Ab Initio Study of AMBO₃ (A = Li, Na and M = Mn, Fe, Co, Ni) as Cathode Materials for Li-Ion and Na-Ion Batteries

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1. INTRODUCTION

Energy is one of the most critical global challenges of the 21st century.¹ So far, rechargeable intercalation batteries (namely Li-ion and Na-ion) are the best choice for energy-storage devices for application in portable electronic devices and (hybrid) electric vehicles. They offer a long lifetime, high volumetric energy density, flexibility, and low-weight design.²⁻⁴ Li-ion batteries (LIBs) were of highest importance for the applications. However, recently, sodium-ion batteries (SIBs) have attracted more attention over LIBs due to their lower toxicity and higher abundance of Na in the earth’s crust.³ The storage mechanism of SIBs is similar to LIBs; therefore, they may be a good alternative to LIBs in large-scale applications.⁵

Despite that the first commercial intercalation battery was a layered oxide cathode material (LiCoO₂), compounds with a polyanionic framework were known as important electrode materials due to their inductive effect.⁶ Polyanion cathode materials may exhibit very interesting properties, including the operating redox voltage that can be tuned by altering the transition metal (TM). A noble approach is used to evaluate electrical conductivity and rate capability. M = Fe compounds exhibit the lowest band gaps (BGs), and M = Mn compounds exhibit almost the highest one. The best electrical rate-capable compounds are estimated to be M = Mn ones and the worst are M = Ni ones. As far as cell potential is not the concern, AMnBO₃, ACoBO₃—AFeBO₃, and ANiBO₃ are the best to the worst considered cathode materials.

LiFePO₄ (170 mAh·g⁻¹) is currently known as the most promising polyanion cathode material for large-scale applications.⁹ Obviously, a polyanion compound with the lightest small oxyanion unit (BO₃)⁻³, for instance, LiFeBO₃, may deliver a larger capacity. Lithium/sodium metal borate (LiMBO₃/NaMBO₃) may form a unique category of insertion electrode materials owning the lowest weight polyanion, thereby delivering the highest possible theoretical capacity (ca. 220 mAh·g⁻¹) among the polyanion cathodes.¹⁰

The use of LiMBO₃ as the cathode material was first reported in 2001, where inferior electrochemical activity (less than 4%) was obtained.¹⁰ For a decade, researchers’ attempts to improve the performance resulted in failure, owing to low conductivity and kinetic limitations.¹⁰,¹¹,¹² Finally, Yamada et al.¹³ obtained a capacity of about 200 mAh·g⁻¹ (near the theoretical capacity) for optimized LiFeBO₃. Afterward, acceptable electrochemical performance was obtained for LiMnBO₃.¹³,¹⁴ Also, the electrochemical activity of LiCoBO₃ was reported.¹⁵ As researchers focused attention on Na-ion batteries, recently, NaMnBO₃ nanoparticles with conductive carbon matrix have been presented as a promising, relatively high-performance cathode material.¹⁵

It is well known that the substitution of TMs in a cathode structure could tune the voltage and performance of the cathode. Also, the replacement of Na by Li in a Li-ion cathode...
structure can present a new cathode for Na-ion batteries. In this study, we evaluate all LiMBO₃ and NaNBO₃ (M = Mn, Fe, Co, and Ni) cathode materials by density functional theory (DFT) as an ab initio study. The relevant properties of the considered cathode materials are compared with each other. The theoretical studies performed could present a new perspective to comprehend the behavior of the materials and shed light on understanding the characterization of the other similar (polyanion) cathode materials of intercalation batteries.

2. RESULTS AND DISCUSSION

The structural characteristics of the considered Li-ion (LiMBO₃, hereinafter called Li-family) and Na-ion (NaNBO₃, hereinafter called Na-family) cathode materials calculated by GGA are given in Table 1. Supplementary data of the table for GGA+U calculations is given in the Supporting Information. In our calculations, using the GGA and GGA+U methods were not cause to remarkable differences for the resulting structural parameters (the differences are lower than the method accuracy) and both of the methods lead to the same conclusions. This phenomenon was also observed in the other relevant investigations as well as for the other similar polyanion cathode materials. However, it is well known that GGA+U has a remarkable advantage over GGA for the prediction of band gap (in fact, extrinsic-like BG). According to Table 1, the maximum change of cell volume under deintercalation of the considered Li-family is about 5%, whereas for the Na-family it is about 14%. Changing the unit-cell volume after the extraction of Li/Na is a criterion for structural stability under charge–discharge. From the table, it is concluded that the Na-family may be structurally unstable (at least in contrast with the Li-family) in the C2/c crystal structure. Possibly, this is the reason that NaNBO₃ (s.g. of C2/c) has not significantly attracted researchers’ attention so far.

According to Table 1, in the lithiated state, by increasing the atomic number of the TM, cell volume (Ω) was increased; however, in the delithiated/desodiated state, cell volume did not change remarkably by changing TM. In contrast with the Li-family, for the intercalated state of the Na-family, increasing the atomic number of the TM led to a little decrease of Ω, excepting Ni. It is noteworthy that using the same calculation approaches, a different trend has been obtained for lithium orthosilicate structures. Therefore, it seems that the effect of the TM on Ω for polyanion cathode materials is not general and related to the structure frame nature as well as the intercalating element (Li/Na).

As was predictable, deintercalation led to the shrinkage of the structures. For the Li-family, increasing the atomic number of the TM increased the structure shrinkage (declining structural stability). For the Na-family, the trend was the same excepting Co. Accordingly, LiMnBO₃/NaCoBO₃ is the most structurally stable cathode during charge–discharge among its own family.

According to Table 1, the most structural changes occurred in the cell parameter c; however, b is the longest cell parameter. According to Figure 1, TM polyhedrals connect each other in their edge along the b axis. Consequently, it seems reasonable that the edge-connected polyhedral frame was avoiding shrinkage of b under extracting Li/Na. On the other hand, open channels for diffusion of Li/Na are in the (110) and (110) directions (Figure 2); both of them are perpendicular to the c axis. According to Table 1, the most shrinkage occurred along the c axis, excepting (Li/Na)NiBO₃.
The occurrence of the most shrinkage in perpendicular to the diffusion directions evokes domino-cascade model presented for LiFePO₄ to justify its V–C flat diagram (ideal voltage behavior). However, it is known that the voltage behavior of LiMBO₃ cathode materials is dramatically nonideal (due to the shape of their V–C curves). Here, it can be concluded that the domino-cascade model is not general. As a matter of fact, the low capacity obtained for this kind of material is due to its nonideal voltage behavior. The decline in the voltage during the discharge process causes reaching cut off voltage, so the capacity would not reach a reasonable value. So far, it is not clear which phenomenon is responsible for a cathode’s ideal or nonideal voltage behavior. Accordingly, a comparison of LiMBO₃ with ideal-behaving cathode materials (i.e., LiFePO₄) would be interesting to find the nature of the phenomenon from the theoretical point of view.

The calculated theoretical voltages of the considered cathode materials are shown in Table 2. Generally, the calculated voltage values of the Li-ion cathode family are higher than those of the Na-ion cathode family. The calculated voltage is increased by increasing the TM atomic number. The highest obtained voltage belongs to LiNiBO₃. Using the same approaches of calculations, for orthosilicate polyanion cathode materials (Li₂MSiO₄), also the highest voltage belongs to M = Ni. However, for layered oxide cathodes (LiMO₂), this trend has not been obtained.

For this kind of the cathode structure, the reported voltage–capacity diagrams in many of the works were not flat enough that the voltage plateau of the cathode could be recognized (it suffers from nonideal voltage behavior). Accordingly, a comparison between the theoretically obtained values and the experimental ones is not so reliable. However, for LiFeBO₃ and LiCoBO₃ cathode materials, the voltage plateau seems to be about 2.8 and 4 V, respectively. Therefore, the voltage values

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Table 2. Calculated Theoretical Voltage for AMBO₃ Cathode Materials, Obtained by the GGA and GGA+U Methods

| material   | GGA   | GGA+U |
|------------|-------|-------|
| LiMnBO₃    | 1.85  | 2.75  |
| LiFeBO₃    | 2.69  | 2.80  |
| LiCoBO₃    | 2.82  | 4.03  |
| LiNiBO₃    | 3.51  | 4.44  |
| NaMnBO₃    | 1.84  | 2.75  |
| NaFeBO₃    | 1.95  | 2.15  |
| NaCoBO₃    | 2.21  | 3.40  |
| NaNiBO₃    | 2.79  | 3.48  |

Supplementary diagrams of the table are given in Supporting Information.
Table 3. Intrinsic-Like Band Gaps (ILBGs) per eV Unit, for Spin-Up and -Down, Calculated by the GGA and GGA+U Methods for AMBO3 Cathode Materials in Their Intercalated (int.) and Deintercalated (deint.) States

| method | material       | spin-up | spin-down | controlling BG |
|--------|----------------|---------|-----------|----------------|
|        |                | int.    | deint.    | int.     | deint. | BG       |
| GGA    | LiMnBO3        | 6.0     | 7.0       | 6.8      | 6.5    | 6.8      |
|        | LiFeBO3        | 4.4     | 4.3       | 6.1      | 6.3    | 4.4      |
|        | LiCoBO3        | 6.1     | 4.9       | 5.9      | 6.5    | 6.1      |
|        | LiNiBO3        | 5.9     | 5.3       | 5.6      | 5.4    | 5.6      |
| GGA+U  | LiMnBO3        | 4.0     | 5.0       | 5.9      | 6.2    | 5.0      |
|        | LiFeBO3        | 3.6     | 5.2       | 6.6      | 6.2    | 5.2      |
|        | LiCoBO3        | 4.0     | 5.5       | 6.2      | 6.2    | 5.5      |
|        | LiNiBO3        | 4.3     | 0         | 5.4      | 6.3    | 4.3      |
| GGA    | NaNiBO3        | 4.8     | 7.0       | 5.9      | 6.5    | 6.5      |
|        | NaFeBO3        | 5.1     | 4.3       | 5.9      | 6.3    | 5.1      |
|        | NaCoBO3        | 5.4     | 4.9       | 5.1      | 6.5    | 5.4      |
|        | NaNiBO3        | 5.1     | 5.3       | 5.0      | 5.4    | 5.3      |
| GGA+U  | NaNiBO3        | 2.4     | 5.0       | 4.2      | 6.2    | 5.0      |
|        | NaFeBO3        | 2.7     | 5.2       | 6.4      | 6.2    | 5.2      |
|        | NaCoBO3        | 3.4     | 5.5       | 5.0      | 6.2    | 5.5      |
|        | NaNiBO3        | 3.5     | 0.0       | 4.9      | 6.3    | 3.5      |

“The intercalated and deintercalated structures in a cathode body are connected in serial manner; therefore, the lower conductivity should control electron (hole) transmission. Accordingly, the higher value among the resulted intercalated and deintercalated should be the governing BG of spin-up and -down, which is highlighted by underline. Among the governing BG values of spin-up and -down, the lower value should control the process, which is highlighted by bold type as the final governing BG for the material (intercalated—deintercalated pair). Supplementary diagrams of the table are given in Supporting Information.”

Table 4. Intrinsic-Like Band Gap (ILBG) Up/Down, Per eV Unit, Calculated by the GGA+U Method for the AMBO3 Cathode Materials in Their Intercalated and Deintercalated States

| material | spin-up | spin-down | controlling BG |
|----------|---------|-----------|----------------|
|          | int.    | deint.    | int.   | deint. | BG |
| LiMnBO3  | 3.5     | 0.8       | 5.1    | 4.0    | 3.5 |
| LiFeBO3  | 3.6     | 0.6       | 2.5    | 2.4    | 2.5 |
| LiCoBO3  | 4.0     | 0.6       | 3.4    | 2.6    | 3.4 |
| NaNiBO3  | 4.3     | 0         | 3.4    | 3.4    | 3.4 |
| NaFeBO3  | 2.4     | 0.8       | 4.2    | 4.0    | 2.4 |
| NaCoBO3  | 2.7     | 0         | 2.0    | 2.4    | 2.4 |
| NaNiBO3  | 3.2     | 0.6       | 3.1    | 2.6    | 3.1 |
| NaNiBO3  | 3.5     | 0         | 3.4    | 3.4    | 3.4 |

“Selection manner for the highlighted values is the same as in Table 3. For ELBG, GGA data are not reliable; thus, to avoid confusion, they are given in Supporting Information. Also, supplementary diagrams of the table are given in Supporting Information.”

obtained by GGA+U calculations seem more relevant than those obtained by GGA calculations (Table 3). Figures 3 and 4 illustrate the density of states (DOS) diagrams for LiMBO3 materials calculated by GGA and GGA+U, respectively. For NaNiBO3 materials, DOS diagrams calculated by GGA and GGA+U are shown in Figures 5 and 6, respectively. The spin is an inherent property of an electron; hence, DOS diagrams of spin-up and -down should be evaluated separately. In these figures, intrinsic-like valence bands are emphasized by the blue color background. Light-blue and dark-blue are related to spin-down and -up, respectively. Intrinsic-like conduction band spin-down and -up is displayed by the orange and yellow background, respectively. To determine intrinsic-like bands (ILBs), the bands created by the 3d orbitals (donors and acceptors) should be ignored. On the other hand, to determine extrinsic-like bands, the 3d orbital bands should be considered. Accordingly, intrinsic-like band gaps (ILBGs) and extrinsic-like band gaps (ELBGs) of the materials were measured, as given in Tables 3 and 4, respectively (see Figures S6 and S7 for better understanding ILBG, ELBG, Δ(C.B.), and Δ(V.B.) determination).

Considering the spin as an inherent property of an electron, between spin-down and -up band gaps (BGs) of a material, the lower value would control the procedure (because the lower energy is more desirable). Among the deintercalated and intercalated pair of a structure, the one that has the higher value of BG should be considered as controlling electron transmission (as far as the semiconductor junction approach” was not considered). Also, spin is an inherent property; therefore, a spin-up electron of the intercalated structure could not transmit to a spin-down state of the deintercalated structure, and vice versa. Therefore, in an intercalated—deintercalated pair, in the first step, we select the highest BG among intercalated spin-up and deintercalated spin-up, considering the resulting value as the governing BG of the spin-up of the pair (denoted by gBGup). Spin-down should be performed in the same manner, and the result should be the governing BG of the spin-down of the pair (denoted by gBGdown). gBGup and gBGdown are highlighted in Tables 3 and 4 by underlines. The lowest value among gBGup and gBGdown is taken as the governing value of rate capability criterion (the lowest value in the row).

Table 5. Values of Δ(C.B.) and Δ(V.B.), Up and Down, Obtained by the GGA and GGA+U Methods in DOS Diagrams for AMBO3 Cathode Materials, in eV Unit

| method | material       | Δ(C.B.) | Δ(V.B.) | controlling value |
|--------|----------------|---------|---------|------------------|
|        |                | up      | down    | up    | down   | BG      |
| GGA    | LiMnBO3        | 1.7     | 0.8     | 0.7    | 1.1    | 0.7     |
|        | LiFeBO3        | 1.3     | 2.3     | 4.2    | 2.1    | 1.3     |
|        | LiCoBO3        | 1.9     | 1.8     | 3.1    | 1.2    | 1.2     |
|        | LiNiBO3        | 1.9     | 1.8     | 2.5    | 2      | 1.8     |
| GGA+U  | LiMnBO3        | 1.5     | 1.1     | 0.5    | 0.8    | 0.5     |
|        | LiFeBO3        | 2.2     | 1.6     | 0.6    | 2      | 0.6     |
|        | LiCoBO3        | 1.5     | 1.2     | 0      | 1.2    | 0       |
|        | LiNiBO3        | 4.3     | 1.1     | 0      | 0.2    | 0       |
| GGA    | NaNiBO3        | 2.8     | 1.7     | 0.6    | 1.1    | 0.6     |
|        | NaFeBO3        | 2.9     | 2       | 3.7    | 1.6    | 1.6     |
|        | NaCoBO3        | 2.5     | 2.3     | 3      | 0.9    | 0.9     |
|        | NaNiBO3        | 2.2     | 2.2     | 2      | 1.8    | 1.8     |
| GGA+U  | NaNiBO3        | 2.4     | 2.9     | 0      | 0.9    | 0       |
|        | NaFeBO3        | 2.8     | 1.3     | 0.3    | 1.5    | 0.3     |
|        | NaNiBO3        | 2.1     | 1       | 0      | 0.2    | 0       |
|        | NaNiBO3        | 3.5     | 2.7     | 0      | 1.3    | 0       |

“For an individual structure, the lowest value between Δ(V.B.) and Δ(C.B.) up/down should be taken as the governing result. The resulted Δ(C.B.) and Δ(V.B.) values are highlighted by underline for each one. The lowest energy among resulted Δ(V.B.) and Δ(C.B.) is highlighted by bold type, which should be taken as the governing value of rate capability criterion (the lowest value in the row).
the governing/controlling BG of the cathode material. These values are highlighted by bold type in Tables 3 and 4. It is noteworthy that if we want to consider only one individual (de)intercalated structure, we should only consider the lowest BG between spin-up and -down. However, the intercalated−deintercalated structures are joint in a particle and they affect electron transmission through each other. This fact led us to use the above-explained approach.

Considering the ILBG of GGA (Table 3), the highest BGs (lowest conductivities) among the materials belong to TM = Mn compounds and the lowest ones to TM = Fe compounds (for both Li and Na-ions). Considering the ILBG of GGA+U (Table 3), TM = Ni and Co compounds exhibit the highest and the lowest electrical conductivity, respectively. However, as far as ILBG is considered, GGA results seem more relevant than GGA+U ones because in GGA+U an on-site Coulomb self-interaction correction potential was applied to the 3d orbitals, but the bands created by these orbitals are supposed to be ignored in the ILBG approach. Therefore, for ILBG, we prefer the conclusion drawn from GGA.

As far as the ELBGo approach is considered, only the GGA +U method should be reported because the well-known effect of the 3d orbitals leads to the underestimation of the ELBG of GGA. In this case, LiFeBO$_3$ and NaFeBO$_3$−NaMnBO$_3$ have the lowest BG (highest conductivity), whereas the lowest conductivities belong to LiMnBO$_3$ and NaNiBO$_3$. Interestingly, for the Li-family, ELBG and ILBG lead to a similar conclusion.

Generally speaking, from Tables 3 and 4, regarding the electron conductivity (band gap) of the structures in their ground states, AFeBO$_3$ compounds exhibit the best properties, while AMnBO$_3$ compounds are the worst (for NaMnBO$_3$ we prefer ILBG rather than ELBG).

Figure 3. Density of states (DOS) diagrams of the LiMBO$_3$ cathode materials calculated by the GGA method. Each pair of diagrams contains a lithiated−delithiated junction. The fermi level is aligned for each pair setting at zero. Spin-up and -down should be considered separately. Intrinsic-like valence-up, valence-down, conduction-up, and conduction-down bands are shown by dark-blue, light-blue, orange, and yellow backgrounds, respectively. The bands that were majorly generated by 3d orbitals were considered as donor/acceptor bands. The value of 0.3 of the horizontal axis was considered to determine the borders of the bands.
Despite the above discussion, considering the intercalated–deintercalated pair as a semiconductor junction is more relevant than considering the BGs. Actually, the final aim of evaluating the electric conductivity is to assess the rate of electron transition (in fact, it is rate capability). However, rate capability is rather controlled by the semiconductor-junction approach. In this case, the values of Δ(V.B.) and Δ(C.B.) up/down should be considered as a criterion of the rate capability. Aligning the Fermi level of the intercalated–deintercalated structures (as illustrated in Figures 3−6), Δ(V.B.) is the difference between their valence-band maxima, while Δ(C.B.) is difference between conduction-band minima of the intercalated–deintercalated structures. In that case, the lowest value among Δ(V.B.) and Δ(C.B.) up/down would control the process (see Figure S7 for a better understanding about Δ(V.B.) and Δ(C.B.) determination). Table 5 shows the results for the considered materials. Moreover, Δ(V.B.) and Δ(C.B.) are based on ILB; therefore, the GGA method seems to be more relevant than the GGA+U method. According to Table 5 and Figure 7, the best compounds for rate capability are TM = Mn ones, whereas the worst are TM = Ni compounds. As it can be seen, this conclusion is in contrast with the conclusion given from BG results.

3. CONCLUSIONS

The properties of AMBO₃ (A = Li and Na, M = Mn, Fe, Co, and Ni) with the monoclinic (C2/c) structure as the intercalation cathode material were evaluated by DFT (GGA and GGA+U methods) and simple physic concepts/rules. Structural properties, theoretical voltage, electrical properties, and electrical rate capability were evaluated as the most important issues of the known cathode substances.

Cell parameters and their change after deintercalation were calculated. Using structural changes by deintercalation as the criterion, structural stability was decreased by increasing the TM atomic number (excepting Co, only in its Na-family). While the structure of the Li-family was remarkably stable after delithiation, the Na-family (with C2/c structure) seemed to lack structural stability under desodiation. The maximum shrinkage was in the c axis, which was perpendicular to the most important diffusion channels.
The calculated theoretical voltages of the cathodes were reported. Generally, the considered Li compounds exhibit higher values of voltage than the Na ones. The voltage value was increased by increasing the TM atomic number in both GGA and GGA+U calculations. The highest obtained voltage belongs to LiNiBO$_3$ and then NaMnBO$_3$.

The recently proposed approach was used to evaluate the electrical properties of the materials. In this approach, ILBs should be considered separately for the calculated spin-down and -up DOSs. Considering the DOS of an intercalated–deintercalated pair, the highest spin-down/-up BG among intercalated and deintercalated DOS of spin-down/up is controlling the electron transition, and the lowest value between spin-down and spin-up is the governing BG. According to the evaluations, TM = Fe compounds exhibit the lowest BGs (highest conductivity) and TM = Mn almost the highest one (lowest conductivity). Nevertheless, the intercalated–deintercalated pair should be considered as a semiconductor junction in the (dis)charge process. Hence, according to the lowest obtained $\Delta(V.B.)/\Delta(C.B.)$ up/down values, the final conclusion is that the best rate-capable compounds are TM = Mn ones and the worst are TM = Ni ones.

In summary, the trend of changing properties by changing the TM in the BO$_3$ cathode family for Li- and Na-ion compounds is almost the same. As far as voltage was not the greatest concern, LiMnBO$_3$, LiCoBO$_3$–LiFeBO$_3$, and LiNiBO$_3$ are the best to the worst Li-ion BO$_3$ cathode materials, respectively. LiCoBO$_3$ is a little better than LiFeBO$_3$ however, Fe compounds have the benefit of lower cost and higher environmental friendliness. For Na-ion considered BO$_3$ cathodes, NaMnBO$_3$, NaCoBO$_3$, NaFeBO$_3$, and NaNiBO$_3$ are the best to the worst materials.

4. COMPUTATIONAL METHODS

All the calculations in this work were performed using the full-potential linear augmented plane-wave (FP-LAPW) method as implemented in the Wien2K code$^{28}$ within the framework of DFT.$^{29}$ Before calculating the DOS, internal energy, and other relevant parameters, full relaxation was performed for atomic positions and cell parameters using the Perdew–Burke–

![Figure 5. Density of states (DOS) diagrams of the NaMBO$_3$ cathode materials calculated by GGA. The other details are the same as in Figure 3.](https://dx.doi.org/10.1021/acs.omega.0c00718)
Ernzerhof generalized gradient approximation (PBE-GGA). The initial structure was taken from ref 31. It was for the LiFeBO₃ monoclinic crystal structure with space group (s.g.) of $C\bar{2}/c$ and cell parameters was 5.12901 Å, 8.8402 Å, 10.1002 Å, and 91.363° for $a$, $b$, $c$, and $\gamma$, respectively. The initial structure of each AMBO₃ compound was produced by replacing the TM atoms in the Fe sites and for NaMBO₃, replacing Na in the Li sites. For these structures, integrals were calculated over the Brillouin zone with k-points based on $7 \times 3 \times 7$ of Monkhorst Pack mesh. For the assessment of the relevant properties (DOS, energy, etc.), the calculations were carried out using PBE-GGA and GGA plus an on-site Coulomb self-interaction correction potential (GGA+U). The $U$ value was considered to be equal to 6 eV for Mn and Co and 5 eV for the Fe atom. The calculations were performed at spin-polarized mode, i.e., ferromagnetic, due to previous investigations about this kind of cathode materials. The major spin was defined as “up” in the calculations.

To estimate the rate capability and electrical conductivities, here we used a noble approach that resulted from applying physic and solid-state physic rules for the obtained DOS diagrams of the intercalated–deintercalated pair of the considered materials.

Inside the nonoverlapping spheres of muffin tin radius ($R_{\text{MT}}$) around each atom, the linear combination of the radial
solution of the Schrödinger equation times the spherical harmonics is used and the plane-wave basis set is used in the interstitial region. To expand the wave functions in the interstitial region, a plane-wave cut off value of $K_{max}R_{cut} = 7.0$ was used, where $R_{cut}$ is the smallest atomic sphere radius in the unit cell and $K_{max}$ is the magnitude of the largest $K$ vector. The Fourier-expanded charge density was truncated at $G_{max} = 12$ (Ryd)$^{1/2}$. The maximum value of the angular momentum ($l_{max}$) was used, where

Fourier-expanded charge density was truncated at

for the wave function expansion inside the atomic spheres. The convergence of the self-consistent iterations was performed within 0.0001 Ry.

Spheres of muffin tin radius ($R_{MT}$) values of Mn, Fe, Co, Ni, Li, B, and O atoms were set at 2.00, 2.00, 2.02, 2.02, 1.75, 1.28, and 1.28 a.u., respectively. The electron and spin configuration of the atoms were the software defaults and were Li: [He] 2s1, [2s2 2p1], O: [He] 2s2 2p4, Mn: [Ar] 3d5 (5s, 0j) 4s2 (1f, 1g), Fe: [Ar] 3d6.5 (4.5j, 2j) 4s2.5 (1j, 0.5l), and Co: [Ar] 3d7 (5j, 2j) 4s2 (1f, 1g).

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