Two-dimensional Obstructed Atomic Insulators with Fractional Corner Charge in MA$_2$Z$_4$ Family

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Abstract: Recently, a series of unique topologically trivial insulators (OAs), in which a portion of valence electrons necessarily have their centers located on some empty Wyckoff positions without atoms occupation in the lattice. The obstruction of centering these electrons coinciding with their host atoms is nontrivial and results in metallic boundary states when the boundary is properly cut. Here, on basis of first-principles calculations in combination with topological quantum chemistry analysis, we propose two dimensional MA$_2$Z$_4$ (M = Cr, Mo and W; A = Si and Ge, Z = N, P and As) monolayer family are all OAs. A typical case is the recently synthesized MoSi$_2$N$_4$. Although it is a topological trivial insulator with the occupied electronic states being integer combination of elementary band representations, it has valence electrons centering empty Wyckoff positions. It exhibits unique OAI-induced metallic edge states along the (110) edge of MoSi$_2$N$_4$ monolayer and the in-gap corner states at three vertices of certain hexagonal nanodisk samples respecting C$_3$ rotation symmetry. The readily synthesized MoSi$_2$N$_4$ is quite stable and has a large bulk band gap of 1.94 eV, which makes the identification of these edge and corner states most possible for experimental clarification.

Introduction. –Topological materials including topological insulators and topological semimetals have attracted intensive attention, mainly due to their nontrivial bulk band dispersion and metallic surface (or edge) states. In recent years, the development of topological quantum chemistry (TQC) and symmetry indicators provides convenient and efficient tools to the high-throughput discoveries of topological quantum material. Within the TQC theory, topological trivial insulators can be defined by band representations (BRs) of valence bands, which are equivalent to a set of exponentially localized Wannier functions. Any BRs can be given by a linear combination of elementary band representations (EBRs), which are induced from irreducible representations at maximal Wyckoff positions (WPs). If some of the coefficients of linear combination of elementary band representations (LCEBRs) are rational fractions, the material is a stable topological insulator or topological semimetal. If all the LCEBRs of a material exhibit non-negative integer coefficients, the materials is then a topological trivial insulator.

Recently, a series of unique topologically trivial insulators, dubbed obstructed atomic insulators (OAs), have been found. In difference from the BRs of atomic insulators induced from the atomic orbitals locating at atom-occupied Wyckoff positions (AOWPs), the BRs of OAs are induced from additional atom-unoccupied Wyckoff positions (AUWPs). In other words, for atomic insulators electrons fill atomic orbitals at the AOWPs, but for OAs a portion of electrons have to occupy those at the AUWPs. Note that in any periodic lattice of solid materials there are many so-called AUWPs, which can be easily identified via the international tables for crystallography. Nevertheless, not all AUWPs are necessary for OAs, while only those electron-filled AUWPs are necessary for OAs. Such electron-filled AUWPs for OAs are also named as obstructed Wannier charge centers (OWCCs). Importantly, when the cleavage termination cuts through those electron-filled AUWPs (namely, OWCCs) in an OAI, the metallic surface states will emerge. This crucial feature makes OAs be potential candidates for superconductivity and catalysis. To date, OAs including 3,383 paramagnetic and 30 magnetic materials are reported in three-dimensional (3D) materials. However, 2D OAs, which could be used in low dimensional devices, have not been systematically investigated.

Recently, 2D monolayer MA$_2$Z$_4$ family with septuple-atomic-layer lattices have been experimentally or theoretically reported. This MA$_2$Z$_4$ family crystallizes in five different crystalline phases, including 72 theoretically suggested stable materials. By inspecting the electronic structure of theoretically predicted stable monolayer $\alpha_1$-WSn$_2$N$_4$ semiconductor with an indirect band gap of 0.18 eV, we found that it possesses the typical inverted energy band between W-$d_{z^2}$ and N-$p_z$ orbitals at the centered $\Gamma$ point of the Brillouin Zone (BZ) around the band gap (Appendix Fig. A1). Although the band inversion typically signals to have nontrivial topological nature, both its topological indictor and mirror chern number equal to zero, indicating a topological trivial insulator. Furthermore, by deriving its electronic band structure of the edge boundary, metallic edge states nevertheless occur, which is very similar to the metallic surface states of 3D OAs. Interestingly, we further revealed that in total 16 monolayer MA$_2$Z$_4$ semiconductors with 34 valence electrons (VEC) including experimentally synthesized $\alpha_1$-MoSi$_2$N$_4$ exhibit sim-
FIG. 1. (Color online) Lattice and electronic structures of MSi\textsubscript{2}N\textsubscript{4} monolayer (M = Mo, W). (a) Lattice structures of \(\alpha\text{-}1\)-MSi\textsubscript{2}N\textsubscript{4} and \(\alpha\text{-}2\)-MSi\textsubscript{2}N\textsubscript{4} monolayers, where the black circle denotes the obstructed wannier charge center (OWCC). (b) The electronic band structures of \(\alpha\text{-}1\)-MoSi\textsubscript{2}N\textsubscript{4} and \(\alpha\text{-}2\)-MoSi\textsubscript{2}N\textsubscript{4} monolayer with the inclusion of spin-orbit coupling, where the red bands correspond to the band representation of \(\mathcal{E}_2@1a\) and \(\mathcal{E}_2@1e\). (c) The electron localization functions (ELF) of \(\alpha\text{-}1\)-MoSi\textsubscript{2}N\textsubscript{4} and \(\alpha\text{-}2\)-WSi\textsubscript{2}N\textsubscript{4} monolayer. \(1a\), \(1c\), and \(1e\) are Wyckoff positions. The solid lines denote the primitive cell of \(\alpha\text{-}1\)-MSi\textsubscript{2}N\textsubscript{4} monolayer materials. (d) The charges distribution of the band representation \(\mathcal{E}_2@1a\) and \(\mathcal{E}_2@1e\) of \(\alpha\text{-}2\)-MoSi\textsubscript{2}N\textsubscript{4}. The green hook face is the isosurface with value of \(0.008\) e\AA\textsuperscript{3} and the black circles denote the OWCCs at both \(1a\) and \(1e\). In the left panel of (d), to show \(1a\) position clearly, the top and bottom Si-N layers of \(\alpha\text{-}1\)-MoSi\textsubscript{2}N\textsubscript{4} monolayer are removed.

iliar electronic band features to \(\alpha\text{-}1\)-WSi\textsubscript{2}N\textsubscript{4} and they all are topological trivial insulators. Their special electronic structures make us think over whether these monolayer MA\textsubscript{2}Z\textsubscript{4} semiconductors are 2D OAIs. If yes, any novel properties will emerge in these 2D OAI family?

With this motivation, by means of first-principles calculations in combination with TQC analysis, we report 16 monolayer 34-VEC MA\textsubscript{2}Z\textsubscript{4} semiconductors as 2D OAIs. By taking the experimentally synthesized MoSi\textsubscript{2}N\textsubscript{4} semiconductor as a typical example, we identify the occurrence of the localized charge at the AuWPs as the crucial fingerprint of OAIs. Additionally, the metallic edge states appear in the band gap along the (110) direction on the boundary of MoSi\textsubscript{2}N\textsubscript{4} monolayer at which cleavage terminations exactly cut through OWCCs. Interestingly, in-gap corner states found in second-order topological insulators also occur in the \(C_3\)-symmetric hexagonal nanodisk of MoSi\textsubscript{2}N\textsubscript{4}.

Lattice structure of MoSi\textsubscript{2}N\textsubscript{4} monolayer. — The experimentally synthesized \(\alpha\text{-}1\)-MoSi\textsubscript{2}N\textsubscript{4} \textsuperscript{85}with 34 VEC belongs to MA\textsubscript{2}Z\textsubscript{4} family\textsuperscript{85}. In our theoretical predictions\textsuperscript{53} there are 15 monolayer 34-VEC MA\textsubscript{2}Z\textsubscript{4} semiconductors, which mainly crystallize in two classes of lattice structures, \(\alpha\text{-}1\) and \(\alpha\text{-}2\)-MA\textsubscript{2}Z\textsubscript{4}. For MoSi\textsubscript{2}N\textsubscript{4}, the formation energy of \(\alpha\text{-}1\)-MoSi\textsubscript{2}N\textsubscript{4} is 24 meV/atom lower than that of \(\alpha\text{-}2\)-MoSi\textsubscript{2}N\textsubscript{4}. Similarly, \(\alpha\text{-}1\) phase of WSi\textsubscript{2}N\textsubscript{4} is energetically more stable by 1.3 meV/atom than its \(\alpha\text{-}2\) phase. Both \(\alpha\text{-}1\) and \(\alpha\text{-}2\)-MoSi\textsubscript{2}N\textsubscript{4} have the hexagonal lattices with the atomic sequence of N-Si-N-Mo-N-Si-N (the space group of \(P\text{6}_3m\text{2}\) (No. 187))\textsuperscript{85}, as shown in Fig. 1(a). This septuple-atom-layer can be viewed as a monolayer with the inclusion of spin-orbit coupling, where the red bands correspond to the band representation \(\mathcal{E}_2@1a\) and \(\mathcal{E}_2@1e\). — The experimental band gap of 0.85 eV, comparable to the DFT-derived gap of 1.74 eV (PBE) and 2.30 eV (HSE\textsuperscript{06})\textsuperscript{53}. It is also a topologically trivial insulator, according to topological analysis using mirror Chern number. Conceptually, the occupied electronic bands
of 3D topological trivial insulator can be expressed by a non-negative integer linear combination of EBRs using the TQC theory.\cite{12,13} Since MoSi$_2$N$_4$ monolayer is a 2D material, only the band representations (BRs) of high symmetry points $\Gamma$, M and K at $k_z=0$ plane are considered. And since the EBRs of Wyckoff positions $2g$, $2h$ and $2i$ can be obtained by the combinations of EBRs of Wyckoff positions $1a$, $1c$, and $1e$, the maximum Wyckoff positions $1a$, $1c$, and $1e$ are chosen to perform the EBRs decomposition. Therefore, the LCEBRs of the occupied electronic bands of $\alpha_1$- and $\alpha_2$-MoSi$_2$N$_4$ have been derived in Table I. Note that we only listed a portion of LCEBRs, and the complete LCEBRs of $\alpha_1$- and $\alpha_2$-MoSi$_2$N$_4$ can be found in Appendix Table A1 and Table A2, respectively. Interestingly, for $\alpha_1$-MoSi$_2$N$_4$, the results of all the LCEBRs show that there are six EBRs ($\bar{E}_1@1a$, $\bar{E}_2@1a$, $\bar{E}_3@1a$, $\bar{E}_2@1c$, $\bar{E}_1@1e$ and $\bar{E}_2@1e$) with the non-zero integer combination. This fact means these six EBRs can not be decomposed and they have to be linked to electron-filled Wyckoff positions $2g$, $2h$ and $2i$. The $1e$ site is occupied by Mo atom whereas the $1a$ and $1e$ sites are null without any atomic occupation. In terms of the OAI definition, $\alpha_1$-MoSi$_2$N$_4$ is an OAI and the $1a$ and $1e$ sites are the OWCC. Similarly, the non-zero integer of LCEBR of the $1a$ and $1e$ AUWPs indicates that $\alpha_2$-MoSi$_2$N$_4$ is also an OAI, and the $1a$ and $1e$ AUWPs are the OWCC.

For the OAI feature, the most key point is to check whether the AUWPs have the localized charges (namely, electron filling). To elucidate the real-space charge localizations of MoSi$_2$N$_4$ we have thus visualized the electron localization function (ELF) (Fig. 1(c)) on the centering Mo-atom layer in which four indecomposable EBRs correspond to both $1a$ (null) and $1c$ (Mo) AUWP. It can be seen that the charges obviously localize at the $1c$ Mo site and the null $1a$ AUWP. The feature is more apparent in $\alpha_1$-WSi$_2$N$_4$ and $\alpha_2$-MoSi$_2$N$_4$ (see Appendix Fig. A2). We find that the localized charges at the $1c$ AOWP are mainly contributed by Mo atoms, whereas the ones at the null $1a$ AUWP originate from the orbital hybridizations between Mo and N$_4$ atoms, which is in good agreement with the observations in 3D OAI.\cite{51,16} By calculating the charge distribution of the OESs at the Fermi level within a...
nanowire model with a width of 20 unit cells, the charges localize around the OWCC-type 1a AUWP and the decay of the OES only has a depth of about 0.4 nm, as seen in Fig. 2(c). Such result is also verified by the first-principles calculations, in Fig. 2(d).

Next we turn to checking whether or not the 2D OAI of monolayer MoSi$_2$N$_4$ has the $d$-2 dimensional (namely zero-dimensional (0D)) in-gap corner states. We derived the electronic structures of the 0D nanodisk modeling of $\alpha_2$-MoSi$_2$N$_4$. By analyzing its structural details (see Appendix Fig. A3, Fig. A4, and Table A4), we constructed a $C_{3v}$-symmetric triangle and hexagonal nanodisk with the armchair edge to keep the electrically neutral stoichiometric ratio of 1:2:4 over Mo:Si:N. Since monolayer MoSi$_2$N$_4$ holds three types of maximum Wyckoff positions, there are three possible geometries for both triangle and hexagonal nanodisks by varying the type of atom at center site. No matter which type of atom sits at the center of the $C_{3v}$-symmetric triangle or hexagonal nanodisk, their stoichiometric ratio is always remained by removing the center atoms (see Appendix Table A4).

To argue whether the monolayer MoSi$_2$N$_4$ holds the in-gap corner states, one has to see the so-called gapped edge states on the boundaries and the in-gap corner states siting the vertexes of the $C_{3v}$-symmetric triangle or hexagonal nanodisk. However, depending on the filling anomaly at the center site, the in-gap corner states certainly occur in $C_{3v}$-symmetric triangle and hexagonal nanodisk.

Recently, a general formula to calculate the corner charges of the $C_{n}$ symmetry nanodisk was developed, as follows,

$$Q_{\text{corner}} = Q^{(n)}_{e-X} = \frac{\left(n^{(e)_X} - n^{(e)_C}\right) |e|}{n} \pmod{|e|}, \quad (1)$$

where $Q^{(n)}_{e-X}$ means the corner charge when the center of the crystal locates at the X site, $n$ is the fold of rotation axis. $n^{(e)_X}$ and $n^{(e)_C}$ are the ionic charges and the number of electronic Wannier functions at the X site, respectively. Applying Eq. (1) to monolayer MoSi$_2$N$_4$, we obtained the corner charge of the $C_{3v}$-symmetric triangle or hexagonal nanodisk of $Q^{(1a)}_{1a} = 1/3 |e|$, $Q^{(1c)}_{1c} = 2/3 |e|$ and $Q^{(1c)}_{1c} = 0 |e|$. Here, the 1a, 1c and 1c sites are responsible for the N, Si and Mo atoms at the center of the $C_{3v}$-symmetric crystals. Furthermore, we derived the energy spectra and charge distributions of our constructed triangle or hexagonal nanodisk. Note that the energy spectra and charge distribution of the N-centered hexagonal nanodisk are further compiled in Fig. 3(a, d), while the others are given in Appendix Fig. A5. It can be seen that three corner states at the N atoms meeting the $C_3$ rotational symmetry are in-gap and nearly zero-energy, labeling Nos. 718, 719 and 720. The other three corners without any charge distribution can be actually viewed as charge neutral "edges". The states of Nos. 718 and 719 are occupied and the No. 720 states are unoccupied. Because this system is spinless and the number of electrons of this system is 1438, we need to add two or subtract four electrons to make this system fully occupied or fully empty so that the system is gapped. The added two or subtracted four electrons correspond to -2/3 $|e|$ and 4/3 $|e|$ corner charge at its each $C_{3v}$-symmetry corner. This result is equivalent to the calculated 1/3 $|e|$ through Eq. (1). We note that the same conditions exist in the corner charge calculations of both Si-centered and Mo-centered hexagonal nanodisks. In Si-centered hexagonal nanodisk, three corner states are separated by one edge state (see Figs. 3b, e and Appendix Fig. A6). The corner state below edge state can be pushed into the gap of edge via an appropriate edge potential. In Mo-centered hexagonal nanodisk, the states near the Fermi level are distributed not only at three corners in similarity to those of N-centered hexagonal nanodisk, but also at three charge neutral "edges". Therefore, no corner states occur in their energy level near the Fermi level, which reflects well the zero corner charge of the Mo-centered hexagonal nanodisk (see Figs. 3c, f and Appendix Fig. A7).

Conclusions. — To summarize, we have identified the 16 MA$_2$Z$_4$ monolayer family materials with 34 valence electrons as 2D obstructed atomic insulators. They are featured by the occurrence of half-filled obstructed metallic edge states in 1D nanowires and in-gap corner states in 0D $C_{3v}$-symmetric hexagonal nanodisks. Moreover, the 2H-MoS$_2$ monolayer and $\alpha$-InSe monolayer, the two basic constituent units for the MA$_2$Z$_4$ monolayer family, are also identified as obstructed atomic insulators. Our work proposes a promising realization of 2D obstructed atomic insulators without inversion symmetry and provides a new platform to explore exotic phases of condensed matter and their associated novel properties.
FIG. 3. (Color online) (a-c) Energy spectra of C$_3$-symmetric hexagonal-shaped nanodisk of α$_1$-MoSi$_2$N$_4$ with the N, Si, and Mo atom in the center, where the occupied energy level is marked by the red arrow and red circles represent corner states. (d-f) The charge distributions of the 718, 722, and 716 energy levels appearing in (a)-(c), respectively.

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Appendix A: Computational methods

Vienna ab initio simulation package (VASP) was used to perform first-principles calculations. 20 Å vacuum was set to exclude the interactions between the layers with periodic images. 500 eV cutoff energy and 10 \( k \)-mesh were chosen in self-consistent calculation process. The structure was optimized until the force and energy less than \( 10^{-3} \) eV/Å and \( 10^{-6} \) eV/Å, respectively. All the \( C_3 \)-symmetric nanodisks were calculated by only \( \Gamma \) points. In addition, combating with Wannier90 code, density functional theory (DFT)-derived Wannier functions (WFs) was constructed. And the Hamiltonians for each compounds were derived. Iterative Green functions method was applied to calculate the semi-infinite spectral function.
FIG. A1. (a) The top view of constructed orthorhombic cell of $\alpha_2$-WSn$_2$N$_4$. The armchair edge is paralleled to mirror $M_x$. $L_{i_{\text{up}}}$ and $L_{i_{\text{down}}}$ ($i = 1, 2, 3$) are the edge above or below line $L_i$. The insert shows the Brillouin zone of orthorhombic and hexagonal cell. (b) The band structure of $\alpha_2$-WSn$_2$N$_4$. The blue circles and red square are the weight of W$^{d_2z}$ and N$^{p_z}$. The spectral function for (c) armchair, (d) $L_{1_{\text{up}}}$, (e) $L_{1_{\text{down}}}$, (f) $L_{2_{\text{up}}}$, (g) $L_{2_{\text{down}}}$, (h) $L_{3_{\text{up}}}$ and (i) $L_{3_{\text{down}}}$ edges. The bright gold, red and navy part represent surface states, bulk states and vacuum, respectively.
FIG. A2. Electronic structure of $\alpha_2$-MoSi$_2$N$_4$ monolayer. (a) The band structure of $\alpha_2$-MoSi$_2$N$_4$ monolayer, where the red bands correspond to the band representation of $E_2@1a$ and $E_2@1e$. (b) The ELF of $\alpha_2$-MoSi$_2$N$_4$ monolayer. 1$a$, 1$c$, and 1$e$ are Wyckoff sites, and charges localize at Wyckoff sites 1$a$ and 1$c$. The diamond solid line are the primitive cell of $\alpha_2$-MoSi$_2$N$_4$ monolayer. The charges distribution of band representation $E_2@1a$ (c) and $E_2@1e$ (d) of $\alpha_2$-MoSi$_2$N$_4$. The green hook face is the isosurface with value of 0.008. The black circles are OWCCs at 1$a$ and 1$e$.

TABLE A1. All possible decompositions of the BR of $\alpha_1$-MoSi$_2$N$_4$ into linear combination of the EBRs in double space group P6$m\overline{2}$ (No. 187). The first column gives the EBRs induced from different orbitals at Wyckoff positions 1$a$, 1$c$, and 1$e$; the numbers below are the multiplicities of each EBR in the corresponding decomposition.

| No. | $E_1@1c$ | $E_2@1c$ | $E_3@1c$ | $E_4@1a$ | $E_5@1a$ | $E_6@1a$ | $E_7@1e$ | $E_8@1e$ | $E_9@1e$ |
|-----|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| #01 | 6       | 7       | 5       | 1       | 0       | 0       | 1       | 1       | 1       |
| #02 | 5       | 6       | 4       | 2       | 1       | 1       | 1       | 1       | 0       |
| #03 | 4       | 5       | 3       | 3       | 2       | 2       | 1       | 1       | 0       |
| #04 | 3       | 4       | 2       | 4       | 3       | 3       | 1       | 1       | 0       |
| #05 | 2       | 3       | 1       | 5       | 4       | 4       | 1       | 1       | 0       |
| #06 | 1       | 2       | 0       | 6       | 5       | 5       | 1       | 1       | 0       |
| #07 | 5       | 6       | 4       | 1       | 0       | 0       | 2       | 2       | 0       |
| #08 | 4       | 5       | 3       | 2       | 1       | 1       | 2       | 2       | 1       |
| #09 | 3       | 4       | 2       | 3       | 2       | 2       | 2       | 2       | 1       |
| #10 | 2       | 3       | 1       | 4       | 3       | 3       | 2       | 2       | 1       |
| #11 | 1       | 2       | 0       | 5       | 4       | 4       | 2       | 2       | 1       |
| #12 | 4       | 5       | 3       | 1       | 0       | 0       | 3       | 3       | 2       |
| #13 | 3       | 4       | 2       | 2       | 1       | 1       | 3       | 3       | 2       |
| #14 | 2       | 3       | 1       | 3       | 2       | 2       | 3       | 3       | 2       |
| #15 | 1       | 2       | 0       | 4       | 3       | 3       | 3       | 3       | 2       |
| #16 | 3       | 4       | 2       | 1       | 0       | 0       | 4       | 4       | 3       |
| #17 | 2       | 3       | 1       | 2       | 1       | 1       | 4       | 4       | 3       |
| #18 | 1       | 2       | 0       | 3       | 2       | 2       | 4       | 4       | 3       |
| #19 | 2       | 3       | 1       | 1       | 0       | 0       | 5       | 5       | 4       |
| #20 | 1       | 2       | 0       | 2       | 1       | 1       | 5       | 5       | 4       |
| #21 | 1       | 2       | 0       | 1       | 0       | 0       | 6       | 6       | 5       |
TABLE A2. All possible decompositions of the BR of $\alpha_2$-MoSi$_2$N$_4$ into linear combination of the EBRs in double space group P$\bar{6}$m2 (No. 187). The first column gives the EBRs induced from different orbitals at Wyckoff positions 1a, 1c, and 1e; the numbers below are the multiplicities of each EBR in the corresponding decomposition.

| No. | $\bar{E}_1$ @1c | $\bar{E}_2$ @1c | $\bar{E}_3$ @1c | $\bar{E}_1$ @1a | $\bar{E}_2$ @1a | $\bar{E}_3$ @1a | $\bar{E}_1$ @1e | $\bar{E}_2$ @1e | $\bar{E}_3$ @1e |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| #01 | 5               | 6               | 5               | 2               | 1               | 0               | 1               | 1               | 0               |
| #02 | 4               | 5               | 4               | 3               | 2               | 1               | 1               | 1               | 0               |
| #03 | 3               | 4               | 3               | 4               | 3               | 2               | 1               | 1               | 0               |
| #04 | 2               | 3               | 2               | 5               | 4               | 3               | 1               | 1               | 0               |
| #05 | 1               | 2               | 1               | 6               | 5               | 4               | 1               | 1               | 0               |
| #06 | 0               | 1               | 0               | 7               | 6               | 5               | 1               | 1               | 0               |
| #07 | 4               | 5               | 4               | 2               | 1               | 0               | 2               | 2               | 0               |
| #08 | 3               | 4               | 3               | 3               | 2               | 1               | 2               | 2               | 1               |
| #09 | 2               | 3               | 2               | 4               | 3               | 2               | 2               | 2               | 1               |
| #10 | 1               | 2               | 1               | 5               | 4               | 3               | 2               | 2               | 1               |
| #11 | 0               | 1               | 0               | 6               | 5               | 4               | 2               | 2               | 1               |
| #12 | 3               | 4               | 3               | 2               | 1               | 0               | 3               | 3               | 2               |
| #13 | 2               | 3               | 2               | 3               | 2               | 1               | 3               | 3               | 2               |
| #14 | 1               | 2               | 1               | 4               | 3               | 2               | 3               | 3               | 2               |
| #15 | 0               | 1               | 0               | 5               | 4               | 3               | 3               | 3               | 2               |
| #16 | 2               | 3               | 2               | 2               | 1               | 0               | 4               | 4               | 3               |
| #17 | 1               | 2               | 1               | 3               | 2               | 1               | 4               | 4               | 3               |
| #18 | 0               | 1               | 0               | 4               | 3               | 2               | 4               | 4               | 3               |
| #19 | 1               | 2               | 1               | 2               | 1               | 0               | 5               | 5               | 4               |
| #20 | 0               | 1               | 0               | 3               | 2               | 1               | 5               | 5               | 4               |
| #21 | 0               | 1               | 0               | 2               | 1               | 0               | 6               | 6               | 5               |

TABLE A3. Summary of OAI features of 17 34-VEC MA$_2$Z$_4$ materials, 2H-MoS$_2$, and $\alpha$-InSe.

| No. | compounds name | phase type | OAI or not | OWCC |
|-----|----------------|------------|------------|------|
| 01  | CrSi$_2$N$_4$  | $\alpha_1$ | Y          | 1a,1e|
| 02  | MoSi$_2$N$_4$  | $\alpha_1$ | Y          | 1a,1e|
| 03  | MoSi$_2$N$_4$  | $\alpha_2$ | Y          | 1a,1e|
| 04  | WSi$_2$N$_4$   | $\alpha_1$ | Y          | 1a,1e|
| 05  | MoGe$_2$N$_4$  | $\alpha_1$ | Y          | 1a    |
| 06  | WGe$_2$N$_4$   | $\alpha_1$ | Y          | 1a    |
| 07  | CrSi$_2$P$_4$  | $\alpha_2$ | Y          | 1a,1e|
| 08  | MoSi$_2$P$_4$  | $\alpha_2$ | Y          | 1a,1e|
| 09  | WSi$_2$P$_4$   | $\alpha_2$ | Y          | 1a,1e|
| 10  | CrGe$_2$P$_4$  | $\alpha_2$ | Y          | 1a    |
| 11  | MoGe$_2$P$_4$  | $\alpha_2$ | Y          | 1a    |
| 12  | WGe$_2$P$_4$   | $\alpha_2$ | Y          | 1a    |
| 13  | MoSi$_2$As$_4$ | $\alpha_2$ | Y          | 1a,1e|
| 14  | WSi$_2$As$_4$  | $\alpha_2$ | Y          | 1a,1e|
| 15  | MoGe$_2$As$_4$ | $\alpha_2$ | Y          | 1a    |
| 16  | WGe$_2$As$_4$  | $\alpha_2$ | Y          | 1a    |
| 17  | WSn$_2$N$_4$   | $\alpha_1$ | Y          | 1a    |
| 18  | MoS$_2$        | 2H          | Y          | 1c,1e|
| 19  | InSe           | $\alpha$    | Y          | 1a,1e|
FIG. A3. (color online) The top left panel is the top view of MoSi$_2$N$_4$ monolayer. There are seven types of edges. Armchair edge is clear shown in figure. Another six edges, L$_{i\text{up}}$ and L$_{i\text{down}}$ ($i = 1, 2, 3$) edge, are obtained by three cutting lines, where subscript up and down are the edge above or below line L$_i$. The projected edge states for L$_{i\text{up}}$ and L$_{i\text{down}}$ ($i = 1, 2, 3$) and armchair edges are shown in another six panels.

TABLE A4. The structural information about nine C$_3$-symmetric nanodisks, where center type “2N” means two N atoms at the center of nanodisk and “2Si 2N” means two N atom and two Si atoms at the center of nanodisk; N$_{Mo}$, N$_{Si}$, and N$_N$ are the number of atoms of Mo, Si, and N in nanodisk; SR is the stoichiometric ratio in nanodisk, normalized down to N atoms.

| No. | C$_n$ | shape    | edge type | center type | N$_{Mo}$ | N$_{Si}$ | N$_N$ | SR       |
|-----|-------|----------|-----------|-------------|----------|----------|-------|----------|
| 01  | C$_3$ | hexagonal| armchair  | 2N          | 42        | 84       | 170   | 1.00:2.00:4.05 |
| 02  | C$_3$ | hexagonal| armchair  | 2Si 2N      | 42        | 86       | 170   | 1.00:2.05:4.05 |
| 03  | C$_3$ | hexagonal| armchair  | 1Mo         | 43        | 84       | 168   | 1.00:1.95:3.91 |
| 04  | C$_3$ | triangle | armchair  | 2N          | 30        | 60       | 122   | 1.00:2.00:4.07 |
| 05  | C$_3$ | triangle | armchair  | 2Si 2N      | 30        | 62       | 122   | 1.00:2.07:4.07 |
| 06  | C$_3$ | triangle | armchair  | 1Mo         | 31        | 60       | 120   | 1.00:1.94:3.87 |
| 07  | C$_3$ | triangle | L$_{2\text{down}}$ | 2N  | 15        | 42       | 98    | 1.00:2.80:6.53 |
| 08  | C$_3$ | triangle | L$_{1\text{down}}$ | 2Si 2N | 21        | 56       | 86    | 1.00:2.67:4.10 |
| 09  | C$_3$ | triangle | L$_{3\text{down}}$ | 1Mo  | 28        | 30       | 72    | 1.00:1.07:2.57 |
FIG. A4. (color online) Hexagonal and triangle $C_3$-symmetric nanodisk with armchair, and L_{down} ($i = 1, 2, 3$) edge, corresponding to Table A4.
FIG. A5. (color online) (a) The energy spectrum of C$_3$-symmetric N-centered hexagonal nanodisk of MoSi$_2$N$_4$. Where red circles is corner states. (b-g) show the charge distribution of its corresponding energy level.

FIG. A6. (color online) (a) The energy spectrum of C$_3$-symmetric Si-centered hexagonal nanodisk of MoSi$_2$N$_4$. Where red circles is corner states. (b-g) show the charge distribution of its corresponding energy level.
FIG. A7. (color online) (a) The energy spectrum of $C_3$-symmetric Mo-centered hexagonal nanodisk of MoSi$_2$N$_4$. (b-g) show the charge distribution of its corresponding energy level.