Layered pnictide-oxide Na$_2$Ti$_2$Pn$_2$O (Pn = As, Sb): a candidate for spin density waves

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Abstract

From first-principles calculations, we have studied the electronic and magnetic structures of compound Na$_2$Ti$_2$Pn$_2$O (Pn = As or Sb), whose crystal structure is a bridge between or a combination of those of high-$T_c$ superconducting cuprates and iron pnictides. We find that in the ground state Na$_2$Ti$_2$As$_2$O is a novel blocked checkerboard antiferromagnetic semiconductor with a small band gap of about 0.15 eV. In contrast, Na$_2$Ti$_2$Sb$_2$O is a bi-collinear antiferromagnetic semimetal, with a small moment of about 0.5 $\mu_B$ around each Ti atom. We show that there is a strong Fermi surface nesting in Na$_2$Ti$_2$Pn$_2$O, and we verify that the blocked checkerboard and bi-collinear antiferromagnetic states both are the spin density waves induced by the Fermi surface nesting. A tetramer structural distortion is found in company with the formation of a blocked checkerboard antiferromagnetic order, in good agreement with the experimentally observed commensurate structural distortion but with space group symmetry retained after the anomaly happens.

(Some figures may appear in colour only in the online journal)

1. Introduction

Layered compounds of transition-metal elements frequently show interesting and novel electrical and magnetic properties and have been studied extensively. Among them, La$_2$CuO$_4$ [1] and LaFeAsO [2] as representatives are widely known because of their superconductivity with high critical temperature after doping or under high pressure, in which the CuO$_2$ square planar layers and the FeAs tetrahedral layers play a substantial role respectively. Now another class of layered compounds, namely layered pnictide oxides, are attracting much attention, which are built from stacking special octahedral layers M$_2$Q$_2$O (M = Fe or Ti; Q = As, Sb, S, or Se) alternating with other layers [3, 4]. Here an M$_2$Q$_2$O layer includes an anti-CuO$_2$-type M$_2$O square planar layer with two Q atoms respectively located above and below the center of each M$_2$O square unit. As shown in figure 1, the M$_2$Q$_2$O layer is in an octahedral layer structure, bridging between (or a combination of) the CuO$_2$ square planar layer and the FeAs tetrahedral layer structures, which is thus expected to show distinct electronic and magnetic properties and possibly superconductivity by doping or under pressure.

Fe$_2$Q$_2$O layer-based (Q = S or Se) oxychalcogenides were first synthesized in 1992 [3] and have recently been characterized to be antiferromagnetic insulators with a magnetic moment of 4 $\mu_B$ on each Fe ion experimentally [5] and with strong correlation effects suggested theoretically [6]. To our knowledge, there has been no any structural distortion found experimentally in these compounds.

Ti$_2$Pn$_2$O layer-based (Pn = As or Sb) oxypnictides have been also studied for some time. Compounds Na$_2$Ti$_2$Pn$_2$O were first synthesized in 1990 [4], and subsequently have been intensively investigated both experimentally and theoretically [7–10]. The temperature-dependent powder neutron diffraction measurement showed that there is a structural distortion in the Ti$_2$Sb$_2$O layer at a temperature of about
The scenario in Ti$_2$As$_2$O layer-based oxypnictide BaTi$_2$As$_2$O has been successfully synthesized [12, 13], which shows similar characteristics to Na$_2$Ti$_2$Pn$_2$O, namely there are anomalies observed as well in the temperature-dependent magnetic susceptibility, electrical resistivity, and heat capacity measurements at a temperature of about 200 K [12, 13].

This is different from the tetragonal-orthorhombic structural distortions observed in the iron pnictides. In particular, the anomalies in the temperature-dependent magnetic susceptibility, electrical resistivity, and heat capacity measurements at a temperature of about 200 K [12, 13]. Considering that the similar anomalies are observed in the iron pnictides, in which the superconductivity takes place when the Ti bond distance ratio of O–Ti–O/Sb–Ti–Sb increases below the transition temperature, but the crystal space group symmetry remains unchanged after the structural distortion [8, 9].

Recently, another new Ti$_2$As$_2$O layer-based oxypnictide BaTi$_2$As$_2$O has been successfully synthesized [12, 13], which shows similar characteristics to Na$_2$Ti$_2$Pn$_2$O, namely there are anomalies observed as well in the temperature-dependent magnetic susceptibility, electrical resistivity, and heat capacity measurements at a temperature of about 200 K [12, 13]. Considering that the similar anomalies are observed in the iron pnictides, in which the superconductivity takes place when the anomaly is suppressed, one thus speculates that the Ti$_2$Pn$_2$O layer-based oxypnictides may also be another parent compound for the high-$T_c$ superconductivity. In the iron pnictides, those anomalies are ascribed to the tetragonal-orthorhombic structural transitions accompanied by the collinear antiferromagnetic ordering [11]. The underlying mechanism is still in debate—either As-bridged antiferromagnetic superexchange interactions between fluctuating Fe local moments [14–16] or spin density wave instability induced by the Fermi surface nesting [17]. There is now more and more evidence in favor of the fluctuating Fe local moment picture. In particular, the neutron inelastic scattering experiments have shown that the low-energy magnetic excitations can be well described by the spin waves based on the quantum Heisenberg model [18, 19].

Here the formation of a local magnetic moment on Fe atom is mainly due to the strong Hund’s rule coupling on Fe 3d-orbitals; meanwhile the formed magnetic moments are embedded in itinerant electrons [14, 20, 21]. Moreover, a spin-fermion model was proposed to consider both the local magnetic moments and itinerant electrons on the same footing with the ferromagnetic double-exchange coupling between them [22–24].

The scenario in Ti$_2$Pn$_2$O layer-based oxypnictides is still very confusing. The experimentally observed anomalies in Na$_2$Ti$_2$Pn$_2$O suggest that there would be an antiferromagnetic transition, but no magnetic ordering has been detected. Theoretically, no ordered magnetic state has been found either for Na$_2$Ti$_2$Sb$_2$O in the first-principles electronic structure calculations reported in [25], which however show that there is Fermi surface nesting. It was then suggested that the experimentally observed anomalies could be due to charge density wave or spin density wave instability induced by such a Fermi surface nesting [25, 26].

In order to clarify the issue, we performed the thorough first-principles electronic structure calculations upon compounds Na$_2$Ti$_2$Pn$_2$O (Pn = As, Sb). We find that the ground state of Na$_2$Ti$_2$As$_2$O is a novel blocked checkerboard antiferromagnetic semiconductor. In contrast, the ground state of Na$_2$Ti$_2$Sb$_2$O is a bi-collinear antiferromagnetic semimetal. We verify that these two antiferromagnetic states both are indeed induced by the Fermi surface nesting.

2. Computational details

In our calculations the plane wave basis method was used [27]. We used the PW91-type [28] generalized gradient approximation for the exchange–correlation functionals. The ultrasoft pseudopotentials [29] were used to model the electron–ion interactions. After the full convergence test, the kinetic energy cut-off and the charge density cut-off of the Brillouin-zone integration in nonmagnetic state. The lattice parameters with the atomic positions were fully optimized by the energy minimization. It was found that the calculated lattice parameters have an excellent agreement with the experimental ones (less than 1.0% variance).

3. Results and analysis

Compound Na$_2$Ti$_2$Pn$_2$O (Pn = As or Sb) crystalizes in tetragonal ($I4/mmm$) symmetry and has a layered structure, as shown in figure 1(a). Its conventional tetragonal unit cell consists of two formula unit cells. However, its primitive unit cell is constructed by considering Na$_2$Ti$_2$Pn$_2$O as a triclinic crystal, in which only one formula unit cell is included, as shown in figure 1(b). On the other hand, Na$_2$Ti$_2$Pn$_2$O can be considered geometrically with an anti-K$_2$NiF$_4$ type structure, where a Ti atom is located between two oxygen atoms in a plane to form a square planar layer of Ti$_2$O, which is an anti-configuration to the CuO$_2$ layer in the high-$T_c$ cuprates. Meanwhile, a Ti atom is also four-coordinated by As atoms, forming a Ti$_2$As$_2$O layer where two As atoms are respectively located above and below the center of a Ti$_2$O square unit. The crystal is formed by stacking such Ti$_2$Pn$_2$O layers in a body-centered manner along the $c$ axis with the separation by a double-layer of Na atoms (figure 1(a)).

3.1. Nonmagnetic states

We first studied the nonmagnetic state of compound Na$_2$Ti$_2$Pn$_2$O (Pn = As or Sb), which would describe the high-temperature phase of these materials. The electronic band

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**Figure 1.** Crystal structure of Na$_2$Ti$_2$As$_2$O: (a) a conventional unit cell composed of two formula cells; (b) a primitive unit cell composed of one formula cell.
structure of this nonmagnetic state also provides a reference to further study the possible low-temperature magnetic phases, by analyzing which we can better understand the underlying mechanism or interactions that drive possible magnetic phase transitions and the related structural transitions. In the calculations, we adopted a primitive unit cell including only one formula cell (figure 1(b)).

3.1.1. Na$_2$Ti$_2$As$_2$O. After the full structural optimization, we find the tetragonal crystal lattice parameters of $a = b = 4.060$ Å and $c = 15.3892$ Å for Na$_2$Ti$_2$As$_2$O, in good agreement with the experimental values of $a = b = 4.0810$ Å and $c = 15.311$ Å measured at a temperature of 310 K [8]. The calculated electronic band structure and Fermi surface in the primitive unit cell are presented in figure 2. As we see, there are three Fermi surface sheets, contributed from the two bands crossing the Fermi energy level (figure 2(a)). Among them, the one sheet is of the hole type, forming an approximate square-shaped pipe centered at each $N$ point in the Brillouin zone (figure 2(b)); the other two are of the electron type—one is a $Γ$-centered box with the windows at its top and bottom, the other is a $X$-centered perfectly fluted pipe around the corner of the Brillouin zone (figure 2(c)). The volumes enclosed by these Fermi surface sheets are 0.186 electrons/cell and 0.186 holes/cell respectively. The electron carrier concentration is the same as the hole carrier concentration. Both are equal to 2.94×$10^{21}$ cm$^{-3}$. Compound Na$_2$Ti$_2$As$_2$O is thus a semimetal with a low carrier concentration between the ones in normal metals and semiconductors, similar to the recent iron pnictides—for example, LaFeAsO and BaFe$_2$As$_2$ [30, 31]. The density of states at the Fermi energy is 3.84 states per eV per formula unit. The corresponding electronic specific heat coefficient is $γ = 9.05$ mJ (K$^{-2}$ mol$^{-1}$) and the Pauli paramagnetic susceptibility is $χ_p = 1.56×10^{-9}$ m$^3$ mol$^{-1}$ (1 mole formula unit), in reasonable agreement with the measured value of $χ = 3.01×10^{-9}$ m$^3$ mol$^{-1}$ [9].

Inspection of the distribution of the density of states will help to clarify the atomic bonding character. Figure 3 plots the calculated total and atomic orbital-resolved partial density of states of Na$_2$Ti$_2$As$_2$O in the nonmagnetic state respectively. As expected, the calculations show that most electrons of the Na 3s-orbitals transfer into the O 2p-orbitals so that the occupied O 2p-orbitals are far below the Fermi energy level while the empty Na 3s-orbitals are much above the Fermi energy level (centered at +5.0 eV). Although the density of states at the Fermi level is dominated by the Ti 3d-orbitals, the density of states around the Fermi energy (from −3.0 to 2.0 eV) consists mainly of both Ti 3d-orbitals and As 4p-orbitals. In particular, the two peaks in the distribution of the As 4p-orbitals coincide with those of the Ti 3d-orbitals, as specifically shown in figure 4, which indicates that there is the hybridization between 4p$_x$ (p$_x$) orbitals and d$_{xz}$ (d$_{2z}$) orbitals,—namely, there is covalent bond formed between them. Figure 4 also specifies that it is the remaining three 3d-orbitals (d$_{xy}$, d$_{xz}$, and d$_{yz}$) that dominate in the density of states at the Fermi energy.

3.1.2. Na$_2$Ti$_2$Sb$_2$O. Likewise, we performed the calculations on Na$_2$Ti$_2$Sb$_2$O. The optimized tetragonal crystal lattice parameters are found to be of $a = b = 4.1369$ Å and $c = 16.6428$ Å, also in good agreement with the experimental values of $a = b = 4.160$ Å and $c = 16.558$ Å measured at a temperature of 150 K [8]. Figure 5 shows the electronic band structure and Fermi surface calculated in a primitive unit cell,
similar to those of Na$_2$Ti$_2$As$_2$O. From the volumes enclosed by these Fermi sheets, we determine that the electron and hole concentrations are 0.140 electrons/cell and 0.140 holes/cell respectively. The corresponding electron (or hole) carrier density is about 1.97 $\times$ 10$^{21}$ cm$^{-3}$. The density of states at the Fermi energy is 4.40 states per eV per formula unit. The corresponding electron specific heat coefficient and Pauli paramagnetic susceptibility are $\gamma = 10.37$ mJ (K$^{-2}$ mol$^{-1}$) and $\chi_p = 1.79 \times 10^{-9}$ m$^3$ mol$^{-1}$ (1 mole formula unit), respectively. The latter is in excellent agreement with the experimental measurement on a high-quality single crystal ($\chi = 1.51 \times 10^{-9}$ m$^3$ mol$^{-1}$) [9].

In figure 6, we plot the calculated total and atomic orbital-resolved partial density of states for Na$_2$Ti$_2$Sb$_2$O in the nonmagnetic state, which are overall similar to the ones of Na$_2$Ti$_2$As$_2$O (figure 3) except that the Sb 5p-orbitals have more contribution to the density of states at the Fermi energy than the As 4p-orbitals do. This is easily understandable because the Sb 5p-orbitals are more diffusive and extended than the As 4p-orbitals. Nevertheless, the atomic bonding character of Na$_2$Ti$_2$Sb$_2$O is basically the same as the one of Na$_2$Ti$_2$As$_2$O, i.e. O and Na atoms are in ionic state while there are covalent bonds formed between Ti and Sb atoms.

3.1.3. Fermi surface nesting. In order to well analyze the Fermi surface symmetry of compounds Na$_2$Ti$_2$Pn$_2$O (Pn = As, Sb) in connection with the crystal symmetry, we replot the calculated Fermi surfaces in the tetragonal conventional Brillouin zone as shown in figure 7, which clearly reflects the two-dimensional character of the electronic structures by the nearly $k_z$-dispersionless Fermi surface sheets, being consistent with the layered crystal structure. As we see, the Fermi surfaces in these two compounds are very similar in shape to each other. There are now six Fermi surface sheets for each Fermi surface, among which there are the two nearly degenerate square-box-like Fermi surface sheets centered around X contributed from the hole-type bands in conjunction with another two similar Fermi surface sheets centered around M but from the electron-type bands. Obviously these two sets of Fermi surface sheets between X and M are strongly nested with each other with a nesting vector of $(\frac{\pi}{a}, 0, 0)$ or $(0, \frac{\pi}{a}, 0)$. This can be directly verified by calculating the Lindhard response function $\chi_0(\vec{q}) = \sum_{i,j} f(\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})$, where $f(\epsilon_{\vec{k}})$ is the Fermi function of energy $\epsilon_{\vec{k}}$ at $\vec{k}$ point in the Brillouin zone for the $i$th band. As shown in figure 8, $\chi_0(\vec{q})$, as a function of $\vec{q} = (q_x, q_y, 0)$, indeed strongly peaks at point of $(\frac{\pi}{a}, 0, 0)$ or $(0, \frac{\pi}{a}, 0)$. Such a nesting between electron-band and hole-band usually means instability of the Fermi surface. Actually the early studies reported in [25, 26] first suggested that such a Fermi surface nesting in Na$_2$Ti$_2$Sb$_2$O could lead to a charge- or spin density wave instability in association with the observed anomalies in the temperature-dependent susceptibility and resistivity [8, 25, 26].

3.2. Magnetic states

The powder neutron diffractions have not yet detected any magnetic spin ordering in compounds Na$_2$Ti$_2$Pn$_2$O (Pn = As, Sb) even though the observed anomalous transitions in the temperature-dependent magnetic susceptibility and electric resistivity strongly suggested an antiferromagnetic transition in the compounds. Nevertheless, the neutron diffractions
found a commensurate structural distortion but without the space group symmetry breakdown.

At this point in time we still cannot exclude any weak magnetic ordering just based on the powder neutron diffraction because of its low resolution\(^3\). Thus, the issue that we meet here is still whether there exists a weak magnetic long-range order based on spin density wave or a completely spin-unpolarized charge density wave, either of which can be induced by the Fermi surface nesting and related to the observed structural distortion. In order to clarify this issue, we have carried out the systematical and extensive calculations on compounds Na\(_2\)Ti\(_2\)Pn\(_2\)O by constructing a wide variety of unit cells and magnetic orders.

We first performed the spin-unpolarized calculations with different unit cells and possible distortions, in particular by elaborately constructing new unit cells in consideration of the nesting vectors between X and M points in the Brillouin zone. It turns out that all the distortions and structures different from the original one are unstable. Thus our calculations do not support spin-unpolarized charge density waves in compounds Na\(_2\)Ti\(_2\)Pn\(_2\)O.

We then investigated whether or not any conventional magnetic order exists, such as the ferromagnetic, checkerboard antiferromagnetic, and collinear antiferromagnetic orders, all of which were found to be stable or metastable in Fe-based superconducting parent compounds [14, 30–32]. Our spin-polarized calculations show that none of these conventional magnetic orders are stable or metastable in compounds Na\(_2\)Ti\(_2\)Pn\(_2\)O, similar to the previous calculations that show no magnetic ordering found in Na\(_2\)Ti\(_2\)Sb\(_2\)O [25]. In the end, we decided to study possible unconventional magnetic orders based on spin density waves induced by the Fermi surface nesting.

3.2.1. Blocked checkerboard antiferromagnetic order and bi-collinear antiferromagnetic order. As presented above, there are two independent and orthogonal but equivalent nesting vectors \(Q_1 = (\frac{\pi}{a}, 0, 0)\) and \(Q_2 = (0, \frac{\pi}{a}, 0)\). Thus a possible linearly polarized spin density wave will be either a single-\(Q\) state described by \(\bar{M} \cos(Q \cdot \bar{R} + \varphi)\) on the Ti–Ti square lattice (\(\bar{R}\) being a lattice site vector, \(\bar{M}\) magnetization vector, and \(\varphi\) phase factor) with a wavevector \(Q\) equal to either \(Q_1\) or \(Q_2\), or a double-\(Q\) state described by \(\bar{M} \cos(Q_1 \cdot \bar{R} + \varphi_1) + \bar{M} \cos(Q_2 \cdot \bar{R} + \varphi_2)\) [34–38]. Accordingly, we elaborately constructed several kinds of magnetic orders. Through the calculations, we eventually found two stable peculiar magnetic orders induced by the Fermi surface nesting, called as blocked checkerboard antiferromagnetic order and bi-collinear antiferromagnetic order respectively, as shown in figure 9.

Figure 9(a) schematically shows the blocked checkerboard antiferromagnetic order, in which the Ti\(_2\)Pn\(_2\)O (Pn = As, Sb) layer is divided into \(\sqrt{2} \times \sqrt{2}\)-squares represented by the dash-dotted thin lines. Each square is a magnetic block with the moments of four Ti atoms being parallel. Between the nearest-neighbor blocks, the block moments are in anti-parallel. It should be emphasized that in each magnetic block the four Ti moments are centered around a Pn atom rather than an O atom. The calculations show that the latter case is unstable or energetically unfavorable. Thus in the blocked checkerboard antiferromagnetic order any pair of the next-nearest-neighbor Ti moments bridged by an O atom is always in anti-parallel. The blocked checkerboard antiferromagnetic order is of double-\(Q\) state, described by \(\bar{M} \cos(Q_1 \cdot \bar{R}) + \bar{M} \cos(Q_2 \cdot \bar{R} - \frac{\pi}{a})\). The magnetic unit cell is thus a \(2a \times 2a\) square. A similar blocked checkerboard antiferromagnetic order was also found in compound K\(_{0.8}\)Fe\(_2\)Se\(_2\) but with a \(\sqrt{5a} \times \sqrt{5a}\) magnetic unit cell and its formation is irrelevant to the Fermi surface nesting [39].

In figure 9(b), we schematically show the bi-collinear antiferromagnetic order, in which the Ti moments align in parallel along a diagonal direction and in anti-parallel along the other diagonal direction on the Ti–Ti square lattice. In other words, if the Ti–Ti square lattice is divided into two square sublattices A and B, the Ti moments on each sublattice take their own collinear antiferromagnetic order with the
same ferro-aligning direction [32]. Unlike in the blocked checkerboard antiferromagnetic order, here half of pairs of the next-nearest-neighbor Ti moments bridged by O atoms are in parallel while the other half are in anti-parallel, and likewise for the Pn atoms. The bi-collinear antiferromagnetic order is of single-\(Q\) state, described by \(\hat{H} \cos (Q_1 \cdot \hat{R}) + M \sin (Q_1 \cdot \hat{R}) = \sqrt{2}M \cos (Q_1 \cdot \hat{R} - \frac{\pi}{4})\). Here the magnetic unit cell is a \(2a \times a\) rectangle.

For a Fermi-surface-induced spin density wave, the issue whether it is a single-\(Q\) or multi-\(Q\) state has been discussed from the very beginning of its study [34–38]. The model study had shown that a multi-\(Q\) spin density wave, namely the superposition of multiple spin density waves with different but equivalent nesting vectors, in a metal having an isotropic Fermi surface nesting is more favorable energetically than a single-\(Q\) one [34–36]. However, an isotropic Fermi surface nesting is rare in realistic materials. For a well-known example of Cr, both hole-type and electron-type Fermi surface sheets are in octahedron-like shape but with considerable size differences. Consequently, a single-\(Q\) spin density wave is more stable in Cr [37, 38]. For compounds Na\(_2\)Ti\(_2\)Pn\(_2\)O, as one sees from figure 7, the Fermi surface nesting in Na\(_2\)Ti\(_2\)As\(_2\)O is nearly perfect between the hole-type surface sheets around X and electron-type surface sheets around M, while the nesting is rather anisotropic in Na\(_2\)Ti\(_2\)Sb\(_2\)O.

Accordingly, one expects that the double-\(Q\) spin density wave may be more favored than the single-\(Q\) one in Na\(_2\)Ti\(_2\)As\(_2\)O, and the single-\(Q\) one more favored than the double-\(Q\) one in Na\(_2\)Ti\(_2\)Sb\(_2\)O, which is indeed confirmed by the calculations presented below.

In addition, the magnetic moment around each Ti atom is found to be about 0.5 \(\mu_B\) in both blocked checkerboard and bi-collinear antiferromagnetic orders for both compounds Na\(_2\)Ti\(_2\)Pn\(_2\)O. This is consistent with the spin density wave mechanism, in which the moment should be small since its formation is only attributed to those states near the Fermi energy. Furthermore, considering that there is a large amount of antiferromagnetic quantum fluctuation in low-dimensional systems, the effective ordering moment around each Ti atom will be further much reduced. This is likely the reason why no magnetic ordering in compounds Na\(_2\)Ti\(_2\)Pn\(_2\)O has so far been detected by powder neutron diffraction (see footnote 3).

A bi-collinear antiferromagnetic order was first introduced in the study of Fe-based superconductors to describe the ground state of \(\beta\)-FeTe [32], very interestingly as strong evidence against the view of spin density waves in the Fe-based superconducting parent compounds, since there is no Fermi surface nesting vector to correspond to such a magnetic order, and moreover there is a large magnetic moment of about 2.5 \(\mu_B\) formed on each Fe atom.

The substantial difference between the two cases lies in the fact that there is only one electron in 3d-orbital for a Ti\(^{3+}\) ion. In contrast, there are five electrons in 3d-orbital for an Fe\(^{2+}\) ion. Accordingly, it is not expected that there is strong electronic correlation effect in Na\(_2\)Ti\(_2\)Pn\(_2\)O. We have performed a GGA + \(U\) calculation. We find that when \(U\) is larger than 2 eV, the ferromagnetic state becomes the lowest energy state for both compounds.

**Figure 10.** Na\(_2\)Ti\(_2\)As\(_2\)O in the blocked checkerboard antiferromagnetic state: (a) band structure; (b) magnetic unit cell; (c) Brillouin zone with selected high-symmetric points. Here the top of the valence band is set to zero.

This contradicts the experimental observation that there is an antiferromagnetic-like transition around 300 K for Na\(_2\)Ti\(_2\)As\(_2\)O and around 120 K for Na\(_2\)Ti\(_2\)Sb\(_2\)O [8–10].

**Figure 11.** Na\(_2\)Ti\(_2\)As\(_2\)O in the bi-collinear antiferromagnetic state: (a) band structure; (b) magnetic unit cell; (c) Brillouin zone with selected high-symmetric points. Here the top of the valence band is set to zero.

3.2.2. Na\(_2\)Ti\(_2\)As\(_2\)O. As aforementioned, the calculations show that any magnetic state, except the blocked checkerboard and bi-collinear antiferromagnetic states, is unstable and will relax into a nonmagnetic state for compound Na\(_2\)Ti\(_2\)As\(_2\)O.

To calculate the blocked checkerboard antiferromagnetic (AFM) order in Na\(_2\)Ti\(_2\)As\(_2\)O, we construct such a crystal unit cell consisting of four formula cells, which is triclinic with three base vectors of (2\(a\), 0, 0), (0, 2\(a\), 0), and (0.5\(a\), 0.5\(a\), 0.5\(c\)) respectively, as shown in figure 10(b). For the bi-collinear AFM order, the crystal unit cell is also constructed as a triclinic cell but with three base vectors of (2\(a\), 0, 0), (0, \(a\), 0), and (0.5\(a\), 0.5\(a\), 0.5\(c\)) respectively (see figure 11(b)).

After the full structural optimization, we find that compound Na\(_2\)Ti\(_2\)As\(_2\)O in the blocked checkerboard AFM order is energetically lower by about 4.5 meV/Ti than in the bi-collinear AFM order. Figures 10 and 11 show the electronic band structures of compound Na\(_2\)Ti\(_2\)As\(_2\)O in the blocked checkerboard AFM and bi-collinear AFM orders respectively. In both AFM orders, Na\(_2\)Ti\(_2\)As\(_2\)O is transformed into a semiconductor from a semimetal, with a small band gap of about 0.15 and 0.05 eV respectively; moreover, the moment around each Ti atom is found to be 0.56 and
Table 1. Calculated energies and magnetic moments of the nonmagnetic, ferromagnetic, checkerboard, collinear, bi-collinear, and blocked checkerboard antiferromagnetic states respectively, for Na$_2$Ti$_2$As$_2$O and Na$_2$Ti$_2$Sb$_2$O. The energy in the nonmagnetic state is set to zero. ‘—’ indicates that the corresponding magnetic state is not stable and will relax into a nonmagnetic state.

| Magnetic order         | Na$_2$Ti$_2$As$_2$O | Na$_2$Ti$_2$Sb$_2$O |
|------------------------|---------------------|---------------------|
|                        | Energy (meV/Ti)     | Moment (µB)         |
| Nonmagnetic            | 0                   | 0                   |
| Ferromagnetic          | —                   | —                   |
| Checkerboard           | —                   | —                   |
| Collinear              | —                   | —                   |
| Bi-collinear           | —20.8               | 0.53                |
| Blocked checkerboard   | —25.3               | 0.56                |

Table 2. Calculated lattice parameters with some selected bond lengths in the blocked checkerboard antiferromagnetic state versus nonmagnetic state for Na$_2$Ti$_2$As$_2$O.

|                  | Nonmagnetic | Blocked checkerboard |
|------------------|-------------|----------------------|
| a                | 4.0597      | 4.0701               |
| c                | 15.389      | 15.364               |
| Ti–O             | 2.0299      | 2.0347/2.0352        |
| Ti–As            | 2.7214      | 2.7175/2.7281        |
| O–Ti–O/(As–Ti–As)| 0.7459      | 0.7474               |

0.53 µB respectively. These calculated results are summarized in table 1.

Table 2 lists the calculated lattice parameters with the selected bond lengths. There is a structural distortion found for compound Na$_2$Ti$_2$As$_2$O in the blocked checkerboard AFM state, in which the four Ti atoms in a magnetic block slightly gather towards their center, an As atom. This gathering leads to the Ti–O bond slightly elongating. Correspondingly, the bond distances among the four Ti atoms in a magnetic block are reduced. These four Ti atoms will form a compact square. As a result, the Ti–Ti and Ti–As chemical bonds within each magnetic block become stronger. Such a tetramer lattice distortion is certainly due to the spin–lattice coupling since it cannot happen in any nonmagnetic state. It can be quantitatively described by the bond distance ratio of O–Ti–O/As–Ti–As, as reported in table 2. Such a distortion is in good agreement with the powder neutron diffraction observation that there is a commensurate structural distortion both space group symmetry is retained after the anomaly occurs [9].

There is also a structural distortion found for compound Na$_2$Ti$_2$As$_2$O in the metastable bi-collinear AFM state, which will be discussed in detail below in association with compound Na$_2$Ti$_2$Sb$_2$O.

3.2.3. Na$_2$Ti$_2$Sb$_2$O. We performed similar calculations on compound Na$_2$Ti$_2$Sb$_2$O. However, we found that compound Na$_2$Ti$_2$Sb$_2$O in the bi-collinear AFM order is the lowest in energy, about 8 meV/Ti lower than in the blocked checkerboard AFM order. In figures 12 and 13, we respectively show the calculated electronic band structures of Na$_2$Ti$_2$Sb$_2$O in the bi-collinear and blocked checkerboard AFM orders. In figure 12(b), the high-symmetry directions $\Gamma$−$Z$ and $\Gamma$−$M$ correspond to the moment parallel and anti-parallel alignments respectively. The shapes of the Fermi surface along these two directions are distinct. The volume enclosed by the electron-type Fermi surface sheets is larger than that enclosed by the hole-type Fermi surface sheets, which means that the electron carrier density is larger than the hole carrier density. It is noticed that the shapes of Fermi surface in both AFM orders are quite similar.

Unlike Na$_2$Ti$_2$As$_2$O, Na$_2$Ti$_2$Sb$_2$O remains semimetallic in both AFM orders. This is consistent with the experimental observation that the electric resistivity of Na$_2$Ti$_2$As$_2$O is higher than that of Na$_2$Ti$_2$Sb$_2$O by approximately a factor of 10 after the anomaly occurs [9]. Examining the Fermi surfaces of Na$_2$Ti$_2$Pn$_2$O in the nonmagnetic state (figure 7), we see that for Na$_2$Ti$_2$As$_2$O both the Fermi surface sheets around $X$ and $M$ are nearly in $C_4$ symmetry (figure 7(c)), which is thus expected to induce a full energy gap to be opened at the Fermi energy after the spin density wave transition. In contrast, for Na$_2$Ti$_2$Sb$_2$O the Fermi surface sheets around $M$
point are still in $C_4$ symmetry, but those around $X$ point take $C_2$ symmetry, especially for nonzero $k_z$ (figure 7(f)). Such a difference may only induce a partial energy gap to be opened at the Fermi energy. This should be the underlying physics that Na$_2$Ti$_2$As$_2$O becomes semiconducting while Na$_2$Ti$_2$Sb$_2$O remains semimetallic after the spin density wave transition, and may explain why the former in the isotropic blocked checkerboard AFM order is more favorable energetically while the latter in the anisotropic bi-collinear AFM order.

Table 3 summarizes the calculated lattice parameters with selected bond lengths. The calculations show that there is also a small structural distortion for compound Na$_2$Ti$_2$Sb$_2$O in the bi-collinear AFM state, similar to the case of $\beta$-FeTe in the bi-collinear AFM state. The lattice constant becomes slightly longer along the spin anti-parallel alignment to lower AFM energy and shorter along the spin-parallel alignment to lower further ferromagnetic energy. As a result, the crystal primitive unit cell on Ti$_2$Sb$_2$O layer deforms from a square to a rectangle.

Compound Na$_2$Ti$_2$Sb$_2$O in the metastable blocked checkerboard AFM state shows a similar tetramer structural distortion as found in Na$_2$Ti$_2$As$_2$O above.

4. Summary

We have presented the first-principles calculations of the electronic structures of layered pnictide oxides Na$_2$Ti$_2$Pn$_2$O (Pn = As, Sb). We find that the ground state of Na$_2$Ti$_2$As$_2$O is a novel blocked checkerboard AFM semiconductor with a small gap of about 0.15 eV, while the ground state of Na$_2$Ti$_2$Sb$_2$O is a bi-collinear AFM semimetal; and both have a small moment of about 0.5 $\mu_B$ around each Ti atom. Moreover, we find that there is a tetramer structural distortion in the blocked checkerboard AFM state, in which the four Ti atoms at each magnetic block gather towards their center of an As atom, in good agreement with the experimental observation of a commensurate structural distortion, but the space group symmetry is retained after the anomaly happening. We confirm that there is a strong Fermi surface nesting in Na$_2$Ti$_2$Pn$_2$O, and have verified that the two AFM states are both induced by the Fermi surface nesting. Actually, these two AFM states are close in energy for each of Na$_2$Ti$_2$Pn$_2$O, in which one is the ground state, and then the other is the metastable state. We thus consider layered pnictide oxide Na$_2$Ti$_2$Pn$_2$O as a strong candidate for spin density waves.

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Note added. While in the preparation of this manuscript, we learnt of a paper by David Singh [40], which reports that the instability at $X$ point associated with the Fermi surface nesting leads to a double striped (namely bi-collinear) antiferromagnetic state in compound BaTi$_2$Pn$_2$O. We have subsequently examined a variety of magnetic states for compounds BaTi$_2$Pn$_2$O (Pn = As, Sb) and find that none of them is stable except the blocked checkerboard and bi-collinear antiferromagnetic states. However, these two antiferromagnetic states are almost degenerated with the nonmagnetic state with a lower energy of less than 0.5 meV/Ti and the moment around each Ti atom is just about 0.2 $\mu_B$. The Fermi surfaces that we obtained for BaTi$_2$Pn$_2$O are similar to those shown in figures 6 and 7 reported in [40], in which the Fermi surface nesting clearly is dramatically weaker than that in compound Na$_2$Ti$_2$Pn$_2$O reported in the present paper (see figure 7).

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