A New Group of 2D Non-van der Waals Materials with Ultra Low Exfoliation Energies

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The exfoliation energy—quantifying the energy required to extract a two-dimensional (2D) sheet from the surface of a bulk material—is a key parameter determining the synthesizability of 2D compounds. Here, using ab initio calculations, a new group of non-van der Waals 2D materials derived from non-layered crystals that exhibit ultra low exfoliation energies is presented. In particular for sulfides, surface relaxations are essential to correctly describe the associated energy gain needed to obtain reliable results. Taking into account long-range dispersive interactions has only a minor effect on the energetics and ultimately proves that the exfoliation energies are close to the ones of traditional van der Waals bound 2D compounds. The candidates with the lowest energies, 2D SbTiO$_3$ and MnNaCl$_3$, exhibit appealing electronic, potential topological, and magnetic features as evident from the calculated band structures making these systems an attractive platform for fundamental and applied nanoscience.

1. Introduction

The discovery of new 2D materials—traditionally derived from bulk layered compounds held together by weak van der Waals (vdW) forces—outlined over the last two decades a diverse zoo of representatives showcasing unique topological,[1] electronic,[2–4] magnetic,[5–7] and superconducting[8,9] properties. The weak interaction between the structural units in their bulk counterparts leads to a natural geometric separation of the 2D subunits in the crystals, giving rise to the possibility of mechanical[10] and liquid-phase[11] exfoliation. This class of nanostructures thus opens up prospects for fundamental research in reduced dimensions as well as for various applications in the energy sector,[12–14] catalysis,[15,16] and optoelectronics.[17,18] The large scale deployment of these vdW 2D materials in modern technologies is, however, still very limited.[19]

In light of the ubiquitous use of many standard non-layered materials in research and technology for which handling and processing is well established, the search for non-vdW 2D materials is appealing.[20] Recently and somewhat unexpectedly, atomically thin 2D sheets derived from non-vdW bonded oxides were indeed manufactured. The first representatives realized in experiment by a special chemical exfoliation process were hematite$^{[21]}$ and ilmenene$^{[22]}$ obtained from the earth-abundant ores hematite ($\alpha$-Fe$_2$O$_3$) and ilmenite (FeTiO$_3$), followed by a few others.$^{[23–36]}$ Their explicit derivation from existing bulk compounds (ores) makes these systems distinct from many other suggested synthetic 2D materials without layered bulk allotropes$^{[37,38]}$ and unlike, e.g., silicene or borophene,$^{[39]}$ these materials do not need to strongly interact with a substrate to be stable. From the computational side, a recent data-driven search on non-vdW 2D systems outlined 28 candidates with a variety of appealing electronic and magnetic properties.$^{[40]}$ First application-oriented studies indicate promising perspectives for opto-electronics,$^{[41]}$ photo-catalytic activity for water splitting,$^{[21,22]}$ and photoco-ductivity.$^{[28]}$ Despite these early successes, the non-vdW 2D materials space is still very narrow, and it remains to be understood what promotes the exfoliability of non-vdW bulk systems into 2D sheets.

A key quantity determining the synthesizability of 2D materials is the exfoliation energy $\Delta E_{\text{exf}}$. It represents the energy needed to peel off one 2D sheet from the surface of the bulk parent material. It can be computed accurately according to the method of Jung et al.$^{[42]}$ at minimal computational cost, who proved that the exfoliation energy is the energy difference between an isolated 2D sheet and one such facet in the bulk, also known as inter-layer binding energy. The approach in particular properly accounts for surface relaxations and reconstructions. For the standard reference material graphene, the exfoliation energy is known to be $\sim$20 meV Å$^{-2}$ from both experiment and advanced density functional theory (DFT).$^{[43,44]}$ It was even found...
that this value appears to be universal for many layered systems largely independent of their electronic structure. However, later on a rather complete screening of the vDW 2D materials space outlined a much wider distribution of exfoliation energies over several 10 meV Å⁻²,[45] likely due to contributions from other interactions than just vDW. Based on detailed energetic and structural considerations, upper bounds of ≈130 meV Å⁻² and 200 meV atom⁻¹ for the exfoliation energy have been proposed to consider a material as (classically) exfoliable.[45,46] As such, the calculated value of ≈140 meV Å⁻² (=310 meV atom⁻³) for hematene[40,47] seems surprisingly high, yet successful liquid-phase isolation of the 2D sheet was reported.[21]

In the recent data-driven search for non-vDW 2D systems, it was indicated that for several of the 28 oxidic candidates, the exfoliation energy is significantly smaller. For a few systems, it even comes close to the one of graphene if the surface cations are in a low (+1) oxidation state[40] suggesting that mechanical peel-off might be feasible. This effect was rationalized through the minimization of electrostatic interactions between the 2D sheets in case of small surface charges. While the consideration of the systems in vacuum is an idealization with respect to experiment, it allows for an assessment of the fundamental exfoliation energetics of these materials. Here, we focus explicitly on novel candidates with surface cations in low oxidation states and generalize the previous efforts by investigating also non-oxides. The goal is to try to find an answer to the question: How small can the exfoliation energy of a non-vDW 2D material get?

2. Results and Discussion

The input structures are retrieved via the AFLOW APIs[48–50] and web interfaces[51,52] as well as the library of crystallographic prototypes.[53] The structures of Al₂S₃ and MnNaCl₃ are depicted in Figure 1ab as examples to visualize the structural prototype of the investigated systems. We decided to focus on the formation of 2D sheets perpendicular to the [001] direction, named [001] facets, (also indicated in the figures) in analogy to hematene and ilmenene realized in experiment[21,22] as well as data-driven study in Ref. [40]. For hematene, also [010] facets were reported but were found to be thermodynamically less stable in agreement with our test calculations. Although different surface terminations of the experimentally realized sheets have been discussed,[45,55] based on various experimental findings[21,23] and from theoretical consideration of a wide range of oxygen chemical potentials,[56] the 2D sheets are expected to be terminated by the surface cations as depicted in Figure 1 ab. This is also corroborated by an intuitive structural argument outlined in Ref. [40], since for the cation termination only weak bonds of the structure need to be broken during exfoliation, which is, however, not the case for the termination by, e.g., oxygen. No further passivation at the surface of the 2D compounds will be considered here based on the experimental result that no chemical modifications were revealed for hematene and ilmenene.[21,22]

The dynamic stability of the outlined 2D systems is verified carefully as follows: First, a 2 × 2 in-plane supercell is constructed from the relaxed structures. Then, the atomic coordinates are randomized (gaussian distribution, standard deviation 50 mÅ)[56,57] and the structures are reoptimized. In all cases, the slabs relax back to the previous geometry. Although they also exhibit the same structure, Yb₂S₃ and Lu₂S₃ are not considered here as the corresponding 2D sheets were found to be dynamically unstable during the test. In addition, also the computed phonon dispersions presented for all candidates in Figure S3 (Supporting Information) together with a detailed discussion confirm the strict vibrational stability of the systems.[58,59] For MnNaCl₃, small imaginary phonon contributions are observed but the system might be readily stabilized on a substrate as it has already been shown for hematene that adsorption on Au(111) essentially preserves its pristine properties.[60] To also check the dynamic stability with respect to structural changes more rigorously as recommended for 2D systems,[61] for one representative sheet, AsLiO₃, we carried out an ab initio molecular dynamics (MD) simulation over 5 ps at 400 K. The system does not lower its potential energy or change its structure during the run as detailed in Section IV (Supporting Information). Although this cannot be considered as a solid proof for all time scales and temperatures, our results can be interpreted as evidence for the dynamic stability of the system.

Figure 1. Structures and exfoliation energies. Atomic structure of a) Al₂S₃ and b) MnNaCl₃.[62] The exfoliable [001] facet (monolayer) is indicated in the orange dashed box. The black line denotes the conventional unit cell. The compass indicating crystal directions applies to both figures. c) Calculated exfoliation energies from SCAN without (as sliced) and with (relaxed) structural optimization of the 2D sheets. As a reference, the exfoliation energy of graphene (Gr)[43,45] as well as for hematene and ilmenene[40] are indicated by the dashed horizontal black lines. For the ternaries, the data for the slabs with the energetically favorable termination are plotted and for all systems, the terminating element is underlined at the bottom axis. The dashed lines connecting the data points are visual guides.
2.1. Ab Initio Exfoliation Energies

In Figure 1c, the calculated exfoliation energies are depicted also including, for comparison to the considered sulfides, the previously obtained values for the corresponding 2D oxides Al₂O₃ and In₂O₃.[46] For the ternaries, the sheets can be terminated by either of the two cation species. Here, only the results for the energetically favorable termination are plotted and a comparison to the unpreferred termination is presented in Figure S1 (Supporting Information). The ΔE_{exf} of the newly considered systems extend over a large range of more than an order of magnitude. Ultra low values are achieved for the systems with surface cations in +1 oxidation states (such as Ag⁺, Li⁺, K⁺, Na⁺, and Tl⁺) being as small as 7 meV Å⁻² for SbTiO₃ and 26 meV Å⁻² for MnNaCl₃. These numbers are comparable to or even below the graphene reference value of ≈20 meV Å⁻². They are significantly smaller than for any other non-vdW 2D system considered before.

In contrast to traditional vdW bound 2D materials, the present systems exhibit ionic and covalent bonds that need to be broken upon exfoliation to obtain the 2D system as successfully achieved in the experiments for hematene and ilmenene.[21,22] Thus, the question of the associated energy barrier to initiate exfoliation arises. While the potential importance of defects (such as dislocations) has been stressed to lower the barrier,[20] to address this issue, we have calculated ΔE_{exf} in two ways. The blue curve denotes the results obtained when omitting structural relaxations of the extracted 2D facets, i.e., keeping them “as sliced” from the bulk, as is common reliable practice for their energy by an inward relaxation of the terminating cations leading to an overall (vertical) thickness reduction from d_{as sliced} to d_{relaxed}. This effect is more pronounced in case of the sulfides as compared to the oxides. While Al₂O₃ (In₂O₃) relaxes from a thickness of 3.84 Å (4.14 Å) to 2.72 Å (3.06 Å), Al₂S₃ (In₂S₃) goes from 4.94 Å (5.16 Å) to 2.96 Å (3.23 Å). Hence, although the absolute thickness of the sulfides is larger, the absolute reduction by ≈2 Å is about twice as large as for the oxides.

2.2. The Role of Structural Relaxations

In many cases, the different extent of structural relaxations for different classes of compounds allows one to better understand the specific energy lowering as the systems minimize their energy on the respective potential energy surface by geometrical reconstructions. As such, the origin of this strong change in energy in case of the sulfides as compared to the oxides can be traced back to intricate structural changes. The side views in Figure 2a–d indicate that the 2D systems lower their energy by an inward relaxation of the terminating cations leading to an overall (vertical) thickness reduction from d_{as sliced} to d_{relaxed}. This effect is more pronounced in case of the sulfides as compared to the oxides. While Al₂O₃ (In₂O₃) relaxes from a thickness of 3.84 Å (4.14 Å) to 2.72 Å (3.06 Å), Al₂S₃ (In₂S₃) goes from 4.94 Å (5.16 Å) to 2.96 Å (3.23 Å). Hence, although the absolute thickness of the sulfides is larger, the absolute reduction by ≈2 Å is about twice as large as for the oxides.

![Figure 2](https://www.advancedsciencenews.com)

Figure 2. Structural Relaxations. Side view of the unit cells of “as sliced” (top) and “relaxed” (bottom) 2D a) Al₂O₃, b) Al₂S₃, c) In₂O₃, and d) In₂S₃. e–h) Top views of the relaxed structures with an indication of the in-plane lattice constant.
As a further comparison, there are seven materials (CdPS₃, CdPSe₃, CrGeTe₃, CrSiTe₃, FePSe₃, MgPSe₃, and MnPSe₃) in the AFLLOW database with the same structural prototype that are clearly layered, i.e., traditional vdW bonded materials as evident from visual inspection of the bulk geometries. Thus, the same structural prototype can host both vdW and non-vdW-bonded 2D materials. The exfoliation energies for these well established 2D systems were also computed with the same methods and are provided in Figure 3b. Here, dispersive interactions are essential to obtain reliable absolute values as the constant shift by ≈10 meV Å⁻² increases the SCAN results by a factor of three. For the non-vdW systems in Figure 3a, the SCAN values account already for 70–80% of the SCAN+rVV10 results since here the largest contribution to the bonding does not derive from long-range interactions. This consideration of the different interaction contributions therefore provides a clear distinction between non-vdW and vdW 2D materials.

SbTIO₃ is a special case at the intersection between the vdW and non-vdW 2D materials spaces. The optimized bulk (layered) structure with the exfoliable facet highlighted is depicted in Figure 3c. It is structurally equivalent to the other non-vdW systems as the TI cations are at the surface of the 2D sheets in contrast to traditional 2D systems such as the ones from Figure 3b which are terminated by the anions (see the side view of CdP₅ in the inset as an example). Yet, the exfoliation energy of SbTIO₃ appears to be largely governed by long-range vdW contributions (see Figure 3a). However, the intermediate range vdW interaction captured by the SCAN exfoliation energy accounts with ≈40% for a larger portion of the total exfoliation energy (from SCAN+rVV10) compared to the traditional vdW 2D compounds of Figure 3b where this amounts on average to only ≈30%. As a result of these characteristics, this compound was already identified as a potential 2D material by Mounet et al.⁴⁵ although not discussed in detail.

An important general remark regarding the exfoliation energies must be made. It is well known that the standard DFT functional PBE(+)U tends to underestimate binding energies (overestimating bond lengths also known as underbinding, see also the comparison including the PBE+U exfoliation energies in Figure S2 (Supporting Information)). There are, on the other hand, several indications that the employed SCAN functional tends to overestimate covalent and ionic binding energy.

**Figure 3.** Contribution of long-range vdW interactions. Comparison of the calculated exfoliation energies from SCAN and SCAN+rVV10 for a) the eight non-vdW 2D candidates and b) seven vdW 2D systems with the same structure. The dashed horizontal black line indicates the graphene reference value.⁴³,⁴⁵ The dashed lines connecting the data points are visual guides. Inset in panel (b): side view of CdP₅. The vertical black line in panel (a) separates binaries from ternaries. c) Atomic structure of SbTIO₃. The exfoliable [001] facet (monolayer) is indicated in the orange dashed box. The black line denotes the conventional unit cell.

(≈ 1.1 Å). In addition, also the relative change defined as \( \frac{d_{\text{relaxed}} - d_{\text{as-relaxed}}}{d_{\text{as-relaxed}}} \) of ≈40% for the sulfides is much larger than for the oxides with ≈30%. Thus, the stronger structural relaxation due to the larger anion allows the surface cation to dive deeper into the anion plane leading to an almost planar coordination of the surface cations in the sulfides. Thereby, due to these pronounced surface reconstructions, the energy is lowered more efficiently leading to stronger reductions in \( \Delta E_{\text{exf}} \).

As a response to the vertical contraction, the oxides stretch laterally, i.e., the in-plane lattice constant of Al₂O₃ (In₂O₃) increases from 4.75 Å (5.51 Å) to 4.86 Å (5.62 Å). For the sulfides, this change is less pronounced as for Al₂S₃ (In₂S₃) the value goes from 6.03 Å (6.59 Å) to 6.07 Å (6.59 Å). Top views of the optimized structures with the relaxed in-plane lattice constant \( a_{\text{relaxed}} \) indicated are presented in Figure 2e–h.

### 2.3. Contribution of Long-Range vdW Interactions

When exfoliation energies get as small as for graphene or even lower, the question of the importance of long-range vdW interactions naturally arises. While the employed SCAN functional has been pointed out to capture intermediate-range vdW interactions relevant for, e.g., hydrogen bonds,⁴³ it does not include long-range dispersion contributions. These can be accounted for within the SCAN+rVV10 scheme.⁴⁶ We have thus also calculated the exfoliation energies for all systems with this approach and compare them to the plane SCAN results in Figure 3a. As expected, inclusion of the long-range interactions increases the exfoliation energies but only by a rather constant shift of 10–15 meV Å⁻²—the typical order of magnitude for dispersive interactions. Hence, no qualitative change in the exfoliation behavior is anticipated from this.

As a further comparison, there are seven materials (CdPS₃, CdPSe₃, CrGeTe₃, CrSiTe₃, FePSe₃, MgPSe₃, and MnPSe₃) in the AFLLOW database with the same structural prototype that are clearly layered, i.e., traditional vdW bonded materials as evident from visual inspection of the bulk geometries. Thus, the same structural prototype can host both vdW and non-vdW-bonded 2D materials. The exfoliation energies for these well established 2D systems were also computed with the same methods and are provided in Figure 3b. Here, dispersive interactions are essential to obtain reliable absolute values as the constant shift by ≈10 meV Å⁻² increases the SCAN results by a factor of three. For the non-vdW systems in Figure 3a, the SCAN values account already for 70–80% of the SCAN+rVV10 results since here the largest contribution to the bonding does not derive from long-range interactions. This consideration of the different interaction contributions therefore provides a clear distinction between non-vdW and vdW 2D materials.

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2.4. Band Structures and Magnetic Properties of SbTlO$_3$ and MnNaCl$_3$

To showcase the potential of these materials, we briefly discuss the band structure and magnetic properties of SbTlO$_3$ and MnNaCl$_3$—the two systems with the lowest exfoliation energies—and present the results for all compounds in comparison to the respective bulk bands in section V., Supporting Information.

According to the band structures in Figure 4, both systems are large gap insulators (calculated bandgaps: 2.94 and 4.01 eV) with valence band maximum and conduction band minimum at the K- and Γ-points, respectively. An appealing feature for SbTlO$_3$ that is absent in the respective bulk bands (see also Figure S10, Supporting Information) is the Dirac cone like linear band crossing at the high-symmetry K-point at ≈1.3 eV above the conduction band minimum. It might be readily accessible via moderate doping since it is relatively well isolated from other bands and is the lowest energy feature in the conduction band manifold at the K-point. This finding might hint at interesting topological properties calling for further investigations for instance addressing the explicit calculation of topological invariants.

MnNaCl$_3$ on the other hand shows ferromagnetic coupling of the Mn moments amounting to ≈4.6 µ$_B$ making it one of the few candidates for a 2D ferromagnet. As there are two nearest neighbor Mn ions in the structural unit cell, also the antiferromagnetic (AFM) alignment of the moments in this cell has been considered. The energy difference to this AFM configuration is ≈14 meV per formula unit (Several longer-range AFM configurations have also been taken into account within a 2 × 2 in-plane supercell and are all found to be higher in energy than the ferromagnetic state as detailed in Section VI, Supporting Information). This energy difference can be mapped onto a nearest-neighbor Heisenberg model $H = \sum_{ij} J_{ij} \mathbf{m}_i \cdot \mathbf{m}_j$ analogously to Refs. [68–71], where $J_{ij}$ is the magnetic exchange coupling constant between ions $i$ and $j$, and $\mathbf{m}_i$ and $\mathbf{m}_j$ stand for the magnetic moments at these centers. From this, one computes the coupling constant between nearest neighbor Mn-ions as $J_{\text{Mn-Mn}} \approx 4.6$ meV. This value can be used to estimate the mean-field Curie temperature $T_{\text{C, MF}}$ according to $k_B T_{\text{C, MF}} = J_0 / 3$ as explained in Ref. [72] ($k_B$ is Boltzmann’s constant) by summing all the coupling constants of one Mn ion as $J_0 = 3J_{\text{Mn-Mn}}$ (Note that our coupling constants are defined as twice the value in Ref. [72]). Thus, we arrive at an estimated Curie temperature of $T_{\text{C, MF}} \approx 54$ K. However, it needs to be stressed that mean-field theory is well known to overestimate Curie temperatures.[22]

The magnetic behavior of MnNaCl$_3$ is also reflected in the spin polarized bandstructure in Figure 4b where both bands at the edges of the gap are derived from majority spin while minority spin states are separated by several hundred meV. In contrast to the previously reported magnetic non-vdW 2D candidates in Ref. [40], the magnetic Mn ions are not at the surface of the slab but in the interior (see also Figure 1b). This is an important difference as the magnetic properties can be expected to be structurally better protected from environmental influences such as adsorbates. Based on the outlined electronic and magnetic characteristics, these systems can thus reveal potential for, e.g., optoelectronic and/or spintronic applications within planar electronic devices.

3. Conclusion

We have outlined a new group of non-vdW 2D materials exhibiting low exfoliation energies—ultimately getting as small as the one of graphene—for which also their dynamic stability has been checked. The investigated sulfides Al$_2$S$_3$ and In$_2$S$_3$ have exfoliation energies a factor of four smaller than the corresponding oxides, which can be traced back to exceptionally strong surface relaxations allowing for a significant energy...
gain. The smallest values close to the ones of traditional 2D systems are found for SbTiO$_3$ and MnNaCl$_3$, as evident from the comparison to several vdW materials. The computed band structures of these most easily exfoliable compounds exhibit appealing electronic, possibly topological, and magnetic properties. Our results may thus be an important guide stimulating experimental investigations for extending the family of non-vdW 2D exfoliable systems representing a new class of low dimensional compounds and for studying their characteristics as well as applications.

4. Methods

The ab initio calculations were performed with AFLOW [71,74] and the Vienna Ab initio Simulation Package (VASP) [75–77] employing the exchange-correlation functionals PBE [78], SCAN [79], SCAN+rVV10 [63], and PBE+U [80–82] with parameter choices in accordance with the AFLOW standard [67] as well as setting the internal VASP precision to ACCURATE. As a reference, the standard $U$ values for PBE+U are provided in Table SIII (Supporting Information). For SCAN, projector-augmented-wave (PAW) pseudopotentials [83] of VASP version 5.4 were used and non-spherical contributions to the gradient of the density in the PAW spheres were included for SCAN and PBE+U. The [001] 2D facets were constructed from the bulk standard conventional unit cell with the respective AFLOW commands [84] resulting in structures with 10 atoms and including at least 20 Å of vacuum perpendicular to the slabs. For all facets, relaxation of both the ionic positions and the cell shape were carried out unless stated otherwise. The AFLOW internal automatic determination of k-point sets was used and for the calculations of the 2D facets, the setting for the number of k-points per reciprocal atom [67] is reduced to 1,000 resulting in Γ-centered 10 × 10 × 1 grids. To properly resolve the Dirac cone-like linear band crossing in the DOS of SbTiO$_3$, the static calculations were carried out with a Γ-centered 70 × 70 × 1 k-point set in this case. The bandstructures and DOS are calculated for the optimized SCAN geometry using PBE+U according to the AFLOW standard [67] as this functional has been successfully employed previously for the electronic properties of non-vdW 2D systems in Ref. [40].

For computational efficiency, the dynamic stability check through the construction of 2 × 2 in-plane supercells as well as the phonon calculations were carried out with PBE+U. The phonon dispersions were computed with AFLOW-API [85] by constructing 5×5 in-plane supercells (containing 250 atoms) without polar corrections. For the ab initio MD simulations for a 4 × 4 in-plane supercell (containing 160 atoms) at 400 K over 5 ps in the canonical (NVT) ensemble, a time step of 1 fs together with an Andersen thermostat with a collision probability of 0.1 was used. The parameters for the associated electronic calculation followed the AFLOW standard but with the number of bands reduced to 700, precision set to NORMAL, symmetry and spin switched off, an electronic convergence criterion of 10$^{-9}$ eV, automatic optimization of the projection operators, and k-point sampling only at the Γ point.

The bulk and 2D candidate systems with expected magnetic ordering (MnNaCl$_3$, CrGeTe$_3$, CrSiTe$_3$, FePSe$_3$, and MnPSe$_3$) were rigorously checked, for magnetism using the algorithm developed within the CCE method, [65,86] i.e., investigating all possible FM and AFM configurations in the structural unit cell for five different sizes of induced magnetic moments each. For MnNaCl$_3$, the three additional AFM configurations depicted in Figure S13 (Supporting Information)b–d were also considered. In each case, the lowest energy magnetic state was used for the further calculations.

The exfoliation energy is computed as

$$\Delta E_{\text{exf}} = \frac{E_{\text{lab}} - E_{\text{bulk}}}{A}$$  \hfill (1)

where $E_{\text{lab}}$ and $E_{\text{bulk}}$ indicate the total energies of the relaxed 2D material and bulk, respectively and $A$ is the in-plane surface area according to the relaxed bulk unit cell. As proven in Ref. [42], the exfoliation energy from the surface of the material is exactly equal to the binding energy between layers/facets in the bulk.

Numerical data for the exfoliation energies are included in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The primary research data of this study are available on the Rossendorf Data Repository (RODARE) via https://doi.org/10.14278/rodare.1852.

Keywords

2D materials, computational materials science, exfoliation

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