Suppression of magnetism and Seebeck effect in Na_{0.875}CoO_2 induced by Sb_{Co} dopants

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Abstract
We examined the electronic property of Sb-doped Na_{0.785}CoO_2 using density functional calculations based on GGA+U formalism. We demonstrated that Sb dopants were the most stable when replacing Co ions within the complex Na_{0.875}CoO_2 lattice structure. We also showed that the Sb_{Co} dopants adopted the +5 oxidation state introducing two electrons into the host Na_{0.875}CoO_2 compound. The newly introduced electrons recombined with holes that were borne on Co^{4+} sites that had been created by sodium vacancies. The elimination of Co^{4+} species, in turn, rendered Na_{0.875}(Co_{0.9375}Sb_{0.0625})O_2 non-magnetic and diminished the compound’s thermoelectric effect. Furthermore, the Sb_{Co} dopants tended to aggregate with the Na vacancies keeping a minimum distance. The conclusions drawn here can be generalised to other highly oxidised dopants in Na_{x}CoO_2 that replace a Co.

Keywords Sodium cobaltate · Sb dopant · Thermoelectric effect · Magnetism · Density functional theory

Introduction
Sodium cobaltate (Na_{x}CoO_2) is an interesting and promising compound for high-efficiency thermoelectric material applications [1–3]. This compound also exhibits a rich magnetic and structural phase diagrams [4, 5]. Na_{x}CoO_2’s unit cell consists of two alternating Na layers and edge-sharing CoO_{6} octahedra. Co ions’ mixed valency in Na deficient Na_{x}CoO_2 (x < 1) creates a large spin entropy flow, and consequently, a large Seebeck coefficient [6]. Additionally, the Na layer in which Na^{+} ions are amorphous and liquid like at room temperature [7] strongly scatters the heat-carrying phonons. The high mobility of Na ions leads to unprecedented freedom to favourably adjust all otherwise interdependent factors of the figure of merit (ZT) independently, giving Na_{x}CoO_2 an advantage over other thermoelectric materials [8, 9].

Controlling Na concentration (x) has been the primary technique to push the ZT of Na_{x}CoO_2 to higher limits [10]. However, given the volatile nature of Na ions, accurate experimental characterisation of Na concentration and its effect on the material’s behaviour is somehow difficult [11]. This experimental difficulty motivated theoretical investigations into the structural and electronic properties of pristine Na_{x}CoO_2 [12–15]. Additionally, doping other elements in Na_{x}CoO_2 has also been utilised to improve sodium cobaltate’s thermoelectric properties [16]. In spite of the efforts, doping Na_{x}CoO_2, as a strategy to enhance the thermoelectric performance, delivered mixed results. For instance, heavier ions such as rare earth Yb and noble metal Ag were successfully used to decrease the lattice thermal conductivity (κ_l) and thus improving ZT [17, 18]. Doping Ru and Mn in Na_{0.5}CoO_2, however, increased the resistivity to ~ 300 µΩ m, three times higher than that of the undoped Na_{0.5}CoO_2 [19]. Similarly, co-doping Ti and Bi almost halved the Seebeck coefficient in Na_{0.6}CoO_2 to ~ 60 µK/V [20].

The mixed experimental results indicate that further progress in realising the functional applications of Na_{x}CoO_2 requires an accurate understanding of the effects of Na concentration and the presence of dopants on the electronic property of Na_{x}CoO_2. More specifically, the effect of the...
dopants on the delicate magnetic interactions in Na$_x$CoO$_2$ is still under debate [21] and needs careful investigation. In this work, therefore, the behaviour of Sb dopants in Na$_{0.875}$CoO$_2$ is examined using density functional theory. Na$_x$CoO$_2$ with higher Na concentration of $x \approx 0.8$, as considered here, possesses excessively higher Seebeck coefficient [22] and exhibits complex Na ordering patterns [5], thus is both appealing and challenging compound to explore. Our choice of Sb dopant was motivated by the successful synthesis of Sb-doped layered metal oxide compounds such as LiMn$_2$O$_4$/LiSbO$_3$ [23], Na$_x$Ni$_5$SbO$_6$ [24] and Na$_x$Sn$_2$Sb$_4$NaO$_6$ [25], all of which share considerable structural features with Na$_x$CoO$_2$. Furthermore, although the Sb-doped Na$_x$CoO$_2$, Na$_{0.75}$CoO$_2$ and Na$_{0.5}$CoO$_2$ compounds have been previously examined [26, 27], Sb doping in Na$_{0.875}$CoO$_2$, which is theroelectrically more critical has not yet been explored in details.

**Computational settings**

Spin-polarised density functional calculations were performed with VASP package [28, 29] based on the projector augmented wave method [30, 31]. The energy cutoff was set to 500 eV. Generalised gradient approximation (GGA) [32, 33] was applied for the exchange–correlation functional. We added on-site Coulomb ($U$) and exchange ($J$) interaction terms of $U = 5$ and $J = 1$ eV to Co 3d electrons using Dudarev’s approach [34]. Among many values reported for $U$ and $J$ in the literature [35–37], the chosen values reproduce the charge disproportionation [38, 39] of the Co ions more accurately. That is clearly distinguishing Co$^{2+}$, Co$^{3+}$ and Co$^{4+}$ from one another in terms of magnetisation and partial density of states. Furthermore, the value of $U_{\text{eff}} = 4$ eV ($U_{\text{eff}} = U - J$) is at a mid-point between the low-end values of $\approx 3$ eV usually proposed for Co$^{3+}$ [40] and the high-end values of $\approx 5$ eV proposed for Co$^{4+}$ [41]. $U_{\text{eff}}$ values close to 4 eV has been successfully applied to multivalent Co oxides [42, 43]. Brillouin zone sampling for the supercells was carried out by choosing a $4 \times 2 \times 2$ k-point set within the Monkhorst–Pack scheme [44]. We have successfully examined the convergence of these settings earlier [45, 46]. Charges localised on cationic centres were examined with Bader charge analysis code [47]. The quoted experimental ionic radii were compiled and reported by Shannon [48].

To obtain the Na$_{0.875}$CoO$_2$ supercell, we first optimised the $P6_3/mmc$ unitcell of the Na$_x$CoO$_2$, which acts as the building block for the Na$_{0.875}$CoO$_2$ structure. The lattice parameters of a fully optimised primitive cell of Na$_x$CoO$_2$ were found to be 2.87 Å for $a$ and 10.90 Å for $c$, which are in good agreement with the measurements [49]. Then two Na ions, one from each Na layer, were removed from the $2a \times 4a \times 1c$ Na$_x$CoO$_2$ supercell to construct the undoped Na$_{0.875}$CoO$_2$ structure. The most stable arrangement of the Na vacancies was adapted from our previous work [46], which is shown in Fig. 1. To obtain the final structures, the internal coordinates of all ions in the supercell were relaxed while the lattice constants were fixed to the calculated values of pristine Na$_x$CoO$_2$. The resulting Na$_{0.875}$CoO$_2$ unit cell had a primitive monoclinic (P2) representation in which all Na ions were at Na2 sites. Although the lattice parameters of Na$_{0.875}$CoO$_2$ were expected to be slightly different from those of Na$_x$CoO$_2$, dopants’ formation energy is not significantly sensitive to this variation [12, 50]. For calculating Sb’s formation energy, after dopant’s placement in the Na$_{0.875}$CoO$_2$ structure, we fixed the lattice parameters of the doped supercell at the theoretical values of the pristine Na$_{0.875}$CoO$_2$, while all internal coordinates were relaxed.

This procedure eliminates the artificial hydrostatic pressure ensuring that the final structures are in equilibrium [51, 52].

**Results and discussion**

We first have to consider the formation energy ($E^f$) of Sb dopants in Na$_x$CoO$_2$. Cationic Sb dopants can either replace a Co or be incorporated in the Na layer. Since Sb’s ionic volume of $2.16 \times 10^{-4}$ nm$^3$ is much larger than the interstitial

![Fig. 1 The spin density of the $2a \times 4a \times 1c$ supercell used for simulating Sb-doped Na$_{0.875}$CoO$_2$ compound in the most stable configuration. Co and O ions occupy the Wyckoff 2a and 4f sites of the hexagonal lattice structure, respectively. In Na$_{0.875}$CoO$_2$, all Na ions occupy 2c (Na2) sites. For smaller Na concentrations, some Na ions occupy 2b (Na1) sites. The distance between $V_{\text{Na}}$ and $\text{Sb}^{4+}$ is marked with dotted brown lines. The spin density isosurfaces were drawn at $\rho = 0.035$ e/Å$^3$. Yellow and cyan surfaces indicate spin-up and spin-down, respectively.](image-url)
cavity in CoO₆ layer of 1.79 × 10⁻⁷ nm³ (marked with a star in Fig. 1), this interstitial site is too small for Sb doping. Furthermore, Sb in Na layer can either be substituted for a Na site (Na1 or Na2 as marked in Fig. 1) or be incorporated interstitially, e.g. occupying a vacant Na site. For x = 0.875, Sb’s formation energy has been reported earlier [26], using the standard supercell defect formation energy approach [53] and the triangular method for obtaining the chemical potentials [54]. The reported values belonged to an O rich environment in which Sb₃O₄ and CoO are the competing phases. The chemical potential (μ) for the oxygen-rich environment was set at μ_O = E'(O₂)/2 in which the E'(O₂) is the total energy of the O₂ molecule [55]. Accordingly, the most stable configuration was found SbCo with an E* of 1.175 eV followed by SnNa₁ with an E* of 4.547 eV, SnNa₂ with an E* of 4.805 eV and finally SnInt with an E* of 5.515 eV. This stability sequence is similar to that of Sb doping in Na₉CoO₂ (x = 1.00) for which SnCo had an E* of 1.356 eV while SnNa₁, SnNa₂ and SnInt each had an E* of 4.798 eV, 4.893 eV and 11.243 eV, respectively.

In the undoped Na₀.₈₇₅CoO₂ compounds, Co⁴⁺ species are produced when the original Co³⁺ ions in the parent Na₁CoO₂ compound are oxidised to bear the holes created by V₄Na₅. As a result, the Na₁₆Co₁₆O₃₂ supercell of the Na₀.₈₇₅CoO₂ compound has two holes borne on two Co⁴⁺ ions, one in each CoO₆ layer of the supercell. Sb dopants can adopt either +3 or +5 oxidation state. The Sb’s partial density of states, as presented in Fig. 2, which corresponds to the configuration in Fig. 1, shows that both 5 s and 5 p states are located above the Fermi level, indicating a +5 oxidation state. Since the supercell of the Na₀.₈₇₅CoO₂·SnCo has a chemical composition of Na₁₆Co₁₆Sb₁O₃₂, charge neutrality implies that on average the oxidation state of Co ions is +3. In the most stable spin alignment, presented in Fig. 1, all Co ions have, indeed, an oxidation state of +3. Additionally, all Co ions were stabilised in the low spin configuration of t¹₂, e¹, further suggesting that this compound is non-magnetic. This is in contrast to the pristine Na₀.₈₇₅CoO₂ compounds in which the Co⁴⁺ ions were antiferromagnetically aligned across the CoO₂ planes [56, 57]. Moreover, we have earlier shown that in Na₅CoO₂ and Na₀.₇₅CoO₂·2NaCo dopant also adopts the higher oxidation state [27].

The partial density of states of SnCo-doped Na₀.₈₇₅CoO₂ [Na₀.₈₇₅(CO₁₆Sb₁O₃₂)] shown in Fig. 2, has some other noticeable features. Here, as expected [58, 59], under octahedral coordination, Co 3dₓ² and 3dₓ²−y² orbitals directly overlap with O 2pₓ, 2pᵧ, and 2p₀ orbitals along the octahedral directions having σ hybridisation. This σ overlap results in low lying bonding e²ₓ states with predominantly p character and high lying antibonding e²ᵧ states with predominantly d character. The remaining Co 3dₓ₁, 3dᵧ, and 3dᵦ orbitals point away from the O 2p orbitals and, therefore, have no significant σ overlap with O 2p orbitals, constituting the nonbonding t²ₓ-states. Moreover, the overlap of O 2p and Co 3p, and O 2p and Co 4 s orbitals form t¹₂ and a¹₂g bands, respectively, both of which located above the e¹-states and have p character. Furthermore, there is a crystal field splitting of 1.01 eV (marked with a red arrow in Fig. 2) between the filled Co³⁺ t¹₂ states at the top of the valence band and the empty antibonding e¹ states at the bottom of the conduction band forcing all Co³⁺ in the low spin state. The bandwidth of 1.01 eV is smaller than that of Na₁CoO₂ (~ 2.2 eV) [45], indicating that Sb doping reduces the fundamental bandgap in Na₀.₈₇₅CoO₂. Additionally, Sb’s empty 5 s states are located at the top of the conduction band at ~ 2.5 eV hybridising with the empty e¹ states while Sb’s empty 5 p states are located even higher at ~ 6 eV hybridising with the high lying Na’s empty 3 s states. This arrangement is different from that of Sb⁵⁺ in Sb₂O₅ in which both Sb 5 s and 5 p states are located within the same range at ~ 4 eV above Fermi level [60].

There is another possibility that the excess electrons introduced by SnCo’s high oxidation state, instead of neutralising all hole introduced by V₄Na₅ in Na deficient compounds, reduce the Co³⁺ species to Co²⁺ in Na₀.₇₅CoO₂, while leaving all or some of the Co⁴⁺ ions unaltered. Co⁴⁺ and Co⁵⁺ are magnetic with a different spin and orbital degeneracies, implying that Na₀.₈₇₅CoO₂·2NaCo might potentially exhibit a
different magnetic and thermoelectric behaviour. We examined the possibility of alternative manifestation of oxidation states for Co ions in Na$_{0.875}$CoO$_2$: Sb$^{5+}$ other than its most stable arrangement as presented in Fig. 1. In doing so, we constructed the alternative spin alignments by fixing the initial magnetic moment on the Co ions in the calculations. Several different configurations were considered of which a more stable spin bearing one is presented in Fig. 3. The partial density of Co ions with distinct oxidation and spin states are presented in Fig. 4. Here, we see that high spin Co$^{4+}$ ($t^2_2 g^2_e$) and low spin Co$^{2+}$ ($t^6_2 g^2_e$) species were both formed at the vicinity of Sb$^{5+}$ dopant. Furthermore, a larger radius of Co$^{2+}$ at octahedral coordination of 0.75 Å introduced significant lattice distortions that forced several Co$^{3+}$ to take high spin configurations ($t^4_2 e^2_g$). The total energy of this configuration was, however, higher than the non-magnetic configuration (Fig. 1) by 46.963 meV/Co, suggesting that Co ions in Sb-doped Na$_{0.875}$CoO$_2$ would be non-magnetic—all Co ions at $t^6_2 g^2_e$ for a wide range of temperatures.

In Sb$_{Co^{5+}}$-doped Na$_{0.875}$CoO$_2$ system [Na$_{0.875}$Co$_{0.9375}$Sb$_{0.0625}$O$_2$], Sb dopants can occupy few distinct positions when substituting Co. For instance, either close to V$_{Na}$, as shown in Fig. 1, which corresponds to the most stable arrangement of Sb dopant, or far from the V$_{Na}$s, as shown in Fig. 5. The distance between Sb$_{Co^{5+}}$ and V$_{Na}$s for the configuration presented in Fig. 1 is 2.23 Å for the V$_{Na}$ at Z = 0 and 2.23 Å for the V$_{Na}$ at Z = 0.5. These distances...
for the configuration presented in Fig. 5 were 5.23 Å for the $V_{Na}$ at $Z=0$ and 5.26 Å for the $V_{Na}$ at $Z=0.5$. We found the total energy of the configuration in Fig. 1 was 27.620 meV/Co lower, and hence more stable than the configuration in Fig. 5. One possible explanation for the aggregation of Sb dopant and the $V_{Na}$ is that the radius of Sb$^{5+}$ in octahedral coordination (0.60 Å) is ~8.3% larger than that of Co$^{3+}$ (0.55 Å). As a consequence, the location of larger Sb ion in the vicinity of $V_{Na}$ results in the cancellation of internal lattice stress leading to greater stability.

In the case where the Sb$^{5+}$ dopant is far away from the $V_{Na}$ as in Fig. 5, unlike the case of the ground state in Fig. 1, the electrons of the Sb$^{5+}$ do not neutralise both of the holes that are borne on the Co$^{4+}$ ions in the supercell. As shown in Fig. 5, only the Co$^{4+}$ at the bottom CoO$_2$ layer which contains the Sb$^{5+}$ dopant has been reduced to Co$^{3+}$ while the Co$^{4+}$ in the top layer has remained unaltered. The extra electron of the Sb dopant, instead, reduces a Co$^{3+}$ in the vicinity of the Sb dopant to Co$^{2+}$. Since the Co$^{4+}$ ions are located near the $V_{Na}$ in the undoped compound [45], doping Sb$^{5+}$ in the vicinity of $V_{Na}$ (as in Fig. 1), facilitates the change charge from Sb to two cationic nearest neighbour Co$^{4+}$ ions. However, when the Sb$^{5+}$ is far away from the $V_{Na}$, as in Fig. 5, there is no cationic nearest neighbour charge transfer possible between Sb and Co$^{4+}$ at the top layer. Consequently, the extra electron of Sb$^{5+}$ is localised on a neighbouring Co$^{3+}$ in the bottom layer converting it to Co$^{2+}$. We verified the stability of this spin alignment for the configuration in Fig. 5 by fixing the spin of all Co to zero ($t_{2g}^{3}e_g^{0}$) which resulted in a 112.6 meV/Co higher total energy.

In Na$_{14}$Co$_{16}$O$_{32}$ the Seebeck effect is facilitated by the spin entropy transfer between Co$^{3+}$ and Co$^{4+}$ ions for which the Seebeck coefficient can be estimated by the modified Heikes formula [61, 62]:

$$S(T \to \infty) = -\frac{k_B}{e} \ln \left( \frac{g(Co^{3+})}{g(Co^{4+})} \cdot \frac{\rho}{1-\rho} \right),$$

in which $k_B$ and $e$ are the Boltzmann constant and electron's charge, respectively, $g(Co^{3+})$ and $g(Co^{4+})$ are the electronic degeneracies of Co$^{3+}$ and Co$^{4+}$ ions, respectively, and $\rho$ is the hole concentration. The electronic degeneracies are calculated by multiplying the orbital ($g_{\text{orbital}}$) and spin ($g_{\text{spin}}$) degeneracies of electrons for a given transition metal ion. In low spin, octahedral coordination for which Co$^{3+}$ and Co$^{4+}$ electrons occupy $t_{2g}$ orbitals only, $g_{\text{orbital}}$ is the total number of permutation of electrons and is calculated as:

$$g_{\text{orbital}} = \frac{3!}{n![(3-n)!]} \cdot \frac{3!}{n![(3-n)!]}$$

in which $n_l$ and $n_t$ are the number of spin-up and spin-down electrons, respectively. $g_{\text{spin}}$ on the other hand, equals to $2\xi + 1$, where $\xi$ is the total spin number of a given ion. Plugging the values for Co$^{3+}$ and Co$^{4+}$ renders $g(Co^{3+}) = 1$ and $g(Co^{4+}) = 6$. Additionally, since conduction in Na$_{0.875}$CoO$_2$ is achieved by holes hopping form a Co$^{4+}$ site to a Co$^{3+}$ site, the hole concentration is proportional to the ratio of Co$^{4+}$ site to the total Co sites. Consequently, $S(T \to \infty) \approx 322.08 \mu\text{K/V}$ in pristine Na$_{0.875}$CoO$_2$. Equation 1 establishes a reverse relationship between $\rho$ and $S$; so that for raising the Seebeck coefficient, one must reduce the concentration of Co$^{4+}$ species [63].

The introduction of one Sb$_{Co}$ dopant into the Na$_{14}$Co$_{16}$O$_{32}$ supercell, however, eliminates the Co$^{4+}$ species and brings the hole concentration to zero resulting in a band insulating character for Na$_{0.875}$CoO$_2$:Sb$_{Co}$. This is inferable from the partial density of states in Fig. 2, which shows a bandgap of 1.01 eV. As a consequence, according to Eq. 1, the Seebeck coefficient diverges. Experimentally, however, Seebeck effect measurements in insulators have indicated that the Seebeck potential approaches zero as carrier concentration diminishes [64]. Mahan has attributed this apparent contradiction to the fact that the Seebeck potential does not diminish but rather a space-charge effect in insulators screens off the Seebeck potential [65, 66]. In any case, in the absence of any carriers, Na$_{0.875}$CoO$_2$:Sb$_{Co}$ is of no use for converting heat gradient to measurable electric energy. Although reducing the concentration of Co$^{4+}$ increases $S$, in choosing the dopant and its concentration for Na$_{0.875}$CoO$_2$, one, nonetheless, must apply due diligence to avoid the catastrophic complete electron–hole recombination.

It is quite instructive to know that several times, similar to the case of Na$_{0.875}$CoO$_2$: Sb$_{Co}$, ineffective doping cases on thermoelectric compounds have been reported in the literature. For example, Al doping plays no effect on Mg$_3$Si$_{10.75}$Sn$_{0.25}$ [67]. In Ni-doped CuInTe$_2$ Ni-doping is rather ineffective regarding the increase of the hole concentration and the decrease of the thermal conductivity [68]. In Mg$_3$Sb$_2$, interstitial doping with Li, Zn, Cu, and Be is found to be ineffective for n-type doping; however, Li is identified as a good p-type dopant [69]. Bi is an ineffective dopant in Mg$_2$Ge and precipitates into Mg$_2$Bi$_3$ [70]. Boron is ineffective as dopant in α-MgAgSb [71].

### Conclusions

In this work, using density functional theory, the formation energy of Sb dopants in Na$_{0.875}$CoO$_2$ was examined. The main findings of this investigation can be summarised as follow: (1) Sb$_{Co}$ is the most stable configuration Na$_{0.875}$CoO$_2$ as it is in Na$_{0.875}$CoO$_2$ as well. This trend is similar to the Sb dopant in other sodium cobaltites with smaller Na concentrations [26, 27]. Moreover, as $x$ increases the margin of the stabilisation of Sb$_{Co}$ configuration increases...
against those other configurations in which Sb is located in the Na layer: (2) the formation energy of SbCo decreases with decreasing $x - E^f(Na_{1-x}CoO_2:SbCo) = 1.356$ eV and $E^f(Na_{0.875}CoO_2:SbCo) = 1.175$ eV. This trend implies that doping Na deficient systems with Sb is practically easier; (3) in $Na_{0.875}CoO_2:SbCo$, Sb’s 5 s states are located above the Fermi level hybridising with Co’s empty $e_g$ states while Sb’s 5p states are located even higher along with Na’s 3 s states implying an oxidation state of $5^+$ for SbCo; (4) in $Na_{0.875}CoO_2:SbCo$, Co tends to aggregate with the $V_{Na}$'s; (5) in the most stable configuration, Sb dopants reduce the magnetic Co$^{3+}$ ion to non-magnetic Co$^{2+}$ abating both the long-range magnetic order and the Seebeck effect which is sustained by spin entropy flow in undoped $Na_{2}CoO_2$; (6) in an excited state, in $Na_{0.875}CoO_2:SbCo$, a pair of non-magnetic Co$^{3+}$ can be transformed into magnetic Co$^{2+}$ and Co$^{4+}$. Such magnetic state is, however, higher in energy by 46.963 meV/Co than the non-magnetic ground state. Finally, we demonstrated how a generally favourable strategy such as reducing carrier concentration for increasing the Seebeck coefficient can suppress the Seebeck effect for a specific dopant and Na concentrations in $Na_{2}CoO_2$.

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