Stability and electronic properties of layered NaMnO₂ using the SCAN(+U)

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Abstract
Considering electron correlation appropriately is important to predict the properties of layered transition metal oxides, which have drawn a lot of attention as cathode materials for sodium-ion batteries. Here, we explore the phonon and electronic properties of layered NaMnO₂ using the recently developed strongly constrained and appropriately normed (SCAN) functional. We also introduce the Coulomb interaction \( U \) to find an accurate description of Mn \( 3d \) orbitals. The phonon dispersion curves show the structural stability with the SCAN, which is consistent with prior experimental stability at high Na concentrations. On the other hand, imaginary phonon frequencies were observed by applying \( U \), which indicates structural instability. Namely, SCAN properly describes the phonon properties of layered NaMnO₂ whereas SCAN + \( U \) does not. We further explore the Jahn–Teller (J–T) stability and magnitude of J–T distortion depending on \( U \) and find that SCAN results are consistent with Perdew–Burke–Ernzerhof functional, PBE + \( U \) results. Our results suggest that SCAN itself properly describes the physical properties of NaMnO₂ without adding \( U \) explicitly.

Keywords Sodium-ion battery · NaMnO₂ · SCAN functional · Jahn–Teller distortion · Phonon · First-principles calculations

1 Introduction
Rechargeable batteries have attracted a lot of interest as the demand for advanced energy storage technology is rapidly increasing around the world [1]. Lithium-ion battery (LIB) is one of the most successful rechargeable batteries and has already been commercialized in many places. However, the uneven distribution of lithium and increase of production cost [2–4] require an alternative energy source, which can replace LIBs. On the other hand, sodium is the second lightest alkali metal with abundant reserves and is readily available worldwide. Because of these advantages, sodium-ion battery (SIB) has been thought of as a promising alternative to LIB [3, 4].
develop the magnetic ordering at low temperature, which shows a strong interaction among Na ion, charge, and magnetic orderings in manganese oxides [14].

Since NaMnO 2 is one of the transition metal oxides, considering strong electron–electron correlation is essential for the accurate description of the physical properties of NaMnO 2 . The use of tunable Hubbard U parameters within DFT+U formalism greatly improves the reproducibility of calculations for experimental physical properties for layered transition metal cathode materials [17–23]. Thus, many previous theoretical studies have been done to explain the properties of NaMnO 2 with the inclusion of parametric Coulomb interaction U in a range of 2.5–5.0 eV under generalized gradient approximation (GGA) or Perdew–Burke–Ernzerhof (PBE) functional [24–29].

Recently, strongly constrained and appropriately normed (SCAN) was developed, a non-empirical meta-GGA functional [30, 31]. This functional does not require external tunable parameter U to describe the properties of many transition metal oxides [32–34]. However, previous studies also reported that SCAN functional still exhibits a self-interaction error [19, 35–39], which requires the Coulomb interaction U to reduce the error. Therefore, it is worth investigating the utility of the SCAN functional for each material.

In this paper, we have investigated the physical properties of layered O‘3-NaMnO 2 using the recently developed SCAN functional, especially focusing on phonon and lattice dynamics. We also considered the Coulomb interaction U to examine the accuracy of SCAN functional for NaMnO 2 . The phonon dispersion curves with the SCAN show the structural stability without imaginary phonon frequencies, while the phonon soft modes are observed with the SCAN+U. Because O‘3-NaMnO 2 is an experimentally synthesized stable structure, the phonon calculations clearly present that SCAN describes the properties of O‘3-NaMnO 2 better than SCAN+U. The calculated lattice parameters within the SCAN(+U) approach are compared with the experimental lattice parameters. Furthermore, we explore the J–T stability and the magnitude of J–T distortion under different U values and compare SCAN(+U) results with PBE+U calculations.

![Fig. 1](image_url)  
**Fig. 1** a Perspective view and b top view of the crystal structure of O‘3-NaMnO 2 . c Octahedral structure of MnO 6 with the J–T distortion and electronic configurations in the d-orbital energy level of Mn 3+ ion. The axis of elongation is the local z-axis. d Brillouin zone of a conventional unit cell of NaMnO 2 with high symmetry points. K1–K7 points correspond to (0.5,0,0), (0.5,0.5,0.0), (0.0,0.5,0.0), (0.0,0.0,0.5), (0.5,0.0,0.5), (0.5,0.5,0.5), and (0.0,0.5,0.5), respectively.
2 Computational method

All spin-polarized density functional theory (DFT) calculations were performed by the Vienna ab initio simulation package (VASP), which implements a pseudo potential band approach [40, 41]. We utilized SCAN (strongly constrained and appropriately normed semilocal density functional) [30, 31] as an exchange–correlation functional and also employed Perdew–Burke–Ernzerhof (PBE) functional for comparison [42]. We further included Coulomb correlation \( U \) to account for the correlated \( d \) orbitals of the Mn atom and used the Dudarev method for the double-counting correction [43]. The effective on-site correlation, \( U_{\text{eff}} = U - J \) of 3.9 eV is chosen unless otherwise specified [44]. To investigate the dependence on \( U \) in SCAN\(+\)U approach, the various \( U_{\text{eff}} \) values were used (0, 1, 2, 3, 3.24, 3.62, and 3.9 eV). \( U_{\text{eff}} \) of 3.24 eV and 3.62 eV are from the previous constrained random phase approximation calculations for layered NaMnO\(_2\) [21]. The energy cutoff for the plane waves is 520 eV. The \( k \)-point sampling is \( 6 \times 13 \times 6 \), which corresponds to the \( k \)-point density of 5000/atom. The monoclinic NaMnO\(_2\) with the space group \( C2/m \) has the experimental lattice parameters: \( a = 5.673 \) Å, \( b = 2.856 \) Å, \( c = 5.807 \) Å, and \( \beta = 113.290^\circ \) [16]. We fully relaxed the lattice parameters and the atomic coordinates from the initial experimental structure until the force was less than 0.01 eV/Å. For each calculation, we used the relaxed structure with the corresponding computational condition. The initial symmetry was maintained while relaxing atomic positions and lattice parameters.

We employed PHONOPY to calculate phonon dispersion and density of states [45, 46]. The force constants and dynamic matrix were calculated from supercells with finite displacements based on the Hellmann–Feynman theorem. The \( 2 \times 4 \times 2 \) supercell and the \( 3 \times 3 \times 3 \) \( k \)-point sampling were used for the phonon calculations.

3 Results and discussion

Figure 2 displays the phonon structures of layered O’3-NaMnO\(_2\) using the SCAN and SCAN\(+\)U methods. The Brillouin zone with high symmetry points used in the phonon dispersion curves is illustrated in Fig. 1d. In our calculations, O’3-NaMnO\(_2\) consists of a total of 8 atoms: 2 Na, 2 Mn, and 4 O atoms. Therefore, 24 modes are generated from three degrees of freedom. Among them, three acoustic modes with zero energy at the \( \Gamma \) point and 21 optical modes can be observed in the phonon bands.

The phonon bands with SCAN (Fig. 2a) show that O’3-NaMnO\(_2\) is dynamically stable, since imaginary phonon frequencies, i.e., soft phonon modes, are not observed in the phonon structure. This stable phonon dispersion is consistent with the experimental result of stable O’3-NaMnO\(_2\) [5, 16]. From the phonon DOS in Fig. 2a, O atoms contribute mostly in the high-frequency region above about 50 meV, while the displacements of Mn and Na ions dominate in the low and medium region in frequency because of their atomic mass. This vibration distribution is similar to the phonon of O’3-NaMnO\(_2\) with the PBE\(+\)U [24] and LiMnO\(_2\) [47].

On the other hand, the phonon structure with SCAN\(+\)U in Fig. 2b exhibits imaginary phonon frequencies through all high symmetry points. This phonon dispersion indicates that O’3-NaMnO\(_2\) is not stable in contrast to the phonon bands with the SCAN and the previous experiments. The soft phonon modes mostly originate from the lattice vibrations of Na and Mn ions as shown in the phonon DOS in Fig. 2b. Namely, the phonon bands with SCAN properly reproduce the experimental stability of O’3-NaMnO\(_2\), whereas those with the SCAN\(+\)U does not. We also tested the \( U \) dependence of the phonon dispersion curves. The phonon soft modes are obtained with \( U_{\text{eff}} > 1 \) eV. It suggests that SCAN\(+\)U is not appropriate to describe the properties of O’3-NaMnO\(_2\).
We have compared the experimental [16] and calculated lattice parameters using different U values. Table 1 shows the structural information of O’3-NaMnO2 and the relative errors of each calculated value compared to the experimental one. The lattice parameters with the SCAN have a relative error of less than 1% compared to the experimental values. It is worth noting that the calculated values with the SCAN have smaller relative errors than those of SCAN+U in all parameters. As U increases, the lattice parameter a and c tend to decrease, while the lattice parameter b increases. The result that the SCAN predicts the lattice parameters better than SCAN+U suggests that the SCAN approach would be more appropriate than SCAN+U for O’3-NaMnO2, which is consistent with our phonon calculations.

We further investigate the electronic DOS of O’3-NaMnO2 within the SCAN and SCAN+U approach as shown in Fig. 3. The Mn⁴⁺ ions in O’3-NaMnO2 are in the high spin states with 3d⁴ electrons. The calculated magnetic moment values of Mn ion from the SCAN and SCAN + U are 3.676 μB and 3.892 μB, respectively. The slight increase of the magnetic moment with U would be from the localization of Mn-d by applying U. The bandgap obtained from SCAN is 1.45 eV, which is similar to the band gap of ~ 1.3 eV from the previous PBE + U (U = 3.9 eV) calculations [24, 28]. The bandgap increases to 1.65 eV with the inclusion of the Coulomb correlation, U. In addition, the down spin states increase in energy with U: the oxygen valence bands and the Mn conduction bands are shifted up from about − 2 eV to − 1 eV and from about 1.5 eV to 3.5 eV, respectively.

Figure 3c, d shows the Mn d orbital decomposed DOS of O’3-NaMnO2 with the SCAN and SCAN+U, respectively. Both DOSs exhibit the clear splitting of d₃z²−r² and dₓ²−y², which results in the opening of the bandgap. This splitting is

| Lattice parameters | SCAN    | SCAN+U (U=3.9 eV) | Exp. [16] |
|-------------------|---------|--------------------|-----------|
| a(Å)              | 5.695 (0.40%) | 5.618 (−0.96%) | 5.673     |
| b(Å)              | 2.859 (0.10%) | 2.896 (1.42%) | 2.856     |
| c(Å)              | 5.754 (−0.91%) | 5.734 (−1.26%) | 5.807     |
| β(°)              | 113.4 (0.17%) | 112.5 (−0.65%) | 113.3     |

The relative errors of calculated values are in parenthesis.

Fig. 3 Total and atomic density of states (DOS) with a SCAN and b SCAN + U. Projected density of states (PDOS) of Mn d orbitals with c SCAN and d SCAN + U. The PDOS curves of d₃z²−r² and dₓ²−y² orbitals are filled with yellow and red colors, respectively.
obtained by the J–T distortion of the elongated Mn–O bonds aligned in the octahedral local z-direction. The inclusion of \( U \) with SCAN functional does not much alter the shape of the orbitals near the Fermi level, but shifts the energy of orbitals, in particular, by increasing the down spin states in conduction bands and decreasing \( t_{2g} \) orbitals in valence bands.

We have analyzed the energy and the magnitude of the J–T distortion using different \( U \) values in SCAN(\(+U\)). To investigate the applicable \( U \) value of this system, SCAN(\(+U\)) results are compared to that of PBE(\(+U\)) calculations as shown in Fig. 4. We compare our SCAN(\(+U\)) results to PBE(\(+U\)) (\( U=3.9 \) eV) instead of comparing each SCAN(\(+U\)) result to the PBE(\(+U\)) for the same \( U \) values, because the SCAN functional in general describes the electron–electron correlation more properly than the PBE functional without adding as large \( U \) as for PBE functional, and the value of 3.9 eV for PBE functional is generally chosen for Mn [24, 28, 44]. Figure 4a shows the energy difference \( \Delta E = E_{JT} - E_0 \) between the structures with and without the J–T distortion, where \( E_{JT} \) and \( E_0 \) indicate the energy with and without the J–T distortion, respectively. The total energy of the J–T distorted structure is lower than that of the undistorted structures regardless of \( U \) values. The energy difference \( \Delta E \) from the J–T distortion is \(-0.372 \) eV at \( U=0 \) eV and slightly becomes larger up to \(-0.434 \) eV at \( U=3.9 \) eV. We have compared the \( \Delta E \) using the SCAN(\(+U\)) with that using the PBE(\(+U\)) (\( U=3.9 \) eV), indicated as a dotted line in Fig. 4a. The \( \Delta E \) difference between PBE(\(+U\)) and SCAN(\(+U\)) becomes larger as \( U \) increases: the \( \Delta E \) differences of two functionals are 0.017 eV and 0.079 eV for SCAN and SCAN(\(+U\)) (\( U=3.9 \) eV). Namely, the results with the SCAN itself exhibit the closest results to that with the PBE(\(+U\)) (\( U=3.9 \) eV). This result is consistent with the prior studies that SCAN in general does not require explicit correction of \( U \) or at least requires smaller \( U \) values than PBE functional to describe the properties of materials [19, 32–34, 37–39].

Furthermore, we evaluated the magnitude of the J–T distortion as a function of the \( U \) value and compared it with the PBE(\(+U\)), as shown in Fig. 4b. The J–T distortion with the elongation along the local z-axis of MnO\(_6\) consists of two long bonds and four short bonds of Mn–O. The magnitude of the J–T distortion is defined as in

\[
\text{J-T distortion} = \frac{6(l_{\text{long}} - l_{\text{short}})}{2l_{\text{long}} + 4l_{\text{short}}},
\]

where \( l_{\text{long}} \) and \( l_{\text{short}} \) indicate the long and short bond lengths of Mn–O, respectively [48]. For example, with the SCAN, the long and short bond lengths are 2.410 Å and 1.927 Å, respectively, which gives the J–T distortion magnitude of 0.231. The relative errors of calculated bond lengths with the SCAN and the experiment [16] are 0.18\% and − 5.07\% for the long and short bond lengths, respectively.

As \( U_{\text{eff}} \) increases, the long bond length decreases, while the short bond length increases. For example, the long and short bond length with \( U=3.9 \) eV is 2.343 Å (−2.63\%) and 1.954 Å (−3.75\%), respectively. The values in parenthesis are the relative errors compared to the experiment. As a result, the J–T distortion slightly decreases as increasing of the \( U_{\text{eff}} \), whose trend is consistent with that using the PBE functional [24]. The relative errors of long and short bond lengths show different tendencies: the error of the long bond length increases and that of the short bond length decreases as increasing \( U_{\text{eff}} \). The relative error of average of long and short bond lengths with SCAN (−2.22\%) is slightly smaller than those of the SCAN(\(+U\)) (−2.53\% to −3.14\% in a range of 1–3.9 eV of \( U_{\text{eff}} \)). SCAN(\(+U\)) (\( U=0–1 \) eV) gives the closest J–T distortion with the PBE(\(+U\)) (\( U=3.9 \) eV). This result also suggests that the SCAN functional itself well describes the strong electron–electron interaction of NaMnO\(_2\) without considering significant explicit \( U \) inclusion as in the PBE functional.

![Fig. 4](image-url)
4 Conclusions

We have explored the lattice dynamics and electronic properties of O$^3$-NaMnO$_2$ using the SCAN($+U$) approach and demonstrate that SCAN without the direct inclusion of the Coulomb interaction $U$ properly reproduces the experimental stability and lattice parameters. The phonon dispersion curve with the SCAN exhibits the dynamical stability of O$^3$-NaMnO$_2$, which is consistent with previous experimental observation. On the other hand, the phonon band with the SCAN + $U$ shows the phonon soft modes implying structural instability. This phonon result suggests that the SCAN functional itself is an appropriate method to describe O$^3$-NaMnO$_2$. The calculated lattice parameters with the SCAN agree well with the experimental lattice parameters. Furthermore, we found that SCAN with smaller $U$ ($U < 1$ eV) gives similar results with the PBE + $U$ ($U = 3.9$ eV) according to the energy difference $\Delta E$ and the magnitude of the J–T distortion, which shows the SCAN functional describes electron correlation of O$^3$-NaMnO$_2$ more appropriately over PBE functional without sizable inclusion of $U$. This work demonstrates that lattice properties, especially phonon structures would be useful to find the appropriate computational approach for materials. We hope that this study can promote further investigation of the performance of SCAN functional for Na-ion cathode materials.

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