j''}}}$$

$$\times \sum_{l'l''} \Phi_{\alpha\beta\gamma} (0k, l'k', l''k'') e^{i\mathbf{q}' \cdot [\mathbf{r}(l'k') - \mathbf{r}(0k)]}$$

$$\times e^{i\mathbf{q}'' \cdot [\mathbf{r}(l''k'') - \mathbf{r}(0k)]} e^{i(\mathbf{q} + \mathbf{q}' + \mathbf{q}'') \cdot \mathbf{r}(0k)} \delta_{q+q'+q'',G},$$
(12)

where $\delta_{q+q'+q'',G}$ is the selection rule for the allowed collisions (e.g., [30], p. 119). In a three-phonon process the wave vectors of the phonons **q**, **q**', and **q**'' must add up to a reciprocal lattice vector **G** in order to preserve the crystal momentum (for more on the selection rules and their implications, see, e.g., [28] pp. 134–145).

B. Thermal conductivity

Macroscopically thermal conductivity κ is defined as the rate of heat energy flow per unit area normal to the thermal gradient ΔT subjected to a solid material, which together form the heat current

$$\mathbf{Q} = -\kappa \Delta T. \tag{13}$$

Generally heat is transferred by several different carriers, and the thermal conductivity can be written as the sum of all individual components,

$$\kappa = \sum_{i} \kappa_i. \tag{14}$$

In solid semiconductor materials it is usually enough to consider heat carried by the phonons (κ_l) and electrons (κ_e). Often even the electron contribution can be neglected: with increasing band gap the electrical conductivity decreases, which also decreases the electronic contribution to the thermal conductivity according to the Wiedemann-Franz law. In a recent study of Cu₂O thin films, the electrical conductivity was found to be around 0.5 Ω^{-1} m⁻¹ [9], allowing the estimation of the total thermal conductivity to a reasonable accuracy based on the lattice contribution alone. It should be noted that in the case of highly doped semiconductor materials κ_e may no longer be negligible.

The problem now is to write out a usable formula for describing heat conduction due to phonons. This is done by solving the linearized Boltzmann transport equation (LBTE). When the single-mode relaxation time approximation is used, the thermal conductivity for a collection of phonons can be written using their heat capacity C, group velocity v, and mean free path between collisions Λ . We can write this for a group of phonons in a finite crystal as

$$\kappa_l = \frac{1}{NV_0} \sum_{\mathbf{q}j} C_{\mathbf{q}j} v_{\mathbf{q}j} \Lambda_{\mathbf{q}j}, \qquad (15)$$

PHYSICAL REVIEW B 96, 014304 (2017)

where V_0 is the volume of the unit cell. Within the harmonic approximation it is already possible to calculate the modedependent heat capacity assuming that phonons obey Bose-Einstein statistics. The group velocity for the modes obtained from Eq. (7) is just the first derivative of the frequencies with respect to the wave vector. The phonon mean free path can be evaluated as a product of the group velocity and relaxation time of a mode (which is assumed to be the same as the lifetime) $v_{qj} \times \tau_{qj}$, and for the latter we need to include the anharmonicity of the crystal.

In the harmonic approximation, phonon lifetimes would be infinite. Anharmonic effects in crystals produce a phonon self-energy $\Delta \omega_{qj} + i\Gamma_{qj}$, where the imaginary part is in fact the reciprocal of the phonon lifetime. An explicit formula for this can be obtained using many-body perturbation theory. Including contributions up to the second order, the imaginary part can be written as

$$\Gamma_{\mathbf{q}j}(\omega) = \frac{18\pi}{\hbar^2} \sum_{\mathbf{q}'j',\mathbf{q}''j''} \left| F_{-\mathbf{q}j,\mathbf{q}'j',\mathbf{q}''j''} \right|^2 \{ (n_{\mathbf{q}'j'} + n_{\mathbf{q}''j''} + 1) \\ \times \delta(\omega - \omega_{\mathbf{q}'j'} - \omega_{\mathbf{q}''j''}) + (n_{\mathbf{q}'j'} - n_{\mathbf{q}''j''}) \\ \times [\delta(\omega + \omega_{\mathbf{q}'j'} - \omega_{\mathbf{q}''j''}) - \delta(\omega - \omega_{\mathbf{q}'j'} + \omega_{\mathbf{q}''j''})] \},$$
(16)

where the terms n_{qj} are phonon occupation numbers [31,32]. Phonons are assumed to obey Bose-Einstein statistics and their occupations as a function of temperature are

$$n_{\mathbf{q}j} = \frac{1}{e^{(\hbar\omega_{\mathbf{q}j}/k_BT)} - 1}.$$
(17)

So far everything about phonons and their behavior is general. In actual calculations carried out in this work, the reciprocal space is discretized to a Γ-point-centered mesh of $N_1 \times N_2 \times N_3$ grid points, and the set of considered collisions is thus truncated to events in the vicinity of these grid points. Additionally, when calculating the imaginary part of the self-energy in Eq. (16), all other phonon modes are assumed to be in their equilibrium distributions (single-mode relaxation time approximation; hereafter RTA). We also checked the accuracy of the RTA in comparison to the full direct solution of the LBTE [16]. Force constants are calculated using the finite-displacement method, where the dynamical matrix is constructed by calculating the forces acting on each atom in a supercell due to the displacement of one atom for the second-order and two atoms for the third-order force constants. The symmetry of the crystal is utilized to reduce the number of supercell calculations required to construct the full set of force constants. Also, only processes of up to three phonons are considered, although the potential energy could be expanded to fourth-order and higher terms. The computational cost scales up rapidly already from the inclusion of third-order interactions, as the number of required force calculations in high-symmetry Cu₂O is only 2 for the harmonic part but 246 for the anharmonic force constants obtained for a $2 \times 2 \times 2$ supercell. Anharmonicity is considered only in the calculation of different scattering processes, and the effect anharmonicity may have on the phonon eigenvalues is neglected, as well as any higher order force constants and decay pathways involving more than three phonons.

C. Computational details

All DFT calculations were carried out with the CRYS-TAL14 program package [26]. Throughout the paper, we compare the performance of two density functionals: (i) the hybrid PBE0 functional, with 25% Hartree-Fock and 75% PBE exchange [33,34]; and (ii) the PBE GGA functional. In addition, we benchmarked three other well-known functionals to provide a more general picture of the DFT performance for Cu₂O: (iii) the hybrid HSE06 functional derived from PBE0 and using an error-function-screened Coulomb potential to calculate the exchange energy [35]; (iv) the Minnesota-type meta-GGA functional M06L; and (v) its hybrid counterpart M06, incorporating 27% exact exchange [36,37]. For all calculations we used all-electron, Gaussian-type basis sets, mainly triple- ζ -valence + polarization level, based on Karlsruhe def2 basis sets (a list of all basis sets used and their derivations is given in the Supplemental Material) [38]. Convergence with respect to reciprocal space k sampling was checked and a mesh of $8 \times 8 \times 8$ points was used for all calculations on the primitive unit cell of Cu₂O [39]. Coulomb and exchange integral tolerance factors (TOLINTEG) were set to tight values of 8, 8, 8, 8, and 16. A default integration grid (XLGRID) was used for the density functional part, along with default total energy convergence thresholds (TOLDEE). TOLDEE was tightened to 10^{-9} a.u. for the Γ -frequency calculation [40,41]. Elastic constants were calculated with the standard method implemented in CRYSTAL14 within the keyword ELASTCON [42,43]. The methodologies used for calculating different physical properties are described in detail in the respective parts of the Results and Discussion section (Sec. III).

Harmonic phonon properties and thermal conductivities were obtained using the Phonopy and Phono3py program packages, respectively [19,44]. Harmonic force constants were calculated using a $4 \times 4 \times 4$ supercell corresponding to a lattice parameter of 17.27 Å, 384 atoms in the cell, and an atomic displacement of 0.01 Å. For k sampling, only the Γ point was considered. To confirm that the localized GTO-type basis set provides accurate force constants, we also calculated second-order force constants with the QUANTUM ESPRESSO plane-wave code both analytically (density functional perturbation theory) and numerically (finite differences with Phonopy). We found a good agreement between the GTO and the plane-wave results, and detailed results from the the QUANTUM ESPRESSO calculations are included in the Supplemental Material [45–52]. When calculating thermal conductivities, the atomic displacement was increased to 0.03 Å for both harmonic and anharmonic force constants. The effect of increasing the atomic displacement was negligible for the harmonic frequencies. A smaller, $2 \times 2 \times 2$, supercell with $2 \times 2 \times 2 k$ sampling was used for the third-order force constants. A **q** mesh $(N_1 = N_2 = N_3)$ for the calculation of κ_l was tested with values varying from 10 to 20, and a mesh of $20 \times 20 \times 20$ q points was used in the final calculations $(18 \times 18 \times 18$ for the full solution of the LBTE). A tight 10^{-10} a.u. total energy convergence threshold was used in all supercell calculations. All Brillouin-zone integrations for calculating the phonon density of states (PDOS) and the imaginary part of the self-energy have been done with the

TABLE I. Optimized lattice parameter a (Å) of Cu₂O for nine combinations of functionals and Gaussian-type basis sets. The SVP basis set is the smallest; the TZVPP, the largest. The difference from the experiment (a = 4.269 Å, T = 295 K) [54] is shown in parentheses.

	SVP	TZVP	TZVPP	
PBE	4.303 (+0.81%)	4.328 (+1.39%)	4.315 (+1.09%)	
PBE0	4.296 (+0.64%)	4.318 (+1.16%)	4.328 (+1.39%)	
HSE06	4.296 (+0.64%)	4.318 (+1.16%)	4.316 (+1.11%)	

tetrahedron method. The nonanalytical contribution when $\mathbf{q} \rightarrow 0$ has been taken into account in all phonon calculations [53].

III. RESULTS AND DISCUSSION

A. Structural analysis and band structure

Cu₂O is one of the oldest and most studied semiconductor materials, and it crystallizes in the cubic $Pn\bar{3}m$ space group. One unit cell has two formula units and consists of copper atoms linearly coordinated with oxygen atoms, which in turn are tetrahedrally coordinated (Fig. 1). Initial structural parameters were taken from a synchrotron radiation study by Kirfel and Eichhorn [54]. The only free structural parameter, the lattice constant a, was optimized and band structure calculations were performed using the three functionals, PBE, PBE0, and HSE06, combined with the SVP, TZVP, and TZVPP level basis sets. Additionally, the mGGA functionals M06L and M06 were tested with the TZVP level basis set, and due to their similar performance to the PBE and PBE0 functionals, respectively, they are discussed in the Supplemental Material. As reported in Table I, each combination performs in a rather similar fashion in the structural optimization. All approaches result in an increase in a that varies between 0.64% and 1.39%. PBE0/TZVP produces a bulk modulus of 107 GPa, while the experimental measurements lie in the range of 106-112 GPa [55,56].

The functional performance starts to diverge when we take a closer look at the electronic properties. The band structures in principle look identical in all nine cases, but the magnitude of the band gap differs significantly between functionals (Fig. S1, Supplemental Material). The difference between the three different basis sets is much smaller. GGAs are somewhat notorious for underestimating band gaps, while hybrids are more likely to overshoot them, a property directly traceable back to the amount of Hartree-Fock exchange used. Band gaps with the TZVP basis set are 0.53, 2.39, and 1.87 eV for PBE, PBE0, and HSE06, respectively. The experimental result most often cited is 2.17 eV (this varies slightly, from 2.0 to 2.2 eV), and the PBE0/TZVP level of theory shows a reasonable agreement with the experiment [57,58]. Results and trends obtained here fall in line with previous calculations reported in the literature [8,59–63].

The PBE0 and PBE electronic band structures and the atom-projected density of states (DOS) shown in Fig. 2 are in line with earlier studies. The valence bands down to -5 eV are dominated by Cu atoms, with some contributions from O



FIG. 2. Band structure and density of states for Cu_2O at the PBE0/TZVP and PBE/TZVP level of theory. The dotted horizontal line marks the top of the valence bands.

atoms, especially for the topmost valence bands (see Fig. S2 in the Supplemental Material for corresponding band-projected densities). Below -5 eV, the contribution of the O atoms increases and both Cu and O contribute almost equally. However, comparison of the DOS plots shows that the valenceband energies predicted by PBE and PBE0 clearly differ. As discussed before for the PBE functional by, e.g., Chen *et al.* [8], the incomplete cancellation of the self-interaction of the *d* orbitals results in their lying too high in energy. The large number of Cu *d* states between -1 and -4 eV are shifted almost 1 eV higher in energy with PBE. This shift to higher energies is still seen in states below -5 eV, although to a smaller degree, because the relative contribution of the oxygen *p* orbitals is larger. As discussed in the following section, the differences in the PBE0 and PBE electronic structures also result in clear differences in the lattice dynamical properties of Cu_2O .

B. Lattice dynamics and phonon dispersions

Harmonic frequencies at the Γ point vary a lot depending on the method of calculation used. Table II extends the list of vibrational frequencies of Cu₂O found in Ref. [64] with the computational results obtained in this study from Phonopy. Γ frequencies were calculated also with the built-in phonon routines of CRYSTAL14, and since the results were practically identical to the results from Phonopy, they are not listed here. Vibrational energies from PBE0 are clearly closer to the experiment in comparison to those from PBE. A noteworthy detail is the systematicity of this study and results from Ref. [65] in column (d). In these studies all values are either within the range of experimental measurements or below them, whereas in other studies some modes are found to be lower and some higher in energy than the experiment.

The full phonon dispersion within the harmonic approximation was calculated for Cu2O with PBE, PBE0, and M06 for their optimized unit cells. Due to the similarity of PBE0 and M06 results, the latter are discussed only in the Supplemental Material (Fig. S4). Considering first the dispersion obtained using the hybrid PBE0 functional, it is in excellent agreement with the early inelastic neutron scattering experiments by Beg and Shapiro, apart from a few data points [70]. One phonon band in each of the measured paths around 150 cm^{-1} differs markedly from the otherwise near-perfect match as shown in Fig 3. These same discrepancies were discovered by Bohnen et al. in their calculations and they deduced them to be errors in the earlier experiments [65]. To verify this, the authors carried out a new set of neutron scattering measurements, which indeed proved to be different along those reciprocal space paths and support both their and our theoretical results. Nonanalytic correction leads to LO-TO splitting in the IR active modes at 144 and 620 cm⁻¹, with values of 4.5 and 35.5 cm⁻¹, respectively. These are somewhat larger than the experimental values of 3 and 29 cm⁻¹. PBE, on the other hand, produces smaller values, 2.7 and 23.9 cm^{-1} , similar to previous PBE calculations [65,71].

When the phonon dispersion throughout the Brillouin zone is considered, a similar softening of modes in comparison to experiment can be seen for PBE. The phonon dispersions

TABLE II. Frequencies of phonon modes at the Γ point. The columns PBE and PBE0 list the frequencies obtained in this study with the given functionals, columns (a)–(d) list other computational results, and column (e) lists experimental values. All values are in wave numbers (cm⁻¹).

Mode	PBE	PBE0	(a) From [64]	(b) From [<mark>66</mark>]	(c) From [67]	(d) From [65]	(e) From [68], [69]
E_u	79	108	119	100	150	86	109-110
F_{1u} (1) (TO)	133	144	142	143	115	147	146-153
F_{1u} (1) (LO)	135	148	146	159	145	148	149–154
B_u	334	340	350	307	328	337	350
F_{2g}	491	497	515	549	515	496	515
F_{1u} (2) (TO)	603	619	635	608	578	609	609-640
F_{1u} (2) (LO)	627	655	654	639	617	629	638–665



FIG. 3. Phonon dispersion of Cu_2O for relevant paths in the reciprocal space (PBE0/TZVP level of theory). Green symbols are data points from Ref. [70] and red lines show theoretical results obtained in this study.

and PDOS for both the PBE and the PBE0 functionals are plotted together with the experimental data from Ref. [65] in Fig. 4. Even though the bands from PBE calculations are in some cases closer to the experimental points than the bands from PBE0, this can probably be attributed to fortuitous cancellation of errors. Generally, the band shapes are very similar to both functionals, although some tendency can be seen for PBE to flatten the bands, as opposed to the higher dispersion obtained with PBE0. This is immediately reflected in the group velocities of the harmonic phonons, e.g., for transverse acoustic modes very near the Γ point, the group velocities obtained with PBE0 are around 20% larger than those obtained with PBE. The PDOS is clearly affected by the softening of the low-frequency modes with PBE. The highest PDOS is found to be about 20 cm⁻¹ lower with the PBE functional in comparison to the PBE0 one, and the shape of the PDOS feature is clearly different for the two functionals.

C. Lattice thermal conductivity

Moving from phonon dispersions to lattice thermal conductivities results in even larger differences between the GGA-PBE and the hybrid PBE0 functionals. Unfortunately, there are only a few experimental single-crystal data available for the lattice thermal conductivity of Cu₂O. However, Fig. 5 shows a clear difference between PBE and PBE0, which would be expected from the differing phonon dispersion results. PBE clearly underestimates the lattice thermal conductivity of Cu₂O, as the calculated values at 300 and 360 K are 3.2 and 2.8 W m⁻¹ K⁻¹, respectively, more than 40% below the experimental values of 5.6 and 4.9 W m⁻¹ K⁻¹ [72]. PBE0, on the other hand, overshoots the experimental values by only about 7%, with predictions of 6.0 and 5.1 W m^{-1} K⁻¹. Since Cu₂O is cubic, the thermal conductivity is the same in all directions. The full solution of the LBTE gives results very similar to those with the RTA. At 300 K, κ_l with the PBE full solution is the same, $3.2 \text{ W} \text{m}^{-1} \text{K}^{-1}$, as with the RTA, and with PBE0 κ_l is increased from 6.0 to 6.1 W m⁻¹ K⁻¹. Dashed lines in Fig. 5 show the lattice thermal conductivities when isotope scattering is included in the calculations. This introduces a mass variance term based on the natural isotope distributions in the respective elements (for details, see Ref. [19]). As a result, κ_l decreases slightly, around a few percent with PBE0 and a little less with PBE, bringing the predictions closer to experimental values with the hybrid PBE0 functional and farther away from experiment with the GGA-PBE. The predicted lattice thermal conductivity at 300 K for PBE0 with isotope scattering is 5.9 W m⁻¹ K⁻¹, and for PBE it rounds up to the same value of 3.2 W m⁻¹ K⁻¹ as without the isotope scattering.

Comparison of the lattice thermal conductivities with the experimental results at 160 K seems to bring PBE closer to the experiment and PBE0 away from it. This is not, however, necessarily a result of one functional performing better than the other. Upon moving to lower temperatures, defect scattering due to point defects and other defects such as dislocations starts to play an increasingly important role in the overall thermal resistance, while at higher T's phonon-phonon



FIG. 4. Phonon dispersion for relevant paths in the reciprocal space. Symbols are data points from Ref. [65] and lines show theoretical results obtained in this study. In each panel, PBE/TZVP results are shown on the left; PBE0/TZVP results, on the right. While the DOS is plotted in arbitrary units, x axes are normalized between the DOS plots to show the actual differences in DOS.



FIG. 5. Lattice thermal conductivity κ_l of Cu₂O between 100 and 600 K. Computational results were obtained at the PBE/TZVP and PBE0/TZVP levels of theory, while experimental values are from Ref. [72].

scattering dominates. Boundary scattering can also play a role at lower temperatures, but our calculations show that in the case of Cu₂O the grains would need to be clearly smaller than 1 μ m to explain the difference at 160 K (experimental data are for a single crystal). Full solution of the LBTE at 160 K does not improve on the RTA result, showing only a 2% increase in κ_l . Cu₂O is rarely stoichiometric, so the computational results shown in Fig. 5 lack a scattering mechanism, which could further decrease the lattice thermal conductivity at lower temperatures. Nonstoichiometricity of Cu₂O has been studied theoretically in some detail, and the feature-rich Raman spectra obtained regardless of the synthesis method give a strong indication of naturally occurring defects (only one vibrational mode is Raman active in pure Cu₂O) [73–76].

As we calculate the thermal conductivity through Eq. (15), it is possible to study the individual factors giving rise to the differences between the PBE and the PBE0 functionals. The heat capacities for Cu₂O are virtually identical with both methods (Fig. S7, Supplemental Material), suggesting that the disparity must be attributed to differences in group velocities and phonon lifetimes. Except for the third-order force constants $\Phi_{\alpha\beta\gamma}$ in Eq. (12), both group velocities and phonon lifetimes are calculated from the harmonic phonon eigenfrequencies and eigenvectors with no anharmonic corrections to phonon eigenfrequencies. Thus, it is very important to have accurate phonon dispersion relations and PDOS values as a basis for the calculation of phonon-phonon interactions. In addition to (i) the accuracy of the DFT forces, it is also important to keep in mind other possible sources of error in comparison to the experiment: (ii) point defect scattering due to impurities or nonstoichiometry is neglected, and (iii) the collision space for determining the processes producing thermal resistance is described using a finite \mathbf{q} mesh. The total contribution arising from these three sources is not easy to estimate and it is possible that some cancellation of errors is also present.

For a symmetric material with a simple structure, Cu₂O has a rather low lattice thermal conductivity. This is usually



FIG. 6. Mode-Grüneisen parameters calculated with (a) PBE0 and (b) PBE functionals, plotted vs the frequency. Red circles show acoustic modes; black circles, optical modes. Note the different *y* axes for PBE and PBE0 functionals.

consistent with compounds that have large mode-dependent Grüneisen parameters, a measure of the anharmonicity of phonons in the system [77,78]. In fact, in continuum theory the phonon lifetime τ_{qj} is inversely proportional to the square of the averaged Grüneisen parameter γ [28]. The dimensionless mode-Grüneisen parameter is often written by relating the shifts in phonon frequencies of modes {q,j} with respect to the varying volume, but a more general way is to define it using strain $\eta_{\mu\nu}$:

$$\gamma_{\mu\nu}(\mathbf{q}j) = -\frac{1}{\omega_{\mathbf{q}j}} \frac{\partial \omega_{\mathbf{q}j}}{\partial \eta_{\mu\nu}}.$$
(18)

Within our DFT-based approach, γ_{qj} can be obtained from third-order force constants using the relation (Ref. [30], pp. 204–205)

$$\gamma_{\mathbf{q}j} = -\frac{1}{2\omega_{\mathbf{q}j}^2} \sum_{l'l''} \sum_{kk'k''} \sum_{\alpha\beta\gamma} \frac{W_{\mathbf{q}j}^{\alpha k*} W_{\mathbf{q}j}^{\beta k'}}{\sqrt{m_k m_{k'}}}$$
$$\times \Phi_{\alpha\beta\gamma}(0k, l'k', l''k'')$$
$$\times e^{i\mathbf{q}\cdot [\mathbf{r}(l'k') - \mathbf{r}(0k)]} \times \mathbf{r}(l''k''\gamma). \tag{19}$$

Calculated mode-Grüneisen parameters are shown in Fig. 6. Data shown in these plots have been obtained using a $10 \times 10 \times 10$ q mesh. A convergence check with respect to a $16 \times 16 \times 16$ mesh showed changes only in the density of data points. PBE0 results are in agreement with previous ab *initio* results obtained using the quasiharmonic approximation. The only notable difference is in the maxima of the modes around $60 \,\mathrm{cm}^{-1}$, where our calculations show values of 3.5 and previous quasiharmonic approximation results reach values as high as 4.5. The γ_{qj} values obtained with PBE0 also compare well with the experimental values of Reimann et al. determined from Raman measurements, which range from -3.4 to +1.7 [79]. With PBE, the maximum value is around 5 and the minimum is -11.5, which is unreasonably low. The distribution of γ_{q_i} with respect to the frequencies becomes almost identical for $\omega \ge 200 \text{ cm}^{-1}$. We would like to note that there is no way to distinguish different modes when the phonon bands cross, and thus the division into acoustic and optical modes in Fig. 6 is based on the listing provided by Phono3py.

Based on Eq. (19), according to which $\gamma_{\mathbf{q}j}$ values are calculated, the reason for the observed discrepancies between PBE and PBE0 is twofold. Lower harmonic frequencies of PBE appear as larger mode-Grüneisen parameters since $\gamma_{\mathbf{q}j} \propto \omega_{\mathbf{q}j}^{-2}$. This alone might not explain the difference of more than a factor of 2, although the relative difference at the lower end of harmonic frequencies between the PBE and the PBE0 functionals is greater than that at higher wave numbers. This results in greater differences in absolute values of $\gamma_{\mathbf{q}j}$. As the vibrational modes associated with the phonons are the same, meaning $e^{i\mathbf{q}\cdot\mathbf{r}}$ and polarization vectors cannot differ significantly, the rest of the differences can be attributed to differences in third-order force constants $\Phi_{\alpha\beta\gamma}$.

To study the range of phonon-phonon interactions in Cu_2O , we also calculated the lattice thermal conductivity with a set of cutoffs, setting the respective third-order force constants to 0 if the separation of any atom pair in a triplet of atoms is longer than the cutoff value. Figure 7 shows the calculated κ_l at temperatures between 100 and 400 K with different cutoff values using PBE0. It is immediately apparent that a cutoff distance of 3 Å will not suffice, as it will take into account only forces between the nearest-neighbor atoms. The majority of the strongest interactions are captured already with a 4-A cutoff, including next-nearest-neighboring atom pairs and oxygens in adjacent oxygen tetrahedra. For accuracy's sake, however, a cutoff distance of at least 5 Å is needed; beyond that, the effects are negligible. If knowledge of the range of interactions were available prior to forming the supercells with finite displacements, the number of required force calculations could be drastically reduced. That said, setting cutoff ranges without testing should generally be avoided. Although some estimates can be made from the structure by choosing the number of neighbor shells to include, a good choice is always heavily material dependent, e.g., a cutoff of 3.8 Å, which is sufficient for WSe₂, would not capture all the relevant interactions in Cu₂O [80].

We also calculated the cumulative lattice thermal conductivity $\kappa_{qj}(\Lambda)$, where only modes with a mean free path smaller than a certain threshold contribute to the thermal conductivity.



FIG. 7. Lattice thermal conductivity calculated with PBE0 using different distance cutoff values for the third-order force constants (normally, all third-order force constants within the supercell were calculated).

In Fig. 8 we have plotted the cumulative lattice thermal conductivity with respect to the phonon mean free path Λ_{qi} for both PBE and PBE0. As the absolute value of κ_l is smaller for PBE, it is natural for it to reach its maximum at a much shorter mean free paths compared to PBE0. The shapes of the curves are rather similar for PBE0 and PBE, with some obvious numerical differences. The curve resembles those of other semiconductors, such as PbTe [80] and ZnO [81], with a slow start before the mean free path grows to relevant magnitudes, followed by a somewhat steep linear regime and, finally, a less steep plateau towards the maximum. For both Cu₂O and PbTe the majority of heat is carried by phonons with a mean free path of less than 20 nm. For ZnO the linear regime continues throughout the plot, indicating a more even distribution of heat-carrying phonons over the whole frequency range. The slope of the plot can be used as an approximate measure of



FIG. 8. Cumulative κ_l with respect to the phonon mean free path Λ_{qj} calculated at 300 K with the functionals PBE and PBE0.



FIG. 9. Cumulative properties with respect to harmonic frequencies at 300 K for PBE and PBE0: (a) lattice thermal conductivity, (b) phonon lifetime, and (c) group velocity.

where the density of heat-carrying phonons lies with respect to Λ_{qj} . Figure 8 does not explicitly show the density of modes, but when comparing the two curves for the same material, general features, such as the bulge with PBE at $\Lambda_{qj} \leq 5$ nm, reveal that the number of modes associated with such mean free paths is greater with PBE than with PBE0.

A more detailed analysis can be made by investigating the different properties through which κ_l is calculated. One way is to plot the cumulative properties with respect to the phonon frequency as in Fig. 9. As shown in Fig. 9(b), for phonons with $\omega_{qj} \leq 250 \text{ cm}^{-1}$, the phonon lifetimes obtained with PBE0 are almost twice as large as the PBE lifetimes. The difference

in lifetimes is even larger in the region below 50 cm^{-1} , which explains the much larger cumulative κ_l of PBE0 in that regime compared to that at higher frequencies, where the differences in τ_{qi} between the PBE and the PBE0 functionals are smaller. Despite the much higher phonon density at frequencies from around 60 to 150 cm^{-1} , the contribution to the thermal conductivity is only half that from the transverse acoustic (TA) modes below 50 cm⁻¹. Group velocities play a bigger role in this regime since, even though the lifetimes are on the same scale as for the TA modes, given the number of modes in the frequency range, the lower group velocity, which is squared in the formula of κ_l , dominates the modes' effect on the thermal conductivity. The phonon modes showing a large dispersion between 150 and 350 cm⁻¹ make up about one-third of the total lattice thermal conductivity despite their rather short lifetimes. Optical modes above 500 cm⁻¹ clearly carry less heat than the modes described above. With PBE, the amount of heat carried by the optical modes is almost negligible due to the short lifetimes.

Another key feature to note in the cumulative properties is that acoustic phonons carry a relatively small portion of the heat in Cu₂O. For comparison, in the case of WS₂ and MoS₂, practically all heat is carried by phonons below 150 cm^{-1} . This region also includes some optical modes, but still it is safe to assume that the heat carried by acoustic phonons is much greater than in Cu₂O. Generally, the lifetimes in Cu₂O are relatively short compared to those in other recently studied semiconductors, such as Si, Si clathrate frameworks, and the aforementioned sulfides [80,82,83]. Lifetimes of different modes are of the order of picoseconds (see Supplemental Material, Figs. S8 and S9), whereas for WS₂ and Si, the lifetimes of some modes are already of nanoseconds. The lifetime of a phonon mode is strongly affected by the number of available phonon-phonon scattering pathways, Eq. 16. In Cu_2O , the relatively low-lying optical modes around 100 cm⁻¹ apparently facilitate the phonon scattering of the acoustic modes. These optical modes are even closer to the TA modes in the case of PBE, which underestimates their energy in comparison to the experiment, increasing the number of scattering pathways and, thus, decreasing the lattice thermal conductivity due to the shorter phonon lifetimes. This is a somewhat similar effect to what Lindroth and Erhart showed for WS₂ by artificially reducing the energy gap between acoustic and optical phonon modes. As the optical modes were brought closer in energy towards the heat-carrying low-frequency phonons, the lifetimes became shorter.

To further investigate the effect, we plotted the imaginary parts of the self-energy, joint density of states (JDOS), and weighted joint density of states (w-JDOS) with respect to the frequency at the *R* point [$\mathbf{q} = (0.5, 0.5, 0.5)$] of the first Brillouin zone. We checked the corresponding values also at 10 points from Γ to the three directions [100], [110], and [111], and the appearances of the plots were similar, so the point *R* serves as a representative point in the reciprocal space. This gives us explicit information on the number of different pathways for phonon scattering through summing the three-phonon events that do not violate the conservation of energy and momentum. The JDOS is split into two types. Class 1 events represent the different collision processes, effectively the delta functions in the third row of Eq. (16),



FIG. 10. (a) Imaginary part of the self-energy, (b) joint density of states (JDOS), and (c) weighted joint density of states (w-JDOS) of Cu₂O calculated at the *R* point in the first Brillouin zone [$\mathbf{q} = (0.5, 0.5, 0.5)$] for both functionals, PBE and PBE0. Solid lines mark class 1 events, and dashed lines class 2 events (see text). Γ and w-JDOS are calculated at 300 K. We show the plot only up to 700 cm⁻¹, although Γ can be nonzero for up to two times the maximum phonon frequency.

and class 2 events represent the decay processes, effectively the delta functions in the second row of Eq. (16). When the effects of temperature, meaning the actual occupations of different modes, are taken into account, we also sum the phonon distribution prefactors of Eq. (16) and this constitutes the w-JDOS.

Figures 10(a) and 9(b) show, to some degree, the same result in reverse. As the imaginary part of the self-energy is inversely proportional to the lifetime, the two plots follow each other in a reciprocal fashion when the two functionals are compared. Figure 10(b) is as expected; there are no decay events until frequencies at which there are optical modes. Between 100 and 200 cm⁻¹ there are some minor differences, mainly shifts in frequency, but based on the JDOS alone, there would not seem to be much difference in the three-phonon scattering events between the two functionals. Major differences between PBE and PBE0 arise in the w-JDOS. Similarly to the JDOS, the peaks appear at lower frequencies for PBE because of the general softening of the modes, but here also the magnitudes differ significantly. Since the calculated w-JDOS shows such clear differences between PBE and PBE0, it could give useful information on the performance of difference functionals for calculating κ_l already based on phonon harmonic properties. However, only one representative point in the Brillouin zone has been discussed here, and in any case, to make a real comparison, one needs to include the anharmonicity in order to see the effect of the interaction strength, which is not included in the w-JDOS.

IV. CONCLUSIONS

We have carried out the first ab initio DFT study on the lattice thermal conductivity of a semiconductor material using a full hybrid density functional method. In the case of Cu₂O, the hybrid DFT-PBE0 method outperforms its GGA counterpart, the DFT-PBE, both in the case of the lattice thermal conductivity and for various other properties studied here. The largest difference is seen for the lattice thermal conductivity, where PBE0 overestimates κ_l by only 5% in comparison to experiment and PBE underestimates it by over 40%. Other quantities, such as the electronic band gap, phonon frequencies at the Γ point, and mode-Grüneisen parameters are also closer to the experiment when calculated with PBE0. Overall, hybrid density functional calculations with Gaussiantype local basis sets provide a rather cost-efficient way of investigating the phonon properties of the challenging 3dtransition metal oxides without any empirical corrections. Work remains to be done to take into account factors such as point defect scattering and anharmonic frequency shifts.

ACKNOWLEDGMENTS

We thank Dr. K.-P. Bohnen and Dr. R. Heid of Karlsruhe Institute of Technology for providing their inelastic neutron scattering data. This work was funded by the Academy of Finland (Strategic Research Council, CloseLoop consortium, Grant No. 303452). Computational resources were provided by CSC, the Finnish IT Center for Science.

- [1] B. Davydov and C.R. Doklady, Acad. Sci. 20, 279 (1938).
- [2] V. Lashkaryov, Ukr. J. Phys. 53, 53 (2008).
- [3] R. N. Briskman, Sol. Energy Mater. Sol. Cells 27, 361 (1992).
- [4] T. Minami, Y. Nishi, T. Miyata, and J. Nomoto, Appl. Phys. Express 4, 062301 (2011).
- [5] M. Le, M. Ren, Z. Zhang, P. T. Sprunger, R. L. Kurtz, and J. C. Flake, J. Electrochem. Soc. **158**, E45 (2011).
- [6] K. W. Frese, J. Electrochem. Soc. 138, 3338 (1991).
- [7] K. Klier, Advances in Catalysis (Elsevier, Amsterdam, 1982).
- [8] X. Chen, D. Parker, M.-H. Du, and D. J. Singh, New J. Phys. 15, 043029 (2013).
- [9] D. Hartung, F. Gather, P. Hering, C. Kandzia, D. Reppin, A. Polity, B. K. Meyer, and P. J. Klar, Appl. Phys. Lett. **106**, 253901 (2015).
- [10] E. A. Mondarte, V. Copa, A. Tuico, C. J. Vergara, E. Estacio, A. Salvador, and A. Somintac, Mater. Sci. Semicond. Process. 45, 27 (2016).
- [11] R. Venkatasubramanian, T. Colpitts, E. Watko, M. Lamvik, and N. El-Masry, J. Cryst. Growth 170, 817 (1997).
- [12] K. Biswas, J. He, I. D. Blum, C.-I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid, and M. G. Kanatzidis, Nature 489, 414 (2012).

- [13] D. A. Broido, A. Ward, and N. Mingo, Phys. Rev. B 72, 014308 (2005).
- [14] D. A. Broido, M. Malorny, G. Birner, N. Mingo, and D. A. Stewart, Appl. Phys. Lett. 91, 231922 (2007).
- [15] L. Chaput, A. Togo, I. Tanaka, and G. Hug, Phys. Rev. B 84, 094302 (2011).
- [16] L. Chaput, Phys. Rev. Lett. 110, 265506 (2013).
- [17] W. Li, J. Carrete, N. A. Katcho, and N. Mingo, Comput. Phys. Commun. 185, 1747 (2014).
- [18] A. Chernatynskiy and S. R. Phillpot, Comput. Phys. Commun. 192, 196 (2015).
- [19] A. Togo, L. Chaput, and I. Tanaka, Phys. Rev. B 91, 094306 (2015).
- [20] J. J. Plata, D. Usanmaz, P. Nath, C. Toher, J. Carrete, M. Asta, M. de Jong, M. B. Nardelli, M. Fornari, and S. Curtarolo, arXiv:1611.05481.
- [21] T. Tadano, Y. Gohda, and S. Tsuneyuki, J. Phys.: Condens. Matter 26, 225402 (2014).
- [22] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B 52, R5467 (1995).
- [23] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
- [24] A. D. Becke, J. Chem. Phys. 98, 5648 (1993).
- [25] A. D. Becke, J. Chem. Phys. 98, 1372 (1993).
- [26] R. Dovesi, R. Orlando, A. Erba, C. M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Maschio, M. Ferrabone, M. De La Pierre, P. D'Arco, Y. Noël, M. Causà, M. Rérat, and B. Kirtman, Int. J. Quantum Chem. 114, 1287 (2014).
- [27] T. Tadano and S. Tsuneyuki, arXiv:1706.04744.
- [28] J. M. Ziman, *Electrons and Phonons: The Theory of Transport Phenomena in Solids* (Oxford University Press, New York, 1960).
- [29] G. P. Srivastava, *The Physics of Phonons* (CRC Press, Boca Raton, FL, 1990).
- [30] D. Wallace, *Thermodynamics of Crystals* (Dover, Mineola, NY, 1990).
- [31] A. A. Maradudin and A. E. Fein, Phys. Rev. 128, 2589 (1962).
- [32] D. C. Wallace, Phys. Rev. 152, 247 (1966).
- [33] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [34] C. Adamo and V. Barone, J. Chem. Phys. 110, 6158 (1999).
- [35] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003).
- [36] Y. Zhao and D. G. Truhlar, J. Chem. Phys. 125, 194101 (2006).
- [37] Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. **120**, 215 (2008).
- [38] F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys. 7, 3297 (2005).
- [39] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
- [40] F. Pascale, C. M. Zicovich-Wilson, F. López Gejo, B. Civalleri, R. Orlando, and R. Dovesi, J. Comput. Chem. 25, 888 (2004).
- [41] C. M. Zicovich-Wilson, F. Pascale, C. Roetti, V. R. Saunders, R. Orlando, and R. Dovesi, J. Comput. Chem. 25, 1873 (2004).
- [42] W. Perger, J. Criswell, B. Civalleri, and R. Dovesi, Comput. Phys. Commun. 180, 1753 (2009).
- [43] A. Erba, A. Mahmoud, R. Orlando, and R. Dovesi, Phys. Chem. Miner. 41, 151 (2014).
- [44] A. Togo and I. Tanaka, Scripta Mater. 108, 1 (2015).
- [45] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.96.014304, which includes Refs. [46–52], for additional information on band structure calculations,

meta-GGA calculations, Quantum Espresso calculations, heat capacities, phonon lifetimes, and GTO basis sets.

- [46] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.: Condens. Matter **21**, 395502 (2009).
- [47] K. F. Garrity, J. W. Bennett, K. M. Rabe, and D. Vanderbilt, Comput. Mater. Sci. 81, 446 (2014).
- [48] X. Gonze, J.-C. Charlier, D. Allan, and M. Teter, Phys. Rev. B 50, 13035 (1994).
- [49] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. 73, 515 (2001).
- [50] K. N. Kudin and G. E. Scuseria, Phys. Rev. B **61**, 16440 (2000).
- [51] A. J. Karttunen, T. Tynell, and M. Karppinen, J. Phys. Chem. C 119, 13105 (2015).
- [52] J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. 115, 036402 (2015).
- [53] Y. Wang, J. J. Wang, W. Y. Wang, Z. G. Mei, S. L. Shang, L. Q. Chen, and Z. K. Liu, J. Phys.: Condens. Matter 22, 202201 (2010).
- [54] A. Kirfel and K. Eichhorn, Acta Crystallogr. Sec. A A46, 271 (1990).
- [55] M. H. Manghnani, W. S. Brower, and H. S. Parker, Phys. Status Solidi A 25, 69 (1974).
- [56] J. Hallberg and R. C. Hanson, Phys. Status Solidi B **42**, 305 (1970).
- [57] A. Önsten, M. Månsson, T. Claesson, T. Muro, T. Matsushita, T. Nakamura, T. Kinoshita, U. O. Karlsson, and O. Tjernberg, Phys. Rev. B 76, 115127 (2007).
- [58] P. W. Baumeister, Phys. Rev. 121, 359 (1961).
- [59] F. Forte, L. J. P. Ament, and J. van den Brink, Phys. Rev. B 77, 134428 (2008).
- [60] E. Ruiz, S. Alvarez, P. Alemany, and R. A. Evarestov, Phys. Rev. B 56, 7189 (1997).
- [61] A. Martínez-Ruiz, M. G. Moren, and N. Takeuchi, Solid State Sci. 5, 291 (2003).
- [62] J. P. Hu, D. J. Payne, R. G. Egdell, P.-A. Glans, T. Learmonth, K. E. Smith, J. Guo, and N. M. Harrison, Phys. Rev. B 77, 155115 (2008).
- [63] D. O. Scanlon, B. J. Morgan, and G. W. Watson, J. Chem. Phys. 131, 124703 (2009).
- [64] A. Sanson, Solid State Comm. 151, 1452 (2011).
- [65] K.-P. Bohnen, R. Heid, L. Pintschovius, A. Soon, and C. Stampfl, Phys. Rev. B 80, 134304 (2009).
- [66] C. Carabatos and B. Prevot, Phys. Status Solidi B 44, 701 (1971).
- [67] R. Mittal, S. L. Chaplot, S. K. Mishra, and P. P. Bose, Phys. Rev. B 75, 174303 (2007).
- [68] Y. Petroff, P. Y. Yu, and Y. R. Shen, Phys. Rev. B 12, 2488 (1975).
- [69] M. Ivanda, D. Waasmaier, A. Endriss, J. Ihringer, A. Kirfel, and W. Kiefer, J. Raman Spectrosc. 28, 487 (1997).
- [70] M. Beg and S. Shapiro, Phys. Rev. B 13, 1728 (1976).
- [71] P. Dawson, M. Hargreave, and G. Wilkinson, J. Phys. Chem. Solids 34, 2201 (1973).

J. LINNERA AND A. J. KARTTUNEN

- [72] D. R. Lide, *CRC Handbook of Chemistry and Physics, Internet Version* (CRC Press, Boca Raton, FL, 2005).
- [73] A. F. Wright and J. S. Nelson, J. Appl. Phys. 92, 5849 (2002).
- [74] M. Nolan and S. D. Elliott, Phys. Chem. Chem. Phys. 8, 5350 (2006).
- [75] A. Soon, X.-Y. Cui, B. Delley, S.-H. Wei, and C. Stampfl, Phys. Rev. B 79, 035205 (2009).
- [76] T. Sander, C. T. Reindl, M. Giar, B. Eifert, M. Heinemann, C. Heiliger, and P. J. Klar, Phys. Rev. B 90, 045203 (2014).
- [77] D. T. Morelli, V. Jovovic, and J. P. Heremans, Phys. Rev. Lett. 101, 035901 (2008).

- [78] Y. Zhang, E. Skoug, J. Cain, V. Ozoliņš, D. Morelli, and C. Wolverton, Phys. Rev. B 85, 054306 (2012).
- [79] K. Reimann and K. Syassen, Phys. Rev. B 39, 11113 (1989).
- [80] D. O. Lindroth and P. Erhart, Phys. Rev. B **94**, 115205 (2016).
- [81] A. J. Karttunen, T. Tynell, and M. Karppinen, Nano Energy 22, 338 (2016).
- [82] V. J. Härkönen and A. J. Karttunen, Phys. Rev. B 94, 054310 (2016).
- [83] V. J. Härkönen and A. J. Karttunen, Phys. Rev. B 93, 024307 (2016).