

Polytypism in LaOBiS₂-type compounds based on different three-dimensional stacking sequences of two-dimensional BiS₂ layers

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Abstract

LaOBiS₂-type materials have drawn much attention recently because of various interesting physical properties, such as low-temperature superconductivity, hidden spin polarization, and electrically tunable Dirac cones. However, it was generally assumed that each LaOBiS₂-type compound has a unique and specific crystallographic structure (with a space group *P4/nmm*) separated from other phases. Using first-principles total energy and stability calculations we confirm that the previous assignment of the centrosymmetric *P4/nmm* structure to LaOBiS₂ is incorrect as a phonon instability renders this structure impossible. Furthermore, we find that the unstable structure is replaced by a *family* of energetically closely spaced modifications (polytypes) differing by the layer sequences and orientations. We find that the local Bi-S distortion leads to three polytypes of LaOBiS₂ with different stacking patterns of the distorted BiS₂ layers. The energy difference between the polytypes of LaOBiS₂ is merely ~1 meV/u.c., indicating the possible coexistence of all polytypes in the real sample and that the particular distribution of polytypes may be growth-induced. The in-plane distortion can be suppressed by pressure, leading to a phase transition from polytypes to the high-symmetry *P4/nmm* structure with a pressure larger than 2.5 GPa. In addition, different choices of the intermediate atoms (replacing La) or active atoms (BiS₂) could also manifest different ground state structures. One can thus tune the distortion and the ground state by pressure or substituting covalence atoms in LaOBiS₂-family.

I. Introduction

LaOBiS₂ represents a group of materials consisting of BiS₂ layers whose states dominate the low-energy spectrum, separated by electronically passive La₂O₂ buffer layers. LaOBiS₂-type materials have drawn attention because of the measured superconductivity¹⁻¹⁴ (up to $T_c = 10.6$ K) and because the BiS₂ layer is spin-orbit active and thus leads to many interesting spin-related properties, including hidden spin polarization¹⁵, spin field effect transistor¹⁶ and electrically tunable Dirac cones¹⁷. The general crystal structure consists of a stack of layers (BiS₂)⁻/(La₂O₂)²⁺/(BiS₂)⁻ made of two BiS₂ rocksalt-like layers and an intermediate fluorite-like La₂O₂ buffer layer separating them¹⁸. Many materials described by this structural scheme have recently been synthesized^{1, 2, 4, 5, 7, 9, 10, 14}, and even more members not listed in inorganic compound data bases (ICSD) can be conceived^{17, 19}. As with many other compounds, here too it was generally assumed that each compound has a unique and specific crystallographic structure separated from other phases. Using first-principles calculations we find that contrary to this view^{1, 6, 8, 11, 12, 18} the three-dimensional (3D) structure of this important family of compounds represents instead a family of energetically closely spaced modifications differing by the layer sequences and orientations. Such *polytypes* are “natural superlattices”, familiar from other areas in condensed matter such as SiC^{20, 21}, ZnX (X = S, Se, Te)²²⁻²⁴, and ATiO₃ (A = Sr and Ba) perovskites^{25, 26}. Polytypes hold a special place as structural phases in that they have very similar (within meV) total energies, yet are distinguished by those physical properties that are sensitive to orientation and stacking such as polarization of light emission and sometimes the magnitude of the zone-folded band gap (for example, the optical band gap of cubic vs wurtzite polytype of SiC differ by nearly 1 eV²⁹). What makes LaOBiS₂ polytypes discovered here particularly interesting is that (i) the characteristic local structural distortions in the electronically active BiS₂ layers could lead to charge fluctuations which may relate to the electron-phonon coupling and the mechanism of superconductivity^{1, 30}; and (ii) different polytypes are either centrosymmetric or noncentrosymmetric, a distinction that carries with it different physical properties related to presence or absence of inversion symmetry, such as band splitting, second harmonic generation and (hidden) spin polarization¹⁵.

In this article we use first-principles total energy calculations to assess the structure and stability of various polytypes in the LaOBiS₂-family of compounds. We find that the local Bi-S distortion leads to three polytypes of LaOBiS₂ according to the different stacking pattern of distorted BiS₂ layers, rather than the previously assumed *P4/nmm* structure. The in-plane distortion is mainly induced by the interaction between the intermediate LaO and the BiS₂ layers, and the electron hybridization in the BiS₂ layer. We performed structural optimization in steps starting from the most restricted degrees of freedom to show how a small distortion can transform the assumed unstable structure to its three polytypes. Since the energy difference between the polytypes of LaOBiS₂ is merely ~ 1 meV/u.c., the real 3D material constructed by stacking up such three types of building blocks could manifest various sequences of polytypes depending sensitively on the growth condition. Furthermore, the in-plane distortion can be suppressed by pressure, leading to a phase transition from polytypes to the high-symmetry *P4/nmm* structure with a pressure larger than 2.5 GPa. In addition, different choices of the buffer atoms (replacing La) or active atoms (BiS₂) manifest different ground state polytypes.

II. The in-plane structure of the 2D BiS₂-like layer and the emergence of possible stacking sequences

LaOBiS₂¹⁸ has been generally accepted to have the ZrCuSiAs-type structure, with a centrosymmetric *P4/nmm* space group. X ray diffraction data was refined^{1, 6} by fitting the measured intensities to this structure type (named T₀ hereafter). In T₀ the BiS₂ layers in the (BiS₂)⁻/(La₂O₂)²⁺/(BiS₂)⁻ stacks have four equal Bi-S bonds, as shown in Fig. 1. However, recent phonon calculations using density functional theory (DFT) found that the T₀ structure with *assumed* equal Bi-S bond lengths of 2.89 Å has soft phonons at the Brillouin zone center Γ point, which indicates dynamic instability and the theoretical impossibility of this T₀ structure¹¹ being stable. Yildirim showed that by shifting the S atoms along the diagonal of the 2D square (*x* or *y* direction in Fig. 1b), forming a ferroelectric-like distortion with two different in-plane Bi-S bonds (bond lengths 2.80 Å and 2.98 Å, see Fig. 1c) one can remove the dynamic instability. In this calculation a deformation parameter Q, which is defined by the normal modes having the unstable phonon was introduced to represent the in-plane displacement of S atoms. The total

energy was minimized with respect to Q , with the remaining structural degrees of freedom other than Q (such as lattice parameter and atomic positions) kept frozen at their $Q = 0$ value (corresponding to the T_0 structure). A subsequent neutron powder diffraction experiment by Athauda et al.³¹ confirmed this predicted *local* distortion within a single BiS_2 layer by observing indeed two different Bi-S bonds (with lengths of 2.68 Å and 3.11 Å). We note that the powder diffraction also suggested another antiferroelectric-like distortion³¹, but such a mode is predicted to induce an instability at M point that is present in F-doped LaOBiS_2 but absent in the parent compound, and is thus excluded by single crystal diffraction very recently³².

However, the in-plane *local distortions* predicted¹¹ and observed³¹ do not define as yet a 3D structure in LaOBiS_2 : there are two BiS_2 layers in a unit cell, and one needs to construct a 3D model of how the various 2D layers are stacked so as to minimize the energy. Yildirim¹¹ suggested a 3D structure that consists of two BiS_2 layers having the *same direction of distortion* (illustrated by the blue arrow shown in Fig. 1c) as a replacement of the unstable T_0 structure. This ferroelectric-like structure removes the phonon instability and thus lowers the energy, turning the 3D structure into non-centrosymmetric T_1 (space group $P2_1mn$) from centrosymmetric T_0 ($P4/nmm$)¹¹. Interestingly, there are additional 3D stacking sequences of the 2D layers possible that were not previously examined in pristine LaOBiS_2 (without doping) by aligning the in-plane distortion in different directions. There are three possible stacking types that fulfill the local Bi-S1 distortion^{11, 31}. In T_1 type, the local distortions of two BiS_2 layers are *along x* direction, in T_2 they occur along x and $-x$ direction, while in T_3 are x and y direction. These distortions lower the system's symmetry from $P4/nmm$ (T_0) to $P2_1mn$ (T_1), or $P2_1m$ (T_2) or $C2$ (T_3). Among T_1 , T_2 , and T_3 , only T_2 is centrosymmetric, whereas T_1 and T_3 are non-centrosymmetric. We next inquire as to the energetic order of stability of the different polytypes in LaOBiS_2 as well as in other compounds from the same general family.

III. Methods of calculation

The geometrical and electronic structures are calculated by the projector-augmented wave (PAW) pseudopotential³³ and the generalized gradient approximation of Perdew,

Burke and Ernzerhof (PBE)³⁴ to the exchange-correlation functional as implemented in the Vienna *ab initio* package (VASP)³⁵. The plane wave energy cutoff is set to 550 eV. Electronic energy minimization was performed with a tolerance of 10^{-6} eV, and all atomic positions were relaxed with a tolerance of 10^{-3} eV/Å.

We note that PBE functional does not take the long-range van der Waals interaction into account, and thus usually overestimate the interlayer space. To overcome this, we also use PBE-D2 exchange-correlation functional, with the implementation of van der Waals (VDW) correction, to optimize the distorted structures (see Sec. VI).

IV. Three levels of approximation for predicting bond relaxation and symmetry breaking

The three polytypes differ in the stacking direction of electronic-active BiS₂ layers along the [001] direction. To gain insight into the various degrees of freedom we perform structural optimization in steps starting from the simplest and most restricted:

Approach (a): If one allows the T₀ structure to relax but without imposing initially any symmetry breaking, only the *a*, *c* lattice vectors and four independent cell-internal atomic coordinate parameters (atomic positions of La, Bi, S1 and S2 sites along the *c* axis) can relax. This restricted relaxation is an artifact of the method of calculation, namely of assuming initially a high symmetry structure. It reflects the fact that the other degrees of freedom in T₀ that could relax are not permitted to do so because a high symmetry (zero force on atoms) is artificially imposed. As a result, the final structure in this relaxation method still has the same space group *P4/nmm* as the initial starting point, denoted by the T₀ point in Fig. 2. Although this is the only optimization treatment in most structure determination step in the DFT community, the result is incorrect because of the artificial restriction to high symmetry.

Approach (b): Next, we allow in-plane relaxation by initially lowering the symmetry but freeze all other degrees of freedom, while seeking the energy minimum under this constrain. To do so we start form T₀ but shift S1 atom of each BiS₂ layer along x or y direction, (depending on the T₁-T₃ type) and artificially *keep all other structural degrees of freedom frozen*. Such frozen Bi-S1 “bond length mismatch” distortion has been used by Ref. ¹¹ for T₁ and is defined by the S1 displacement Δ . This is not the most general

procedure, and is used here to observe what its physical consequence is. This simplified procedure of allowing just one mode to drive distortion is common in simple models of phase transitions. The results of this simplified model are the three curves in Fig. 2. They show that if one scans the energy as a function of Δ , each of these structures has different energy minima shown as solid dots in T_1 - T_3 curves. *This is clear evidence that in $LaOBiS_2$ T_0 structure is a saddle point and thus not able to exist stably.*

Approach (c) – Most general: The in-plane Bi-S1 distortion can enable additional degrees of freedom, including the lattice parameters and atomic positions. For example, T_1 -type distortion will elongate the axis, while T_2 -type distortion will twist the rectangular x-z plane of the unit cell into a parallelogram. Therefore, in the most general approach (c) we further relax all degrees of freedom starting from the energy-minimum structures of T_1 - T_3 , and get three final structures that are several meV/unit cell (u.c.) lower in energy, T_1^* , T_2^* and T_3^* indicated in Fig. 2 by diamond shapes. Unlike the T_0 structure, the T_1^* , T_2^* and T_3^* structures are thermodynamically stable. We also considered full relaxation starting from a generic symmetry breaking of the T_0 structure by randomly adding small distortions on both lattice vectors and atomic positions. We find from a few such starting points that the relaxed structures all become T_1^* , T_2^* or T_3^* structure, indicating that T_1^* - T_3^* structure are the only three local minima around T_0 phase.

Comparision between different fully relaxed polytypes: Table I shows the total energy, space group, lattice parameter and Bi-S bond length of T_0 , T_1^* - T_3^* structure as well as the experimental refinement using T_0 structure. Several observations are found: (i) Although T_0 structure has a good agreement and a reasonable fit⁶ (R factor < 0.1) with experiment regarding the in-plane lattice constant, there is only one kind of Bi-S bond, which is inconsistent with the results by neutron diffraction³¹. On the other hand, all of T_1^* to T_3^* suggests two kinds of in-plane Bi-S1 bonds, with the bond lengths 2.76-2.77 and 3.03-3.04 Å, respectively. These bond lengths agree with the experiments well³¹. (ii) With the presence of the in-plane distortion for T_1^* - T_3^* structures relative to T_0 , the buckling nature of the Bi-S1 plane is nearly unchanged. The calculated S1-Bi-S1 angle varies from 165° for T_0 to 164° for all T_1^* - T_3^* structures, including one type of S1-Bi-S1 angle in T_1^* and T_2^* , and two types in T_3^* . (iii) The T_2^* structure is centrosymmetric and

has the lowest energy, but only 1-2 meV/u.c. lower than the non-centrosymmetric T_1^* and T_3^* . Such a small energy difference originates from the weak van der Waals interaction between adjacent BiS_2 layers. The total energies of the polytypes are so close that theoretical stability could be significantly affected by the temperature or crystal growing conditions. On the other hand, T_0 structure has the highest energy, about 10 meV/u.c. higher than T_2^* .

In order to visualize the transformation path from the saddle point T_0 to the stable structures (e.g., T_1^* or T_2^*) in LaOBiS_2 , we show in Fig. 3 the feasibility of converting LaOBiS_2 from T_1^* to T_2^* structure with T_0 structure as an intermediate state. In $T_0 \rightarrow T_1^*$ and $T_0 \rightarrow T_2^*$ path we start from T_0 structure and impose a tiny T_1 - or T_2 -type distortion on T_0 . Then we record each step of DFT relaxation process from T_0 to T_1^* (T_2^*) as the reaction coordinate, i.e., the geometric parameter that changes during the conversion between T_1^* and T_2^* , by gradually changing the cell and the atomic position using conjugate gradient method. We find that T_0 structure stays at a saddle point, so it is unstable and will spontaneously relax to a distorted structure T_1^* or T_2^* (also probably T_3^*). On the other hand, the potential barrier between the transition of T_1^* and T_2^* structures is about 10 meV, which is not large enough to make T_2^* as a unique structure. Instead, all T_1^* to T_3^* structures or their mixed phases are possible to happen in room temperature.

V. Pressure-induced phase transition and polytypes in other LaOBiS_2 -type compounds

In order to unveil the physical origin of the polytypism, we investigated the ground-state structure of LaOBiS_2 under hydrostatic pressure. Figure 4(a) shows the in-plane distortion of T_1 - T_3 structures presented by the Bi-S1 bond difference as a function of hydrostatic pressure. Zero pressure $P = 0$ corresponds to T_1^* - T_3^* structures with PBE-calculated equilibrium lattice constant. We find that the pressure indeed suppresses the in-plane distortion for all T_1 - T_3 structures. Above $P = 2.5$ GPa (corresponding an in-plane lattice constant $a = b = 4.02$ Å) the high-symmetry T_0 structure becomes the ground state of LaOBiS_2 .

Following LaOBiS_2 , many compounds having similar structure are reported for the purpose of exploring the BiS_2 -based superconductivity^{7, 10}. Therefore, it is interesting to

ask if the other compounds in this family also have such polytypes or not, and what determines T_0 structure or distorted structures as a ground state. We substitute La (with Y), Bi (with Sb, As) or S (with Se, Te) site at one time and fix the other 3 sites the same as LaOBiS_2 . Figure 4(b) shows the relative energy of the polytypes of these materials. We found that when substituting La with lighter elements or substituting S with heavier elements, the undistorted T_0 structures are the ground states, which means there is no polytypes in these materials. On the other hand, when substituting Bi with lighter elements Sb and As, T_0 structures are no longer dynamic stable (dash lines), while distorted T_1^* - T_3^* are local minima. Among them T_2^* is the ground state, with the total energy 10-15 meV lower than that of T_1^* . The energy differences between T_2^* and T_0 for LaOSbS_2 and LaOAsS_2 are 167 and 718 meV, respectively, which is much larger than the counterpart of LaOBiS_2 . Moreover, the in-plane M-S1 bonds (M: Bi, Sb or As) also reveals that LaOSbS_2 and LaOAsS_2 suffer larger distortion. The two As-S1 bond lengths in LaOAsS_2 are 2.43 Å and 3.31 Å. As a result, such large distortion breaks the 2D As-S square and forms individual zigzag As-S chains, as shown in the inset of Fig. 4(b).

From the study of pressure and various LaOBiS_2 -type compounds we conclude that the polytypism in LaOBiS_2 -family is mainly attributed to two reasons: the “substrate” effect of the intermediate layer (e.g., LaO) and hybridization effect of the active layer (e.g., BiS_2). In LaOMS_2 compounds (M: Bi, Sb, As), the mismatch between the optimum lattice constants of LaO (larger) and MS_2 (smaller) layers tends to stretch the M-S square and thus cause distortion. When the lattice of MS_2 layers becomes smaller without changing LaO layer, the stretching effect becomes stronger. Interestingly, although this effect originates from the interaction between LaO and MS_2 layers, the distortion in LaO layer is insignificant. It is because the bond energy of La-O is large so that the LaO network remains stable when suffering distortions. On the other hand, enlarging the lattice parameter of the side layer or reducing the lattice parameter of the intermediate layer induce better lattice match between side and intermediate layer so that the distortion is unlikely to happen, as the case in LaOBiSe_2 , LaOBiTe_2 and YOBiS_2 . For LaOBiS_2 under pressure, the BiS_2 and LaO layers are simultaneously compressed, in which case the enhanced Bi-S1 bond strength could stabilize the T_0 structure and prevent distortion.

The other factor that can lead to distortion is within the local structure of the side layer. For the trend from Bi to As, the group-V cations behave more covalent character while less ionic character. As a result, they are inclined to form sp^3 hybridization with 3 S atoms and the other bond is the lone-pair electron. The lone-pair bond usually has larger repulsive force than the other bonds, and thus breaks two M-S1 bonds to form zigzag chains.

VI. The results of VDW correction

VDW interactions represent the interaction of an **induced moment** (dipole, quadropole, etc) with itself. This is strictly zero in mean field Hartree -Fock or DFT. From Table I we find that DFT without VDW gives the length of c axis (T_0 and $T_1^* - T_3^*$) as 14.25 Å, much larger than the observed 13.83 Å. This is because the PBE functional didn't take the long-range van der Waals interaction into account, and thus usually overestimate the interlayer space.

To overcome this, we also use PBE-D2 exchange-correlation functional that includes a rough VDW term to optimize the distorted structures. We find that the a and c axis of T_0 structure are 3.99 Å and 13.62 Å, respectively. Although PBE-D2 gives a better agreement with experiments on c axis (13.83 Å), it underestimate the a axis by 1.5% than that of experiments or PBE results (4.05 Å). More importantly, because of the biaxial strain effect within x - y plane under PBE-D2 method, the undistorted structure T_0 becomes the ground state. We performed the relaxation starting from the PBE relaxed $T_1^* - T_3^*$ structure and find that the final configuration is the T_0 structure. Phonon calculations of LaOBiS₂ for smaller in-plane lattice parameters also suggested that the undistorted structure T_0 is dynamic stable¹¹. Since the accuracy of a axis is more important to investigate the in-plane distortion, we used PBE functional for the base of calculation and analysis.

VII. Summary

By using first-principles total energy and stability calculations, we predict that the local Bi-S distortion leads to three polytypes of LaOBiS₂-type materials according to the different stacking pattern of BiS₂-like layers. The in-plane distortion, mainly induced by

the interaction between the intermediate and the side layers and the electron hybridization in the side layer, can lower the total energy comparing with the conventional accepted *P4/nmm* structure. In LaOBiS₂, the energy difference between the polytypes is small, indicating the possible coexistence of all polytypes in the real sample. While we cannot determine if the superposition is dynamic in nature (time-dependent doping), we note that such a superstructure with the combination of *T*₁, *T*₂ and *T*₃ polytypes will effectively lower the symmetry to the P1 space group. Such a superstructure symmetry has been recently suggested by a single-crystal neutron-diffraction experiment of Athauda *et al.*³² Finally, external pressure and different choices of the intermediate atoms (replacing La) or active atoms (BiS₂) manifest different ground state polytypes. One can thus tune the distortion and the ground state by both physical and chemical means. Our findings provide a clear picture on the complexity of the crystal structure of LaOBiS₂-type materials, which might be relevant to the mechanism of the recently found BiS₂-based superconductivity.

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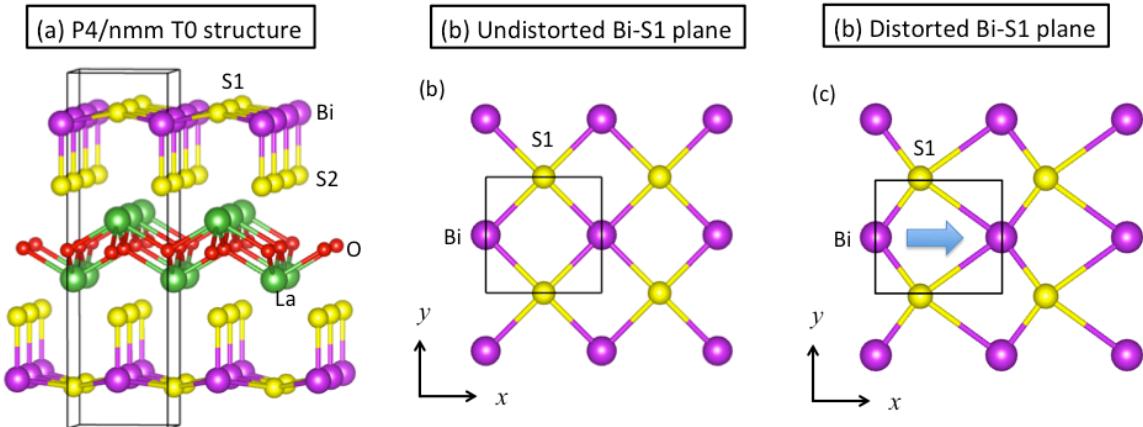


Fig. 1: (a) P4/nmm T₀ structure of LaOBiS₂. (b) Top view of Bi-S1 2D square consisting of Bi and S1 atoms in T₀ structure. (c) Top view of Bi-S1 2D square with distortion. The blue arrow along *x* direction indicates the displacement of S1 and the spontaneous polarization. The black frame indicates the unit cell.

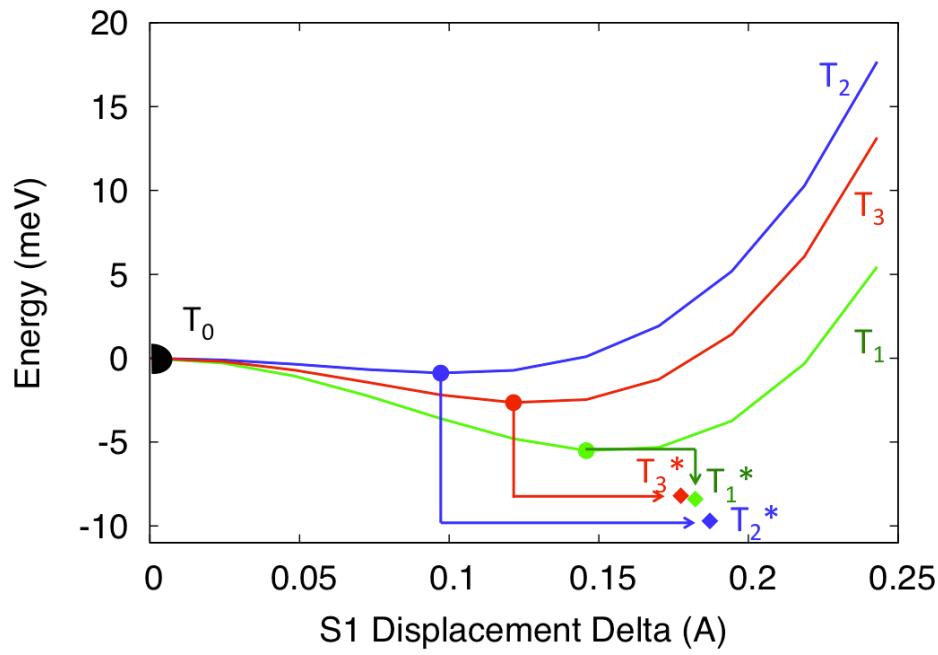


Fig. 2: Total energy as a function of S1 displacement in T_1 - T_3 stacking types of LaOBiS_2 . T_1^* - T_3^* indicate the complete relaxed structures of T_1 - T_3 type (approach c), respectively.

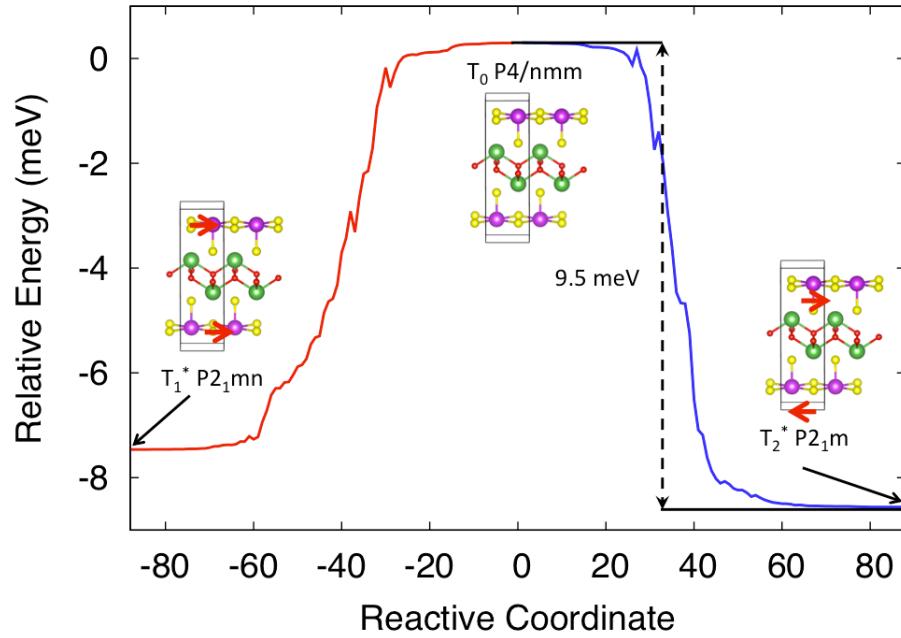


Fig. 3: Total energy change during the transformation from T_1^* to T_2^* structure with T_0 structure as an intermediate state. The reaction coordinate in x -axis is presented by the DFT relaxation steps from T_0 to T_1^* and T_2^* . The red and blue lines denote the transition from T_0 to T_1^* and T_2^* , respectively. The red arrows in the crystal structure denote the direction of the BiS_2 in-plane distortion.

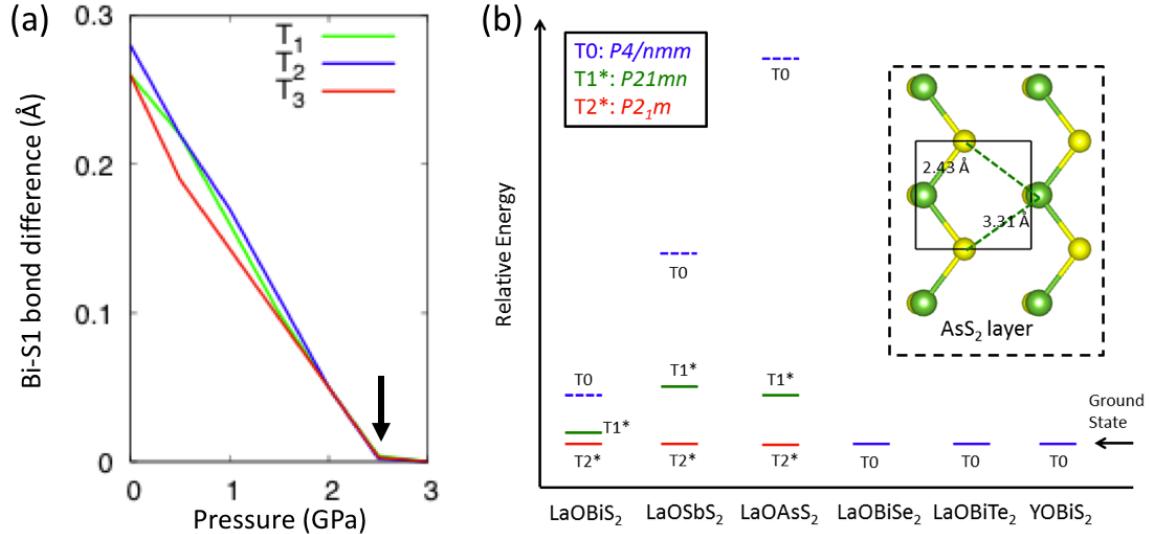


Fig. 4: (a) The difference of bond length within Bi-S1 plane of distorted T_1 - T_3 structures as a function of hydrostatic pressure. The black arrow corresponds to 2.5 GPa where the Bi-S1 bond length become isotropic, indicating a phase transition from a distorted structure to high-symmetry T_0 structure. Since the difference between a distorted T_1 - T_3 and T_0 structure is just a stretched Bi-S1 plane (but no bond breaking), different pressure will lead to a structure with either larger or smaller in-plane distortion. If the distortion vanishes under pressure, then a phase transition will ensue from T_1 - T_3 to T_0 . (b) Schematic illustration of the relative energy of different polytypes in LaOBiS₂-family. The dashed horizontal lines denote structures that are dynamic unstable. Dashed box: top view of AsS_2 layer in LaOAsS₂, in which the unit cell is denoted by the solid frame. The strong distortion separates the layer into individual zigzag chains.

Table I: The stacking configurations of in-plane distortion, space group, inversion symmetry, total energy per u.c., Bi-S bond lengths and lattice parameters of LaOBiS₂, including experimental results and DFT calculations T₀ and T₁^{*}-T₃^{*} on PBE level. The total energy of T₀ structure is set to zero as a reference.

	Expt. ³¹	T ₀	T ₁ [*]	T ₂ [*]	T ₃ [*]
Stacking of distortion	---	No distortion	(x, x)	(x, -x)	(x, y)
Space group	P4/nmm	P4/nmm	P21mn	P2 ₁ m	C2
Inversion symmetry	Unknown	Yes	No	Yes	No
Energy (meV)	---	0	-8.4	-9.7	-8.2
Bi-S bond (Å)	2.68/ 3.11	2.89/ 2.89	2.77/ 3.03	2.76/ 3.04	2.77/ 3.03
a (Å)	4.054	4.050	4.071	4.073	4.060
b (Å)	4.054	4.050	4.051	4.051	4.060
c (Å)	13.825	14.250	14.266	14.273	14.266