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Lattice thermal conductivity of NaCoO₂ and LiCoO₂ intercalation materials studied by hybrid density functional theory

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Abstract
We have studied the lattice dynamics and lattice thermal conductivity of NaCoO₂ intercalation material with first-principles hybrid density functional methods. The lattice thermal conductivity has been obtained using linearized Boltzmann transport theory and the contributions to the lattice thermal conductivity have been analyzed in detail. The results obtained for NaCoO₂ have been systematically compared with LiCoO₂ to shed light on the effect of the alkali metal atom. The room-temperature in-plane lattice thermal conductivities within relaxation time approximation are 78 W m⁻¹ K⁻¹ and 46 W m⁻¹ K⁻¹ for NaCoO₂ and LiCoO₂, respectively. The respective room-temperature cross-plane lattice-thermal conductivities are 25.0 W m⁻¹ K⁻¹ and 6.6 W m⁻¹ K⁻¹. The predicted lattice thermal conductivities for fully alkali-occupied single crystals are clearly larger in comparison to the experimental values obtained for single-crystal NaCoO₂ and polycrystalline LiCoO₂. Analysis of the lattice thermal conductivity reveals that the differences between NaCoO₂ and LiCoO₂ can be explained by significantly shorter phonon lifetimes in LiCoO₂.

1. Introduction

Alkali metal cobalt oxides NaₙCoO₂ and LiₙCoO₂ are widely studied materials that show a variety of electronic and magnetic properties with respect to the alkali metal content x [1]. NaₙCoO₂ phases with x < 1 are promising thermoelectric materials due to high thermopower combined with low resistivity and low thermal conductivity [2, 3]. The hydrated form NaₙCoO₂·yH₂O has attracted interest due to superconductivity observed below 5 K [4]. Finally, LiCoO₂ is a widely used positive electrode material in lithium-ion batteries [5, 6].

NaCoO₂ and LiCoO₂ are the end members of AₙCoO₂ phases, adopting layered trigonal crystal structure that corresponds to the Delafossite-NaFeO₂ structure type (space group R3m). The unit cell consists of three layers of edge-sharing CoO₆ octahedra and the alkali metal atoms occupy octahedral interstitial positions in the interlayer space (figure 1). The Co atom is in low-spin + III oxidation state, resulting in non-magnetic materials [1, 7].

Phonon-related properties of NaCoO₂ and LiCoO₂ have been studied rather widely using various experimental and theoretical approaches (table 1). In the case of thermal conductivity, the available literature values vary clearly within both materials. In the case of NaCoO₂, Takahata et al and Lee et al reported in-plane κₐ of 19 W m⁻¹ K⁻¹ and 38 W m⁻¹ K⁻¹, respectively, for a single crystal at 300 K [8, 9]. Tada et al and Fujii et al reported rather similar in-plane κₐ values of 42 W m⁻¹ K⁻¹ and 44 W m⁻¹ K⁻¹, respectively, based on classical molecular dynamics [10, 11]. In the case of LiCoO₂, Takahata et al reported the lattice thermal conductivity of polycrystalline LiCoO₂ at 280 K to be 4 W m⁻¹ K⁻¹, while Mizuno et al reported a value of 22 W m⁻¹ K⁻¹ at 300 K [8, 12]. For comparison, Cho et al reported in-plane (ab-plane) and cross-plane (c direction) thermal conductivities of 9.2 and 3.5 W m⁻¹ K⁻¹, respectively, for thin-film samples [13]. Yang et al studied the lattice thermal conductivity of LiCoO₂ using first-principles Density Functional Theory (DFT-HSE06), reporting in-plane κₐ to be 53.6 W m⁻¹ K⁻¹ at 300 K, about two times larger than the largest reported experimental value [14]. The difference between the experimental and the computational results was explained by the grain boundaries in...
polycrystalline samples, causing additional scattering process and decreasing thermal conductivity. Finally, Tada et al reported in-plane $\kappa_l$ of 40 W m$^{-1}$ K$^{-1}$ for LiCoO$_2$ using perturbed classical molecular dynamics simulations [10].

Here, we investigate the lattice thermal conductivity of NaCoO$_2$ using hybrid density functional theory and systematically compare the lattice dynamics and lattice thermal conductivity of NaCoO$_2$ with the isotypic LiCoO$_2$. We study the d-metal oxides with hybrid DFT to avoid the DFT-GGA self-interaction error which
results in the over-delocalization of the electrons on d-metal 3d and oxygen 2p orbitals [20]. We examine the components of the \( \kappa \) to shed light on the origin of different thermal conductivities of the two materials.

2. Computational details

Quantum chemical calculations have been carried out using the CRYSTAL17 code [21]. We applied PBE0 hybrid density functional method[22, 23] and Gaussian-type triple-ζ-valence + polarization level basis set (TZVP) (split-valence + polarization for Na) [24]. Detailed basis set listings are given in the Supplemental Material [25]. Recent studies on several layered d-metal disulfides and bulk d-metal oxides have shown the DFT-PBE0/TZVP level of theory to provide a balanced description of their electronic properties and lattice thermal conductivity [26–29]. The reciprocal space of the primitive cell was sampled using 8 \( \times \) 8 \( \times \) 8 Monkhorst-Packtype \( k \)-mesh (the total energy is converged to \( \mu \) Hartree accuracy with this mesh) [30]. The calculations were carried out with Coulomb and exchange integral tolerance factors (TOLINTEG) set to tight values of 8, 8, 8, 8, and 16 (phonon supercell calculations of LiCoO\(_2\) required values of 10, 10, 10, 10 and 20 to achieve converged third-order force constants). The LiCoO\(_2\) and NaCoO\(_2\) structures have been fully optimized within \( R^3 m \) space group, using the experimental crystal structures as starting points [31, 32]. The DFT-PBE0 optimized structures are reported in the Supplemental Material [25].

The harmonic vibrational frequencies at the \( \Gamma \) point were obtained by using the finite displacement method implemented in CRYSTAL. Here, the second derivatives of the energy with respect to atomic displacements are obtained from numerical differentiation of the analytical first derivatives [33, 34]. Infrared (IR) and Raman intensities were obtained with the Coupled Perturbed Kohn–Sham method implemented in CRYSTAL [35, 36]. The IR spectra were convoluted using Lorenzian peak profile with FWHM of 16 cm\(^{-1}\). The Raman spectra were convoluted using pseudo-Voigt peak profile (50:50 Lorenzian:Gaussian) and FWHM of 16 cm\(^{-1}\).

The second-order force constants and phonon dispersions were calculated within the harmonic approximation using the finite displacement supercell method as implemented in the Phonopy code [37, 38]. Tight SCF convergence criterion of 10\(^{-10}\) a.u. was applied in all phonon supercell calculations. For both LiCoO\(_2\) and NaCoO\(_2\), we used a \( 4 \times 4 \times 4 \) phonon supercell, 0.03 Å atomic displacements, and \( 2 \times 2 \times 2 \) \( q \)-sampling. The convergence of the phonon dispersion relations with respect to the phonon supercell size is discussed in the Supplemental Material, where we show the convergence with respect to a smaller \( 3 \times 3 \times 3 \) phonon supercell [25]. The non-analytical contribution (NAC) as \( q \rightarrow 0 \) has been taken into account in all phonon dispersion calculations [39]. The effect of including NAC on the phonon dispersion relations is illustrated in Supplemental Material [25].

The lattice thermal conductivities (\( \kappa \)) were calculated with the Phono3py code [40]. Phono3py uses the same finite displacement supercell method as Phonopy, but enables the investigation of third-order force constants and phonon anharmonicity by displacing two atoms simultaneously. The computational cost of third-order force constants is significantly larger compared to second-order force constants and a smaller supercell of \( 3 \times 3 \times 3 \) with 0.03 Å displacement amplitude was used. Additionally, an interatomic cut-off distance of 4 Å was imposed for the calculation of the third-order force constants. Convergence tests with a smaller \( 2 \times 2 \times 2 \) supercell showed that the lattice thermal conductivity converges within the applied cut-off distance (see Supplemental Material) [25]. NAC has been taken into account in the lattice thermal conductivity calculations. Including NAC changed both the in-plane and cross-plane lattice thermal conductivity of LiCoO\(_2\) by 1 Wm\(^{-1}\)K\(^{-1}\) (17% difference for the cross-plane direction, see Results section).

\( \kappa \) was solved both within the relaxation time approximation (RTA) and using the full solution for the linearized Boltzmann Transport equation (LBTE) [41]. The convergence of \( \kappa \) with respect to phonon \( q \)-point sampling is illustrated in the Supplemental Material [25]. The results discussed below have been obtained using a \( 20 \times 20 \times 20 \) \( q \)-point mesh.

3. Results

3.1. Geometry and electronic properties

The optimized lattice parameters of LiCoO\(_2\) and NaCoO\(_2\) agree well with the experimental crystal structures. In the case of LiCoO\(_2\), the lattice parameters \( a \) (2.80 Å) and \( c \) (13.98 Å) are underestimated by 0.5%. In the case of NaCoO\(_2\), the lattice parameters \( a \) (2.87 Å) and \( c \) (15.62 Å) differ from the experiment by −0.6% and +0.1%, respectively. The primitive unit cell volumes of LiCoO\(_2\) and NaCoO\(_2\) are 32 Å\(^3\) and 37 Å\(^3\), respectively. The electronic band structures of LiCoO\(_2\) and NaCoO\(_2\) are presented in figure 2. Overall, the electronic properties are rather similar: both materials are insulators with indirect band gap of 4.9 eV for LiCoO\(_2\) and 4.8 eV for NaCoO\(_2\), which is in a good agreement with previous reports [42, 43]. For comparison, a DFT-PBE calculation on LiCoO\(_2\) yields a significantly smaller band gap of 1.0 eV. From the density of states, we can conclude that the
Co and O atoms have the largest contribution to the highest-energy valence bands, while the lowest-energy conduction band is dominated by the Co atom (3d-orbitals). For both materials, the alkali metal contributions near the Fermi level are negligible.

3.2. IR and Raman spectra
The primitive unit cell of LiCoO2 and NaCoO2 consists of four atoms, resulting in 12 vibrational modes that are divided into irreducible representations as follows:

\[ \Gamma = A_{1g} + 3A_{2u} + E_{g} + 3E_{u}. \]  

The \( E_{g} \) and \( E_{u} \) modes are doubly degenerate. \( A_{1g} \) and \( E_{g} \) modes are Raman-active, while \( A_{2u} \) and \( E_{u} \) are IR-active. We calculated the \( \Gamma \) point phonons of LiCoO2 and NaCoO2 together with their IR and Raman tensors. The IR and Raman spectra are simulated based on these results and illustrated in figure 3. The optical vibrational modes are further characterized in table 2.

The Raman-active \( E_{g} \) and \( A_{1g} \) modes correspond to Co–O stretching vibrations in the in-plane and cross-plane directions, respectively. These modes with frequencies larger than 500 cm\(^{-1}\) are paired with IR-active \( E_{u} \) and \( A_{2u} \) modes corresponding to Co–O stretching vibrations. These Co–O stretching modes show rather similar frequency both for LiCoO2 and NaCoO2. The lower-energy \( E_{g} \) and \( A_{2u} \) modes correspond to vibrations of alkali metal atoms in the in-plane and cross-plane directions, respectively. This also explains why these modes show much smaller frequencies in the case of NaCoO2 with heavier alkali metal atoms. The calculated Raman-active modes for LiCoO2 are in a good agreement with previously reported DFT-HSE06 values, but are 5%–7% overestimated in comparison to experiments (see table 1).

For Na\(_x\)CoO\(_2\), the majority of the IR and Raman spectra have been reported with systems with \( x < 1 \). Lupi \textit{et al} did study the in-plane infrared conductivity of Na\(_x\)CO\(_3\) single crystals for 0.5 \( \leq x \leq 1 \) at various temperatures and their spectrum with \( x = 1 \) obtained at 12 K revealed a single peak at \( \approx 590 \) cm\(^{-1}\) [15]. The observed frequency is within 6% of the calculated harmonic frequency of the IR-active \( E_{g} \) mode (vibrations of the CoO\(_6\) octahedra). The nominally \( x = 1 \) crystal did show slightly metallic behavior at low temperatures, this was ascribed to slight non-stoichiometry.

3.3. Phonon dispersions and heat capacity
The phonon dispersion relations of LiCoO2 and NaCoO2 are illustrated in figure 4. The differences in the \( \Gamma \) point phonon frequencies compared to the values reported in previous section are mainly due to the non-analytical correction applied for the full phonon dispersion relations (LO-TO splitting was not considered for the IR and Raman spectra). When Non-analytical correction is not included, the \( \Gamma \)-point frequencies from

\[ \text{Figure 2. Electronic band structure and density of states (DOS) of LiCoO2 (top) and NaCoO2 (bottom). The following reciprocal space coordinates were used: } T = (0, 0, 0), T = (1/2, 1/2, 1/2), L = (1/2, 0, 0), F = (1/2, 0, 1/2) [44–46]. \]
CRYSTAL and Phonopy agree within 2%, except for the lowest-frequency Eu mode, where the supercell approach used by Phonopy yields a frequency of 248 cm$^{-1}$ for LiCoO$_2$ and 212 cm$^{-1}$ for NaCoO$_2$.

The phonon dispersion relations of LiCoO$_2$ and NaCoO$_2$ show similar trends, but similar to Γ point phonons listed in table 2, the NaCoO$_2$ optical modes in the range of 200–500 cm$^{-1}$ are clearly lower in energy compared to LiCoO$_2$. At higher frequencies above 500 cm$^{-1}$, the difference becomes smaller. Notably, NaCoO$_2$ shows a phonon band gap approximately between 420 and 460 cm$^{-1}$, while LiCoO$_2$ does not. The phonon density of states show that the lower-energy optical modes below 500 cm$^{-1}$ are dominated by the alkali metal atoms and the modes above 500 cm$^{-1}$ arise from the CoO$_6$ octahedra.

We calculated the constant volume heat capacities ($C_v$) of both materials from the phonon dispersion relations using a dense q-mesh of $40 \times 40 \times 40$ (figure 5). The heat capacity of LiCoO$_2$ is slightly smaller compared to NaCoO$_2$, the $C_v$ values at 300 K being 69 J K$^{-1}$ mol$^{-1}$ for LiCoO$_2$ and 71 J K$^{-1}$ mol$^{-1}$ for NaCoO$_2$. The $C_v$ values are slightly smaller in comparison to the experimental $C_p$ values of 71.6 and 75.2 J K$^{-1}$ mol$^{-1}$ (table 1). At high temperatures ($T > 700$ K), the $C_v$ values normalized by the number of atoms in the primitive...

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**Table 2.** Γ point vibrational modes of LiCoO$_2$ and NaCoO$_2$. A = Active, I = Inactive. LO-TO splitting is not included here.

| Mode (irrep.) | Frequency, cm$^{-1}$ | LiCoO$_2$ | NaCoO$_2$ | IR | Raman |
|--------------|----------------------|------------|------------|----|-------|
| $E_u$        | 271                  | 182        | A          | I  |       |
| $A_{2u}$     | 429                  | 323        | A          | I  |       |
| $E_g$        | 520                  | 512        | I          | A  |       |
| $E_u$        | 567                  | 557        | A          | I  |       |
| $A_{1g}$     | 629                  | 624        | I          | A  |       |
| $A_{2u}$     | 644                  | 642        | A          | I  |       |

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**Figure 3.** Infrared and Raman spectra of LiCoO$_2$ and NaCoO$_2$. LO-TO splitting is not included here.
unit cell (4) converge towards 24 J K$^{-1}$ mol$^{-1}$ per atom, which is close to the value of 3R expected from the Dulong-Petit law.

3.4. Mode Grüneisen parameter

Mode Grüneisen parameter is a dimensionless quantity defined as the change of phonon frequency with respect to the change of volume [47]:

$$\gamma_q = -\frac{V}{\omega_q} \frac{\partial \omega_q}{\partial V}. \tag{2}$$

The mode Grüneisen parameters can be considered as a measure of the phonon anharmonicity. Figure 6 shows the mode Grüneisen parameters for LiCoO$_2$ and NaCoO$_2$ calculated directly from the third-order force constants, utilizing the approach described in detail in [48]. The current Phono3py implementation enables the calculation of mode Grüneisen parameters within this approach only when the second- and third-order force constants have been calculated using the same phonon supercell. Therefore, the mode Grüneisen parameters presented in figure 6 have been calculated using $3 \times 3 \times 3$ supercells both for the second- and third-order force constants.

In both LiCoO$_2$ and NaCoO$_2$, the majority of the modes possess a positive mode Grüneisen parameter, corresponding to typical phonon behavior where the phonon frequency decreases as the volume increases. However, at low phonon frequencies below 150 cm$^{-1}$, the acoustic modes of LiCoO$_2$ show much larger number of negative mode Grüneisen parameters, that is, modes where the phonon energy increases as the volume
increases. In turn, NaCoO$_2$ shows few very large $\gamma_{q,j}$ values for acoustic phonon modes close to $\Gamma$ point. Between 200 and 400 cm$^{-1}$, LiCoO$_2$ shows clearly larger mode Grüneisen parameter values which peak at about 250 cm$^{-1}$. The phonon band gap of NaCoO$_2$ is clearly visible at around 450 cm$^{-1}$. Overall, as the mode Grüneisen parameters are a measure of the phonon anharmonicity, the mode Grüneisen parameters suggest LiCoO$_2$ to show larger phonon anharmonicity in comparison to NaCoO$_2$.

### 3.5. Lattice thermal conductivity

Within the single-mode relaxation time approximation (RTA), the lattice thermal conductivity $\kappa_l$ can be expressed as:

$$\kappa_l = \frac{1}{N V_0} \sum_{q,j} C_{q,j} V_{q,j} \otimes \tau_{q,j},$$

(3)

where $N$ is the number of $q$ points sampled, $V_0$ is the volume of the unit cell and $C_{q,j}, V_{q,j}$ and $\tau_{q,j}$ are the heat capacity, group velocity, and relaxation time of phonon mode $(q,j)$, respectively. Within RTA, the phonon relaxation time is equal to the phonon lifetime.

The lattice thermal conductivities of LiCoO$_2$ and NaCoO$_2$ obtained within RTA are plotted in figure 7. Even though the materials are isotypic, the lattice thermal conductivities are rather different. At 300 K, the in-plane $\kappa_l$ is 45.7 W m$^{-1}$ K$^{-1}$ for LiCoO$_2$ and 77.6 W m$^{-1}$ K$^{-1}$ for NaCoO$_2$. The cross-plane $\kappa_l$ values show even larger relative difference: 6.6 W m$^{-1}$ K$^{-1}$ for LiCoO$_2$ against 25.0 W m$^{-1}$ K$^{-1}$ for NaCoO$_2$. The full solution of linearized Boltzmann transport equation (LBTE) yields even larger in-plane $\kappa_l$ values of 56 W m$^{-1}$ K$^{-1}$ and 83.4 W m$^{-1}$ K$^{-1}$ for LiCoO$_2$ and NaCoO$_2$, respectively. The cross-plane LBTE $\kappa_l$ values of 6.6 W m$^{-1}$ K$^{-1}$ and 25.3 W m$^{-1}$ K$^{-1}$ are almost identical to the RTA values.
Within RTA, the ratio $k_{l \parallel} / k_{l \perp}$ at 300 K is 6.9 for LiCoO$_2$ and 3.1 for NaCoO$_2$, suggesting a clearly more anisotropic $\kappa_l$ in LiCoO$_2$. Yang et al observed very similar $k_{l \parallel} / k_{l \perp}$ ratio of 6.7 for LiCoO$_2$, even though their absolute $\kappa_l$ values obtained with DFT-HSE06 are somewhat larger (56.6 W m$^{-1}$ K$^{-1}$ and 8.4 W m$^{-1}$ K$^{-1}$ for in-plane and cross-plane $\kappa_l$, respectively) [14]. The predicted room-temperature in-plane $\kappa_l$ of 45.7 W m$^{-1}$ K$^{-1}$ for LiCoO$_2$ is two times larger than the largest experimental value reported for a polycrystalline sample and almost five times larger than the value reported for a thin-film sample (table 1). It has been suggested that the difference between the theory and experiments on polycrystalline samples can be explained by imposing a boundary scattering limit of 2 nm [14]. For NaCoO$_2$, the in-plane $\kappa_l$ values obtained here are larger than the experimental values reported previously (table 1). Our values are also larger than the previous theoretical results obtained from classical MD simulations where the interatomic potential was derived using DFT-PBE functional. Generally, the experimental $\kappa_l$ values are very sensitive to Na occupancy: the in-plane $\kappa_l$ for thin-film Na$_{0.8}$CoO$_2$ was reported to be $5.5 \pm 0.7$ W m$^{-1}$ K$^{-1}$, which is significantly smaller than the single-crystal NaCoO$_2$ values reported before (19–38 W m$^{-1}$ K$^{-1}$) [13]. Thus, even very small Na deficiency may decrease $\kappa_l$ compared to the ideal single crystals studied here.

3.6. Analysis of the lattice thermal conductivity

To understand the differences in the lattice thermal conductivity of structurally isotopic LiCoO$_2$ and NaCoO$_2$, we carried out a detailed analysis of the individual components of equation (3) and related phonon properties (except for constant volume heat capacities, which are rather similar for both materials). To facilitate comparisons with previous studies on LiCoO$_2$ [14] the detailed analysis was carried out within the relaxation time approximation, using a $20 \times 20 \times 20$ q-mesh. The studied phonon properties are illustrated in figure 8 and discussed below.

The cumulative lattice thermal conductivity $\kappa_l$ of LiCoO$_2$ and NaCoO$_2$ as a function of phonon frequency is shown in the panel a) of figure 8. The in-plane $\kappa_l$ for LiCoO$_2$ reaches its maximum value already at about 380 cm$^{-1}$, the higher-frequency optical modes contributing very little beyond this point. 380 cm$^{-1}$ corresponds also to the peak frequency of acoustic phonons in the $\Gamma$–L direction, which equals to in-plane direction in the real space. In the case of NaCoO$_2$, in-plane $\kappa_l$ increases more rapidly in comparison to LiCoO$_2$ up to 200 cm$^{-1}$, after
which $\kappa_l$ reaches its maximum value at about 430 cm$^{-1}$. The acoustic modes of NaCoO$_2$ in the $\Gamma$-L direction peak at about 300 cm$^{-1}$, suggesting that the optical modes between 300 and 430 cm$^{-1}$ do also contribute to the in-plane $\kappa_l$. In the cross-plane direction, the cumulative $\kappa_l$ of LiCoO$_2$ reaches its maximum value already at about 180 cm$^{-1}$, while in the case of NaCoO$_2$ there is some increase beyond this point. This is in line with the phonon dispersion relations, as the acoustic phonons of both materials peak at about 180 cm$^{-1}$ in the $\Gamma$-T direction corresponding to the cross-plane direction in the real space. To summarize, practically all heat is carried by acoustic phonons in the case of LiCoO$_2$, while in the case of NaCoO$_2$ the optical phonons do have a small contribution to the thermal conductivity both in the in-plane and cross-plane directions. According to the phonon density of states presented in figure 4, Na atoms have a major contribution to these optical modes.

The cumulative phonon group velocity $v_{qj}$ is presented in the panel b) in figure 8. The in-plane cumulative $v_{qj}$ of LiCoO$_2$ (5.8 km/s) is slightly higher compared to NaCoO$_2$ (5.4 km/s). The cross-plane cumulative $v_{qj}$ values are rather similar, being 2.5 km/s and 2.4 km/s for LiCoO$_2$ and NaCoO$_2$, respectively. While the cumulative phonon group velocities are anisotropic, phonon group velocities alone not enough to explain the seven-fold anisotropy of in-plane and cross-plane $\kappa_l$ in the case of LiCoO$_2$.

The cumulative phonon lifetime $\tau_{qj}$ presented in the panel c) of figure 8 shows significant differences between LiCoO$_2$ and NaCoO$_2$. The total cumulative phonon lifetime of NaCoO$_2$ is about two times larger compared to LiCoO$_2$, mainly due to the phonon modes below 300 cm$^{-1}$. Thus, the shorter phonon lifetime of the acoustic modes in LiCoO$_2$ appears to determine the smaller $\kappa_l$ values in comparison to NaCoO$_2$.

The phonon lifetime $\tau$ presents an inverse relationship with the imaginary part of phonon self-energy $\Gamma_{qj}$:

$$\tau_{qj} = \frac{1}{2\Gamma_{qj}}.$$  \hspace{1cm} (4)

$\Gamma_{qj}$ is in turn calculated from the squared three-phonon interaction strength and the weighted joint density of states, w-JDOS (equation (11) in [40]). w-JDOS describes the three-phonon collision and decay processes as a function of phonon frequency. The collision events refer to three-phonon events, where two interacting phonons are annihilated, creating a third phonon (equation (23) in [40]). In the case of a decay event, one phonon is annihilated and two phonons are created (equation (24) in [40]). Both types of events, weighted by

Figure 8. Phonon properties behind the lattice thermal conductivity at 300 K (RTA, 20 × 20 × 20 q-mesh). Properties for LiCoO$_2$ are shown on the left and the properties for NaCoO$_2$ on the right. The following properties are plotted as a function of phonon frequency: a) Cumulative lattice thermal conductivity ($\kappa_l$); b) cumulative phonon group velocity ($v_{qj}$); c) cumulative phonon lifetime ($\tau_{qj}$); d) imaginary part of phonon self-energy ($\Gamma_{qj}$); e) weighted joint density of states (w-JDOS), where solid and dotted lines represent collision and decay events, respectively (see text). $\Gamma_{qj}$ and w-JDOS are shown at representative $q = (0.5, 0.0, 0.0)$ and $q = (0.5, 0.5, 0.5)$ points of the first Brillouin zone, corresponding to in-plane and cross-plane directions (the primitive unit cell is rhombohedral).
phonon mode occupations, are taken into account in the calculation of w-JDOS and eventually in the calculation of $\Gamma_{q_j}$.

$\Gamma_{q_j}$ and w-JDOS at representative $\mathbf{q}$-points are illustrated in panels d) and e) in figure 8, respectively (data at other $\mathbf{q}$-points are available as Supplemental Material [25]). $\Gamma_{q_j}$ values of LiCoO$_2$ are larger in comparison to NaCoO$_2$ at all frequencies, explaining the shorter phonon lifetimes for LiCoO$_2$. In contrast to NaCoO$_2$, $\Gamma_{q_j}$ values are anisotropic in the case of LiCoO$_2$. The anisotropy is smaller at low frequencies, but the cross-plane direction consistently shows larger $\Gamma_{q_j}$ below 200 cm$^{-1}$. Together with the anisotropic phonon group velocities, the anisotropic $\Gamma_{q_j}$ values contribute to the larger $\kappa_l$ anisotropy in the case of LiCoO$_2$ [14].

The w-JDOS values do not reveal any major differences between LiCoO$_2$ and NaCoO$_2$, but below 200 cm$^{-1}$ the w-JDOS values are larger for LiCoO$_2$ contributing in part to the larger $\Gamma_{q_j}$ values and shorter phonon lifetimes for the heat-carrying acoustic modes. The phonon band gap in NaCoO$_2$ may affect the number of possible three-phonon interactions between acoustic and optical phonons, reducing phonon-phonon scattering and increasing phonon lifetimes. However, the phonon band gap is not large and as the w-JDOS plots do not show significant differences, the differences in $\Gamma_{q_j}$ values are more likely determined by the three-phonon interaction strength. This quantity is calculated from the third-order force constants and harmonic phonon properties and as shown above, the mode Grüneisen parameters, calculated directly from the third-order force constants, suggest larger phonon anharmonicity in LiCoO$_2$. For comparison, strong phonon anharmonicity has been recently reported as a major limiting factor for lattice conductivity in the case of ternary thallium telluride TlInTe$_2$ [49].

4. Conclusion

We have studied the phonon properties and lattice thermal conductivity of NaCoO$_2$ intercalation material by combining hybrid density functional method and linearized Boltzmann Transport equation. The obtained properties were systematically compared with isotopic LiCoO$_2$ to understand the effect of the alkali metal. Even though the two materials are isotopic, $\kappa_l$ of NaCoO$_2$ is almost two times larger in the in-plane direction and almost four times larger in the cross-plane direction. Analysis of mode Grüneisen parameters and the components of $\kappa_l$ showed that the differences are mainly due to the larger phonon anharmonicity and shorter phonon lifetimes in LiCoO$_2$. The anisotropic thermal transport in LiCoO$_2$ was found to be due to the anisotropic phonon group velocities and shorter phonon lifetimes, in agreement with previous studies [14].

Recent experiments on various A$_x$CoO$_2$ thin films illustrate that $\kappa_l$ can be very sensitive to the A atom occupancy [13] and explaining the remaining differences between the predicted and measured $\kappa_l$ values may require careful consideration of point defects (vacancies) and higher-order anharmonic terms Another interesting challenge is the effect of thermal expansion on the lattice thermal conductivity, as thermal expansion plays a significant role in the performance of LiCoO$_2$-based batteries [50].

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