Electronic Supplementary Information

\( d_z^2 \) Orbital character of polyhedra in complex solid-state transition-metal compounds

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Contents

1. Description of calculations S2

2. Electronic structure of 2H-type hexagonal perovskite SrTiS\(_3\) composed of face-sharing octahedra S3–S4

3. Electronic structure of \( \alpha \)-NaFeO\(_2\)-type SrHfN\(_2\) consisting of edge-sharing octahedral layers S4

4. Electronic structure of LiWN\(_2\) consisting of edge-sharing trigonal prismatic layers S5–S6

5. Supplementary references S6

List of Figures

1. Figure S1 (page S2) Brillouin zones for 4H-type hexagonal perovskite BaTiO\(_3\) and 2H-type hexagonal perovskites BaTiS\(_3\), 2H-SrTiS\(_3\), LiWN\(_2\), and LiMoN\(_2\)

2. Figure S2 (page S3) Electronic band structure and orbital characters for a lowest conduction band of 2H-type hexagonal perovskite SrTiS\(_3\)

3. Figure S3 (page S4) Density of states (DOS) of 2H-type hexagonal perovskite SrTiS\(_3\)

4. Figure S4 (page S4) Density of states (DOS) of \( \alpha \)-NaFeO\(_2\)-type SrHfN\(_2\)

5. Figure S5 (page S5) Electronic band structure and orbital characters for the lowest conduction band of LiWN\(_2\)

6. Figure S6 (page S6) Density of states (DOS) of LiWN\(_2\)
1. Description of calculations

The electronic-structure calculations were performed by using the L/APW+lo method, as implemented in the WIEN2k code. The generalized gradient approximation-Perdew-Burke-Ernzerhof functional (GGA-PBE) and the modified Becke-Johnson exchange potential (mBJ) were used. A GGA-PBE+U approach was also adopted, where U is the effective on-site Coulomb interaction correction. All calculations were performed by using experimental structural coordinates and lattice constants taken from powder neutron and X-ray diffraction measurements. The 4H-type hexagonal perovskite BaTiO3 crystallizes with a $P6_3/mmc$ structure (space group No. 194) with Ba atoms situated at the (0, 0, 0) and (1/3, 2/3, 0.096715) sites, Ti atoms at the (0, 0, 0) and (1/3, 2/3, 0.8463314) sites, and O atoms at the (0.51856, 0.0370, 0.14) and (0.83496, 0.6698, 0.08022) sites. The lattice parameters are $a = 5.72387$ Å and $c = 13.96497$ Å. The 2H-type hexagonal perovskites BaTiS3 and SrTiS3 also crystallize with a $P6_3/mmc$ structure (space group No. 194), with Ba (Sr) atoms situated at the (1/3, 2/3, 1/4) site, Ti atoms at the (0, 0, 0) site, and S at the (0.16551, 0.33212, 1/4) site for BaTiS3 or the (0.166, 0.332, 1/4) site for SrTiS3. The lattice constants are $a = 6.756$ Å, $c = 5.798$ Å for BaTiS3 and $a = 6.59$ Å, $c = 5.708$ Å for SrTiS3.

To calculate the electronic structures of $\alpha$-NaFeO2-type SrMN2 (M = Zr, Hf) and LiMoN2 by using the WIEN2k code, the lattice constants of the hexagonal system and the atomic positions of the rhombohedral system were used. $\alpha$-NaFeO2-type SrMN2 (M = Zr, Hf) crystallizes in the $R-3m$ structure (space group No. 166), with the Sr atoms situated at the (1/2, 1/2, 1/2) site, M-type atoms at the (0, 0, 0) site, and N at the (0, 0, $z$) site ($z = 0.23502$ for SrZrN2, $z = 0.23463$ for SrHfN2). The hexagonal lattice constants for these calculations are $a = 3.373$ Å, $c = 17.676$ Å for SrZrN2, and $a = 3.345$ Å, $c = 17.678$ Å for SrHfN2. LiMoN2 crystallizes in the $R3$ structure (space group No. 146), with the Li atoms situated at the (0.829018, 0.829018, 0.829018) site, Mo atoms at the (0, 0, 0) site, and N at the (0.25204, 0.25204, 0.25204) site and the (0.41414, 0.41414, 0.41414) site. The lattice constants are $a = 2.86723$ Å, $c = 15.813$ Å. LiWN2 crystallizes in the $P6_3/mmc$ structure (space group No. 194), with the Li atoms situated at the (0, 0, 0) site, W atoms at the (1/3, 2/3, 1/4) site, and N at the (0.12652, 0.65253) site. The lattice constants are $a = 2.881$ Å, $c = 10.346$ Å. The parameter $R_{mt}K_{max}$, where $R_{mt}$ is the smallest muffin-tin radius (in atomic units) and $K_{max}$ is the plane wave cutoff, controls the size of the basis, which was set to a high value of 7.0 for all materials. The values of $R_{mt}$ for the atomic spheres were 2.5 (Ba), 1.93 (Ti), 1.75 (O) for 4H-BaTiO3; 2.5 (Ba), 2.45 (Ti), 2.11 (S) for 2H-BaTiS3; 2.5 (Sr), 2.39 (Ti), 2.06 (S) for 2H-SrTiS3; 2.26 (Sr), 2.08 (Zr), 1.79 (N) for SrZrN2; 2.25 (Sr), 2.11 (Hf), 1.73 (N) for SrHfN2; 1.82 (Li), 2.11 (Mo), 1.82 (N) for LiMoN2; and 1.83 (Li), 2.17 (W), 1.78 (N) for LiWN2. 100 $k$-points in the Brillouin zones were used in calculating the electronic structures. The Brillouin zones for the electronic band structures of $\alpha$-NaFeO2-type SrMN2, 2H-type hexagonal perovskite BaTiS3, 2H-SrTiS3, LiWN2, and LiMoN2 are shown in Figure S1.

Figure S1. Brillouin zones for the electronic band structures of (a) 4H-type hexagonal perovskite BaTiO3, 2H-type hexagonal perovskite BaTiS3, 2H-SrTiS3, and LiWN2 and (b) of LiMoN2.
2. Electronic structure of 2H-type hexagonal perovskite SrTiS$_3$ composed of face-sharing octahedra

Figure S2 shows the electronic band structure and the orbital characters for the lowest conduction band of the 2H-type hexagonal perovskite SrTiS$_3$, which consists of face-sharing TiS$_6$ octahedral blocks. The results of electronic calculations for 2H-SrTiS$_3$ using the GGA-PBE functional and the mBJ exchange potential do not show energy-band gaps if the on-site Coulomb interaction is not considered. Energy-band gaps in 2H-SrTiS$_3$ are observed in the electronic structures calculated by the GGA-PBE+U method if the effective Coulombic interaction $U_{\text{eff}} > 8$ eV: an effective on-site $U_{\text{eff}}$ was therefore taken into account for the Ti site. The calculated energy-band gap (direct) of 2H-SrTiS$_3$ at the $\Gamma$-point is 0.18 eV ($U_{\text{eff}} = 9$ eV). The energy-band gaps vary depending on the value of $U_{\text{eff}}$. Figure S3 shows the density of states (DOS) in 2H-SrTiS$_3$. The lowest conduction band and the highest valence band in 2H-SrTiS$_3$ have mainly Ti 3d and S 3p orbital characters, respectively. Orbital characters for the lowest conduction band are shown in Figures S2b. Ti 3$d^2$ ($a_{1g}$) orbital character predominates in the lowest conduction band, except for the L–H directions. In the L–H directions of the electronic band structures, the Ti 3$d_x^2$ orbital character is dominant.

![Figure S2](image-url)

Figure S2. (a) Electronic band structure and (b) orbital characters for the lowest conduction band in the 2H-hexagonal perovskite SrTiS$_3$. The amount of Ti 3$d^2$ orbital character is shown by the width of the lines in the lowest conduction band. In Figure S2b, all s orbitals, p orbitals ($p_z$, $p_x + p_y$ for Sr and Ti, $p_x$, $p_y$, $p_z$ for S), and d orbitals ($d_z^2$, $d_x^2$–$d_y^2$, $d_{xy} + d_{xz}$) for Sr and Ti) are plotted. The electronic band structure was calculated by the GGA-PBE+U method ($U_{\text{eff}} = 9$ eV).
Figure S3. Total and partial density of states (DOS) of d orbitals in the 2H-hexagonal perovskite SrTiS$_3$. (a) Total DOS and partial DOS of Sr and S 3p orbitals, (b) d$_{z^2}$, (c) d$_{x^2}$, (d) d$_{xy}$, (e) d$_{xz}$ + d$_{yz}$ orbitals. The DOSs were calculated by the GGA-PBE+$U$ method ($U_{	ext{eff}} = 9$ eV).

3. Electronic structure of α-NaFeO$_2$-type SrHfN$_2$ consisting of edge-sharing octahedral layers

Figure S4 shows the density of states (DOS) in the α-NaFeO$_2$-type d$^0$-layered complex metal nitride SrHfN$_2$, which consists of edge-sharing HfN$_6$ octahedral layers. The DOSs of SrHfN$_2$ were calculated by using the mBJ exchange potential. The main contributors to the valence bands and the conduction bands are N 2p orbitals and Hf 5d orbitals, respectively. As with the other α-NaFeO$_2$-type d$^0$-layered complex metal nitrides SrZrN$_2$, NaNbN$_2$, and NaTaN$_2$, the Hf 5d$_{z^2}$ orbital characters predominate at the bottom of the conduction band (F-point).

Figure S4. Total and partial density of states (DOS) of d orbitals in α-NaFeO$_2$-type SrHfN$_2$. (a) Total DOS and partial DOS of Sr and N 2p orbitals, (b) d$_{z^2}$, (c) d$_{x^2}$, (d) d$_{xy}$, (e) d$_{xz}$ + d$_{yz}$ orbitals. These DOSs were calculated by using the mBJ exchange potential.
4. **Electronic structure of LiWN₂ consisting of edge-sharing trigonal prismatic layers**

The electronic band structure and the orbital characters for the lowest conduction band in LiWN₂ are shown in Figure S5. Electronic structures of LiWN₂ were calculated by using the GGA-PBE functional. In LiWN₂, three electronic bands (Bands C, D, and E) cross the Fermi level (0 eV). In Bands C and D, the predominant orbital characters are \( W 5d_{\sigma} \) near the Fermi level and near the K- and H-points, and \( W 5d_z \) below the Fermi level and near the \( \Gamma \)- and A-points. In Band E, N 2p orbital character predominates.

In Bands A and B, the dominant orbital characters are \( W 5d_z \) near the K- and H-points, and \( W 5d_{\sigma} \) in the \( \Gamma \)-A direction and near the K-point. As shown in Figure S6, large contributions from \( W 5d_z \) and \( 5d_{\sigma} + 5d_{\pi} \) orbitals are separately present near the Fermi level (0 eV) and at about 4 eV, corresponding to locations of Bands C and D near the Fermi level and of Bands A and B at about 5 eV. The electronic structure also contains some N 2p orbital character near the Fermi level and at about 4 eV (Figure S6).

Hybridized orbital characters combining \( W 5d_z \), \( 5d_{\sigma} + 5d_{\pi} \) with N 2p are present in the electronic bands near the Fermi level (0 eV) and at about 4 eV.

![Figure S5](image-url)

**Figure S5.** (a) Electronic band structure and (b–f) orbital characters of electronic bands (Bands A–E) near the Fermi level in LiWN₂. The amounts of \( W 5d_z \) orbital characters are shown in the electronic band structures by the widths of the line (Bands A–E near the Fermi level). All s orbitals, p orbitals (\( p_x, p_y, p_z \) for W, \( p_x, p_y, p_z \) for N), and d orbitals (\( d_z^2, d_{\sigma} + d_{\pi} + d_{\pi} \) for W) are plotted in Figures S5b–S5f. The electronic band structure was calculated by using the GGA-PBE functional.
Figure S6. Total and partial density of states (DOS) of d orbitals in LiWN\(_2\). (a) Total DOS and partial DOS of Li and N 2p orbitals, (b) d\(_{z^2}\), (c) d\(_{x^2-y^2}\) + d\(_{xy}\), (d) d\(_{xz}\) + d\(_{yz}\). The DOSs were calculated by using the GGA-PBE functional.

5. Supplementary references