Abundance of Second Order Topology in Two-dimensional Insulators

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We have screened 71 two-dimensional (2D) materials with \(C_3\) symmetry for non-trivial second order topological order and find that 28 compounds exhibit an obstructed atomic limit (OAL). In the case of \(C_3\) symmetry, the second order topology can be calculated from bulk symmetry indicator invariants, which predict the value of fractional corner charges in symmetry conserving nanoflakes. The procedure is exemplified by MoS\(_2\) in the H-phase, which constitutes a generic example of a 2D OAL material and the predicted fractional corner charges is verified by direct calculations of nanoflakes with armchair edges. We also determine the bulk topological polarization, which always lead to gapless states at zigzag edges and thus deteriorates the concept of fractional corner charges in nanoflakes with zigzag edges. We then consider the case of TiCl\(_2\), which has vanishing polarization as well as an OAL and we verify that the edge states of nanoflakes with zigzag edges may indeed by passivated such that the edges remain insulating and the corner charges are well defined. For the 28 OAL materials we find that 16 have vanishing polarization and these materials thus constitute a promising starting point for experimental verification of second order topology in a 2D material.

The discovery of the quantum spin Hall effect in 2005 \(^1\)\(^2\) has initiated an immense interest in the topological properties of crystalline solids \(^3\)\(^9\). The initial \(Z_2\) classification of time-reversal invariant two-dimensional (2D) insulators was rapidly generalized to three-dimensional (3D) insulators \(^10\)\(^13\) and in 2011 it was shown that non-trivial topology may be protected by crystalline symmetries as well \(^14\)\(^16\). A common signature of such "first order" topological insulators is the appearance of gapless states that are guaranteed to exist at symmetry-conserving edges and surfaces in 2D and 3D materials respectively \(^7\)\(^17\)\(^19\).

In addition to the topological classification scheme based on time-reversal symmetry and crystalline symmetries, certain non-polar space groups allow for quantized values of the spontaneous polarization, which can thus be regarded as a topological index in itself \(^20\). The simplest example is comprised by the one-dimensional Su-Schrieffer-Heeger (SSH) chain \(^21\), which yields a polarization of either 0 or \(e/2\). The two phases correspond to Wannier charge centers being localized at inversion symmetric lattice sites or on bonds between sites. The latter case is referred to as a obstructed atomic limit (OAL) because the system cannot be adiabatically dissociated without breaking the symmetry. In a chain with open boundary conditions that preserve the symmetry and charge neutrality, the OAL phase will have Wannier charge centers at the end points that cannot both be occupied implying that the symmetry is either spontaneously broken or that the degenerate edge states are partially occupied. Alternatively, one may relax the condition of charge neutrality and the edge states will be fully occupied with a resulting fractional boundary charge of \(e/2\). The concept of topological polarization is readily generalized to higher dimensions and the ubiquitous metallic edge states in nanoparticles of 2D MoS\(_2\) have been attributed to a non-trivial topological polarization \(^22\). However, in 2D it is possible to obtain a different OAL phase where the edges are insulating, but carry a finite dipole moment that results in fractional corner states \(^20\)\(^23\)\(^27\). and the topology is then referred to as being of second order. In 3D, non-trivial second order topology gives rise to gapless hinge states that has been observed in bulk Bi \(^28\), but so far there is no direct experimental evidence for second order topology and the resulting fractional corner charges in a 2D material.

In the present letter we have screened 71 2D materials with \(C_3\) symmetry for non-trivial second order topology. Of these we find that 28 is in the OAL phase, which thus appears to be a rather common feature of 2D materials. We start by analyzing 2D MoS\(_2\) in the H-phase, which comprises a prototypical example of a material which can be characterized by an OAL phase as well as by a topological polarization in the armchair direction \(^22\)\(^23\)\(^30\). The OAL phase can be predicted from the bulk material and the emergence of fractional corner charges in symmetry-conserving flakes with armchair edges is explicitly verified. It is also shown that the topological...
polarization of MoS$_2$ yields metallic edges at any zigzag edge in agreement with previous predictions. We then consider the case of TiCl$_2$, which also exhibits an OAL phase, but has vanishing polarization and we show that in that case all nanotriangles exhibit fractional corner charges and edges that are either insulating or may be made so by including appropriate edge adsorbates. Finally, we summarize our results on the 28 OAL materials and we find that 16 of these have vanishing polarization and may therefore comprise good candidates for experimental verification of second order topology in 2D.

The unit cell of 2D MoS$_2$ is shown in Fig. 1 where the atomic positions and maximal Wyckoff positions are indicated. The OAL phase is related to occupancy of the 1b site, which may give rise to non-trivial fractional corner charges. The occupation of the maximal Wyckoff positions can be calculated from the symmetry indicator invariants [31]

$$\chi^{(3)} = \{[K_1^{(3)}], [K_2^{(3)}]\},$$

where $[K_1^{(3)}]$ is the difference in the number of occupied $C_3$ rotation eigenvalues between $K$ and $\Gamma$ (see Fig. 1). Here $i = 1$ refers to the rotation eigenvalue $e^{i\pi/3}$ and $i = 2$ refers to the rotation eigenvalue $-1$. The symmetry indicator [1] in itself constitutes a topological invariant, but depends on the choice of unit cell and non-trivial values (different from $(0, 0)$) do not in general describe OAL phases. Instead, the OAL phase can be related to appearance of fractional corner charges which can be calculated from [31]

$$Q_c(C_3) = \frac{2e}{3}([K_1^{(3)}] + [K_2^{(3)}]) \mod 2e,$$

and thus comprises a $Z_3$ classification of the second order topology. In addition, if the unit cell is chosen with the origin at a three-fold rotation axis the electronic part of the 2D polarization becomes quantized according to

$$P_{el}^{(3)} = \frac{e}{3A} \left(2[K_1^{(3)}] + [K_2^{(3)}]\right) (2a_1 + a_2) \mod eR_j/A,$$

where $A$ is the unit cell area, $R_j$ is an arbitrary lattice vector and the lattice constants are chosen as $a_1 = a\hat{x}$ and $a_2 = -\frac{1}{2}a\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$ with the lattice constant $a$. The polarization thus constitutes a distinct $Z_3$ topological index in that dimensionless units may take values of $(0, 0)$, $(2/3, 1/3)$ and $(1/3, 2/3)$, which are just the high symmetry points of the Wigner-Seitz cell. For a single band these values thus correspond to Wannier charge centers located at 1a, 1b or 1c respectively.

In the present work we have computed the symmetry indicator invariant [1] in MoS$_2$ and 70 other 2D insulators with the same space group taken from the computational 2D materials database (C2DB) [32]. We have used the electronic structure software package GPAW [33, 34] using the PAW method and a plane wave basis. The computational parameters and lattice parameters are the same as those used in the C2DB. In Fig. 2 we show the band structure of MoS$_2$ and in Tab. 1 we show the contributions to the symmetry indicator invariants from the different groups of bands. The total invariant is simply a sum of the different contributions and is given by $\chi^{(3)} = (-2, 3)$. The OAL phase thus emerges from the two upper valence bands that yields a Wannier center on the 1b Wyckooff position. The resulting Wannier functions originate from hybridization of $d$-orbitals from the three adjacent Molybdenum atoms [22] and give rise to a fractional corner charge of $Q_c = \frac{2e}{3}$ in MoS$_2$. It should be emphasized that unlike the case of quantum spin Hall insulators, the OAL phase is not driven by spin-orbit coupling and OAL phases are thus expected to be rather common in other transition metal dichalcogenides and dihalides with similar electronic structure. The four deep valence bands that are mainly composed of $S$ $s$-orbitals have a non-vanishing symmetry indicator invariant and simply corresponds to four states located at the S atom (the 1c site). These states have trivial second order topology, but contributes to the topological polarization. With the choice of unit cell in Fig. 1 the charges of the nuclei do not contribute to the polariza-
FIG. 3. Eigenvalue spectrum of a $C_3$ symmetric MoS$_2$ flake with armchair edges. The greyscale indicates the weight of a given state at edges (black is full edge localization). The top inset shows the three (Kramers degenerate) eigenvalues at the Fermi level, which are filled by four electrons at charge neutrality. At the bottom right we show the flake with the sum of the norm-squared wavefunctions of the states located at the Fermi level marked in red.

FIG. 4. Prototypical examples of 2D materials from the C2DB with space group $P6m2$ for non-trivial second order topology. In Fig. 4 we show examples of the different prototypes included in the search and we have tabulated all results in the supplementary. To summarize, we find 28 materials in the OAL phase and 16 of these have vanishing polarization. For materials with the same stoichiometry we obtain a picture similar to that of MoS$_2$. For example the band structure of HfTe$_2$ is highly similar to that of MoS$_2$ except there is two valence electrons less. The non-trivial bands are thus above the Fermi level, which yields a trivial topology and a polarization of (2/3, 1/3) instead of (1/3, 2/3). Another example is comprised by TiCl$_2$ which has the same number of valence electrons and fractional corner charges as MoS$_2$, but in that case the charge of the nuclei exactly cancels the electronic polarization, such that the total polarization vanishes (see supplementary for DFT calculations of TiCl$_2$ ribbons). TiCl$_2$ thus comprises a good example of a material where the corner charges might be observable in real (zigzag terminated) triangles. The material has not yet been synthesized experimentally.

In order to verify the emergence of fractional corner charges we have constructed tight-binding models of triangular MoS$_2$ nanoflakes. The tight-binding parameters were obtained from the Kohn-Sham Hamiltonian of bulk MoS$_2$ in a Wannier function representation obtained with Wannier90 package [35, 36]. An example with armchair edges is shown in Fig. 3 along with the eigenvalues colored according to weight on edges and corners. We see that the spectrum is gapped except for three (Kramers degenerate) eigenvalues that are pinned to the Fermi level. The associated wavefunctions are localized at the corners of the triangle and becomes pinned because there are only four available electrons for filling the triangle to the neutrality point. The fractional corner charges thus arise as a consequence of this filling anomaly. We find that explicit integration of the charge density over each symmetry related sector yields exponentially localized corner charges of $Q_c = 2e/3$, when the degenerate levels are filled. At the neutrality point such flakes will exhibit anomalous polarizability [37] since a small electric field will break the symmetry and localize four states at two corners. This will give rise to a total flake dipole moment of $Q_c L$, where $L$ is the height of the triangle.

Triangular nanoparticles of MoS$_2$ have been synthesized on Au surfaces and characterized by STM [38]. The metallic edges always carry gapless states, which can be attributed to a non-trivial topological polarization orthogonal to the zigzag direction in MoS$_2$ [22]. The metallic edge states thus cannot be passivated by adsorbates and the fractional corner charges will always be unobservable. In the supplementary material we show an example of a flake calculation with zigzag edges where the lack of a gap at the Fermi level is evident. We also present DFT calculations of band structures and potential profiles of MoS$_2$ nanoribbons, which explicitly shows that the bulk polarization gives rise to charge transfer between edges and that gapless bands at zigzag edges are enforced by the polarization.

For other similar materials the zigzag terminated nanotriangles are expected to be more stable than armchair terminated triangles as well and it is therefore pertinent to look for 2D materials that have non-trivial second order topology and associated fractional corner charges, but trivial polarization. We have thus screened 71 stable materials from the C2DB with the space group $P6m2$ for non-trivial second order topology. In Fig. 4 we show examples of the different prototypes included in the search and we have tabulated all results in the supplementary. To summarize, we find 28 materials in the OAL phase and 16 of these have vanishing polarization. For materials with the same stoichiometry we obtain a picture similar to that of MoS$_2$. For example the band structure of HfTe$_2$ is highly similar to that of MoS$_2$ except there is two valence electrons less. The non-trivial bands are thus above the Fermi level, which yields a trivial topology and a polarization of (2/3, 1/3) instead of (1/3, 2/3). Another example is comprised by TiCl$_2$ which has the same number of valence electrons and fractional corner charges as MoS$_2$, but in that case the charge of the nuclei exactly cancels the electronic polarization, such that the total polarization vanishes (see supplementary for DFT calculations of TiCl$_2$ ribbons). TiCl$_2$ thus comprises a good example of a material where the corner charges might be observable in real (zigzag terminated) triangles. The material has not yet been synthesized experimentally.

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FIG. 5. Eigenvalue spectrum of a $C_3$ symmetric TiCl$_2$ flake with Cl$_2$ terminated zigzag edges. The color indicates the weight of a given state at edges. The Fermi level at zero energy (grey dashed line) corresponds to the bare flake and the Fermi level at 1.2 eV results from passivating all Cl dimers at edges with two electrons. The top inset shows a zoom in on the three (Kramers degenerate) eigenvalues pinned to the Fermi level (in the edge-passivated system).

To conclude, we have calculated polarization and fractional corner charges of 71 stable 2D materials with three-fold rotational symmetry and found 16 materials that have an OAL phase and a vanishing polarization. It has been argued that only these materials are relevant for experimental verification, since the fractional corner charges of OAL materials with non-trivial polarization will be obscured by edged states in nanotriangles with zigzag edges. We note that this was already concluded in the seminal work of Benalcazar et al. [24], but in that study the polarization and OAL was considered in the context of a single band and the non-trivial topological polarization is then always associated with an OAL phase. It should be emphasized that we have only included materials that are predicted to be dynamically and thermodynamically stable and all of the 16 materials could thus be relevant for experimental verification of second order topology. Of particular interest, however, are materials that are known to exist as bulk van der Waals structures, since these are expected to be directly exfoliable from bulk. In Tab. II we list all such materials (from the 71 materials) along with their identifier from the databases of experimental structures ICSD [40] or COD [41]. We find one material - ZrCl$_2$ - that has been experimentally characterized in bulk form [42] and is predicted to have an OAL phase as well trivial polarization. This material may thus comprise an optimal starting point for the observation of second order topology in 2D.

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| Material | $\chi^{(3)}$ | $Q_c$ | P | ID |
|----------|--------------|------|---|----|
| BN       | (0, 0)       | 0    | (0, 0) | 186248 |
| Ga$_2$S$_2$ | (-2, 2) | 0 | (2/3, 1/3) | 635254 |
| Ga$_2$Se$_2$ | (-2, 2) | 0 | (2/3, 1/3) | 2002 |
| Ga$_2$Te$_2$ | (-2, 2) | 0 | (2/3, 1/3) | 43328 |
| GaN      | (0, 0)       | 0    | (0, 0) | 159250 |
| In$_2$Se$_2$ | (-2, 2) | 0 | (2/3, 1/3) | 640503 |
| MoS$_2$  | (-2, 3)      | 2/3  | (1/3, 2/3) | 38401 |
| MoSe$_2$ | (-2, 3)      | 2/3  | (1/3, 2/3) | 49800 |
| MoTe$_2$ | (-2, 3)      | 2/3  | (1/3, 2/3) | 15431 |
| WS$_2$   | (-2, 3)      | 2/3  | (1/3, 2/3) | 202367 |
| WSe$_2$  | (-2, 3)      | 2/3  | (1/3, 2/3) | 84182 |
| WTe$_2$  | (-2, 3)      | 2/3  | (1/3, 2/3) | 653170 |
| ZrCl$_2$ | (-2, 3)      | 2/3  | (0, 0)  | 1530902 |

TABLE II. 2D insulators that are experimentally known as van der Waals bonded 3D materials. The columns are the symmetry indicator $\chi^{(3)}$, fractional corner charges $Q_c$ (in units of e), polarization P, band gap and ICSD/COD identifier (ID).
Supplementary material

DFT CALCULATIONS FOR NANORIBBONS

Here we present DFT calculations for the MoS$_2$ and TiCl$_2$ nanoribbons shown in Fig. 6. The main difference between these two materials is that the former has non-trivial topological polarization while the latter does not. Tight binding calculations for ribbons of polar materials are unreliable due to the electronic redistribution originating from the polarization and a proper description of charge transfer requires a self-consistent approach.

In Fig. 7 we show the band structures and electrostatic potentials for ribbons of MoS$_2$. The color code in the band structures measures the weight of states on different edges highlighted in Fig. 6. The potentials are evaluated at a representative point in the direction orthogonal to the atomic plane (close to the plane) and averaged over the periodic direction. In the direction across the ribbons we carried out a sliding window average to obtain a smooth function. The band structures have been colored according to the weight of states at the two edges. The metallic edges are evident in the two cases of zigzag terminated ribbons, since both blue and red bands (corresponding to states at the two edges) cross the Fermi level. In both cases there is a small hole pocket at the S-edge signifying transfer of electrons from the S-edge to the Mo-edge, which is a direct consequence of the bulk topological polarization of the material. This is also reflected in the potential, which increases linearly across the ribbon. The potential shift across the ribbon, however, is strongly dependent on the edge terminations, which may or may not introduce dipole densities at the edges. In general, the bulk polarization gives rise to bound charge at edges, which leads to a potential difference between the edges that increases with the width of the ribbon. Beyond a certain width (smaller than the ribbons considered here) the potential difference exceeds the band gap and charge is transferred between the edges, which results in metallic edges. For the armchair ribbon the potential is flat across the ribbon since the topological polarization is parallel to the edges and the band structure of the ribbon is gapped.

In the case of TiCl$_2$ the electronic structure of the ribbons shows significant differences compared to MoS$_2$. We show the band structures and potential profiles of the ribbons shown in Fig. 8. For the zigzag ribbon with Cl dimers at the Ti-edge we again observe a gapless spectrum. It is, however, only the dimer edge that becomes metallic, which is due to the fact that the Cl dimers have a strong electronegativity. Since the Cl-edge band is unoccupied, charge is taken from bulk, which pins both bulk and dimer bands to the Fermi level. The metallic edges states thus arise solely from the structure at the edge and such states may be passivated by appropriate adsorbates that donate the desired electrons to the Cl dimers. For the stoichiometric zigzag ribbon there is a difference in electronegativity between the Ti-edge and Cl-edge, which pins both of the edge states to the Fermi level, but the pinning again originates from the detailed structures of the edges and such states may be passivated. This conclusion is corroborated by the potential profiles of the ribbons, which show that the potential in the bulk of the ribbons becomes flat due to the absence of bulk polarization. We note that there is a significant amount of variation in the potential in the vicinity of the edges as well as a constant potential shift across the ribbons, but these effects arise as a consequence of dipoles residing at the edges.

MODELS OF POLAR AND NON-POLAR NANOTRIANGLES WITH FRACTIONAL CORNER CHARGES

It is perhaps not obvious that the bulk topological polarization have any physical consequences for nanotriangles, which are intrinsically non-polar due to symmetry. To illustrate that this is indeed the case we consider simple models of one and two electron systems with and without topological polarization. In Fig. 9 we show cartoons of nanotriangles representing the case of MoS$_2$ where a single electron has been taken from the transition metal atom and placed in the 1b site. This corresponds to the case of $Q_e = 1/3$ (not taking Kramers degeneracy into account) and a polarization of $(1/3, 2/3)$. In the case of the armchair ribbon the edges become fully compensated such that the only fractional charge resides at corners. For the zigzag triangle the edge states become
fractionally occupied and dispersive edge states thus appear, which cannot be passivated by adsorbates. The charge at a given edge is $2(N - 1)/3$, where $N$ is the number of edge unit cells. Similarly, with a corner charge of $2/3$ any zigzag ribbon would acquire fractionally occupied edge states with an edge charge of $(N - 1)/3$.

In Fig. 10 we show the corresponding situation for a zigzag triangle of a non-polar material. In this example, we consider the case where two electrons are removed from the transition metal atom and one is added at the 1b site and another one at the 1c site. This gives a vanishing polarization and a fractional corner charge of $1/3$. For clarity we show the construction (left) where all 1b and 1c sites receive one third of an electron from all adjacent transition metal atoms. The resulting structure is shown to the right where it is evident that the edges become fully compensated and the only fractional charge resides at corners.

**TIGHT-BINDING CALCULATION OF MoS$_2$ NANOTRIANGLE WITH ZIGZAG EDGES.**

In Fig. 11 we show a calculation of a MoS$_2$ nanotriangle with zigzag edges. The spectrum is clearly gapless and the states transversing the bulk band gap are localized at edges. However, in contrast to the non-polar case of TiCl$_2$ (see main text) these cannot be passivated by adsorbates. This follows from the fractional occupation of edge states illustrated in Fig. 11. Adding either one or two electrons per edge unit cell cannot move the Fermi level into a gap with pinned eigenvalues corresponding to corner states. The details of the spectrum are highly dependent on the edge terminations, but the fact that the edges cannot be passivated remains valid for any termination.

**2D MATERIALS WITH C$_3$ SYMMETRY AND FRACTIONAL CORNER CHARGES FROM THE C2DB**

We have taken 71 materials with space group $P\bar{6}m2$ from the C2DB and calculated the fractional corner charges and spontaneous polarization as well as the band gap. In Tab. III we present the results for materials exhibiting non-trivial corner charges. For materials that has been experimentally characterized as bulk van der Waals bonded materials we supply the identifier for either ICSD or COD. In Tab. IV we show the same data for the 43 materials that are not in an OAL phase. We note that only 13 of these have vanishing polarization and may be regarded as having trivial topology.
FIG. 7. Band structures and potential profiles of the three MoS$_2$ nanoribbons shown in Fig. 6. Left: Weight of states localized on the Mo-edge with S dimer termination marked in red and weight on S-edge in blue. Middle: Weight of states localized on zigzag termination with Mo-edge marked in red and weight on S-edge marked in blue. Right: armchair termination. The zero energy marks the Fermi level.

FIG. 8. Band structures and potential profiles of the three TiCl$_2$ nanoribbons shown in Fig. 6. Left: Weight of states localized on Ti-edge with Cl dimer termination marked in red and weight on Cl-edge marked in blue. Middle: Weight of states localized on zigzag termination with Ti-edge marked in red and weight Cl-edge marked in blue. Right: armchair termination. The zero energy marks the Fermi level.
FIG. 9. $C_3$ symmetric triangles with a topological polarization of $(1/3, 2/3)$. The bulk structure has a single occupied state at 1b (center of hexagons) which is taken from the 1a position (blue atoms), while the yellow sites (1c) are neutral. Left: triangle with armchair edges, which are fully occupied, whereas the corners have fractional occupancy of 2/3. Right: triangle with zigzag edges. The corners states again have fractional occupancy of 2/3, but the 1b sites at edges are also fractionally occupied and the edges thus host metallic states that cannot be passivated.

FIG. 10. $C_3$ symmetric triangles with vanishing polarization. The bulk structure has one occupied state at 1b (center of hexagons) and one occupied state at 1b, which are both taken from the 1a position (blue atoms). Left: result of assigning 1/3 of an electron to all 1b sites adjacent to 1a sites and 1/3 of an electron to all 1c sites adjacent to 1a sites. Right: same as left, but now with all fractionally occupied sites at edges merged into integer occupied sites. This results in passivated edges and corner states with a fractional occupation of 2/3.
FIG. 11. Nanotriangle of MoS$_2$ with Mo zigzag edges and S dimers. The edge states give rise to a gapless spectrum that gapped be passivated by the introduction of suitable adsorbates. The grey dashed line indicates the Fermi level of the bare triangle and the blue dashed line indicates the Fermi level where one electron has been added per S dimer at the edges. The upper inset shows two states at the Fermi level, which are localized at all edges as indicated in the lower inset.
| Material      | $\chi^{(3)}$ | $Q_c$ | $P$ | ID         |
|---------------|--------------|-------|-----|------------|
| CrO$_2$       | (-2, 3)      | 2/3   | (1/3, 2/3) |            |
| CrS$_2$       | (-2, 3)      | 2/3   | (1/3, 2/3) |            |
| CrSe$_2$      | (-2, 3)      | 2/3   | (1/3, 2/3) |            |
| CrTe$_2$      | (-2, 3)      | 2/3   | (1/3, 2/3) |            |
| Hf$_2$C$_2$O$_4$ | (-2, 4) | 4/3   | (0, 0) |            |
| Hf$_2$N$_2$O$_4$ | (-3, 5) | 4/3   | (0, 0) |            |
| HfBr$_2$      | (-2, 3)      | 2/3   | (0, 0) |            |
| HfCl$_2$      | (-2, 3)      | 2/3   | (0, 0) |            |
| HfI$_2$       | (-2, 3)      | 2/3   | (0, 0) |            |
| MoO$_2$       | (-2, 3)      | 2/3   | (1/3, 2/3) |            |
| MoS$_2$       | (-2, 3)      | 2/3   | (1/3, 2/3) | 38401      |
| MoSe$_2$      | (-2, 3)      | 2/3   | (1/3, 2/3) | 49800      |
| MoTe$_2$      | (-2, 3)      | 2/3   | (1/3, 2/3) | 15431      |
| Ti$_2$Te$_2$  | (-3, 4)      | 2/3   | (0, 0) |            |
| TiBr$_2$      | (-2, 3)      | 2/3   | (0, 0) |            |
| TiCl$_2$      | (-2, 3)      | 2/3   | (0, 0) |            |
| TiH$_2$       | (-2, 3)      | 2/3   | (0, 0) |            |
| Ti$_2$        | (-2, 3)      | 2/3   | (0, 0) |            |
| WO$_2$        | (-2, 3)      | 2/3   | (1/3, 2/3) |            |
| WS$_2$        | (-2, 3)      | 2/3   | (1/3, 2/3) | 202367     |
| WSe$_2$       | (-2, 3)      | 2/3   | (1/3, 2/3) | 84182      |
| WTe$_2$       | (-2, 3)      | 2/3   | (1/3, 2/3) | 653170     |
| Zr$_2$Se$_2$  | (-3, 4)      | 2/3   | (0, 0) |            |
| Zr$_2$Te$_2$  | (-3, 4)      | 2/3   | (0, 0) |            |
| Zr$_2$C$_2$O$_4$ | (-2, 4) | 4/3   | (0, 0) |            |
| ZrBr$_2$      | (-2, 3)      | 2/3   | (0, 0) |            |
| ZrCl$_2$      | (-2, 3)      | 2/3   | (0, 0) | 1530902    |
| ZrI$_2$       | (-2, 3)      | 2/3   | (0, 0) |            |

TABLE III. 2D materials with space group $P\bar{6}m2$ that exhibits non-trivial fractional corner charges. We have stated the symmetry indicators $\chi^{(3)}$, the fractional corner charges $Q_c$, the polarization in dimensionless units $P$ and the ICSD/COD identifier (ID) for materials that are experimentally known in bulk form.
| Material | $\chi^{(3)}$ | $Q_c$ | $P$ | ID       |
|----------|-------------|------|-----|---------|
| AlN      | (0, 0)      | 0    | (0, 0) |         |
| Al$_2$O$_2$ | (-2, 2)    | 0    | (0, 0) |         |
| Al$_2$S$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| Al$_2$Se$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| Al$_2$Te$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| BaBr$_2$  | (-2, 2)    | 0    | (1/3, 2/3) |       |
| BaCl$_2$  | (-2, 2)    | 0    | (0, 0) |         |
| BaI$_2$   | (-2, 2)    | 0    | (1/3, 2/3) |       |
| Bi$_2$O$_2$ | (-2, 2)    | 0    | (0, 0) |         |
| BN       | (0, 0)     | 0    | (0, 0) | 186248  |
| BP       | (0, 0)     | 0    | (0, 0) |         |
| CaBr$_2$ | (-2, 2)    | 0    | (1/3, 2/3) |       |
| CaCl$_2$ | (-2, 2)    | 0    | (1/3, 2/3) |       |
| CaI$_2$  | (-2, 2)    | 0    | (1/3, 2/3) |       |
| GaN      | (0, 0)     | 0    | (0, 0) | 159250  |
| Ga$_2$O$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| Ga$_2$S$_2$ | (-2, 2)    | 0    | (2/3, 1/3) | 635254 |
| Ga$_2$Se$_2$ | (-2, 2)    | 0    | (2/3, 1/3) | 2002   |
| Ga$_2$Te$_2$ | (-2, 2)    | 0    | (2/3, 1/3) | 43328  |
| HfSe$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| HfTe$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| In$_2$O$_2$ | (-2, 2)    | 0    | (0, 0) |         |
| In$_2$S$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| In$_2$Se$_2$ | (-2, 2)    | 0    | (2/3, 1/3) | 640503 |
| In$_2$Te$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| Mo$_2$Cl$_6$ | (-1, 1)    | 0    | (0, 0) |         |
| PbBr$_2$ | (-2, 2)    | 0    | (1/3, 2/3) |       |
| PbCl$_2$ | (-2, 2)    | 0    | (1/3, 2/3) |       |
| Pb$_2$  | (-2, 2)    | 0    | (1/3, 2/3) |       |
| PbS$_2$  | (-1, 1)    | 0    | (1/3, 2/3) |       |
| PbSe$_2$ | (-1, 1)    | 0    | (1/3, 2/3) |       |
| SnI$_2$  | (-2, 2)    | 0    | (1/3, 2/3) |       |
| SrBr$_2$ | (-2, 2)    | 0    | (1/3, 2/3) |       |
| SrCl$_2$ | (-2, 2)    | 0    | (1/3, 2/3) |       |
| SrI$_2$  | (-2, 2)    | 0    | (1/3, 2/3) |       |
| TiSe$_2$ | (-2, 2)    | 0    | (0, 0) |         |
| TiTe$_2$ | (-2, 2)    | 0    | (0, 0) |         |
| Tl$_2$S$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| Tl$_2$Se$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| Tl$_2$Te$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |
| W$_2$Br$_6$ | (-1, 1)    | 0    | (0, 0) |         |
| W$_2$Cl$_6$ | (-1, 1)    | 0    | (0, 0) |         |
| ZrTe$_2$ | (-2, 2)    | 0    | (2/3, 1/3) |       |

**TABLE IV.** 2D materials with space group $P\bar{6}m2$ that exhibits non-trivial fractional corner charges. We have stated the symmetry indicators $\chi^{(3)}$, the fractional corner charges $Q_c$, the polarization in dimensionless units $P$ and the ICSD/COD identifier (ID) for materials that are experimentally known in bulk form.