

## Analysis of point defect formation in $\text{Na}_x\text{CoO}_2$ by first principle calculation

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$\text{Na}_x\text{CoO}_2$  based materials are thermoelectric conversion materials that exhibit relatively high figure of merit. Of three parameters that determine the figure of merit, it is reported that high Seebeck coefficient is originated from a proper coexistence of  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions [1], while high electronic conductivity is a result of high concentration of electron holes [2]. As for the low thermal conductivity, it is reported that Na vacancies are responsible for the decrease in the phonon thermal conductivity [3]. All of the three parameters are related to the states of point defects including electronic defects. In order to acquire a guideline for further improvement of the materials or to search for new materials having higher figure of merit, it is necessary to obtain physical insight as to why and how those defects are present in this series of materials. These are the rationale for studying point defects by first principles calculations in this study, which would reveal energetics of the defects formation and electronic states from which the energetics are originated from.

In the present study, we have examined the state of possible point defects by adding one point defect to a perfect state, with a variable  $x$ , since it is easily expected that interaction among point defects, whether intrinsic or extrinsic, is too complicated to acquire clear picture as to what is the influence of a defect on the system. Thus, we have calculated the formation energies of point defects by the first principle calculation using a GGA exchange-correlation functional [4]. Although it is well known that relatively strong electronic correlation is responsible for the unique electronic states especially near Fermi level in this series of materials, one-electron picture is at first necessary to be obtained before discussing further details of the electronic correlation. Thus, in the present study, we started with the GGA formalism as a first step and we did not taken into account the electronic correlation in an extrinsic manner other than those already included in the GGA formalism.

Within wide range of composition, or Na content, calculations were carried out for  $\text{NaCoO}_2$  having no Na vacancy and  $\text{Na}_{0.5}\text{CoO}_2$  in which half of Na sites are unoccupied. In order to minimize defect-defect interaction due to three periodic boundary conditions, supercells of which lengths are longer than 10 Å were used in this study. Plane wave cutoff energy, the number of k-points, and FFT mesh size were determined so that total energy was converged sufficiently enough within a several meV per atom.

Formation energy of a point defect,  $\Delta E_{\text{formation}}$ , was calculated as

$$\Delta E_{\text{formation}} = \{E_{T,\text{defective}} + \mu_M + q\mu_e\} - E_{T,\text{perfect}} \quad (1)$$

where  $E_{T,\text{defective}}$  and  $E_{T,\text{perfect}}$  are the total energy of a defective supercell and a perfect supercell.  $\mu_M$  and  $\mu_e$  are chemical potentials of defective atoms and electron, respectively and  $q$  is a charge state of the defective supercell. To determine chemical potential of an electron, we surveyed the electronic density of states of  $\text{NaCoO}_2$  and  $\text{Na}_{0.5}\text{CoO}_2$ . While  $\text{NaCoO}_2$  exhibited small band gap below which bands are occupied by electrons, the gap was completely filled in  $\text{Na}_{0.5}\text{CoO}_2$ , in accordance with metallic behavior of electric resistance reported by experiment. Filled band gap enables to uniquely determine  $\mu_e$ , leading to the formation energy as a function only of  $\mu_M$ .

The chemical potentials of constituting atoms were calculated by the following equations:

$$x\mu_{\text{Na}} + \mu_{\text{Co}} + 2\mu_{\text{O}} = \mu_{\text{Na}_x\text{CoO}_2(\text{bulk})} \quad (2)$$

$$2\mu_{\text{Na}} + \mu_{\text{O}} = \mu_{\text{Na}_2\text{O}(\text{bulk})} \quad (3)$$

$$\mu_{\text{Co}} + \mu_{\text{O}} = \mu_{\text{CoO}(\text{bulk})} \quad (4)$$

where  $\mu_{\text{Na}_x\text{CoO}_2(\text{bulk})}$ ,  $\mu_{\text{Na}_2\text{O}(\text{bulk})}$  and  $\mu_{\text{CoO}(\text{bulk})}$  are the energies of the each bulk material and are constant values that can be calculated as the total energy per unit formula. Then, chemical potentials of

Na and Co can be calculated as a function of chemical potential of O which can be calculated from

$$\mu_O = \mu_O^0 + kT \ln(P / P_0) \quad (5)$$

where  $P$  is partial pressure of oxygen and  $P_0$  is that in standard state, fixed at 0.2 atm, and  $k_B$  and  $T$  is Boltzmann constant and temperature, respectively. The value of  $\mu_O^0$  was assumed to be equal to energy per atom of  $O_2$  molecule at 0 K, which was also calculated independently.

Figure 1 shows the calculated formation energies of a vacancy in  $NaCoO_2$  and  $Na_{0.5}CoO_2$ . In the figure, among various charge states of defects, only a charge states that shows minimal energy was shown for each defect species. Namely,  $Co^{3+}$  is the most stable among various valence states of Co in  $NaCoO_2$  in whole range of partial pressure of  $O_2$  while  $Co^{4+}$  is the most stable one in  $Na_{0.5}CoO_2$ . In whole range of the oxygen partial pressure, the formation energies of the point defect from Na site were lower than the others for both  $NaCoO_2$  and  $Na_{0.5}CoO_2$ , indicating that  $Na^+$  vacancies can be easily formed. It is interesting to note that the formation energy of  $Na^+$  vacancy showed negative value, though entropy contribution is not taken into account, indicating that Na tends to be depleted to some extent under an ordinary condition.

Through analyzing charge distribution of defective states, it is found that, when a  $Na^+$  vacancy is formed, a Na atom is removed leaving one electron which greatly localized at around the vacancies, and slight depletion of charge around Co atoms were found, which indicates that a portion of electrons around Co is attracted to the  $Na^+$  vacancy. In other words, a portion of electron hole is supplied from the  $Na^+$  vacancies, which might be responsible for the high concentration of carrier, and, in turn, high electronic conductivity of this series of materials when Na is deficient. Although further calculation with proper treatment of electronic correlation is needed to discuss further details, it is the beyond of the present study and it will be revealed by ongoing calculations by GGA+U method.

#### References

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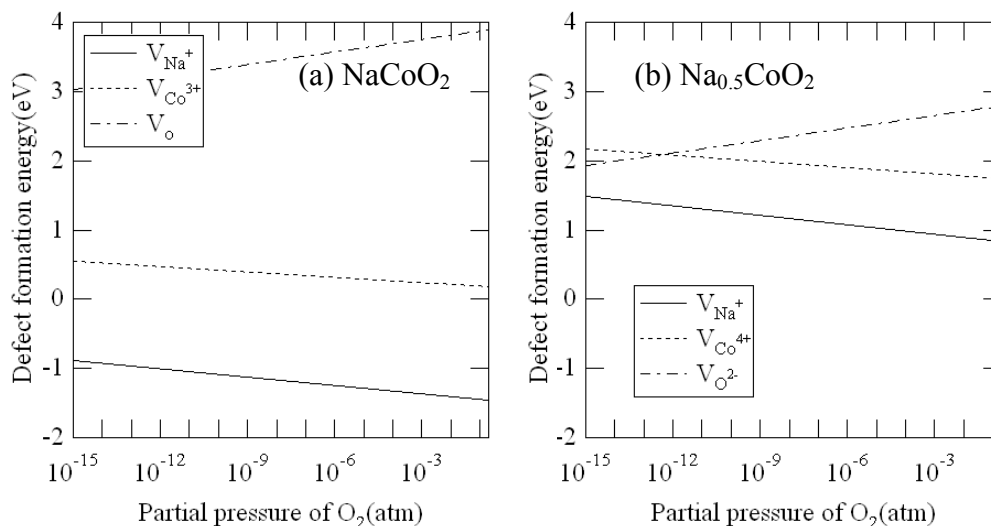


Figure 1. Formation energies of various charge states of vacancies in (a)  $NaCoO_2$  and (b)  $Na_{0.5}CoO_2$  as a function of oxygen partial pressure.