

# Comparative study of dopants' formation energies in thermoelectric sodium cobaltate

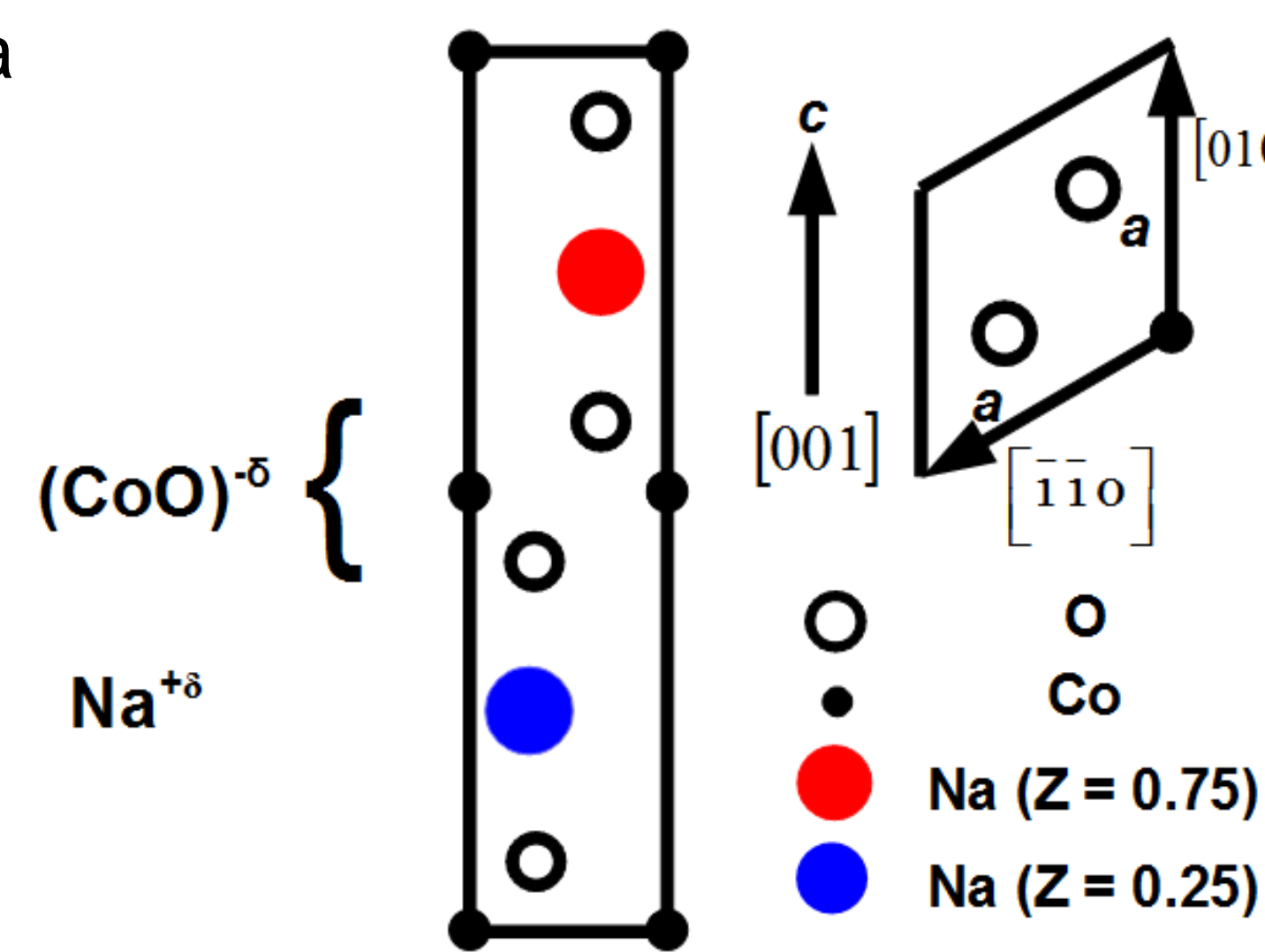
M. H. N. Assadi and H. Katayama-Yoshida

Graduate School of Engineering Science, Osaka University, Osaka 560-8531, Japan

assadi@aquarius.mp.es.osaka-u.ac.jp

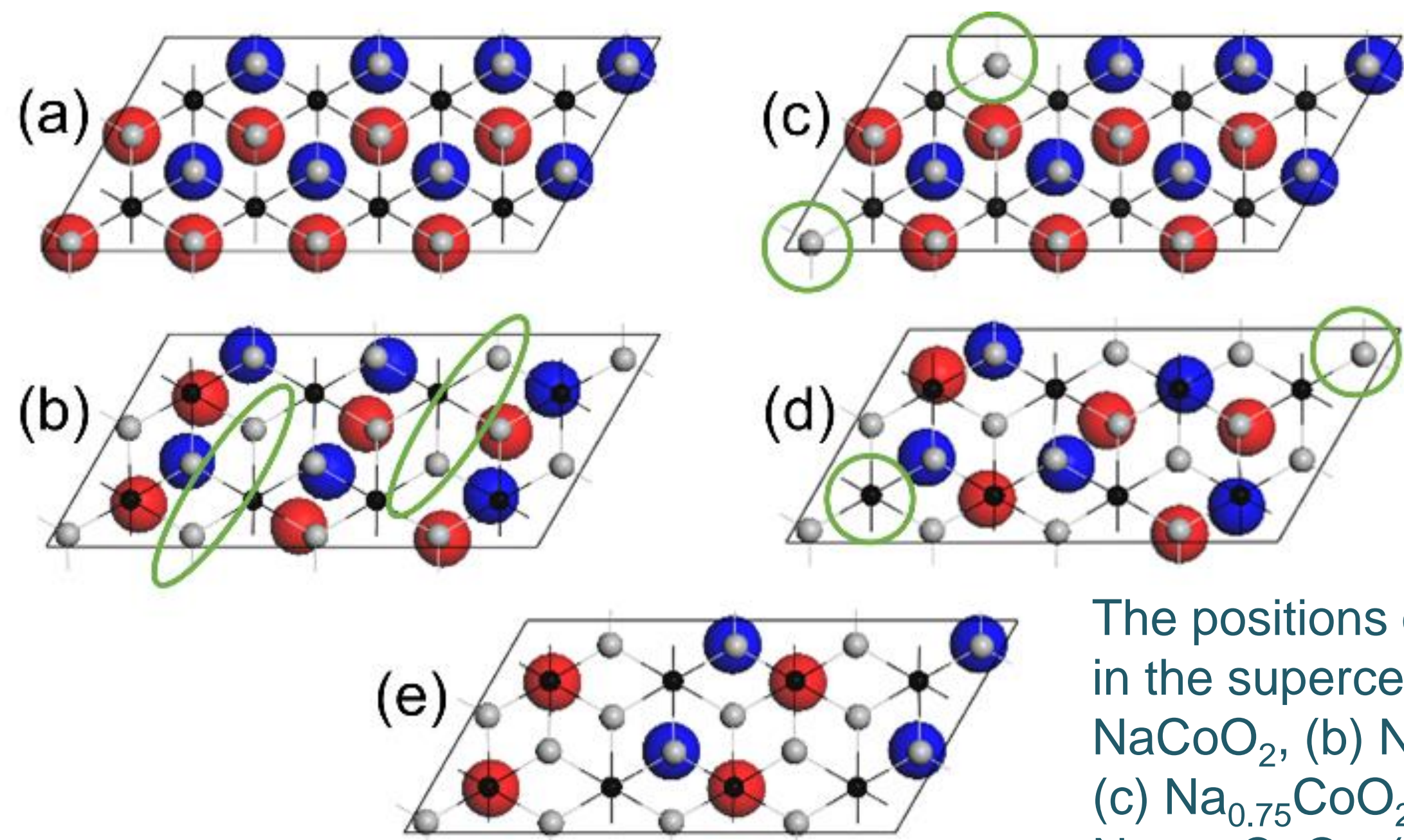
## Introduction

Layered cobaltate  $\text{Na}_x\text{CoO}_2$  has recently attracted intense research attention as a promising material for high efficiency thermoelectric systems.  $\text{Na}_x\text{CoO}_2$  lattice is made of alternating Na layers and edge-sharing  $\text{CoO}_6$  octahedra. The triangular nature of  $\text{CoO}_6$  layer in  $\text{Na}_x\text{CoO}_2$  possesses high degree of electronic frustration, resulting in large spin entropy and thus creating large Seebeck coefficient. Additionally, in  $\text{Na}_x\text{CoO}_2$ , phonons are strongly scattered by the  $\text{Na}^+$  ions which are mostly mobile at room temperature. From materials engineering viewpoint, controlling Na content has been a prime tool to push the  $ZT$  of  $\text{Na}_x\text{CoO}_2$  to higher limits. Additionally, doping has also been utilized to improve the sodium cobaltate system's properties. In order to further advance the field, fundamental atomistic understanding of electric behaviour as a function of Na content in  $\text{Na}_x\text{CoO}_2$  should be established. One particular concern is that due to the difference in the bonding nature and lattice structures of the  $\text{CoO}_2$  and Na layers in  $\text{Na}_x\text{CoO}_2$  systems, a particular dopant may be stable at different lattice sites as Na content varies.

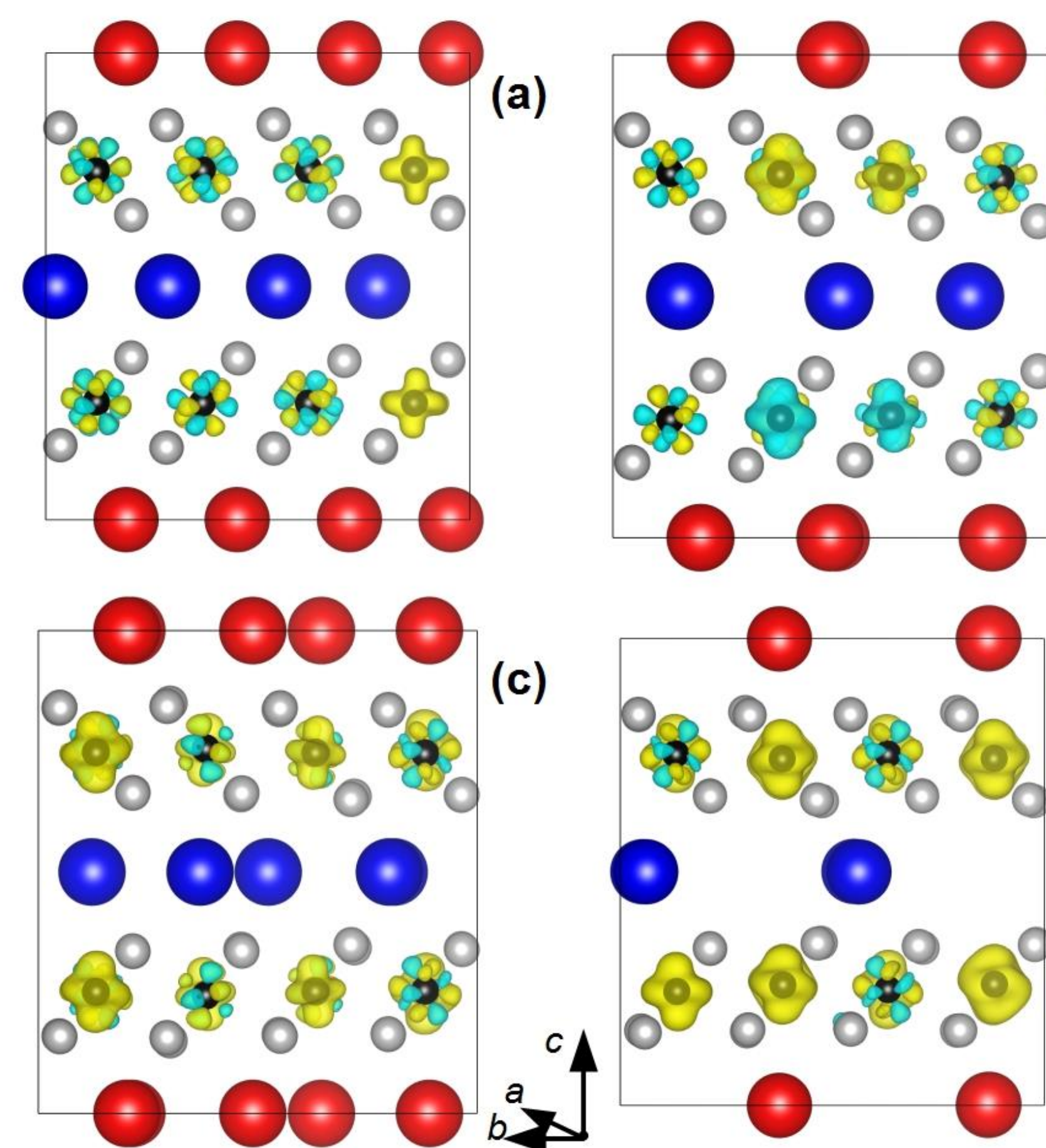


The primitive cell and lattice vectors of the  $\text{NaCoO}_2$  crystal. There are two  $\text{Na}^+$  ions in each primitive cell, one at  $Z = 0.25$  and the other at  $Z = 0.75$ . In ambient, depending on the concentration of Na vacancy, usually Na ions are not strongly bound to their sites and take an amorphous configuration. Each Na donates an electron to a neighboring Co creating a  $\text{Na}^{+\delta}$  layer and a  $(\text{CoO})^{-\delta}$  layer. As a result in Na deficient systems, Co ions exist in mixed valance state.

## Pristine $\text{Na}_x\text{CoO}_2$

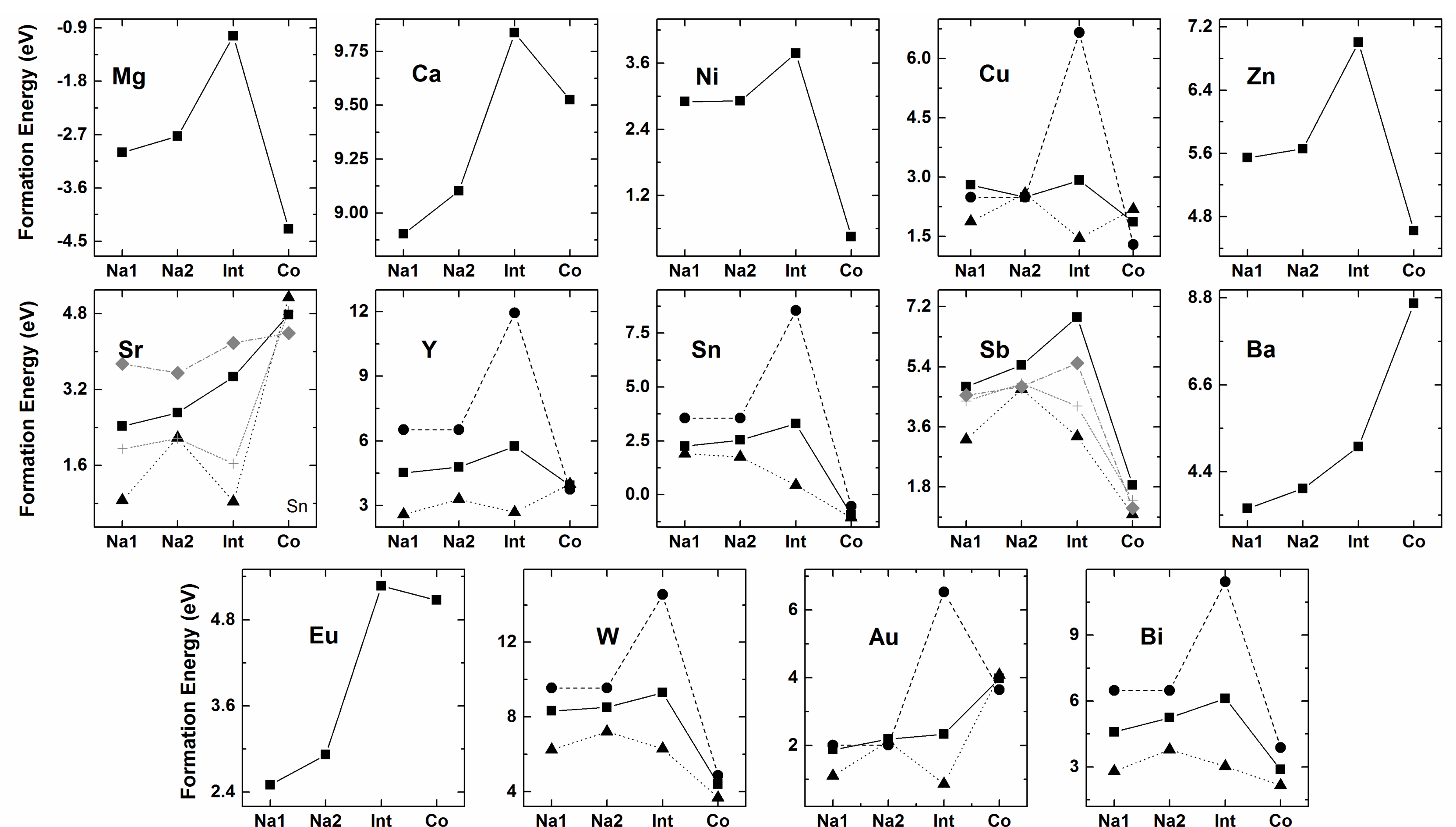


The positions of the  $\text{Na}^+$  ions in the supercell for (a) the  $\text{NaCoO}_2$ , (b)  $\text{Na}_{0.875}\text{CoO}_2$  and (c)  $\text{Na}_{0.75}\text{CoO}_2$ , (d)  $\text{Na}_{0.625}\text{CoO}_2$ , (e)  $\text{Na}_{0.50}\text{CoO}_2$  systems. Note the change in Na patterning as Na concentration changes.

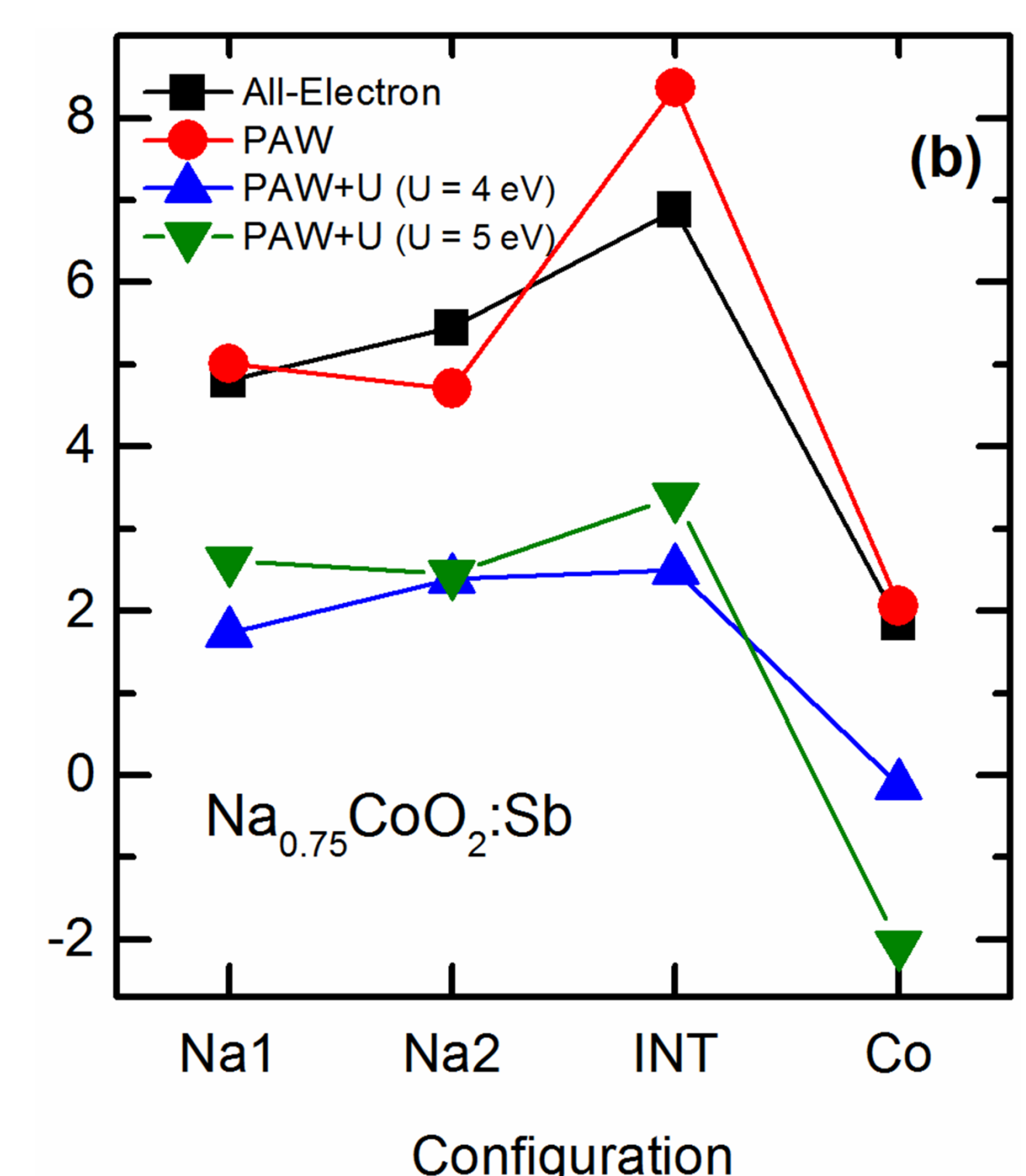


(b) The charge density isosurfaces of the (a)  $\text{Na}_{0.875}\text{CoO}_2$ , (b)  $\text{Na}_{0.75}\text{CoO}_2$ , (c)  $\text{Na}_{0.625}\text{CoO}_2$  and (d)  $\text{Na}_{0.50}\text{CoO}_2$ . The isosurfaces were plotted for charge density of  $0.025 \text{ e}/\text{\AA}^3$ . The larger red and blue spheres represent  $\text{Na}^+$  ions with fractional coordinate of  $Z = 0$  and  $Z = 0.5$  respectively. The cyan and yellow shades represent the spin-up and spin-down charge isosurfaces respectively.

## Doped $\text{Na}_x\text{CoO}_2$



The formation energy of various dopants in  $\text{Na}_x\text{CoO}_2$ . The upright triangle, the plus sign, the solid square, diamond and the circle symbols correspond to  $x$  values of 0.5, 0.625, 0.75, 0.875 and 1.00 respectively in  $\text{Na}_x\text{CoO}_2$ .  $\text{Na}_x\text{CoO}_2$  has two distinct Na sites labeled  $\text{Na}1$  and  $\text{Na}2$ . Na interstitial site is labeled  $\text{Int}$ .



## Conclusions

- For full Na occupancy in the pristine systems, all sodium ions are located at Na1 sites. In contrast, for 87.5% Na occupancy Na ions are located at Na2 sites. For 75% sodium occupancy, the ratio of Na2/Na1 is 5.
- Systematic density functional calculations showed that the Ni and Zn were more stable when substituting Co with formation energy 2.35 eV, 2.08 eV. While Eu and Mg and Sb are more stable when it substitutes Na.
- In sodium rich systems of full and 87.5% occupancy, Sb dopants stabilizes at the  $\text{CoO}_2$  layer in the form of  $\text{Sb}_{\text{Co}}$  (5+). However the margin of stability of  $\text{Sb}_{\text{Co}}$  (5+) with respect to the next stable configuration decreases as Na occupancy decreases. In Sodium poor  $\text{Na}_{0.75}\text{CoO}_2$ , Sb dopant is stable in the form of  $\text{Sb}_{\text{Na1}}$  (5+).
- By varying Na occupancy, one can dictate the incorporation lattice site of Sb dopants. For lower Na content, positively charged Sb dopants tend to reside in the Na layer to compensate for vacant Na ions. However, as Na content increases, these dopants will be stabilized in Co's substitutional site. This conclusion may be generalized to other positively charged dopants in Na deficient sodium cobaltate.

## Further readings and acknowledgments

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- M. H. N. Assadi, H. Katayama-Yoshida "Interplay between magnetism and Na concentration in  $\text{Na}_x\text{CoO}_2$ " Functional Materials Letters 8 (2015) 1540016; arXiv:1504.00456
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Thank you very much

Osaka University