The effect of octahedral distortions on the electronic properties and magnetic interactions in O3 NaTMO2 compounds (TM = Ti–Ni & Zr–Pd)

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Layered hexagonal compounds with formula NaTMO2, in which TM is a transition metal, often exhibit interesting magnetic, thermoelectric, and electrochemical properties. One obstacle in studying these compounds is the rich variety of their polymorphs, each with distinct symmetry and local coordination for the transition metal ions, which complicates finding general property trends for this family of materials. One area of research that lacks a concise overview is the magnetic properties of the NaTMO2 compounds. For instance, reports of conflicting experimental observations of the magnetic properties for the same compound is not unheard of. Such contradictions often stem from coarse structural characterization, restricted by instruments' range and resolution, which falls short in capturing the delicate structural details that dictate the magnetic ground state in these compounds. This study therefore presents a detailed and focused density functional insight into one important family of such layered materials, namely O3 NaTMO2 compounds in which TM is a fourth or fifth row transition metal element.

We start our investigations with compounds of R3m symmetry which is a common symmetry group among layered compounds. As shown in Fig. 1(a) and (b), the hexagonal representation of this structure consists of three alternating TMO2 and Na layers. The notation “O3” indicates that oxygen ions are stacked in ABCABC order and Na ions occupy the octahedral site with respect to the surrounding O ions. The primitive cell of the R3m O3 structure, presented in Fig. 1(c), has rhombohedral symmetry and the TM ion is located in the center of the primitive cell coordinated by six oxygen ions. The O–TM–O angles, marked η in Fig. 1(c), depend on the lattice parameters of the rhombohedral primitive cell (a and α) and the fractional coordinates of oxygen. If this angle is not exactly 90°, then it follows that the O–TM–O angles alternate between values smaller and larger than 90° resulting in a rhombohedral distortion to the TMO2 octahedra. These angles are marked η and θ in Fig. 1(d). This distortion decreases the octahedral symmetry and splits the energy levels of the t2g orbitals of the TM ions into a single a1g orbital and doubly degenerate e_g orbitals. The sequence of stabilization of the a1g and e_g orbitals is not however trivial. In addition to the rhombohedral distortion which is inherent to the R3m symmetry, NaTMO2 compounds may also experience additional distortions that further reduce the overall symmetry and influence the electronic structure. We will thoroughly examine all such distortions and determine how they influence the electronic and magnetic properties of O3 NaTMO2 compounds.

2. Computational and system settings

Spin polarized density functional theory (DFT) calculations were carried out within augmented plane-wave potential formalism as implemented in VASP code. Brillouin zone was sampled using a mesh generated by Monkhorst-Pack scheme with spacing of ~0.02 Å^{-1} among k points while the energy cutoff was set to 550 eV. The threshold for energy convergence was...
set to 10⁻⁷ eV per atom. Orbital population and bonding characteristics were examined using LOBSTER code.²⁵

The exchange-correlation functional was approximated by the Perdew–Burke–Ernzerhof method.¹⁶,¹⁷ To improve the electronic description of the compounds in term of localizing the d shell electrons of the transition metal elements, an orbital description of the compounds in terms of localizing the electrons justifies the smaller $U_{\text{eff}}$ value for the 4d elements. Among the different elements of the 3d and the 4d rows, a small variation in $U_{\text{eff}}$ is naturally expected. However, the choice of constant $U_{\text{eff}}$ for each row allows a more straightforward comparison.¹⁸ This procedure is further justified by the fact that the localization effects in NaVO$_2$ are not affected by slight variation of $U_{\text{eff}}$.¹⁹ Furthermore, as shown in Table 1, the applied $U_{\text{eff}}$ values reproduce the lattice constants reported in earlier experiments within ~1% deviation indicating the adequacy of the chosen values.

O₃ NaTMO$_2$ structure with R̅₃m symmetry in hexagonal representation, as shown in Fig. 1(a) and (b), was initially used for all compounds. To find the final geometries of NaTMO$_2$ compounds, the lattice parameters and all internal coordinates of the primitive cell were allowed to relax to forces smaller than 0.001 eV Å⁻¹. Furthermore, the geometry optimization was repeated with $2a \times 2a \times 1c$, $3a \times 3a \times 1c$ and $4a \times 4a \times 1c$ supercells with symmetry restrictions turned off, to detect any possible distortion that may lower the total energy by breaking the symmetry.

The magnetic phase stability was examined by comparing the total energies of the ferromagnetic system ($E_{\text{FM}}$) with those of competing antiferromagnetic phases. The energy of the ferromagnetic state was calculated by aligning the spin of all TM ions in the hexagonal cell parallel. The total energy of the C-type antiferromagnetic state ($E_{\text{AFM}}$) was calculated by aligning the spin of adjacent TM ions within the basal planes of a $2a \times 1a \times 1c$ supercell antiparallel. $\Delta E_{\text{AFM}}$ is defined as the difference between total energies $E_{\text{AFM}}$ and $E_{\text{FM}}$ the per TM ion:

$$\Delta E_{\text{AFM}} = \left| E_{\text{AFM}} - E_{\text{FM}} \right|$$  \hspace{1cm} (1)

Here, $n$ is the total number of the TM ions in the ferromagnetic supercell which is 3 for systems without distortions but larger for distorted systems. The energy of the A-type antiferromagnetic states ($E_{\text{AFM}}$) calculated by aligning the spin of TM ions in a $1a \times 1a \times 1c$ supercell antiparallel in alternating manner. $\Delta E_{\text{AFM}}$ is defined as the difference between $E_{\text{AFM}}$ and $E_{\text{FM}}$ the per TM ion:

$$\Delta E_{\text{AFM}} = \left| E_{\text{AFM}} - E_{\text{FM}} \right|$$  \hspace{1cm} (2)

Positive $\Delta E_{\text{AFM}}$ values indicate the preference of TM ion to align ferromagnetically within a TMO$_2$ plane (inter-plane) while positive $E_{\text{AFM}}$ indicate the preference of ferromagnetic coupling across TMO$_2$ planes (intra-plane).

3. Results and discussions

3.1. TM spin state

Based on the calculated spin populations presented in Table 2, the early 3d TM ions in NaTiO$_2$, NaVO$_2$ and NaCrO$_2$ generally conform to the octahedral crystal field splitting $t_{2g}e_g$. However, as we will see later, there are finer splittings among $t_{2g}$ states caused by symmetry considerations. Later TM ions in NaMnO$_2$, NaFeO$_2$ and NaCoO$_2$ compounds stabilize in high spin configuration. We found that the total energy of the NaMnO$_2$ compound rose by 1.306 eV/f.u. (f.u. is formula unit) when the Mn ion was set to low spin configuration ($t_{2g}^3e_g^0$). Similarly, the total energy of the NaFeO$_2$ ($t_{2g}^5e_g^0$) rose by 0.889 eV/f.u. and the total energy of the NaCoO$_2$ ($t_{2g}^5e_g^0$) rose by 0.157 eV/f.u. with respect to their corresponding high spin configurations. Ni ions in NaNiO$_2$, nonetheless, are stabilized in low spin configuration as setting Ni to high spin configuration ($t_{2g}^0e_g^0$) raised the total energy by 0.777 eV/f.u. Our calculations for Ni is agreement with the experimental observation of low spin NaNiO$_2$.²⁴

Unlike their 3d counterparts, early 4d TM ions in NaZrO$_2$ and NaNbO$_2$, deviate from $t_{2g}e_g$ splitting as Zr bears no magnetic moment and Nb adopts two distinct magnetic moments both significantly smaller than the anticipated $t_{2g}^0e_g^0$. NaZrO$_2$ in which Zr set to $t_{2g}^1e_g^0$ was 0.317 eV/f.u. higher in energy than...
Table 1 | Calculated and observed lattice parameters and structural data for NaTMO₂ compounds in hexagonal representation

| System       | Calculated $a$ (Å) | Calculated $c$ (Å) | Experimental $a$ (Å) | Experimental $c$ (Å) | Ref. TM-O (Å) | $\eta$ (°) |
|--------------|-------------------|-------------------|----------------------|----------------------|---------------|------------|
| NaTiO₂       | 3.042             | 16.551            | 3.037                | 16.260               | 10            | 2.11       | 92.25   |
| NaVO₂        | 3.055             | 16.242            | 2.996                | 16.100               | 11            | 2.10       | 95.57   |
| NaCrO₂       | 3.052             | 16.146            | 3.030                | 16.000               | 20            | 2.06       | 96.66   |
| NaMnO₂       | 3.087             | 16.234            | —                    | —                    | —             | 2.01, 2.26 | 92.16   |
| NaFeO₂       | 3.061             | 16.286            | 3.029                | 16.113               | 21            | 2.03       | 94.86   |
| NaCoO₂       | 2.908             | 15.776            | 2.891                | 15.612               | 21            | 1.95       | 96.13   |
| NaNiO₂       | 3.000             | 15.899            | 2.960                | 15.780               | 6             | 2.02       | 95.89   |
| NaZrO₂       | 3.206             | 17.217            | —                    | —                    | —             | 2.24       | 90.63   |
| NaNbO₂       | 3.298             | 17.817            | —                    | —                    | —             | 2.22 (unpuckered), 2.18 (puckered) | 91.15 |
| NaMoO₂       | 3.272             | 16.128            | —                    | —                    | —             | 2.19       | 96.90   |
| NaTeO₂       | 3.111             | 16.466            | —                    | —                    | —             | 2.14       | 93.12   |
| NaRuO₂       | 3.121             | 15.968            | 3.124                | 16.037               | 22            | 2.11       | 96.29   |
| NaRhO₂       | 3.151             | 15.725            | 3.097                | 15.527               | 23            | 2.10       | 97.03   |
| NaPdO₂       | 3.235             | 15.854            | —                    | —                    | —             | 2.07 (Pd⁴⁺), 2.10 (Pd⁵⁺), | 90.00 |

$^a$ The lattice parameter $a$ of the supercell has been divided by the number of hexagonal unit cells in corresponding dimensions of the supercell.

$^b$ These values correspond to the angles closest in value to 90° in distorted systems.

non-magnetic NaZrO₂ while NaNbO₂ with Nb fixed to $t_2g^{1−}$ configurations was 0.649 eV/f.u. higher than the presented ground state. Moreover, contrarily to the 3d TM ions, the later 4d TM ions in NaTMO₂ stabilized in low spin configuration. The total energy of NaTeO₂ rose by 1.086 eV/f.u. when Tc was set to high spin configuration ($t_{2g}^0$). Similarly, the high spin NaRuO₂ ($t_{2g}^0$ $e_g^0$) and NaRhO₂ ($t_{2g}^0$ $e_g^0$) were higher in energy than their low spin counterparts by 1.937 eV/f.u. and 4.642 eV/f.u. respectively.

### 3.2. Electronic structures

Fig. 2 shows the total and partial density of states (DOS) of 3d TM containing NaTMO₂ compounds. In the NaTiO₂, rhombohedral distortion in the TiO₆ octahedra splits the $t_{2g}$ orbitals of the spin-up channel into lower single fold $a_{1g}$ orbital which is occupied by Ti³⁺’s lone 3d electron and higher empty $e_g$ orbitals. Furthermore, $a_{1g}$ orbital is detached from the lower O 2p states and creates a pseudo-gap within the valence band. Consequently, the complete separation of Ti 3d states from O 2p states implies that Ti-O bond is highly ionic. In NaVO₂, the rhombohedral splitting is still dominant. However, contrary to the Ti case, the occupied $e_g$ orbitals have lower energy than the empty $a_{1g}$ orbital. Moreover, since the gap between $e_g$ states and O 2p states is now closed, there is a greater hybridization between $e_g$ and O 2p states which reduces the ionicity of the V-O bond compared to that of Ti-O bond. In NaCrO₂, through the energy of NaTcO₂ rose by 1.086 eV/f.u. when Tc was set to high spin configuration ($t_{2g}^0$).

Table 2 | Nominal electronic configuration of the d shell in NaTMO₂ compound, calculated number of unpaired d electrons (spin population) and the energy difference between ferromagnetic and antiferromagnetic states ($\Delta E$) are given. The nominal electronic configuration corresponds to the hypothetical complete ionic bonding. The magnetic ground state and the conduction type of all compounds also summarized here. FM, AAFM, GAFM stand for ferromagnetic, A-type and G-type antiferromagnetic states respectively.

| Compound      | Nominal configuration | Calculated unpaired d electrons | $\Delta E_{CAFM}$ (mEV) | $\Delta E_{AAMF}$ (mEV) | Magnetic ground state | Conduction |
|---------------|-----------------------|---------------------------------|-------------------------|-------------------------|----------------------|------------|
| NaTiO₂        | $t_{2g}^0$ $e_g^0$    | 0.897                           | $–395.365$              | $–0.228$                | GAFM                 | Insulator |
| NaVO₂         | $t_{2g}^0$ $e_g^0$    | 1.879                           | $–18.163$               | $–3.190$                | GAFM                 | Insulator |
| NaCrO₂        | $t_{2g}^0$ $e_g^0$    | 2.925                           | $–4.341$                | $–0.323$                | GAFM                 | Insulator |
| NaMnO₂        | $t_{2g}^0$ $e_g^0$    | 3.922                           | $–51.657$               | $0.197$                 | FM                   | Insulator |
| NaFeO₂        | $t_{2g}^0$ $e_g^0$    | 4.277                           | $–4.738$                | $–1.894$                | GAFM                 | Insulator |
| NaCoO₂        | $t_{2g}^0$ $e_g^0$    | 3.149                           | $–152.238$              | $–2.410$                | AAFM                 | Half metallic |
| NaNiO₂        | $t_{2g}^0$ $e_g^0$    | 1.378                           | $–24.564$               | $0.826$                 | FM                   | Half metallic |
| NaZrO₂        | $t_{2g}^0$ $e_g^0$    | 1.110, 0.350                    | $–12.68$                | $–1.240$                | Nonmagnetic          | Metallic |
| NaNbO₂        | $t_{2g}^0$ $e_g^0$    | 2.567                           | $–117.653$              | $–2.272$                | GAFM                 | Insulator |
| NaMoO₂        | $t_{2g}^0$ $e_g^0$    | 1.721                           | $–65.860$               | $2.565$                 | FM                   | Half metallic |
| NaNiO₂        | $t_{2g}^0$ $e_g^0$    | 0.858                           | $–13.462$               | $–5.030$                | Nonmagnetic          | Insulator |
| NaPdO₂        | $t_{2g}^0$ $e_g^0$    | 1.339                           | $11.315$                | $–2.750$                | AAFM                 | Insulator |
The merging of the \(e'_g\) and \(a_{1g}\) states in the spin-up channel, the band structure resembles conventional octahedral splitting where the spin-up \(t_{2g}\) states in the valence band are all occupied while the empty \(e_g\) states constitute the bottom of the conduction band. The DOS of NaMnO\(_2\) corresponds to the elongated Jahn–Teller distortion. The lower region of the valence band (\(-7 \text{ eV} \leq E \leq -4 \text{ eV}\)) is occupied by \(d_{xy}\) and \(d_{xz}\) states while the middle part (\(-4 \text{ eV} \leq E \leq -1.2 \text{ eV}\)) is occupied by \(d_{yg}\) states. The top of valence band is nevertheless occupied by \(d_{yz}\) states. As inferred from the DOS, the proximity of \(d_{xy}\) and \(d_{z^2}\) favors the high spin configuration for the Mn ions.

The DOS of the half-filled Fe 3d shell (\(t_{2g}^0e_{g}^2\)) in NaFeO\(_2\) exhibits a different arrangement when compared to earlier compounds. Here, due to strong electron–electron repulsion between the half-filled Fe 3d\(^5\) states and O 2p states, all of the occupied Fe 3d states are shifted downwards below O 2p states.

The proximity of the \(t_{2g}\) and \(e_{g}\) states in the spin-up channel to one another favors the high spin configuration for Fe ions as the spin-down \(t_{2g}\) states are \(\approx 11 \text{ eV}\) higher in energy than spin-up \(e_g\) states. In NaCoO\(_2\), the \(t_{2g}\) states of the spin-up channel, although mainly concentrate at the bottom of the valence band, still stretch over the entire valence band width and strongly hybridize with O 2p states. Furthermore, the tale of the spin-up \(t_{2g}\) states crosses the Fermi level creating half metallic conduction. Similarly, in NaNiO\(_2\), the spin-up \(t_{2g}\) states stretch over the valence band and cross the Fermi level while the spin-down \(t_{2g}\) states and \(d_{z^2}\) states remain confined within the middle of the valence band without crossing the Fermi level.

Fig. 3 show the total and partial DOS in 4d TM containing compounds. NaZrO\(_2\) exhibits strong metallic character as its Fermi level intercepts the Zr 4d states in the conduction band. Metallicity in NaZrO\(_2\) is facilitated by a metallic Zr–Zr bond which is caused by extraordinarily large Zr\(^{3+}\) ionic radius of NaZrO\(_2\).
~0.89 Å (ref. 25) and the Zr–Zr distance of 3.21 Å which is comparable to that in Zr metal. The metallic character of NaZrO$_2$ explains the lack of magnetic moment as there is no significant hybridization between Zr with O. NaNbO$_2$ also exhibits metallic conduction as the Fermi level crosses through the 4d states in the conduction band. However, as we will discuss later, due to puckering distortion, there are two distinct Nb species in this compound each with different levels of metallicity. The band structure of the NaMoO$_2$ shows a conventional octahedral distortion where the half-filed t$_{2g}$ states constitute the top of the valence band while the empty e$_g$ states are separated by ~1 eV above the Fermi level. In NaTcO$_2$, NaRuO$_2$ and NaRhO$_2$ compounds the spin-down channel of the t$_{2g}$ states is progressively filled as expected for the TM ions in low spin configuration. As will be discussed in detail in the next section, Pd in NaPdO$_2$ undergoes charge disproportionation among Pd ions. As shown in Fig. 4, two out of six Mn–O bonds in all MnO$_2$ octahedra are elongated causing a deviation from perfect R$_{3m}$ symmetry. This distortion is similar to the Jahn–Teller distortion depicted in Fig. 1(e). The long Mn–O bond is 2.26 Å while the short Mn–O bonds is 2.01 Å implying a 12.4% elongation. We found that perfectly R$_{3m}$ symmetric NaMnO$_2$ primitive cell with no elongation had a total energy 0.763 eV/f.u. higher than the distorted compound indicating that this distortion leads to significant stabilization.

### 3.3. Octahedral distortions

The geometry optimization conducted with larger supercells revealed that NaNbO$_2$, NaNbO$_2$ and NaPdO$_2$ compounds, each to a different extent, exhibits additional distortions in their TMO$_6$ octahedra. In NaMnO$_2$, as indicated by purple arrows in Fig. 4, two out of six Mn–O bonds in all MnO$_2$ octahedra are elongated causing a deviation from perfect R$_{3m}$ symmetry. This distortion is similar to the Jahn–Teller distortion depicted in Fig. 1(e). The long Mn–O bond is 2.26 Å while the short Mn–O bonds is 2.01 Å implying a 12.4% elongation. We found that perfectly R$_{3m}$ symmetric NaMnO$_2$ primitive cell with no elongation had a total energy 0.763 eV/f.u. higher than the distorted compound indicating that this distortion leads to significant stabilization.

NaNbO$_2$ showed puckering distortion [Fig. 1(f)] in half of its NbO$_6$ octahedra. As marked by blue arrows in Fig. 5(a), NbO$_6$ octahedra on every second row in [100] direction are alternately puckered to the left and the right along [010] direction while the octahedra on the adjacent row only had rhombohedral distortion. In the puckered NbO$_6$ octahedra, the short Nb–O bond was 2.18 Å while the long Nb–O bond was 2.23 Å indicating a 2.2% puckering distortion in bond lengths. The bond length in unpuckered NbO$_6$ octahedra had a median value of 2.22 Å. The puckering altered the electronic structure of the NaNbO$_2$ compound as ions in the puckered and unpuckered octahedra had distinct spin populations of 1.051e and 0.350e respectively. According to Fig. 5(b), Nb ions in the puckered octahedra has a significantly larger spin-up population (marked with red arrow) and smaller spin-down population (marked with blue arrow) compared to the Nb ions in unpuckered octahedra. To examine the stability induced by this distortion, we once set all Nb ions to low magnetization equal to that in the unpuckered octahedra and once again to high magnetization equal to that in the puckered octahedra and recalculated the total energy. The earlier setting raised the total energy of NaNbO$_2$ compound by 0.230 eV/f.u. while the latter setting raised the total energy by 0.649 eV/f.u. demonstrating the stabilizing effect of puckering distortion. Given that Nb’s total electronic population does not significantly depend on the puckering of NbO$_6$ octahedra, we infer that this relatively minor distortion does not cause charge disproportionation but rather only alters the magnetization of Nb ions.

The distortion in PdO$_6$ octahedra in NbPdO$_2$ were accompanied with charge disproportionation among Pd ions. As

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**Fig. 4** Jahn–Teller distortion in NaMnO$_2$ system. The elongated bonds are marked with black arrows while the shorter bonds are marked with purple arrows.

**Fig. 5** (a) The spin density isosurface of NaNbO$_2$ drown at 0.025 e Å$^{-2}$. Half of the NbO$_6$ octahedra undergo puckering distortion. The compressed bonds are marked with blue arrows. (b) The site-projected Nb 4d states for high magnetization (top panel) and low magnetization (bottom panel) Nb species.
different spin alignments result in the same energy, the compound is paramagnetic. Furthermore, $\Delta E_{\text{CAFM}}$ and $\Delta E_{\text{AFM}}$ are functions of the magnetic exchange integrals ($J$) which determine the Curie and Néel temperatures ($T_C$ and $T_N$) in compounds with long range magnetic ordering. According to the mean field approximation these critical temperatures depends linearly on the $J$. For instance, room temperature ferromagnetism requires positive $\Delta E_{\text{CAFM}}$ and $\Delta E_{\text{AFM}}$ values of $\sim 12$ meV.

As presented in Table 2, NaMnO$_2$, NaNbO$_2$, NaNiO$_2$, NaCoO$_2$ and NaPdO$_2$ have positive $\Delta E_{\text{CAFM}}$ values indicating inter-plane ferromagnetism which is defined as the ferromagnetic coupling among TM ions within the basal TMO$_6$ planes. This ferromagnetic coupling can be attributed to one of two distinct mechanisms: the kinetic p–d exchange interaction and the superexchange interaction. The density of states in Fig. 2(f)–(g) and Fig. 3(d) reveals a special p–d hybridization in NaCoO$_2$, NaNiO$_2$ and NaTcO$_2$ compounds. Because of this hybridization, the spin majority p states are shifted to higher energies, while the spin minority p states are shifted to lower energies. This hybridization scheme therefore creates spin polarized p states which mediate the ferromagnetic coupling. In NaMnO$_2$, NaNbO$_2$ and NaPdO$_2$, on the other hand, positive $\Delta E_{\text{CAFM}}$ values are caused by ferromagnetic superexchange. The prerequisite for ferromagnetic superexchange is a $\sim 90^\circ$ TM–O–TM angle which stabilizes the ferromagnetic coupling through $\pi$ TM–O bonds in TM–O–TM trimers. The octahedral distortions in these compounds orient the TM–O–TM angles in these compounds to $\sim 90^\circ$. Under perfect $\bar{R}3m$ symmetry, as shown in Fig. 1(c), the TM–O–TM angle is determined by O’s fractional coordinates and alternates between the supplementary angles $\eta$ and $\theta$ [defined in Fig. 1(c) and (d)] preventing the stabilization of the ferromagnetic phase. If a distortion, however, breaks the symmetry and brings the TM–O–TM angle closer to $90^\circ$, ferromagnetic superexchange can prevail. One should note that, as indicated in Table 1, the octahedral distortions in these compounds basically bring the O–TM–O angle closer to $90^\circ$. However, since these compounds do not have any octahedral tilting, the TM–O–TM angle, at least in certain planes, also approaches $90^\circ$ due to the similar distortion in neighbouring TM$_6$ octahedra. Those TM–O–TM angles assisting the ferromagnetic superexchange are marked $\alpha$ in Fig. 4–6. $\alpha$ is $91.67^\circ$ in NaMnO$_2$, $89.86^\circ$ in NaNbO$_2$ and $88.48^\circ$ in NaPdO$_2$. Contrary to our results, earlier DFT calculation of the NaMnO$_2$ compound using a small supercell restricted to C2/m symmetry, predicted weak frustrated antiferromagnetic ground state. This discrepancy shows the importance of taking into account the octahedral distortions that stabilizes the ferromagnetic ground state. Inferred from $\Delta E_{\text{CAFM}}$ values, the kinetic p–d exchange interaction seems to be generally stronger than the ferromagnetic superexchange interaction.

The magnetic coupling across the TMO$_6$ planes or intra-plane coupling, in principle, can be mediated a by second nearest neighbour superexchange interaction through TM–O–Na–O–TM chain via O’s p orbitals and Na sp$^2$ hybrid orbitals. Because of anisotropy in the $\bar{R}3m$ crystal structure which prevents the hybridization of TM d states with the p
states of adjacent TMO$_2$ layers, p–d kinetic exchange is not expected to result in significant intra-plane coupling. Among all compounds only NaMnO$_2$, NaNiO$_2$ and NaTeO$_2$ had small positive $\Delta E_{\text{AFM}}$ values indicating weak ferromagnetic intra-plane coupling resulting in $T_c$ values lower than $\sim$20 K. This prediction, particularly for the NaNiO$_2$ compound, is agreement with the earlier observation that measured a $T_c$ of $\sim$20 K. In the case of NaNbO$_2$, NaPdO$_2$ and NaCoO$_2$ compounds, the negative $\Delta E_{\text{AFM}}$ values along with positive $\Delta E_{\text{CAF}}$ values predict A-type antiferromagnetic ground state. For the rest of compounds for which both $\Delta E_{\text{AFM}}$ and $\Delta E_{\text{CAF}}$ are negative, G-type antiferromagnetic ground state prevails. Such antiferromagnetism has been observed in NaCrO$_2$ with $T_N$ = 40–50 K, NaVO$_2$ [ref. 35 and 38] and NaTiO$_2$ (ref. 39).

Last, note that relativistic spin–orbit interaction can play a significant role in determining the structural and magnetic properties of isolated TM octahedral complexes. However, in the context of bulk NaTMO$_2$ compounds that have been studied here, the role of spin–orbit interaction on the calculated $\Delta E_{\text{CAF}}$ and $\Delta E_{\text{AFM}}$ values is negligibly small. Spin–orbit interaction constant is proportional to the mass of the interacting ions and can be significant in 5d TM oxides such as iridates. However, experimental studies have shown that the magnitude of the spin–orbit interaction in 3d and 4d TM oxides such as cobaltates and rhenates is generally small. To verify this notion, we recalculated the $\Delta E_{\text{CAF}}$ and $\Delta E_{\text{AFM}}$ for NaPdO$_2$ with the inclusion of the spin–orbit calculation and obtained $\Delta E_{\text{CAF}} = 11.492$ meV and $\Delta E_{\text{AFM}} = -2.841$ meV. These values differ only by $\sim$0.1 meV from the values of Table 2 which have been obtained without including spin–orbit interaction. The role of spin–orbit interaction is expected to be even smaller for the rest of the compounds, especially for 3d NaTMO$_2$ as their molecular mass is considerably smaller than that of NaPdO$_2$.

4. Conclusions

We demonstrated that the rhombohedral distortion inherent to the 3$I_6$m symmetry stabilizes G-type antiferromagnetism in NaTiO$_2$, NaVO$_2$, NaCrO$_2$, NaFeO$_2$, NaMnO$_2$ and NaRuO$_2$ compounds. Inter-plane ferromagnetism however can be stabilized if the 3$I_6$m symmetry breaks due to additional octahedral distortions which is the case for NaMnO$_2$, NaNiO$_2$ and NbPdO$_2$. Here, because of favorable orbital orientation, the superexchange interaction stabilizes ferromagnetism instead of antiferromagnetism among the TM ions of the same TMO$_2$ plane. Additionally, strong p–d hybridization, as in NaCoO$_2$, NaNiO$_2$ and NaTeO$_2$ can also result in inter-plane ferromagnetism. In this case, due to its strength, the kinetic p–d exchange mechanism overcomes the underlying inter-plane antiferromagnetism. The intra-plane ferromagnetic coupling is mediated by a weak second neighbor coupling which prevails only in NaMnO$_2$, NaTeO$_2$ and NaNiO$_2$ giving rise to bulk ferromagnetism with low $T_c$.

The weak intra-plane coupling appears to be a general feature of O3 compounds. This is in contrast to the P2$_1$ structures in which the magnitudes of inter-plane and intra-plane coupling are of the same order. This is probably because this interaction strongly depends on Na’s coordination environment. This line of enquiry warrants further research.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work was supported in part by MEXT as a social and scientific priority issue: creation of new functional devices and high-performance materials to support next-generation industries to be tackled by using post-K computer. Computational resources were provided by Kyushu University’s high performance computing center and supercomputers at the Institute for Solid State Physics at the University of Tokyo and at the Center for Computational Sciences at University of Tsukuba.

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