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Electronic Properties and Lattice Dynamics of Li$_x$CoO$_2$ and Na$_x$CoO$_2$ ($x = 0$, 0.5, 1) Studied by Hybrid Density Functional Theory

Nina Mattila and Antti J. Karttunen*

A systematic hybrid density functional theory study on the electronic and vibrational properties of M$_x$CoO$_2$ compounds with M = Li, Na and $x = 0$, 0.5, 1 is reported. The used DFT-PBE0 method describes the structural parameters of the studied compounds well in comparison to experimental data. All studied magnetic species are treated as ferromagnets and the Co(IV) atoms possess a magnetic moment of 1.2 $\mu_B$. At 0 K, CoO$_2$ favors a monoclinic structure very close to trigonal symmetry and behaves as a Mott insulator. The electronic bandgap increases as $x$ increases from 0 to 1. The simulated infrared and Raman spectra together with full phonon dispersion relations show that the intercalation of Li and Na ions affects the lattice dynamics of CoO$_2$ in a different way.

1. Introduction

Layered alkali metal oxides Li$_x$CoO$_2$ and Na$_x$CoO$_2$ are representatives of the vast group of compounds derived from the layered parent compound CoO$_2$ (see Figure 1). The Co–O layers in these compounds are formed by edge-sharing Co$_6$ octahedra. It is well known that the electronic and magnetic properties of Li$_x$CoO$_2$ and Na$_x$CoO$_2$ are very dependent on the alkali metal composition ($x$) and they have attracted a lot of scientific and technological interest, for example, as Li-ion battery materials and thermoelectric energy conversion materials.\[1\]–\[7\]

Even though Li$_x$CoO$_2$ and Na$_x$CoO$_2$ have been extensively studied both experimentally and computationally, there have been some differences in the reported electronic and magnetic properties. In the case of CoO$_2$, the $x = 0$ end member, each Co(IV) atom would possess one unpaired electron in the low-spin $d^5$ configuration. CoO$_2$ without alkali metals was first reported by Amatucci et al. in 1996. They obtained the compound via chemical deintercalation of LiCoO$_2$ and reported it to be a nonmagnetic metal.\[8\]–\[9\]

In 2007, Motohashi et al. synthesized CoO$_2$ by electrochemical deintercalation of LiCoO$_2$ and reported it to be Pauli paramagnetic metal with itinerant electrons.\[10\]

Vaulx et al. studied CoO$_2$ with $^{59}$Co NMR and described it as a metal, while magnetic susceptibility measurements revealed antiferromagnetic spin fluctuations and suggested the vicinity of a Mott insulator transition at low temperatures of about 7 K.\[11\]

Kawasaki et al. also studied CoO$_2$ using $^{59}$Co nuclear magnetic resonance (NMR) together with nuclear quadrupole resonance (NQR).\[12\]

They reported CoO$_2$ to be a non-correlated metal satisfying Korringa law for a Fermi liquid and reproduced the findings of Vaulx et al. for a Li$_0$CoO$_2$ sample.

Theoretical studies on CoO$_2$ have also produced rather varying results. Zhang et al. studied the electronic and structural properties of a single CoO$_2$ layer with density functional theory (DFT) within the local spin density approximation and $U$ correction (DFT-LSDA+$U$). As expected, they observed a strong dependency on the $U$ correction. LSDA+$U$ with $U = 5.5$ eV resulted in CoO$_2$ being a charge transfer insulator with Co(IV) magnetic moment of about 1 $\mu_B$. With plain LSDA, CoO$_2$ was a metal with high density of states (DOS) at the Fermi level and $\mu$ of 0.58 $\mu_B$.\[13\] Lee and Pickett studied the strength of correlation effects in Na$_x$CoO$_2$ $\rightarrow$ 0 using LSDA+$U$. Comparing their results with the experimental observations of Amatucci et al.,\[8\] they concluded that $U$ has to be smaller than 2.3 eV to obtain a nonmagnetic metal, while above 2.3 eV a Mott insulating state is obtained.\[9\]

Half-filled Na$_{0.5}$CoO$_2$ possesses remarkable electronic properties and has been studied intensively. Terasaki et al. studied the transport properties of a single crystal.\[4\] Similar to previous reports,\[14\] they described the compound as metallic, with in-plane thermopower of 100 $\mu$V K$^{-1}$ at room temperature and low resistivity of 200 $\mu$Ω cm, making it a promising thermoelectric material. They also observed high electrical anisotropy and described a metal–semiconductor transition in the cross-plane at 200 K.

Ray et al. proposed a possible magnetic structure for Na$_{0.5}$CoO$_2$ based on $^{23}$Na and $^{59}$Co NMR studies, suggesting that the magnetic Co(IV) atoms alternate with diamagnetic Co(III) atoms.\[15\]

In 2004, Foo et al. reported the phase diagram of Na$_x$CoO$_2$ for $0.3 \leq x \leq 0.75$.\[5\] According to their results, Na$_0$CoO$_2$ is generally a metal for whole doping range except for the half-filled Na$_{0.5}$CoO$_2$ where charge-ordered insulating state separates the low-doped paramagnetic phase and the highly doped Curie–Weiss metallic
phase. At the doping level of $x = 0.75$, weak magnetization explained by spin density wave occurs.$^{[16]}$

Huang et al. conducted electronic, magnetic, and specific heat measurements on Na$_{0.5}$CoO$_2$ and observed phase transitions at temperatures of 87, 53, and 20 K.$^{[17]}$ Similar phenomena were reported by Viciu et al. who studied Na$_x$CoO$_2$ compounds with $0.32 \leq x \leq 0.92$. The orthorhombic crystal structure determined for Na$_{0.5}$CoO$_2$ leads in two symmetry-independent Co sites and an insulating charge-ordered state. Williams et al. have noted that the diffraction data reported for Na$_{0.5}$CoO$_2$ were insufficient for full understanding of the CoO$_2$ lattice.$^{[18]}$ They studied Na$_{0.5}$CoO$_2$ within high-resolution powder neutron diffraction at temperatures 10–300 K, concluding that the electron density of the two Co sites is only slightly different and a conventional charge-ordered state might not be a proper model.

From a computational point of view, Singh applied DFT-LDA to study electronic and magnetic properties of Na$_{0.5}$CoO$_2$.$^{[20]}$ The paramagnetic metallic hexagonal structure proposed by Jansen and Hoppe,$^{[21]}$ with arbitrarily placed Na atoms, was used as a starting point. DFT-LSDA yielded a half-metallic ferromagnetic configuration with magnetic moment of 0.5 $\mu_B$ per Co.

Turning to Li$_x$CoO$_2$, Hertz et al. investigated the magnetic properties and structure of Li$_x$CoO$_2$ for $0.5 < x < 1$. From the magnetic susceptibility measurements, they observed a small anomaly for some samples at 175 K, apart from which all Li$_x$CoO$_2$ samples exhibited Curie–Weiss behavior. Remeasurement of same samples after 4 months revealed significant suppression of the anomaly and therefore it was proposed that origin of the anomaly can be a small impurity phase slowly decomposing in air, or subtle structure defect that diminishes in time, e.g., through homogeneous Li$^+$ distribution. From small negative values of Curie–Weiss temperature $\Theta_\kappa$, they concluded that Li$_x$CoO$_2$ at $0.5 < x < 1$ exhibits a small antiferromagnetic behavior increasing with Li deintercalation and low spin–high spin Co(IV) transition at $x > 0.5$. The structure of Li$_x$CoO$_2$ was thoroughly analyzed by neutron diffraction methods and revealed significant structural differences of CoO$_2$ layers compared with Li$_x$CoO$_2$, implying higher distortion of CoO$_6$ octahedra in Li$_x$CoO$_2$.

The electronic phase diagram of Li$_x$CoO$_2$ reported by Motohashi et al. has seven stable phases and appears more complicated in comparison to Li$_x$CoO$_2$. Starting from CoO$_2$, Li$_x$CoO$_2$ is Pauli paramagnetic metal up to $x = 0.35$. Lithium intercalation increases the energy of the conduction band and the number of nonmagnetic Co(III) ions. Li$_x$CoO$_2$ with $0.40 \leq x \leq 0.70$ is generally discussed as a Curie–Weiss metal which turns to a band semiconductor with further intercalation. The end member LiCoO$_2$ is a nonmagnetic band insulator. We have discussed the literature related to the fully intercalated, nonmagnetic LiCoO$_2$ and NaCoO$_2$ in a recent article and will not repeat them here.$^{[24]}

Here, we investigate the electronic properties and lattice dynamics of layered alkali metal oxides Li$_x$CoO$_2$ and Na$_x$CoO$_2$ using hybrid density functional methods. We study the effect of the doping level $x$ ($x = 0, 0.5, 1$) and the alkali metal type (Li vs Na). Using the same hybrid density functional method for all studied compounds enables the systematic comparison of the trends in the electronic, magnetic, and vibrational properties.

2. Results

2.1. Geometry and Magnetic Ordering

The optimized lattice parameters of the Co atom are reported in Table 1 (DFT-PBE0 method, see Computational Details). The optimized lattice parameters compare well with the experimental values, except for the $c$ parameter of CoO$_2$, which is overestimated.

![Figure 1. Crystal structures of the studied M$_x$CoO$_2$ structures. Blue: Co; red: O; purple: Li/Na.](image)

| Compound | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\Theta_\kappa$ (K) |
|----------|--------|--------|--------|------------------|
| CoO$_2$  | 2.79   | 5.36   | 15.62  | -                  |
| Li$_{0.5}$CoO$_2$ | 2.80 (−0.6) | 4.83 (−0.7) | 4.84 (−0.8) | 2.80 (−0.5) |
| Na$_{0.5}$CoO$_2$ | 2.80 (−0.6) | 5.61 (−0.4) | 2.80 (−0.5) | 2.87 (−0.6) |
| LiCoO$_2$ | 4.42 (+4.2) | 5.13 (+1.4) | 11.05 (−0.1) | 13.98 (−0.5) |
| NaCoO$_2$ | 4.42 (+4.2) | 5.13 (+1.4) | 11.05 (−0.1) | 15.62 (+0.1) |
by 4.2% despite the D3 dispersion correction. We also benchmarked the D3 dispersion correction with Becke-Johnson damping, but this led to even larger overestimation by 5.1%. The lattice parameters and coordinates of the optimized structures are given as Supporting Information.[25] The magnetic moment of the Co(IV) ion is practically the same 1.2 μB for all materials.

While the ideal space group of the end member CoO2 is P3m1, this structure is not a true local minimum at the DFT-PBE-D3/TZVP level of theory, as a Γ-point frequency calculation revealed a twofold degenerate imaginary vibrational frequency of ~414 cm\(^{-1}\) (at 0 K). The c lattice parameter of the trigonal geometry is 4.02 Å, which is underestimated by over 5% compared to the experiment. Lowering the symmetry to monoclinic subgroup C12/m1 leads in a structure that is close to the original trigonal structure and in reasonable agreement with the experimental lattice constants (lattice parameter c is overestimated). The monoclinic structure is ~0.2 kJ mol\(^{-1}\) lower in energy and does not show any imaginary frequencies. We studied both ferromagnetic (FM) and antiferromagnetic (AFM) magnetic ordering for CoO2. To achieve an AFM ordering, we had to create a supercell, ending up in P\(\overline{1}\) space group. The AFM ordering is slightly lower in energy in comparison to the FM ordering (2 kJ mol\(^{-1}\)), but we carried out the majority of our calculations using the higher symmetry FM ordering to enable comparisons with the intercalated systems and the experiments. The structural and magnetic details of the antiferromagnetic configuration are reported in the Supporting Information.

Na-intercalated Na\(_{0.5}\)CoO\(_2\) crystallizes in orthorhombic space group Pm\(\overline{1}m\) and has both nonmagnetic Co(III) and magnetic Co(IV) ions. We tested both FM and AFM ordering for Na\(_{0.5}\)CoO\(_2\) (for AFM, the symmetry had to be reduced to P1\(\overline{2}\)_1/m1). The energy difference between FM and AFM is very small; FM is 0.2 kJ mol\(^{-1}\) lower in energy. We used the higher symmetry FM configuration in our calculations. The structural and magnetic details of the antiferromagnetic configuration are reported in the Supporting Information. FM ordering was also used for the magnetic Co(IV) ions in the lithium-intercalated Li\(_{0.5}\)CoO\(_2\) crystallizing in lower symmetry monoclinic space group P1\(\overline{2}\)_1/m1. The nonmagnetic end members LiCoO\(_2\) and NaCoO\(_2\) both crystallize in a trigonal crystal structure (\(\Gamma\overline{3}\))m. The alkali metal ions occupy octahedral sites between the oxygen atoms of the adjacent layers.

2.2. Band Structures

The electronic band structures are presented in Figure 2 and 3 for magnetic and nonmagnetic compounds, respectively. At 0 K, the CoO\(_2\) end member is an insulator with a bandgap of 2.9 and 2.8 eV for α and β spin channels, respectively, suggesting Mott insulator-type situation. Topmost valence bands are dominated by oxygen and the lowest energy conduction band of the β spin channel is dominated by Co, as expected. If nonhybrid DFT-PBE method is used for CoO\(_2\), the optimized lattice parameters agree well with experiments (difference of +0.2% and +1.9% for α and c, respectively), but the system is metallic at 0 K. The optimized lattice parameter c of CoO\(_2\) appears to be rather sensitive with respect to the electronic ground state.

Alkali metal intercalation into CoO\(_2\) increases the bandgap. For the \(x = 0.5\) systems, the increase is still rather small: the α and β spin channel band gaps are 3.1 and 2.8 eV for Li\(_{0.5}\)CoO\(_2\) and 3.0 and 2.8 eV for Na\(_{0.5}\)CoO\(_2\). The contribution from the Li and Na ions to the DOS is negligible both for the topmost valence bands and the lowest energy conduction bands. The fully intercalated end members LiCoO\(_2\) and NaCoO\(_2\) show the largest bandgaps of 4.9 and 4.8 eV, respectively.

2.3. IR and Raman Spectroscopy

We calculated the harmonic vibrational frequencies at the Γ-point for all studied systems, together with IR and Raman intensities. The number of optical modes for different systems is as follows: CoO\(_2\): 6; Li\(_{0.5}\)CoO\(_2\): 18; Na\(_{0.5}\)CoO\(_2\): 81; (Li,Na)CoO\(_2\): 6. The calculated IR and Raman spectra are plotted in Figure 4 and full details are given in tabulated form in the Supporting Information.[25]

Direct comparisons of the spectra of different materials are complicated by the differences in their symmetry properties. However, it is possible to observe the general trends on how the spectra of CoO\(_2\) change as result of alkali metal intercalation.

In the case of Li\(_2\)CoO\(_2\), the low-energy IR-active peaks 100–300 cm\(^{-1}\) arise from the alkali atoms, while the modes at 500–700 cm\(^{-1}\) represent modes of the CoO\(_2\) octahedra (Co–O bond stretching, O–Co–O bending and twisting, etc.). The modes at 300–400 cm\(^{-1}\) involve both Li atoms and CoO\(_2\) layers. As expected, based on their atomic masses, the energy of the modes involving Li is higher than that for Na. The modes of Na\(_{0.5}\)CoO\(_2\) can be described as follows: Na atom vibrates in the range 100–200, 200–300 cm\(^{-1}\) range involves both Na atoms and CoO\(_2\) layers, and the modes at 500–700 cm\(^{-1}\) range arise from the CoO\(_2\) layers. The intensity difference of Li- and Na-based modes can be observed for LiCoO\(_2\) and NaCoO\(_2\) at the range 100–500 cm\(^{-1}\).

The alkali metal-based modes are less visible in Raman spectra compared to the IR spectra. For all compounds, mainly modes in the range 400–700 cm\(^{-1}\), arising from CoO\(_2\) layers, are clearly visible. Only in Na\(_{0.5}\)CoO\(_2\), low-intensity Na-based modes can be observed at 100–300 cm\(^{-1}\).

Yang et al. have conducted Raman measurements for Na\(_{0.5}\)CoO\(_2\) single crystal at various temperatures. They observed phase transition upon cooling from high-temperature hexagonal structure to the orthorhombic low-temperature structure, starting at about 200 K.[26] In the spectrum obtained at 80 K, they observed only three Raman peaks at 439, 476, and 573 cm\(^{-1}\). Later, Zhang et al. reported five Raman peaks at 10 K: 414, 437, 475, 497 (low intensity), and 570 cm\(^{-1}\).[27]

The in-plane infrared reflectance of a Na\(_{0.5}\)CoO\(_2\) single crystal has been studied by Wang et al. at various temperatures.[28] They observed a charge-ordered state appearing with lowering temperature to 100 K, followed by a charge density wave that is responsible for metal–insulator transition at 50 K. They reported IR-active peaks at 10 K with frequencies of 102, 282, 435, 530, and 535 cm\(^{-1}\). Lupi et al. measured in-plane infrared conductivity of Na\(_{0.5}\)CoO\(_2\), 0.5 ≤ \(x\) ≤ 1 as a function of x and temperature.[29] The spectrum obtained at 12 K is similar with the spectrum presented here: peaks at about 180–400 cm\(^{-1}\) vanish with increasing x, while the peak at 590 cm\(^{-1}\) is visible for all cases, but decreases in intensity with increasing x. The slightly metallic behavior observed at low temperatures for nominally insulating NaCoO\(_2\) was ascribed to nonstoichiometry. A detailed
Theoretical analysis of phonon properties of NaCoO$_2$ has also been carried out in space group $P6_3/mmc$ by Jha et al., but direct comparison to our results is not feasible due to lack of intensity data.\cite{ref30}

For Li$_x$CoO$_2$, Inaba et al. have recorded polarized and unpolarized Raman spectra of $c$-axis oriented 0.8 $\mu$m-thick thin film at room temperature.\cite{ref31} They reported two intense peaks at 486 and 596 cm$^{-1}$ for LiCoO$_2$, which is in agreement with calculated spectra (the calculated harmonic frequencies are overestimated by about 7%). During Li deintercalation, the two peaks broadened and shifted toward lower energy. Despite the fact that a monoclinic structure has been observed for Li$_{0.5}$CoO$_2$, no additional peaks besides 475 and 575 cm$^{-1}$ were observed. This was ascribed to random Li atom occupation.

### 2.4. Phonon Dispersions and DOS

The phonon dispersion relations and the phonon DOS of the studied systems are plotted in Figure 5 and 6. The optical modes at the $\Gamma$-point differ slightly from the infrared and Raman spectra shown above due to the nonanalytical correction term for $\mathbf{q} \to \mathbf{0}$ included in the phonon dispersions.

The atom-projected phonon DOS show that the high energy phonons at about 450–750 cm$^{-1}$ are governed by oxygen and cobalt atoms, while Li and Na contribute at lower phonon energies. This is in line with the above discussion for the $\Gamma$-point phonons. In the case of CoO$_2$, there is a clear phonon bandgap between the acoustic and optical phonons at about 450 cm$^{-1}$. The dispersion of the acoustic phonons is clearly smaller in the $\Gamma$–$A$ direction that corresponds to the cross-plane direction. Introducing alkali metal atoms into the interlayer space with $x = 0.5$ increases the number of phonon modes, filling up the phonon bandgap and decreasing the maximum frequency of the acoustic modes in the in-plane direction. These changes are expected to have a clear influence on the lattice thermal conductivity in the in-plane direction, as the number of phonon scattering channels increases and the phonon group velocity may...
decrease. For the cross-plane direction, the comparison of CoO$_2$ and the intercalated systems with $x = 0.5$ is not straightforward and detailed studies on the lattice thermal conductivity are needed. For the $x = 1$ systems, a phonon bandgap opens up in the case of NaCoO$_2$, while in the case of LiCoO$_2$, the Li modes prevent the opening of a phonon bandgap. To summarize, the nature of the alkali metal atom has a clear effect on the lattice dynamics of the studied M$_x$CoO$_2$ systems.

Alkali metal atom intercalation into the parent CoO$_2$ crystal structure has clear effects on the phonon group velocities. The largest acoustic phonon group velocity in the in-plane direction is 3.25 km s$^{-1}$ for CoO$_2$ (Γ–Y$_2$ direction). The in-plane group velocity decreases to 2.77 and 2.79 km s$^{-1}$ for Li$_{0.5}$CoO$_2$ (Γ–Y$_2$) and Na$_{0.5}$CoO$_2$ (Γ–X), respectively. For $x = 1$ systems LiCoO$_2$ and NaCoO$_2$, the in-plane group velocity in the Γ–L direction increases to 3.20 and 3.09 km s$^{-1}$, respectively. In the cross-plane direction, the largest acoustic phonon group velocity of CoO$_2$ is only 0.99 km s$^{-1}$ (Γ–A). In the intercalated materials, the cross-plane group velocity of Na$_{0.5}$CoO$_2$ is lower in comparison to Li$_{0.5}$CoO$_2$ (1.84 vs 2.25 km s$^{-1}$, Γ–Z and Γ–B, respectively), but the group velocity of NaCoO$_2$ is larger in comparison to LiCoO$_2$ (2.43 vs 2.34 km s$^{-1}$, Γ–T for both).

Figure 3. Electronic band structure and DOS of nonmagnetic LiCoO$_2$ (top) and NaCoO$_2$ (bottom).
Figure 4. IR (left) and Raman (right) spectra of the studied systems. The intensity scale is different for IR and Raman spectra. LO–TO splitting has not been considered in the plotted spectra.
Figure 5. Phonon dispersion and density of states of CoO$_2$ and Li$_x$CoO$_2$. 

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3. Conclusion

We have studied the electronic properties and lattice dynamics of Li$_x$CoO$_2$ and Na$_x$CoO$_2$ intercalation materials ($x = 0, 0.5, 1$) with hybrid density functional theory. The end member CoO$_2$ favors a monoclinic structure at 0 K and behaves in accordance with Mott insulator theory. All magnetic species were treated as ferromagnets and the Co(IV) atoms possessed a magnetic moment of 1.2 $\mu_B$. Intercalating CoO$_2$ with Li and Na atoms leads to the increase of the electronic band gap and the intercalation can be observed both in IR and Raman spectra. The alkali atom intercalation also has a clear impact on the lattice dynamics of the parent CoO$_2$ compound, leading also in clear differences between the Li- and Na-intercalated species.

Figure 6. Phonon dispersion and density of states of Na$_{0.5}$CoO$_2$. 
4. Computational Details

The quantum chemical calculations have been carried out using the CRYSTAL17 code and PBE0 hybrid density functional method. We applied Gaussian-type triple-$\zeta$-valence + polarization level basis set (TZVP) for Co, O, and Li and split-valence + polarization level basis set for (SVP) for Na. The used basis sets have been derived from the molecular Karlsruhe basis sets and are identical to our previous study on fully intercalated, nonmagnetic LiCoO$_2$ and NaCoO$_2$.\textsuperscript{24,35}

In order to take into account the weak interlayer van der Waals interactions between adjacent layers in CoO$_2$, we used the empirical D3 dispersion correction with zero-damping and three-body interaction term (ABC) in the geometry optimization and phonon calculations for the CoO$_2$ end member with $x = 0$.\textsuperscript{36,37} The zero-damping scheme was utilized as we have previously reported the Becke–Johnson damping to overestimate the interlayer interaction in TiS$_2$, ZrS$_2$, and HfS$_2$.\textsuperscript{38}

The following Monkhorst–Pack-type $k$-meshes for sampling the reciprocal space were used: CoO$_2$: 12 $\times$ 12 $\times$ 8; Li$_0.5$CoO$_2$: 8 $\times$ 12 $\times$ 8; Na$_0.5$CoO$_2$: 8 $\times$ 8 $\times$ 4; LiCoO$_2$ and NaCoO$_2$: 8 $\times$ 8 $\times$ 8. A double-density mesh was used in the evaluation of the Fermi energy for the $x = 0$ and $x = 0.5$ systems. Obtaining the correct electronic ground state for the magnetic $x = 0$ and $x = 0.5$ systems required careful tuning of the initial guess. The full input examples with the initial guess settings are included as Supporting Information.\textsuperscript{29} Both the atomic positions and lattice parameters were fully optimized within the constraints imposed by the space group symmetry. Default DFT integration grids and optimization convergence thresholds of CRYSTAL17 were applied in all calculations. The calculations were carried out with Coulomb and exchange integral tolerance factors (TOLINTEG) set to tight values of 8, 8, 8, 8, and 16. The phonon dispersion relations of Li$_{0.5}$CoO$_2$ required even tighter TOLINTEG values of 10, 10, 10, 10, and 20.

The $\Gamma$-point vibrational frequencies were obtained within the harmonic approximation by using the scheme implemented in CRYSTAL.\textsuperscript{40,41} IR and Raman intensities for simulating vibrational spectra were obtained within the coupled perturbed Kohn–Sham method as implemented in CRYSTAL code.\textsuperscript{42,43} The IR absorbances are reported with units of km mol$^{-1}$ and the spectra have been broadened by Lorentzian line shape and FWHM of 16 cm$^{-1}$. The Raman intensities are reported in arbitrary units and spectra have been broadened using pseudo-Voigt peak profile (50:50 Lorentzian:Gaussian) and FWHM of 16 cm$^{-1}$.

Phonon dispersion relations were calculated within the harmonic approximation using Phonopy code.\textsuperscript{44} Phonopy uses a supercell approach in combination with atomic finite displacement method. Based on our previous benchmark calculations for LiCoO$_2$ and NaCoO$_2$,\textsuperscript{24} phonon supercell dimensions of about 10 Å were considered sufficient to obtain converged phonon dispersion relations. The following phonon supercells were applied: 3 $\times$ 3 $\times$ 2 for CoO$_2$, 3 $\times$ 4 $\times$ 2 for Li$_0.5$CoO$_2$, 2 $\times$ 2 $\times$ 1 for Na$_0.5$CoO$_2$, and 4 $\times$ 4 $\times$ 4 for Li$_0.5$CoO$_2$, Na$_0.5$CoO$_2$, and LiCoO$_2$, respectively. The phonon supercells were created with a displacement amplitude of 0.03 Å. Nonanalytical correction (NAC) as $q \to 0$ has been included in all phonon calculations using the method of Wang et al.\textsuperscript{45} except for Li$_0.5$CoO$_2$, where the method of Gonze et al.\textsuperscript{46} had to be used to avoid imaginary phonon modes. 3 $\times$ 3 $\times$ 3 $k$-sampling was used for $x = 0$ and 2 $\times$ 2 $\times$ 2 sampling for the $x = 1$ systems. For the $x = 0.5$ case, 2 $\times$ 3 $\times$ 3 and 3 $\times$ 3 $\times$ 3 sampling was used for Li$_0.5$CoO$_2$ and Na$_0.5$CoO$_2$, respectively. For the lattice dynamics calculations, tight SCF convergence criterion of 10$^{-10}$ a.u. was applied. The Li$_{0.5}$CoO$_2$ phonon supercell calculations required Fermi surface smearing of 0.001 a.u. (315 K) to converge. The reciprocal space coordinates used for plotting the electronic and phonon band structures were obtained from the SeeK-path service.\textsuperscript{47–49}

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

density functional calculations, electronic properties, lattice dynamics, layered compounds, magnetism

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