Competing rhombohedral and monoclinic crystal structures in MnPn2Ch4 compounds: an ab-initio study

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Based on the relativistic spin-polarized density functional theory calculations we investigate the crystal structure, electronic and magnetic properties of a family MnPn2Ch4 compounds, where pnictogen metal atoms (Pn) are Sb and Bi; chalcogens (Ch) are Se, Te. We show that in the series the compounds of this family with heavier elements prefer to adopt rhombohedral crystal structure composed of weakly bonded septuple monoatomic layers while those with lighter elements tend to be in the monoclinic structure. Irrespective of the crystal structure all compounds of the MnPn2Ch4 series demonstrate a weak energy gain (of a few meV per formula unit or even smaller than meV) for antiferromagnetic (AFM) coupling for magnetic moments on Mn atoms with respect to their ferromagnetic (FM) state. For rhombohedral structures the interlayer AFM coupling is preferable while in monoclinic phases intralayer AFM configuration with ferromagnetic ordering along the Mn chain and antiferromagnetic ordering between the chains has a minimum energy. Over the series the monoclinic compounds are characterized by substantially wider bandgap than compounds with rhombohedral structure.

I. INTRODUCTION

The ternary chalcogenides MPn2Ch4 (M = Fe, Mn; Pn = Sb, Bi; and Ch = S, Se)1–9 which include a large number of synthetic and natural metal chalcogenides are promising for applications in thermoelectricity10, spintronics11, and nonlinear optics12. These compounds crystallize in the monoclinic space group C2/m. This structure is characterized by a presence of the M atoms chains along one of the crystallographic directions where the distances between M atoms are 1.5–2 times shorter than in other directions. As shown by magnetic measurements, the iron containing chalcogenides are ferromagnetic semiconductors3, while the Mn-based compounds are antiferromagnets9. However, recently a new ternary chalcogenide semiconductor of the same series containing a heavier chalcogen atom (Te), MnBi2Te4, and possessing different crystal structure has been reported13. It was shown that the compound crystallizes in the rhombohedral structure (R3m) and can be described as the one composed of septuple layer (SL) slabs with a stacking sequence of Te1–Bi–Te2–Mn–Te2–Bi–Te1 along the c-axis and with van der Waals gaps between the slabs. The structure may also be described by using the Bi2Te3 structure, where the central Te layer is substituted with Te–Mn–Te layers. The obtained phase, as established by using high-temperature XRD analysis, is stable up to 423 K while above this temperature it starts to be spontaneously decomposed into Bi2Te3 and MnTe2 phases. It should be noted that the magnetic state of MnBi2Te4 has not been studied.

In the present study we scrutinize the crystal structure of compounds of the MnPn2Ch4 series (Pn = Sb, Bi; Ch = Se, Te) by means of the density functional theory (DFT) calculations with taking into account their magnetic state.

II. METHODS

For calculations we use the Vienna Ab Initio Simulation Package (VASP)14,15 with generalized gradient approximation (GGA)16 for the exchange correlation potential. The interaction between the ion cores and valence electrons is described by the projector augmented-wave method17,18. Owing to presence of heavy Pn atoms (Sb,Bi) in the ternary chalcogenides MPn2Ch4 the relativistic effects are expected to have a significant impact on electronic and crystal structures. For this reason the relativistic effects, including spin-orbit interaction, were taken into account in the calculations. To determine equilibrium state of the systems, we accurately optimized the lattice parameters as well as the atomic positions of the rhombohedral and monoclinic structures of MnPn2Ch4 in ferromagnetic (FM) and different antiferromagnetic states. For rhombohedral structure we have considered a collinear antiferromagnetic state with interlayer antiferromagnetic coupling (AFM) and noncollinear antiferromagnetic (NCAFM) state in which three spin sublattices form angles of 120° with respect to each other19. To consider the FM and AFM ordering in the rhombohedral phase we use doubled along c axis
FIG. 1. Rhombohedral (a) and respective hexagonal (b) representations of the crystal structure as was found for MnBi₂Te₄ compound in Ref. 13. Parts of the doubled along c axis hexagonal cells, containing two SL blocks with FM (c) and AFM (d) ordering for Mn atoms (red arrows show mutual orientations of the magnetic moment). (e) NCAFM ordering in the $\sqrt{3} \times \sqrt{3}$ hexagonal cell. (f) Monoclinic cell as was found for MnBi₂Te₄ compound in Ref. 8. Triclinic Niggli-reduced cell for the monoclinic structure with FM (g) and interlayer AFM (AFM-1) (h) magnetic ordering. (i-k) Intralayer magnetic configurations: antiferromagnetically ordered Mn chains with ferromagnetic interchain coupling (AFM-2), ferromagnetically ordered chains with antiferromagnetic interchain coupling (AFM-3), and checkerboard-like magnetic configuration with antiferromagnetic both intrachain and interchain coupling (AFM-4).
hexagonal cell containing six Mn atoms. The NCAFM configuration was treated within larger supercell, which is $\sqrt{3} \times \sqrt{3}$ in the hexagonal plane. For monoclinic phase we studied four AFM configurations on the base of triclinic Niggli-reduced cell, containing two Mn atoms, which was $2 \times 2$ expanded in the basal plane. The considered AFM configurations are the interlayer antiferromagnetic configuration with antiferromagnetic coupling through the longest Mn–Mn distance (along monoclinic c axis) between ferromagnetic layers (AFM-1) and three intralayer configurations: antiferromagnetically ordered Mn chains with ferromagnetic interchain coupling (AFM-2), ferromagnetically ordered chains with antiferromagnetic interchain coupling (AFM-3), and checkerboard-like magnetic configuration where both intrachain and interchain coupling are antiferromagnetic (AFM-4). DFT-D3 van der Walls corrections were applied for accurate structure optimization. To describe the strongly correlated Mn–d electrons we include the correlation effects within the GGA+U method in the Dudarev implementation. Since the nearest neighbors for Mn atom in both rhombohedral and monoclinic structures are Te(Se) atoms we have chosen the $U^* = U - J = 5.34 \pm 0.33$ eV values to be the same as in bulk MnTe($\text{MnSe}$).

III. RESULTS AND DISCUSSION

A. MnBi$_2$Te$_4$

The MnBi$_2$Te$_4$ compound was grown for the first time and its crystal structure was determined in Ref. 13. It was found to crystallize in the rhombohedral crystal phase (space group $R\overline{3}m$) and have a layered structure composed of septuple layer (SL) slabs with a stacking sequence of Te$_1$–Bi–Te$_2$–Mn–Te$_2$–Bi–Te$_1$ along the hexagonal axis with van der Waals gaps between them (Fig. 1 (a,b)). According to the powder X-ray diffraction (XRD) data the unit cell parameters are $a = 4.334$ Å and $c = 40.910$ Å. The atomic positional parameters were also determined. The DFT calculations performed in Ref. 13 reproduced well the a parameter while noticeably overestimated (by 5.06 %) the c one. Such an overestimation is typical for the DFT calculations performed for the layered structures without taking the van der Waals corrections into account. Besides, only FM state was considered in that calculation. In order to find out the ground state of MnBi$_2$Te$_4$ we consider FM, AFM, and NCAFM magnetic ordering in the rhombohedral structure (Figs. 1 (c–e)) as well as FM and four above described AFM alignments in the monoclinic structure (Figs. 1 (g–k)) which is typical for MnPn$_2$Ch$_4$ ($Ch = S, Se$). For each configuration the lattice parameters and atomic positions were optimized. According to the calculations the lowest energy structure is the rhombohedral one with an AFM interlayer coupling of the Mn magnetic moments which were found to be 4.607 $\mu_B$. The obtained equilibrium lattice constants $a = 4.336$ Å and $c = 40.221$ Å as well as the atomic positions (Table I) agree well with the experimental parameters. It is worth to note that other magnetic configurations of the rhombohedral structure, FM and NCAFM, are 4.5 meV and 11.8 meV per formula unit, respectively higher in energy than the AFM ground state. On the other hand the FM (Fig. 1 (g)) and different AFM configurations (Figs. 1 (h–k)) of the monoclinic structure have the total energy of more than 200 meV higher than that of the ground state although they differ between themselves by few meV only. We remind, that all calculations were done for the same $U^*$ value as in bulk MnTe (see Methods section). Additionally, an extensive testing was performed for the rhombohedral phase in order to ensure stability of the results against the $U^*$ value change. At that, the crystal structure was fully optimized for each $U^*$ considered. It was found that neither intra- nor interlayer magnetic ordering changes qualitatively when $U^*$ varies from 3 to 5.34 eV and the energy gain for AFM phase as compared to ferromagnetic ordering is larger for smaller $U^*$.

| site         | Wyckoff symbol | x   | y   | z (exp) | z (calc) |
|--------------|----------------|-----|-----|---------|----------|
| Mn           | 3a             | 0.0 | 0.0 | 0.0     | 0.0      |
| Bi           | 6c             | 0.0 | 0.0 | 0.42488(4) | 0.424306 |
| Te$_1$       | 6c             | 0.0 | 0.0 | 0.13333(6) | 0.134649 |
| Te$_2$       | 6c             | 0.0 | 0.0 | 0.29436(6) | 0.294763 |

FIG. 2. Calculated total (black line) and partial density of states (color lines) for the rhombohedral AFM MnBi$_2$Te$_4$. Zero energy corresponds to the Fermi level.
The calculated total density of states (DOS) for the rhombohedral AFM MnBi₂Te₄ (Fig. 2) shows that the compound is a narrow gap semiconductor with a bandgap of 217 meV in which the valence band maximum (VBM) as follows from the atom-projected DOS is composed by Te and Bi p-orbitals while the conduction band minimum (CBM) is formed mainly by empty orbitals. The observed experimentally for p-doped sample optical bandgap was estimated by using diffuse reflectance spectrum via the Kubelka-Munk method at room temperature to be equal to ~0.4 eV\textsuperscript{13}. In view of the p doping in the experiment the calculated energy gap agrees reasonably with the measured value.

### B. MnBi₂Se₄

The MnBi₂Se₄ compound was reported to be semiconducting antiferromagnet which adopts the monoclinic crystal structure\textsuperscript{8} (see Fig. 1 (f)). According to the X-ray Powder Diffraction measurements the monoclinic unit cell containing four MnBi₂Se₄ formula units (Z=4) belongs to the space group C2/m and is characterized by parameters: \(a = 13.319(3)\) Å, \(b = 4.0703(8)\) Å, \(c = 15.179(3)\) Å, and \(\beta = 115.5(1)°\). A triclinic Niggli-reduced cell (Z=2, see Fig. 1 (g,h)) for this structure can be described by the parameters: \(a = 4.07030\) Å, \(b = 6.96350\) Å, \(c = 13.85240\) Å, and \(\alpha = 87.0360°, \beta = 81.5520°, \gamma = 73.0070°\).

Our calculations for this structure confirm the antiferromagnetic configuration state for monoclinic MnBi₂Se₄. However, in contrast to the experimental finding of Ref.\textsuperscript{8} the intrachain AFM ordering (AFM-2 in our notation, see Fig. 1 (i)) is the second favorable configuration after AFM-3 (Fig. 1 (j)) being 0.9 meV/f.u. higher in energy. The optimized crystal cell parameters \((a = 4.0640\) Å, \(b = 6.93876\) Å, \(c = 13.81183\) Å, and \(\alpha = 87.3886°, \beta = 81.5400°, \gamma = 72.9718°\)) as well as atomic coordinates (see Table II) are in good agreement with the experimental data.

However, the calculations for the MnBi₂Se₄ compound in rhombohedral structure, performed similar to the MnBi₂Te₄ case for FM, AFM, and NCAFAM magnetic ordering, revealed that the AFM rhombohedral structure is the lowest energy structure. It is of 39.2 meV (per formula unit) lower than the AFM-3 monoclinic structure. Note that the cell volume in the rhombohedral structure is 1.45 % (per formula unit) smaller than that in the monoclinic MnBi₂Se₄. At the same time the equilibrium rhombohedral structure with FM and NCAFAM magnetic configurations has higher energies than the AFM ground state by only 0.6 meV and 7.8 meV, respectively. The optimized lattice constants \(a = 4.0782\) Å and \(c = 37.8059\) Å are smaller than the respective parameters of the rhombohedral MnBi₂Te₄ owing to the smaller radius of the \(Ch\) atom while the equilibrium atomic positions (Se₁, \(z = 0.133816\); Se₂, \(z = 0.295154\); Bi, \(z = 0.424624\)) are comparable with those in MnBi₂Te₄ (see Table I).

It is worth noting that in both structures the coordination of Mn atoms by six nearest Se atoms, which form MnSe₆ octahedra, is similar. However, while in the rhombohedral structure the octahedra are hexagonally packed, in the monoclinic phase adjacent MnSe₆ share edges to form one-dimensional chains along \(b\) axis (see Figs. 1 (b and f)). At the same time Mn-Mn bond lengths in hexagonal layer of rhombohedral structure and that in the chain of monoclinic structure are very close: 4.0782 Å and 4.0640 Å, respectively. In this regard, the fact that we found interlayer AFM configuration for rhombohedral structure and AFM-3 one for monoclinic structure the most energetically preferable magnetic configurations looks reasonable. In both cases the ferromagnetic ordering along the short Mn-Mn bonds is favorable while along the long bonds (between hexagonal layers in rhombohedral structure and between chains in monoclinic structure) the antiferromagnetic coupling is preferred.

The reason for the discrepancy between the experimentally determined and calculated crystal structure can consist in that a mixed Mn/Bi occupancy where 6 % of Mn occupy Bi sublattice (and vice versa)\textsuperscript{8} was found in the studied sample. Such a disordering in the Bi and Mn sublattices can presumably stabilize the monoclinic phase in the experiment. In other words, the growth of the rhombohedral phase can be achieved under appropriate synthesis conditions providing suppression of the Mn/Bi intermixing. The disordering factor can be responsible also for different type of antiferromagnetic ordering (interchain vs. intrachain) in the monoclinic structure.

Owing to similarity in the crystal structures of rhombohedral MnBi₂Ch₄ and the band structure of MnBi₂Se₄ in general is similar to that of MnBi₂Te₄.

| atom | exp. calc. | exp. calc. | exp. calc. |
|------|------------|------------|------------|
| Se₁  | 0.01145    | 0.01540    | 0.16220    | 0.15282 |
| Se₂  | 0.98855    | 0.98460    | 0.83780    | 0.84718 |
| Se₃  | 0.11384    | 0.11373    | 0.22719    | 0.22757 |
| Se₄  | 0.88616    | 0.88627    | 0.77281    | 0.77243 |
| Se₅  | 0.34158    | 0.34263    | 0.25614    | 0.25339 |
| Se₆  | 0.65842    | 0.65737    | 0.74568    | 0.74667 |
| Se₇  | 0.34166    | 0.33676    | 0.64172    | 0.64818 |
| Se₈  | 0.65834    | 0.66324    | 0.35528    | 0.35182 |

### TABLE II. Experimental (recalculated for Niggli-reduced cell from the data of Ref. 8) and calculated atomic coordinates for monoclinic MnBi₂Se₄ structure.
The calculated DOS for rhombohedral AFM MnBi$_2$Se$_4$ (Fig. 3 (a)) demonstrates semiconducting spectrum with very narrow bandgap of 22 meV, where, like in the MnBi$_2$Te$_4$ case, gap edges are determined by the \(p\)-orbitals of Se and Bi (VBM) and mostly Bi (CBM). The values of the Mn magnetic moments in the AFM-3 case) in agreement with experimental finding\(^8\) that is 4-5 times smaller than the calculated value for any AFM configuration. This discrepancy can be attributed to non-stoichiometric composition of the measured samples.

We emphasize again that for both rhombohedral and monoclinic phases the interlayer/interchain antiferromagnetic coupling is only slightly more favorable than the ferromagnetic one. This result is in line with experimental observation\(^8\) which suggests the existence of residual ferromagnetic ordering in the MnBi$_2$Se$_4$ sample. The small energy difference between magnetic configurations is explained by the fact that in both phases the distance between Mn layers (Mn chains) is too long for strong magnetic exchange interaction and hence the Mn atoms of adjacent structural blocks are magnetically coupled by indirect exchange interactions through the Se and Bi atoms.

### C. MnSb$_2$Te$_4$

The reliable data on the crystal structure of MnSb$_2$Te$_4$ are absent with exception of the paper published in the early eighties, Ref. 24, where an unusual for the Mn\(Pn\)\(n\)\(Ch\)\(4\) series tetragonal symmetry of the crystal structure was identified and nothing about atomic parameters was reported. For this reason we consider this compound within the same rhombohedral and monoclinic phases, that are typical for related MnSb\(Ch\)\(4\).

The total energy calculations show that like in the MnBi$_2$Te$_4$ case the rhombohedral phase is strongly preferred. At the same time, among magnetic configurations of the monoclinic structure, AFM-3 is energetically favorable, as in the previously described cases of MnBi$_2$Ch$_4$. The rhombohedral AFM structure is by 162.2 meV per formula unit lower in energy than the monoclinic structure with AFM-3 coupling. This result unambiguously indicates that MnSb$_2$Te$_4$ can be grown in the rhombohedral phase. At the same time, as in the other MnBi$_2$Ch$_4$ compounds, the energy difference between ferromagnetic and antiferromagnetic configurations is small for both rhombohedral and monoclinic phases and NCAFM phase is the most unfavorable among magnetic configurations of the rhombohedral structure. The optimized lattice constants for the rhombohedral AFM structure are \(a = 4.2626 \text{ Å}\) and \(c = 39.6572 \text{ Å}\), and the atomic positions (Te\(_1\), \(z = 0.133900\); Te\(_2\), \(z = 0.293205\); Sb, \(z = 0.424323\); Mn, \(z = 0\)) are close to those in MnBi$_2$Te$_4$ (see Table I).

The band structure of the MnSb$_2$Te$_4$ compound is characterized by a bandgap of 123 meV (Fig. 4) that is about two times smaller than the gap in MnBi$_2$Te$_4$. Alike the case of MnBi$_2$Te$_4$ gap edges are contributed by the \(Pn\) and Te (VBM) and \(Pn\) only (CBM) states. Owing to

\[ \text{Energy (eV)} \]

\[ \begin{array}{cccc}
  \text{Mn} & \text{Se} & \text{total} \\
  3.0 & 3.5 & 3.0 & 3.5 \\
  \text{Bi} & \text{Mn} & \text{Se} & \text{total} \\
  2.0 & 2.5 & 2.0 & 2.5 \\
  \end{array} \]
similarity of the crystal structure with the MnBi$_2$Te$_4$ case and the same local atomic surrounding for the Mn atoms the Mn magnetic moments, 4.590 $\mu_B$, are very close to those in the Bi-containing compound.

D. MnSb$_2$Se$_4$

The MnSb$_2$Se$_4$ compound was synthesized and its structural, electronic and magnetic properties were studied in Ref. 9. Single-crystal X-ray diffraction revealed that MnSb$_2$Se$_4$ crystallizes like MnBi$_2$Se$_4$ in the monoclinic space group C2/m with the parameters $a = 13.076(3)$ Å, $b = 3.965(1)$ Å, $c = 15.236(3)$ Å, and $\beta = 115.1(3)^\circ$ (Z=4). This structure can be conveniently represented in the Niggli-reduced form as triclinic cell (Z=2) with parameters $a = 3.96500$ Å, $b = 6.83200$ Å, $c = 13.93920$ Å, and $\alpha = 87.3400^\circ$, $\beta = 81.8230^\circ$, $\gamma = 73.1310^\circ$.

Similarly to the above considered MnPn$_2$Ch$_4$ compounds we performed the optimization of the crystal structure of MnSb$_2$Se$_4$ within rhombohedral and monoclinic phases with taking into account the magnetic ordering. Irrespective the magnetic ordering monoclinic phase has the lower energy than rhombohedral structure. Among the considered spin configurations for monoclinic structure we found out that the ferromagnetic configuration is less favorable that is in agreement with the experimental result. As it happens for the compounds considered above the AFM-3 configuration has the lowest energy among others. The optimized lattice parameters for the Niggli-reduced cell are $a = 3.98107$ Å, $b = 6.87504$ Å, $c = 13.67025$ Å, and $\alpha = 87.6610^\circ$, $\beta = 81.6250^\circ$, $\gamma = 73.1697^\circ$.

| atom | $x$ exp. | $x$ calc. | $y$ exp. | $y$ calc. | $z$ exp. | $z$ calc. |
|------|----------|-----------|----------|-----------|----------|-----------|
| Se$_1$ | 0.01230 | 0.01199 | 0.15530 | 0.16060 | 0.32010 | 0.31550 |
| Se$_2$ | 0.98770 | 0.98801 | 0.84470 | 0.83940 | 0.67990 | 0.68450 |
| Se$_3$ | 0.11430 | 0.11647 | 0.22890 | 0.22199 | 0.04250 | 0.04503 |
| Se$_4$ | 0.88570 | 0.88355 | 0.77110 | 0.77801 | 0.95750 | 0.95497 |
| Se$_5$ | 0.34510 | 0.34087 | 0.25650 | 0.25946 | 0.55330 | 0.55880 |
| Se$_6$ | 0.65490 | 0.65913 | 0.74350 | 0.74054 | 0.44670 | 0.44120 |
| Se$_7$ | 0.34460 | 0.33405 | 0.63850 | 0.65225 | 0.17230 | 0.17967 |
| Se$_8$ | 0.65540 | 0.66595 | 0.08580 | 0.07050 | 0.86660 | 0.86184 |
| Sb$_1$ | 0.27380 | 0.28382 | 0.08580 | 0.07050 | 0.86660 | 0.86184 |
| Sb$_2$ | 0.72620 | 0.71618 | 0.91420 | 0.92950 | 0.13340 | 0.13816 |
| Sb$_3$ | 0.35540 | 0.35164 | 0.41520 | 0.42240 | 0.37400 | 0.37437 |
| Sb$_4$ | 0.64460 | 0.64836 | 0.58480 | 0.57760 | 0.62600 | 0.62563 |
| Mn$_1$ | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.50000 | 0.50000 |
| Mn$_2$ | 0.50000 | 0.50000 | 0.50000 | 0.50000 | 0.00000 | 0.00000 |

These parameters as well as the atomic coordinates (see Table III) nicely reproduce the experimental structural parameters.

FIG. 4. Calculated DOS for the rhombohedral AFM MnSb$_2$Te$_4$.

FIG. 5. Calculated DOS for the monoclinic structure of MnSb$_2$Se$_4$ with AFM-3 magnetic ordering.

Like in case of other MnPn$_2$Ch$_4$ the antiferromagnetic ordering of the Mn magnetic moments is only slightly more favorable than the ferromagnetic configuration. According to the magnetic susceptibility measurements performed in Ref. 9 the interaction between the Mn magnetic moments is predominantly antiferromagnetic, however, the slight increase in the susceptibility observed below 5 K was explained by the existence of a residual ferromagnetic ordering in the sample at
very low temperatures. Our results showing small energy difference between ferro- and antiferromagnetic configurations confirm the competition between AFM and FM ordering in the compound. The calculated magnetic moment on the Mn atoms for the most favorable AFM-3 structure is 4.596 $\mu_B$, which is almost the same as that in monoclinic MnBi$_2$Se$_4$.

Experimental estimation with using the diffuse reflectance infrared spectroscopy measurements at room temperature gave the value of the bandgap in the MnSb$_2$Se$_4$ sample of $\sim$0.32 eV$^9$. On the other hand, from the temperature dependent electrical resistivity measurements the bandgap value was estimated to be of 0.52 eV$^9$. Our calculations of the electronic structure provide a bandgap, which is closer to the experimental value derived from the charge-transport data. As can be seen from the calculated DOS for monoclinic AFM-3 structure presented in Fig. 5, in MnSb$_2$Se$_4$ the gap is of 757 meV that is comparable with the value in the monoclinic MnBi$_2$Se$_4$ (772 meV). Like in the case of MnBi$_2$Se$_4$ Se/Bi states dominate at the gap edges.

IV. DISCUSSION AND CONCLUDING REMARKS

In summary, we have performed DFT calculations of electronic, magnetic and crystal structure of the MnP$_n$Ch$_4$ series of ternary transition metal chalcogenides ($Pn = Sb, Bi; Ch = Se, Te$). All MnP$_n$Ch$_4$ compounds were considered within the rhombohedral and monoclinic phases, which were shown experimentally to be typical for some compounds of the series. The FM, interlayer AFM and NCAFM spin structures have been taken into account in the calculations for rhombohedral structure and FM and four different AFM configurations for monoclinic phase. The obtained total energies for MnP$_n$Ch$_4$ phases are summarized in the Table IV. We have found that the compounds containing the heavier chalcogen atom, Te, show a strong trend to adopt the layered rhombohedral structure.

TABLE IV. Relative total energies (in meV) per formula unit (zero energy corresponds to rhombohedral AFM case) for different magnetic states of rhombohedral and monoclinic structures of MnP$_n$Ch$_4$ compounds.

| compound     | rhombohedral | monoclinic |
|--------------|--------------|------------|
|              | AFM FM NCAFM | FM AFM-1 AFM-2 AFM-3 AFM-4 |
| MnBi$_2$Te$_4$ | 0.0 +4.5 +11.8 | +206.4 +209.6 +204.6 +202.7 +205.2 |
| MnBi$_2$Se$_4$ | 0.0 +0.6 +7.8 | +43.0 +41.7 +40.1 +39.2 +40.6 |
| MnSb$_2$Te$_4$ | 0.0 +1.3 +11.2 | +165.9 +165.1 +164.7 +162.2 +165.3 |
| MnSb$_2$Se$_4$ | 0.0 +0.8 +8.1 | -11.3 -12.7 -13.7 -15.1 -13.3 |

Thus, our results confirm the structure of MnBi$_2$Te$_4$, recently determined by the experiment and predict the similar crystal structure for MnSb$_2$Te$_4$, which has not been studied in details earlier. For the compound with lighter both pnictogen and chalcogen atoms, MnSb$_2$Se$_4$, our result, predicting the lowest energy state for monoclinic structure, is in agreement with experimental data. A similar change in the crystal structure from the rhombohedral layered phase to the monoclinic structure was reported earlier for compounds with substitution between Se and Te in FeSb$_2$Te$_4−x$Se$_x$ ($x = 1,2,3,4$)$^{25}$. At the same time our total energy calculations for MnBi$_2$Se$_4$, which contains heavier pnictogen and lighter chalcogen atoms, predicting the rhombohedral phase as the stable structure contradict the experimentally determined monoclinic structure. However, it should be noted that the energy gain for the rhombohedral over monoclinic structure in MnBi$_2$Se$_4$ is five times smaller than in the MnBi$_2$Te$_4$ compound (39.2 vs. 202.7 meV, see Table IV). This discrepancy can be an indication that the rhombohedral phase of MnBi$_2$Se$_4$ can be obtained at the growth conditions that are different from those used in Ref.$^{9}$. E.g. it could probably be stabilized by using MBE. We have also shown, that irrespective of the crystal structure, all compounds of the MnP$_n$Ch$_4$ family are antiferromagnetic semiconductors. In accordance with the experimental findings for MnP$_n$Se$_4$, indicating the competition between AFM and FM ordering, the energy gain for the AFM coupling with respect to ferromagnetic state is very weak – it is just a few meV per formula unit or even smaller. The small energy difference between antiferromagnetic and ferromagnetic configurations is explained by the fact that in both phases the distance between Mn layers is too long for strong magnetic exchange interactions. At the same time among considered antiferromagnetic configurations for monoclinic structure AFM-3, in which ferromagnetically ordered Mn chains couple to each other, is the most favorable. Owing to similarity in the local atomic surrounding for the Mn atoms the Mn magnetic moments are almost the same through the MnP$_n$Ch$_4$ series regardless of the structure. On the other hand, the type of crystal structure, rhombohedral or monoclinic, significantly influences the bandgap width. In the rhombohedral MnP$_n$Ch$_4$ phases the gap is of 22-217 meV while in the compounds with monoclinic structure this value is significantly larger and amounts to about 750-770 meV.

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