# First-principles study on Small Polaron and Li diffusion in layered $LiCoO_2$

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## 1. Polaron stability depending on the Li composition

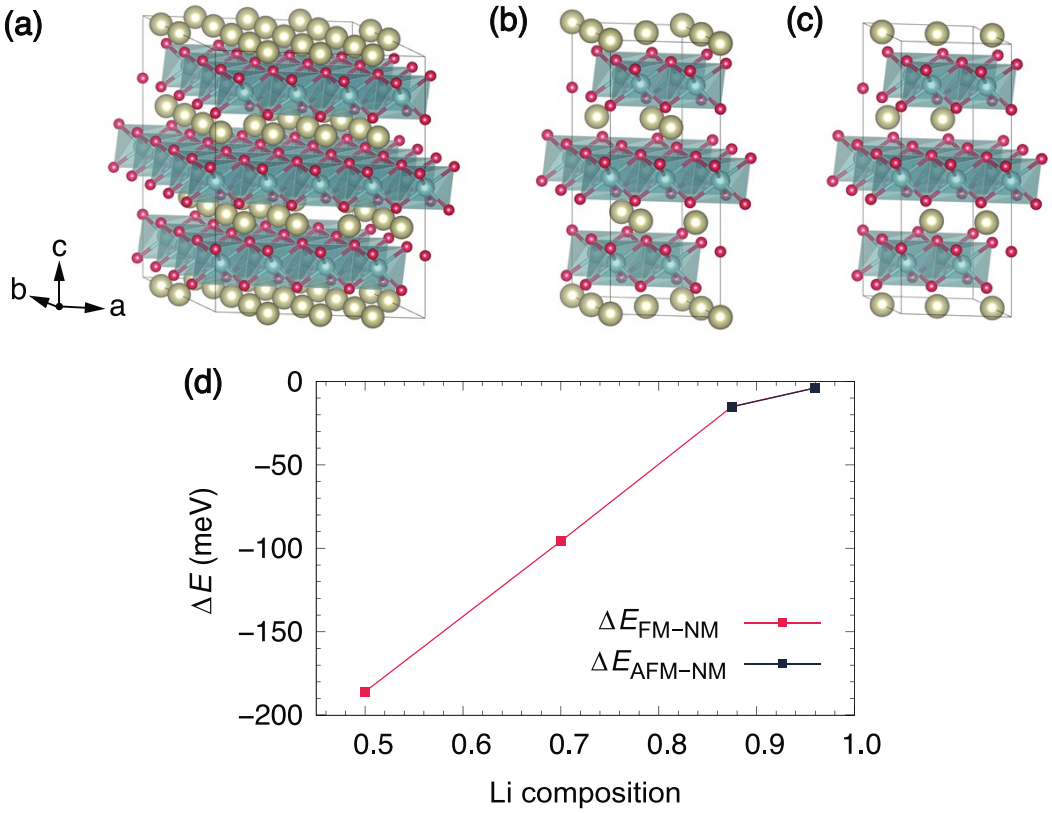


**Fig. S1** Crystal structures of (a) $Li_{0.875}CoO_2$, (b) $Li_{0.75}CoO_2$, and (c) $Li_{0.5}CoO_2$. (d) The energy difference between polaron and non-polaron structures per formula unit depending on the Li composition.

We have investigated the energy difference between polaron and non-polaron structures, $\Delta E$ at the intermediate charge levels. Figure S1(a-c) shows the generated structures of $Li_{0.875}CoO_2$, $Li_{0.75}CoO_2$, and $Li_{0.5}CoO_2$. As in the case of $Li_{0.96}CoO_2$, the small polarons only appear in the magnetic structures, and the polaronic structures are energetically more stable regardless of Li composition as shown in Fig. S1(d). Also, note that the more the Li vacancies are the more stable the small polarons are. The energy difference between FM and AFM in $Li_{0.875}CoO_2$ is almost negligible, whose value is 0.2 meV/f.u.. Thus, the $\Delta E$ from the FM and AFM cases are almost the same as in Fig. S1.

## 2. Electronic structures of the AFM phase

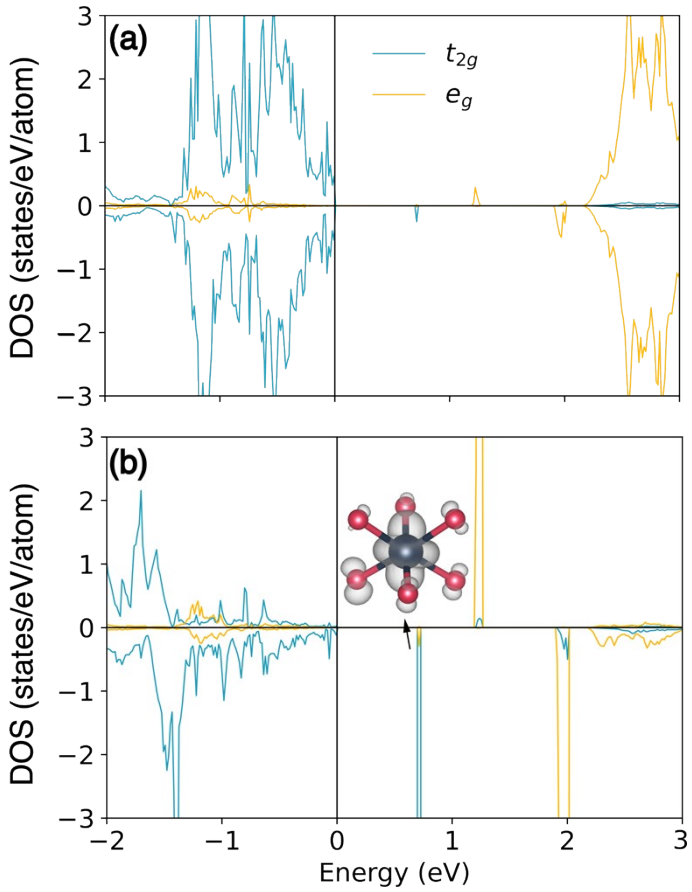


**Fig. S2** Projected density of states (PDOS) of 3*d* orbitals (a) $Co^{3+}$ and (b) $Co^{4+}$ in the AFM structure. (Inset) Charge density isosurface of $CoO_6$ octahedral $t_{2g}$ hole band.

Figure S2 shows the electronic structure of $Co^{3+}$ and $Co^{4+}$ ions in the AFM phase. The partial density of states (DOS) and the charge density are nearly identical to FM in Fig. 4. This result is consistent with the energy calculation, which has an insignificant difference of 0.06 meV/f.u,. Like the electronic structure of FM, the $t_{2g}$ orbitals of $Co^{3+}$ are fully occupied with the low spin state whereas the unoccupied $t_{2g}$ band appears in $Co^{4+}$ ion. The AFM phase exbibits a band gap of 0.69 eV from the gap between $t_{2g}$ orbitals of the $Co^{4+}$ ion. The unoccupied $Co^{4+}$ $t_{2g}$ orbital is the $a_{1g}$ orbital as indicated in the charge density. The charge density in Fig. S2(b) also shows the oxygen hole around $Co^{4+}$.