

Theoretical study of fluorine doping in layered LaOBiS₂-type compounds

Naomi Hirayama,^{*} Masayuki Ochi, and Kazuhiko Kuroki

Osaka University, 1-1 Machikaneyama-cho, Toyonaka-shi, Osaka 560-0043, Japan



(Received 23 March 2019; revised manuscript received 3 July 2019; published 5 September 2019)

We theoretically investigate the fluorine doping in LaOBiS₂-type quaternary compounds (LaOBiS₂, NdOBiS₂, LaOBiSe₂, and LaOSbSe₂), which are promising candidates for thermoelectric and superconducting materials. These compounds possess a layered structure comprising blocking LnO ($Ln = \text{La, Nd, etc.}$) layers and conducting $PnCh_2$ ($Pn = \text{Bi, Sb; } Ch = \text{S, Se}$) layers. Their carrier concentration is generally tuned via substitutional doping of F atoms in the O site for improving the thermoelectric performance or the superconductivity; however, the tunability of the electrical properties via F doping strongly depends on constituent elements. In order to elucidate the difference, we theoretically examine the electronic and structural properties of these F-doped systems using first-principles calculation. Our results show that the monoclinic distortion of the mother compound, which is closely related to the Pn element, can drastically decrease the capability of F doping. Replacement of the Ln atom from La to Nd in $Ln\text{OBiS}_2$ makes F doping difficult, which is consistent with experimental observation. We also find that the tetragonal structure is gradually stabilized by F doping for all the systems investigated in this study. Our results will be important knowledge for controlling the electrical properties of LaOBiS₂-type compounds both as thermoelectric and superconducting materials.

DOI: [10.1103/PhysRevB.100.125201](https://doi.org/10.1103/PhysRevB.100.125201)

I. INTRODUCTION

Materials science for solving the energy problem is currently of crucial importance. To this end, several technologies have been actively developed such as the thermoelectric effects, the direct conversion between thermal and electric energy, and the superconductivity, which enables efficient power transmission. For these technologies, efficient thermoelectric conversion enabled by a high value of the dimensionless figure of merit (ZT) and high superconducting transition temperature are the central objectives, respectively, for which materials search has been conducted by many researchers. In the search for such materials, the controllability of the carrier concentration is often an essential aspect of candidate materials to optimize their functionalities.

LaOBiS₂ [1], which comprises blocking LaO layers and conducting BiS₂ layers, has attracted much attention as a superconducting [2–10] and thermoelectric [11–18] material. One of the remarkable features of this material is a relatively low thermal conductivity, $\sim 2 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature [19], which is advantageous for increasing ZT . Another important characteristic is a rich variety of constituent elements. For example, a capability of substitution of F atoms with O atoms in LaO layers offers a high controllability of carrier concentration. Since LaOBiS₂ has a large band gap without doping carriers, [20,21] the capability of the carrier doping is indispensable for employing it as a superconducting or thermoelectric material. For instance, a high superconducting transition temperature was observed in LaO_{1-x}F_xBiS₂ with $x = 0.5$ [1]. Also, the thermoelectric performance of LaOBiS₂ can be improved by utilizing the large degrees of freedom of

constituent elements not limited to O atoms. An experimental study revealed that the thermoelectric performance can be improved by partial replacement of S atoms with Se atoms, where $ZT = 0.17$ at 723 K is realized in LaOBiS_{2-x}Se_x with $x = 0.8$ [19]. A further high ZT of approximately 0.36 with low thermal conductivity of $0.8\text{--}1.2 \text{ W m}^{-1} \text{ K}^{-1}$ at around 650 K was achieved in a densified sample of LaOBiS₂Se [22]. It was also shown that the Se substitution reduces the lattice thermal conductivity by softening the rattling phonon modes in LaOBiS_{2-x}Se_x [15]. In addition, a theoretical study [23] predicted that replacing Bi with Sb or As together with replacing S with Se can considerably improve the power factor of this compound. From this viewpoint, a recent experimental study that reported a successful synthesis of $Ln\text{OSbSe}_2$ ($Ln = \text{La, Ce}$) is intriguing [24]. While low thermal conductivity of 1.5 and $0.8 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature were found for $Ln = \text{La and Ce}$, respectively, there remains a difficulty in lowering their high electrical resistivity, which was also reported in Ce(O, F)SbS₂ [25]. Although a recent experimental study on NdO_{0.8}F_{0.2}Sb_{1-x}Bi_xSe₂ ($x \leq 0.4$) revealed that the electrical conductivity of the SbSe₂-based compound can be improved by Bi doping, [26] the microscopic origin of the dependence of the transport properties on constituent elements such as pnictogen has been unclear. It is of great importance to investigate what determines the controllability of the carrier concentration and the electrical conductivity in various kinds of the pnictogen dichalcogenide layered compounds.

In this study, we theoretically investigate the electronic and structural properties of several LaOBiS₂-type quaternary compounds (LaOBiS₂, NdOBiS₂, LaOBiSe₂, and LaOSbSe₂) for undoped and F-doped states using first-principles calculation. Our results suggest that the monoclinic distortion, which is closely related to the Pn ($Pn = \text{Bi, Sb}$) element, drastically decreases the F-doping capacity. The change in the Ln atom

^{*}hirayama@presto.phys.sci.osaka-u.ac.jp

from La to Nd in $LnOBiS_2$ makes F doping difficult, which may have some relevance to experimental findings. We also find that the tetragonal structure is gradually stabilized by F doping for all the compounds investigated in this study. The present calculation provides important information on the F-doping capability in the $LaOBiS_2$ -type compounds.

This paper is organized as follows. In Sec. II, we outline some computational conditions for crystal structure optimization and calculation of the formation energy of F-doped systems. In Sec. III A, we demonstrate the electronic and structural properties of compounds that have the same layered structure as $LaOBiS_2$ and different compositions, such as $NdOBiS_2$ and $LaOBiSe_2$, using the first-principles calculation with the generalized gradient approximation (GGA). Subsequently, the feasibility of F doping in the systems is examined in terms of the formation energy. In Sec. III B, we demonstrate the electronic properties of $LaOBiS_2$ and $LaOSbSe_2$ obtained using the first-principles calculation with a hybrid exchange-correlation functional. Their stable structures with and without F doping are also examined. Finally, we discuss the origin of the different doping abilities of these systems in view of their structural properties. Section IV presents the conclusions.

II. CALCULATION METHOD

A. Structural description and computational conditions for supercell calculations

The $LaOBiS_2$ crystal is composed of alternate stacking of LaO blocking and BiS_2 conducting layers as shown in Fig. 1. Because $LaOBiS_2$ and related compounds were reported to be the tetragonal crystal structure with the $P4/nmm$ space group (No. 129) or the monoclinic structure with the $P2_1/m$ space group (No. 11) [28], we performed the cell-relaxation calculation considering monoclinic as well as tetragonal symmetries in order to elucidate the effect of the crystal symmetry onto the capability of the F doping.

We utilized the $2 \times 2 \times 1$, $2 \times 2 \times 2$, $3 \times 3 \times 1$, $4 \times 4 \times 1$, and $\sqrt{2} \times \sqrt{2} \times 1$ supercells to deal with systems doped with F at the O sites with the doping concentration x , e.g., $LaO_{1-x}F_xBiS_2$. When one of O atoms in these supercells is replaced by F, x is given as 0.125, 0.0625, 0.0556, 0.03125, and 0.25, respectively. In Sec. III A, we performed cell relaxation and band structure calculations using the Perdew-Burke-Ernzerhof parametrization of the GGA functional [29] for $LaOBiS_2$, $NdOBiS_2$, and $LaOBiSe_2$. In Sec. III B, we performed these calculations using Heyd, Scuseria, and Ernzerhof (HSE06) hybrid functional [30] for $LaOSbSe_2$ and $LaOBiS_2$, because we found that $LaOSbSe_2$ becomes metallic in the GGA calculation by a well-known underestimation of the band gap. Hybrid-functional calculation of $LaOBiS_2$ was performed to compare it with $LaOSbSe_2$. Owing to the high computational cost of calculations using the hybrid functional, we used only the unit cell and the $\sqrt{2} \times \sqrt{2} \times 1$ and $2 \times 2 \times 1$ supercells in the analysis of $LaOSbSe_2$ and $LaOBiS_2$ shown in Sec. III B.

For all the calculations in this paper, we used the projector augmented wave method as implemented in Vienna *ab initio* simulation package [31–34]. In crystal structure

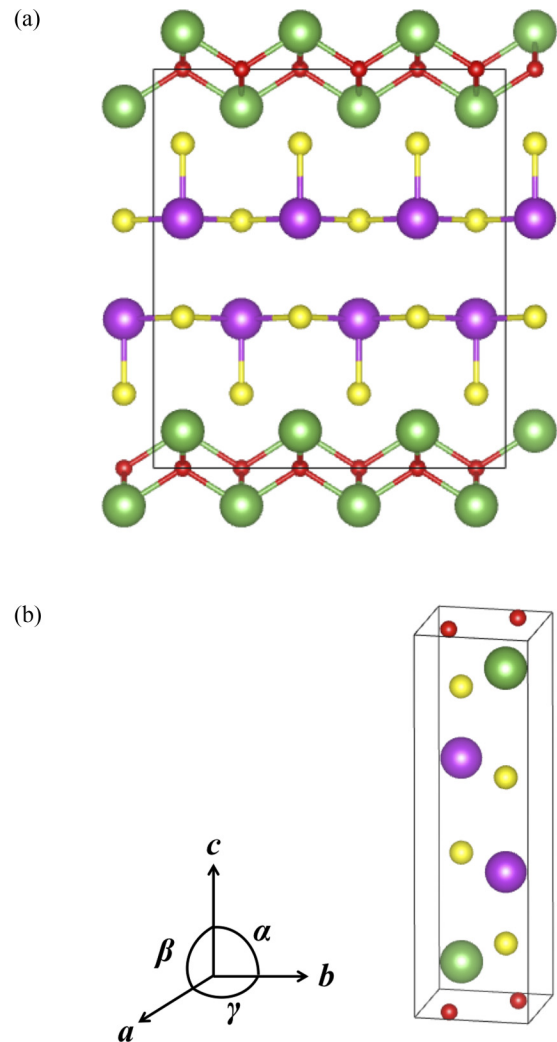


FIG. 1. (a) Crystallographic structure of $LnOPnCh_2$, which consists of alternate stacking of LnO blocking and $PnCh_2$ conduction layers. Here, the Ln (green), O (red), Pn (purple), and Ch (yellow) atoms are displayed. (b) Unit cell shown with the lattice parameters. The lattice parameters follow the conditions $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ for the tetragonal ($P4/nmm$ space group) structure and $a \neq b \neq c$ and $\beta \neq 90^\circ$ for the monoclinic ($P2_1/m$ space group) structure. Depicted using the VESTA software [27].

optimization, both the atomic coordinates and the cell shapes were optimized by keeping the crystal symmetry. The plane-wave cutoff energy was 550 eV. Brillouin zone sampling was performed by the k -points grid with the following meshes: (12 12 3) for the unit cell; (6 6 3) for the $2 \times 2 \times 1$ supercell; (6 6 2) for the $2 \times 2 \times 2$ supercell; (4 4 3) for the $3 \times 3 \times 1$ supercell; (3 3 3) for the $4 \times 4 \times 1$ supercell; and (8 8 3) for the $\sqrt{2} \times \sqrt{2} \times 1$ supercells. For self-consistent field calculations, the convergence threshold of the total energy was 10^{-7} eV. The ionic relaxation was performed until the Hellmann-Feynman force acting on each atom becomes less than 10^{-2} eV/Å. To represent the strongly localized $4f$ orbitals of Nd atoms, we adopted an open-core treatment where $4f^3$ are included in the core. Spin-orbit coupling was not included in this study, the effect of which on the doping capability will be an important future issue.

B. Formation energy of F-doped system

We will discuss how the structural properties influence the doping ability by comparing the formation energy of all the examined compounds. In order to identify the energy stability of F-doped systems, we evaluated the following formation energy:

$$\Delta E_{\text{form}} = E(\text{LnO}_{1-x}\text{F}_x\text{PnCh}_2) + x\mu(\text{O}) - E(\text{LnOPnCh}_2) - x\mu(\text{F}), \quad (1)$$

where $\text{Ln} = \text{La}, \text{Nd}$, $\text{Pn} = \text{Bi}, \text{Sb}$, and $\text{Ch} = \text{S}, \text{Se}$ in this study. Here, $E(A)$ is the total energy that was calculated by assuming a single-crystalline structure of the system. $\mu(\text{O})$ and $\mu(\text{F})$ denote chemical potentials of O and F, respectively. For simplicity, we assumed $\mu(\text{O}) = E(\text{O}_2)/2$ and $\mu(\text{F}) = E(\text{F}_2)/2$, which corresponds to the O-rich and F-rich conditions. The way of estimating $\mu(\text{O})$ and $\mu(\text{F})$ does not affect the following discussion because, in the present study, we aim to examine differences of ΔE_{form} among the compounds rather than the values of ΔE_{form} themselves. In order to obtain $E(\text{O}_2)$ and $E(\text{F}_2)$, we calculated the total energy of the $\text{O}_2(\text{F}_2)$ single molecule in the $10 \text{ \AA} \times 10 \text{ \AA} \times 10 \text{ \AA}$ unit cell, where the interatom distance was optimized in the calculation. We considered a spin-polarized state for the O_2 molecule. For calculations of these molecules, we only took the Γ point in the reciprocal space. We used the same exchange-correlation functional for evaluating all the total energies $E(A)$ in Eq. (1), i.e., GGA in Sec. III A -3 and HSE06 in Sec. III B 3. Other computational conditions are the same as those shown in Sec. II A.

We note that Eq. (1) estimates the difference in total energy between the system before and after the F doping, without considering the charged states. Although the estimation of the defect formation energy generally requires consideration of the charged states of the defect (see Ref. [35], for instance), we used Eq. (1) for simplicity. This can be reasonable for a system where carriers are doped with high concentrations because, in such a case, the doped carriers can be regarded as being within the unit cell. Several experimental studies [2,36,37] suggested that substantial electron carriers generated by partial substitution of F for O were doped in the conduction band in $\text{La}(\text{O}, \text{F})\text{BiS}_2$. Although Eq. (1) is quite simplistic, these experimental results may verify the validity of using it in the present study because we are interested in the stability of systems with relatively high doping concentrations.

Furthermore, although the chemical reaction presented with Eq. (1) is not very realistic, it suffices for our aim of comparing the doping abilities of the compounds, where only the relative values of ΔE are needed. For LaOSbSe_2 , we also evaluated the energy difference between the nondoped and F-doped systems using more realistic chemical reaction as shown in Sec. III B 3.

III. RESULTS AND DISCUSSION

A. Comparison of LaOBiS_2 , NdOBiS_2 , and LaOBiSe_2 using the GGA functional

1. Electronic band structure of mother compounds

First, we have examined the electronic band structure of LaOBiS_2 , NdOBiS_2 , and LaOBiSe_2 using first-principles

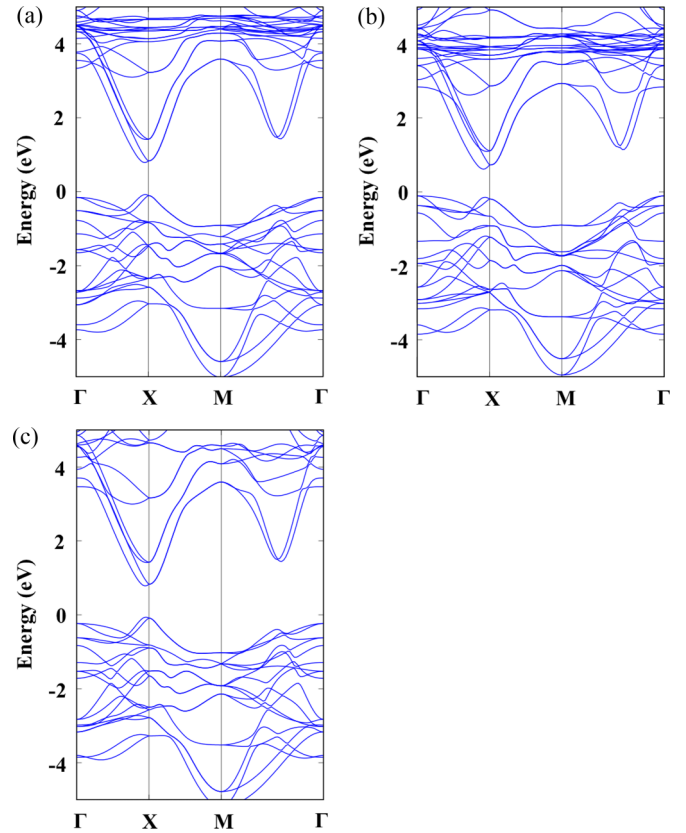


FIG. 2. Electronic band structures of tetragonal (a) LaOBiS_2 , (b) NdOBiS_2 , and (c) LaOBiSe_2 crystals obtained using the first-principles calculation with the GGA functional.

calculation with the GGA functional. The electronic band structures of the undoped systems with the tetragonal structure are shown in Fig. 2. Since all the systems shown here are gapped, we can safely investigate the F-doping effects in the following analysis using the GGA.

The electronic band structures of doped unit cells— $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$, $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$, and $\text{LaO}_{1-x}\text{F}_x\text{BiSe}_2$ with $x = 0.5$ —are plotted in Fig. 3. By comparing Figs. 2 and 3, the addition of F atoms results in n -type conductivity without substantially altering the conduction band dispersion around the Fermi level of pure systems even at a high doping level such as $x = 0.5$. Moreover, from local density of states calculation, it has been revealed that the F atoms form deep impurity states over 6 eV lower than the Fermi level. It suggests that the thermoelectric transport calculation under the rigid-band assumption, where the Fermi level is shifted according to the carrier concentration based on the band structure of a pure system, is valid for these compounds. We note that, while the validity of this approximation was already checked for LaOBiS_2 [38], the present calculation shows that it is valid also for other compounds (NdOBiS_2 and LaOBiSe_2). Several theoretical studies adopted the rigid band approach to analyze thermoelectric properties (see Refs. [23] and [39], for instance); the above result assures us that the good performance of LaOBiS_2 -type materials that was predicted by the previous studies is convincing.

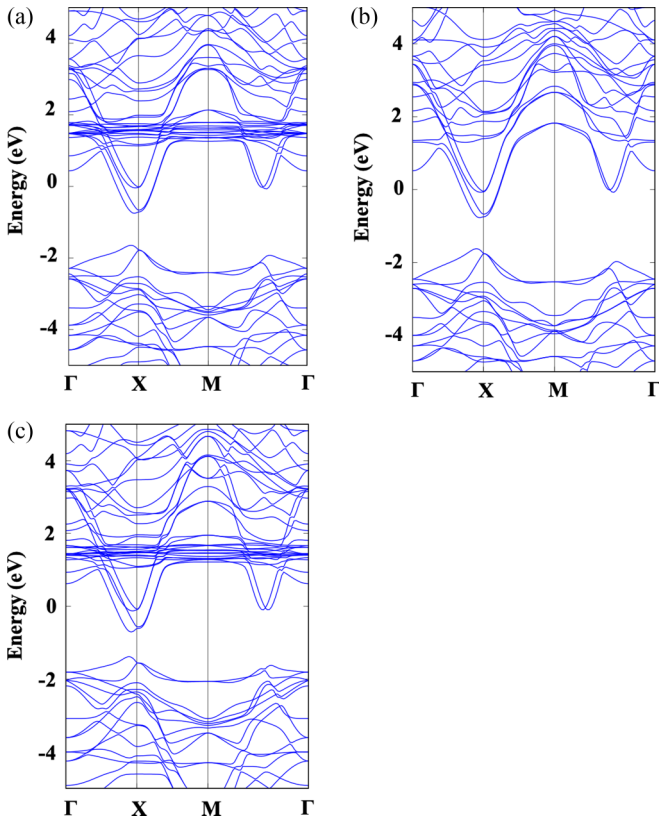


FIG. 3. Electronic band structures of tetragonal (a) $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$, (b) $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$, and (c) $\text{LaO}_{1-x}\text{F}_x\text{BiSe}_2$ crystals with $x = 0.5$, obtained from first-principles calculation with the GGA functional. The Fermi level is set to the origin of the energy axis.

2. Structural properties of the optimized structure with F doping

Figure 4 presents the total energy difference between the monoclinic and tetragonal structures for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$,

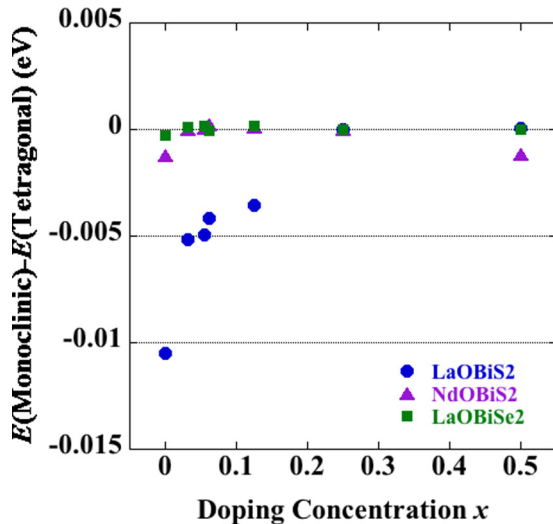


FIG. 4. Total energy difference between the monoclinic and tetragonal structures for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ (circles), $\text{NdO}_{1-x}\text{F}_x\text{BiSe}_2$ (triangles), and $\text{LaO}_{1-x}\text{F}_x\text{BiSe}_2$ (squares), calculated using GGA.

$\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$, and $\text{LaO}_{1-x}\text{F}_x\text{BiSe}_2$ with several values of the doping concentration x . It is noteworthy that the total energy of pure LaOBiS_2 is lower for the monoclinic phase with $\beta = 91.02^\circ$ than for the tetragonal phase, which indicates that the stable structure is monoclinic rather than tetragonal. The obtained lattice constants of pure LaOBiS_2 ($a = 4.073 \text{ \AA}$, $b = 4.050 \text{ \AA}$, and $c = 14.295 \text{ \AA}$) well reproduce the experimental results [$a = 4.0769(4) \text{ \AA}$, $b = 4.0618(3) \text{ \AA}$, and $c = 13.885(2) \text{ \AA}$; $\beta = 90.12(2)^\circ$] [28]. This result indicates the validity of the present calculation for examining these systems.

On the other hand, NdOBiS_2 and LaOBiSe_2 exhibit smaller energy differences between the tetragonal and monoclinic phases than LaOBiS_2 . For example, the energy difference between the two phases for NdOBiS_2 is around 1.2 meV, which is negligibly small, i.e., can be regarded as a numerical error, for the present computational conditions, such as the number of k points. According to experimental studies, LaOBiSe_2 crystallizes in the tetragonal phase [40]. Furthermore, NdOBiS_2 was also reported to be the tetragonal structure [41–44]. The lattice parameters were obtained as $a = b = 4.009 \text{ \AA}$ and $c = 14.244 \text{ \AA}$ for NdOBiS_2 ; $a = b = 4.146 \text{ \AA}$ and $c = 14.96 \text{ \AA}$ for LaOBiSe_2 through the cell optimization calculation. The calculation results well reproduced the experimental results: $a = b = 3.98 \text{ \AA}$ and $c = 13.56 \text{ \AA}$ [41] for NdOBiS_2 and $a = b = 4.1565(1) \text{ \AA}$ and $c = 14.1074(3) \text{ \AA}$ [40] for LaOBiSe_2 . Our results are also consistent with the previous theoretical calculation showing that the $P2_1/m$ (monoclinic) and $P4/nmm$ (tetragonal) phases are the most stable for LaOBiS_2 and LaOBiSe_2 , respectively [45].

However, we note here that the calculated values of c were approximately 3–6% overestimated when compared with the experimental values, in contrast to a and b , where the discrepancies between the calculated and experimental values were within 1%. This overestimation of c might be attributed to the van der Waals interaction between the stacking layers, which is not easy to describe accurately by popular energy functionals.

The dependence of the lattice constants of LaOBiS_2 on the doping concentration x is shown in Fig. 5. Here, the crystal symmetry was assumed to be $P2_1/m$ (monoclinic). Our results are consistent with an experimental report [2], which revealed that the value of c sizably decreases with increasing x . Similarly, F doping for the other two compounds (NdOBiS_2 and LaOBiSe_2) induced the shrinkage of these cells along the c axis, which also replicates experimental data [40,44]. Although the magnitudes of c tend to be overestimated, as described above, the good agreement between the theoretical and experimental behaviors after F doping assures us that our analysis is suitable for comparing the stability of F-doped compounds. More interestingly, our results indicate that LaOBiS_2 gradually falls into the tetragonal phase by the F doping, that is, the lattice constants a and b become closer and the angle β approaches 90° . This tendency is also inferred from Fig. 5, where the energy difference between the tetragonal and monoclinic structures vanishes by increasing x .

3. Formation energy of F-doped systems

The formation energies ΔE_{form} of the systems doped with F are presented in Fig. 6. The figure contains the calculation

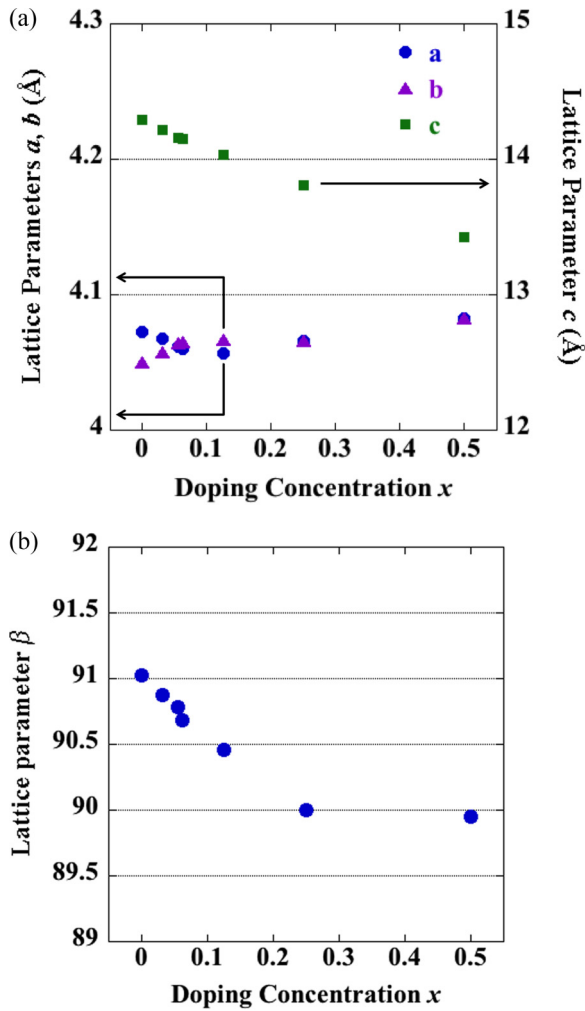


FIG. 5. Dependences of the lattice constants (a) a , b , c , and (b) β on the F-doping concentration x for the optimized structures of $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$.

results obtained for LaOBiS_2 , NdOBiS_2 , and LaOBiSe_2 for two different cases: structures optimized assuming the tetragonal and monoclinic phases. For example, a plot for “Tetragonal LaOBiS_2 ” means that we assumed the tetragonal structure when evaluating $E(\text{LaOBiS}_2)$ and $E(\text{LaO}_{1-x}\text{F}_x\text{BiS}_2)$ in Eq. (1). Among these compounds, LaOBiS_2 has the lowest values of ΔE_{form} , as shown in Fig. 6. This good doping ability agrees with experimental facts [2], which indicates that the electrical properties are easily controlled by doping with F for LaOBiS_2 . The next lowest ΔE_{form} was obtained for NdOBiS_2 and the largest was for LaOBiSe_2 . That is, the change in chalcogens from S to Se led to a larger increase in ΔE_{form} than the change in lanthanoids from La to Nd. We note that, on the basis of experimental studies that reported successful F doping into NdOBiS_2 [41–44] and LaOBiSe_2 [40,46], the F doping into all these systems are still possible while the solubility can be different among them.

As shown in Fig. 6, the ΔE_{form} values of monoclinic LaOBiS_2 are slightly higher than those of the tetragonal one. This can be understood in terms of structural changes induced by F doping. As shown in Fig. 6, F doping decreases

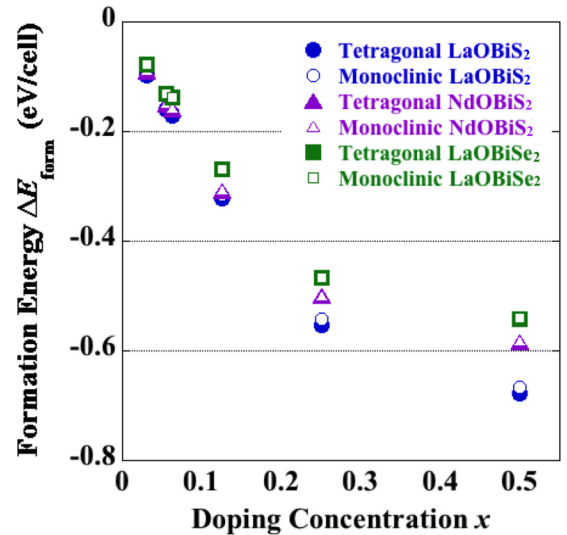


FIG. 6. Dependency of the formation energy ΔE_{form} on the F-doping concentration x for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$, $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$, and $\text{LaO}_{1-x}\text{F}_x\text{BiSe}_2$, calculated using GGA. The plot shows each compound with the tetragonal (solid symbols) and monoclinic crystallographic (open symbols) structures.

the monoclinic distortion of the system; i.e., the system approaches the tetragonal structure. Therefore, in Eq. (1), allowing the monoclinic distortion in calculation mainly lowers $E(\text{LaOBiS}_2)$, while a change in $E(\text{LaO}_{1-x}\text{F}_x\text{BiS}_2)$ is smaller. As a result, a higher formation energy is obtained when one allows the monoclinic distortion in calculation. NdOBiS_2 and LaOBiSe_2 exhibit negligibly small differences between the ΔE_{form} values of the tetragonal and monoclinic phases because the structures of these optimized cells are almost the same as discussed in Sec. III A 2. We note that, for these systems, the effect of the monoclinic distortion onto the F-doping capability seems to be smaller than that introduced by changing the constituent elements of Ln and Ch .

Before proceeding to the next section, we point out that the $x-\Delta E_{\text{form}}$ plots in Fig. 6 exhibit good linearity up to x of 12.5%. In contrast, the plots show nonlinear relationships for larger x . Because calculation of heavily doped systems with sizable interaction among dopant atoms is challenging owing to the necessity of trying several dopant configurations, we shall focus on x up to 25% in the remainder of this paper.

B. Comparison of LaOBiS_2 and LaOSbSe_2 using hybrid functional

1. Electronic band structure of mother compounds

The band structures of the undoped LaOSbSe_2 and LaOBiS_2 with the tetragonal structure calculated using the HSE06 hybrid functional are shown in Fig. 7. The band dispersion of LaOBiS_2 in Fig. 7(a) closely resembles that obtained using GGA shown in Fig. 2(a). The band dispersion of LaOSbSe_2 shown in Fig. 7(b) is also similar to them, while the band gap is much narrower. In fact, this small band gap ~ 0.23 eV obtained by HSE06 disappears for GGA because of its well-known underestimation of the band gap, while the experimental study reported the insulating behavior for

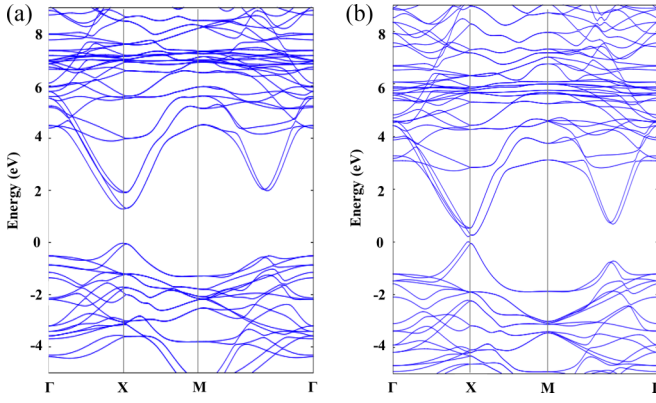


FIG. 7. Electronic band structures of (a) LaOBiS₂ and (b) LaOSbSe₂ for the tetragonal structure obtained using the HSE06 hybrid functional.

LaOSbSe₂ [24]. This is the reason why we adopted HSE06 here rather than GGA.

2. Structural properties of the optimized structure with F doping

The lattice constants of the pure LaOBiS₂ and LaOSbSe₂ optimized using HSE06 are listed in Table I. The results show that the monoclinic instability is enhanced in LaOSbSe₂ than LaOBiS₂, as seen from the large energy difference between the tetragonal and monoclinic phases, the large difference between the lattice constants a and b , and a larger β in monoclinic LaOSbSe₂. The energy difference between the tetragonal and monoclinic phases in LaOBiS₂ is of the same order of magnitude as that obtained by GGA, which is also listed in Table I. Table I also demonstrates that F doping reduces the monoclinic distortion for both systems, which is consistent with GGA analysis performed for LaOBiS₂ shown in the previous section. We note that, although we obtain a positive total energy of the monoclinic LaO_{1-x}F_xSbSe₂ ($x = 0.25$) relative to that for the tetragonal phase, this might be due to a numerical error since $P2_1/m$ is a subgroup of $P4/nmm$. Nevertheless, we can safely say that the tetragonal structure is actually stabilized by F doping also for LaOSbSe₂ because of the large total energy difference between the two phases for

$x = 0$ and the change in the lattice parameters from $x = 0$ to 0.25, which suggests that the system falls into (at least closely approaches) the tetragonal phase by F doping.

According to an experimental work [24], the x-ray diffraction analysis revealed that LaOSbSe₂ has a tetragonal ($P4/nmm$ space group) structure with $a = b = 4.14340(3)$ Å and $c = 14.34480(14)$ Å. The calculated lattice constants listed in Table I agree with these experimental values within an error of 3%. We note that, however, the lattice structure determined in this experimental study differs from that predicted in our calculation, to say, the monoclinic lattice. Nevertheless, on the basis of our calculation results, which offer reasonable agreement with experimental observation for $Pn = Bi$ systems as we have seen in Sec. III A, we can speculate that a strong instability toward the monoclinic structure should be present in LaOSbSe₂. As a matter of fact, some experimental studies reported that Ce(O, F)Sb(S, Se)₂, where S : Se = 1:0 or around 1:1, has the monoclinic structure [25,47]. Also in the previous theoretical calculation, replacement of Pn atom from Bi to Sb or As tends to stabilize the $P2_1/m$ (monoclinic) phase [45]. Further discussion will be presented in the following section.

3. Formation energy of F-doped systems

The formation energies ΔE_{form} of F-doped LaOSbSe₂ and LaOBiS₂ are shown in Fig. 8. For calculating the formation energies, we assumed the tetragonal or monoclinic structures just as in Sec. III A 3. We can see two important features: monoclinic distortion remarkably increases the formation energy for LaOSbSe₂, and the tetragonal structures of LaOSbSe₂ and LaOBiS₂ have rather close values of ΔE_{form} . Since the experimental study reported the tetragonal structure for LaOSbSe₂, our calculation results suggest that the capability of F doping is not so different between LaOBiS₂ and LaOSbSe₂. In fact, the experimental observation that the F doping induced some change of the transport properties in LaOSbSe₂ [24] suggests that F atoms are indeed doped in the system although the system remains insulating. Our calculation suggests that the structural instability in tetragonal LaOSbSe₂ can play some role in its insulating behavior through the local structural distortion leading to the difficulty in F doping. It is also

TABLE I. Calculated total energies and lattice constants of LaO_{1-x}F_xBiS₂ and LaO_{1-x}F_xSbSe₂ for $x = 0$ and 0.25. Total energy relative to that for the tetragonal structure is shown for the monoclinic structure.

Material (functional)	Doping concentration x	Structure	Total energy (eV/cell)	a (Å)	b (Å)	c (Å)	β
LaOBiS ₂ (hybrid)	$x = 0$	Tetragonal	–	4.026	4.026	14.15	90°
		Monoclinic	–0.03	4.065	4.025	14.19	91.2°
	$x = 0.25$	Tetragonal	–	4.038	4.038	13.74	90°
		Monoclinic	–0.01	4.046	4.046	13.69	90.3°
LaOBiS ₂ (GGA)	$x = 0$	Tetragonal	–	4.050	4.050	14.25	90°
		Monoclinic	–0.01	4.073	4.050	14.30	91.0°
	$x = 0.25$	Tetragonal	–	4.066	4.066	13.81	90°
		Monoclinic	0.00	4.066	4.066	13.81	90.0°
LaOSbSe ₂ (hybrid)	$x = 0$	Tetragonal	–	4.071	4.071	14.59	90°
		Monoclinic	–0.18	4.157	4.062	14.76	92.0°
	$x = 0.25$	Tetragonal	–	4.118	4.118	13.85	90°
		Monoclinic	0.04	4.117	4.117	14.09	90.2°

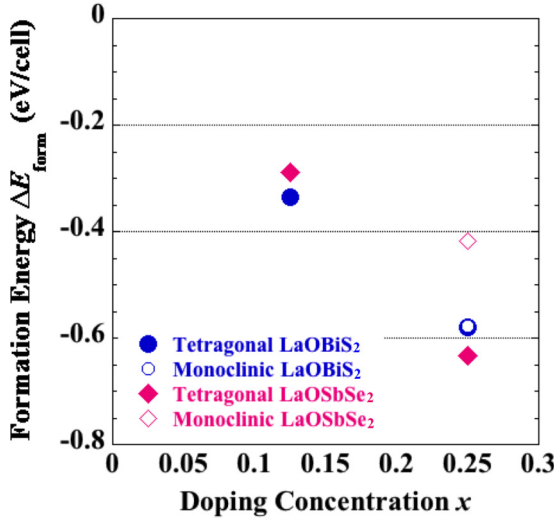


FIG. 8. Dependency of the formation energy ΔE_{form} on the F-doping concentration x for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ and $\text{LaO}_{1-x}\text{F}_x\text{SbSe}_2$, calculated using the HSE06 hybrid functional. The graph contains different crystallographic structures for each compound, the tetragonal (solid symbols) and monoclinic (open symbols) structures. For the monoclinic structure, only the case of $x = 0.25$ is shown.

noteworthy that the monoclinic distortion in LnOPnCh_2 results in the deformation of the conducting layer from the two-dimensional square lattice to the (quasi-)one-dimensional chains [28] (Fig. 9), where the transport could be more easily disturbed by several scattering processes due to its low dimensionality.

While the formation energies calculated so far in this paper are all negative, this does not necessarily indicate that this impurity doping was achieved without any hindrance because of our simple treatment of F doping. For example, the chemical reaction used in Eq. (1) is clearly different from the actual synthesis. Whereas our analysis should be sufficient to roughly see the material dependence of the F-doping capability and the strength of the monoclinic distortion, we here evaluated ΔE_{form} based on a more practical chemical reaction for LaOSbSe_2 . In its experimental synthesis, La_2O_3 ,

Sb_2Se_3 , LaSe , LaSe_2 , and LaF_3 were used [24]. Using these precursors, we evaluated the total energies before and after synthesizing $\text{LaO}_{1-x}\text{F}_x\text{SbSe}_2$ as follows:

$$\begin{aligned} & \frac{1-x}{3}E(\text{La}_2\text{O}_3) + \frac{1}{8}E(\text{Sb}_2\text{Se}_3) + \frac{1+4x}{24}E(\text{LaSe}) \\ & + \frac{1-2x}{24}E(\text{LaSe}_2) + \frac{x}{18}E(\text{LaF}_3) \\ & \rightarrow E(\text{LaO}_{1-x}\text{F}_x\text{SbSe}_2). \end{aligned} \quad (2)$$

Thus, by taking the difference between the left-hand side with a finite x and that for $x = 0$, the capability of the F doping into LaOSbSe_2 can be evaluated by the following energy difference:

$$\begin{aligned} & E(\text{LaO}_{1-x}\text{F}_x\text{SbSe}_2) - \left[E(\text{LaOSbSe}_2) - \frac{x}{3}E(\text{La}_2\text{O}_3) \right. \\ & \left. + \frac{x}{6}E(\text{LaSe}) - \frac{x}{12}E(\text{LaSe}_2) + \frac{x}{18}E(\text{LaF}_3) \right]. \end{aligned} \quad (3)$$

We computed Eq. (3) and obtained the values of 0.42 and 0.64 eV for tetragonal and monoclinic $\text{LaO}_{0.75}\text{F}_{0.25}\text{SbSe}_2$, respectively. This suggests that the F doping into LaOSbSe_2 seems difficult, at least for relatively large $x = 0.25$. More careful analysis on a dilute F-doped system would be an important future study.

IV. CONCLUSIONS

We have theoretically investigated the structural properties of LnOPnCh_2 -type quaternary compounds (LaOBiS_2 , NdOBiS_2 , LaOBiSe_2 , and LaOSbSe_2) and examined their influences on F doping. Our results show that replacement of atoms from La to Nd and S to Se in LaOBiS_2 crystal makes F doping difficult, which may have some relevance to experimental observation. We also find that replacement of the Pn element from Bi to Sb increases the monoclinic distortion of the mother compound and, in consequence, decreases the capability of F doping. That is, large formation energy is necessary for doping the monoclinic LaOSbSe_2 with F owing to the monoclinic-to-tetragonal transformation induced by F doping. Therefore, it is suggested that the difficulty in controlling the electrical properties of LaOSbSe_2 by F doping, which was experimentally observed, is partly attributed to its low doping ability related to the predisposition towards distortion. Our theoretical work can provide important information on carrier density control in LnOPnCh_2 systems.

Although the present paper focuses on the substitutional doping of F in the O site as the primary structure of F-doped LaOBiS_2 -type compounds, it would be important to discuss the possibility of occupying the interstitial site in future studies. If this occurs, the interstitial F atoms can be charged as F^- , which results in unintentional hole doping. In addition, intrinsic charged defects of the parent compounds can be formed and affect the carrier concentration. Thus, these defects could be associated with the low electrical conductivity of LaOSbSe_2 . Further studies are necessary to clarify this point.

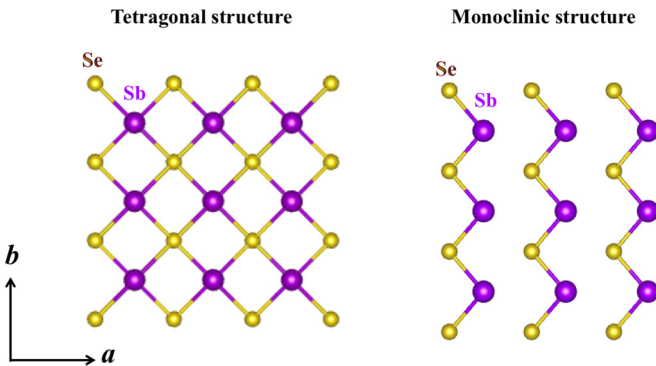


FIG. 9. The SbSe_2 conductive layer in LaOSbSe_2 crystal structures optimized assuming (left) the tetragonal and (right) the monoclinic phases. The bonds are displayed between the nearest Sb and Se atoms that are separated by a distance of 3 Å or less.

ACKNOWLEDGMENTS

We appreciate the fruitful discussions with Prof. Y. Mizuguchi and Prof. Y. Goto. This work was supported by JSPS KAKENHI (Grant No. JP17H05481 and Grant No.

JP19H04697) and JST CREST (Grant No. JPMJCR16Q6), Japan. A part of the computation in this work has been done using the facilities of the Supercomputer Center, the Institute for Solid State Physics, the University of Tokyo.

-
- [1] Y. Mizuguchi, *J. Phys. Soc. Jpn* **88**, 041001 (2019).
- [2] Y. Mizuguchi, S. Demura, K. Deguchi, Y. Takano, H. Fujihisa, Y. Gotoh, H. Izawa, and O. Miura, *J. Phys. Soc. Jpn* **81**, 114725 (2012).
- [3] K. Deguchi, Y. Takano, and Y. Mizuguchi, *Sci. Technol. Adv. Mater.* **13**, 054303 (2012).
- [4] Y. Mizuguchi, *Phys. Proc.* **58**, 94 (2014).
- [5] Y. Mizuguchi, *J. Phys. Chem. Solids* **84**, 34 (2015).
- [6] D. Yazici, I. Jeon, B. D. White, and M. B. Maple, *Physica C* **514**, 218 (2015).
- [7] H. Usui and K. Kuroki, *Novel Supercond. Mater.* **1**, 50 (2015).
- [8] Y. Mizuguchi, *Condens. Matter* **2**, 6 (2017).
- [9] N. Kase, K. Kondo, M. Koike, S. Watanabe, and N. Miyakawa, *AIP Adv.* **8**, 101322 (2018).
- [10] K. Suzuki, H. Usui, K. Kuroki, T. Nomoto, K. Hattori, and H. Ikeda, *J. Phys. Soc. Jpn* **88**, 041008 (2019).
- [11] A. Omachi, J. Kajitani, T. Hiroi, O. Miura, and Y. Mizuguchi, *J. Appl. Phys.* **115**, 083909 (2014).
- [12] I. Pallicchi, G. Lamura, M. Putti, J. Kajitani, Y. Mizuguchi, O. Miura, S. Demura, K. Deguchi, and Y. Takano, *Phys. Rev. B* **89**, 214513 (2014).
- [13] Y. Mizuguchi, A. Miura, A. Nishida, O. Miura, K. Tadanaga, N. Kumada, C. H. Lee, E. Magome, C. Moriyoshi, and Y. Kuroiwa, *J. Appl. Phys.* **119**, 155103 (2016).
- [14] A. Nishida, H. Nishiate, C. H. Lee, O. Miura, and Y. Mizuguchi, *J. Phys. Soc. Jpn* **85**, 074702 (2016).
- [15] C. H. Lee, A. Nishida, T. Hasegawa, H. Nishiate, H. Kunioka, S. Ohira-Kawamura, M. Nakamura, K. Nakajima, and Y. Mizuguchi, *Appl. Phys. Lett.* **112**, 023903 (2018).
- [16] Y. Mizuguchi, A. Nishida, A. Omachi, and O. Miura, *Cog. Phys.* **3**, 1156281 (2016).
- [17] C.-H. Lee, *J. Phys. Soc. Jpn* **88**, 041009 (2019).
- [18] M. Ochi, H. Usui, and K. Kuroki, *J. Phys. Soc. Jpn* **88**, 041010 (2019).
- [19] Y. Mizuguchi, A. Omachi, Y. Goto, Y. Kamihara, M. Matoba, T. Hiroi, J. Kajitani, and O. Miura, *J. Appl. Phys.* **116**, 163915 (2014).
- [20] K. Terashima, J. Sonoyama, T. Wakita, M. Sunagawa, K. Ono, H. Kumigashira, T. Muro, M. Nagao, S. Watauchi, I. Tanaka, H. Okazaki, Y. Takano, O. Miura, Y. Mizuguchi, H. Usui, K. Suzuki, K. Kuroki, Y. Muraoka, and T. Yokoya, *Phys. Rev. B* **90**, 220512(R) (2014).
- [21] A. Miura, Y. Mizuguchi, T. Takei, N. Kumada, E. Magome, C. Moriyoshi, Y. Kuroiwa, and K. Tadanaga, *Solid State Commun.* **227**, 19 (2016).
- [22] A. Nishida, O. Miura, C. H. Lee, and Y. Mizuguchi, *Appl. Phys. Exp.* **8**, 111801 (2015).
- [23] M. Ochi, H. Usui, and K. Kuroki, *Phys. Rev. Appl.* **8**, 064020 (2017).
- [24] Y. Goto, A. Miura, R. Sakagami, Y. Kamihara, C. Moriyoshi, Y. Kuroiwa, and Y. Mizuguchi, *J. Phys. Soc. Jpn* **87**, 074703 (2018).
- [25] M. Nagao, M. Tanaka, R. Matsumoto, H. Tanaka, S. Watauchi, Y. Takano, and I. Tanaka, *Cryst. Growth Des.* **16**, 3037 (2016).
- [26] Y. Goto, A. Miura, C. Moriyoshi, Y. Kuroiwa, and Y. Mizuguchi, *J. Phys. Soc. Jpn* **88**, 024705 (2019).
- [27] K. Momma and F. Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).
- [28] R. Sagayama, H. Sagayama, R. Kumai, Y. Murakami, T. Asano, J. Kajitani, R. Higashinaka, T. D. Matsuda, and Y. Aoki, *J. Phys. Soc. Jpn* **84**, 123703 (2015).
- [29] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [30] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, *J. Chem. Phys.* **125**, 224106 (2006).
- [31] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558(R) (1993).
- [32] G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
- [33] G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- [34] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [35] S. Lany and A. Zunger, *Phys. Rev. B* **78**, 235104 (2008).
- [36] Y. Y. Chin, H.-J. Lin, Z. Hu, M. Nagao, Y. Du, X. Wan, B.-J. Su, L. Y. Jang, T. S. Chan, H.-Y. Chen, Y. L. Soo, and C. T. Chen, *Phys. Rev. B* **94**, 035150 (2016).
- [37] S. Nagira, J. Sonoyama, T. Wakita, M. Sunagawa, Y. Izumi, T. Muro, H. Kumigashira, M. Oshima, K. Deguchi, H. Okazaki, Y. Takano, O. Miura, Y. Mizuguchi, K. Suzuki, H. Usui, K. Kuroki, K. Okada, Y. Muraoka, and T. Yokoya, *J. Phys. Soc. Jpn* **83**, 033703 (2014).
- [38] B. Li, Z. W. Xing, and G. Q. Huang, *Europhys. Lett.* **101**, 47002 (2013).
- [39] G. Wang, D. Wang, X. Shi, and Y. Peng, *Mod. Phys. Lett. B* **31**, 1750265 (2017).
- [40] S. L. Wu, Z. A. Sun, F. K. Chiang, C. Ma, H. F. Tian, R. X. Zhang, B. Zhang, J. Q. Li, and H. X. Yang, *Solid State Commun.* **205**, 14 (2015).
- [41] V. S. Tanryverdiev, O. M. Aliev, and I. I. Aliev, *Inorg. Mater.* **31**, 1497 (1995).
- [42] D. Yazici, K. Huang, B. D. White, A. H. Chang, A. J. Eriedman, and M. B. Maple, *Philos. Mag.* **93**, 673 (2012).
- [43] M. Nagao, S. Demura, K. Deguchi, A. Miura, S. Watauchi, T. Takei, Y. Takano, N. Kumada, and I. Tanaka, *J. Phys. Soc. Jpn* **82**, 113701 (2013).
- [44] S. Demura, Y. Mizuguchi, K. Deguchi, H. Okazaki, H. Hara, T. Watanabe, S. J. Denholme, M. Fujioka, T. Ozaki, H. Fujihisa, Y. Gotoh, O. Miura, T. Yamaguchi, H. Takeya, and Y. Takano, *J. Phys. Soc. Jpn* **82**, 033708 (2013).
- [45] Q. Liu, X. Zhang, and A. Zunger, *Phys. Rev. B* **93**, 174119 (2016).
- [46] M. Nagao, M. Tanaka, S. Watauchi, I. Tanaka, and Y. Takano, *J. Phys. Soc. Jpn* **83**, 114709 (2014).
- [47] M. Nagao, M. Tanaka, A. Miura, M. Kitamura, K. Horiba, S. Watauchi, Y. Takano, H. Kumigashira, and I. Tanaka, *Solid State Commun.* **289**, 38 (2019).