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Theoretical study of crystal and electronic structures of BiI₃

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Abstract

The electronic band structure as well as the crystal structure of the BiI₃ semiconductor is investigated by performing first-principles pseudopotential calculations for the space group D_{3d}¹ or C_{3i}². The optimized structures were determined through total-energy calculations. The calculated results indicate that a rhombohedral structure (C_{3i}²) forms a flatter band at the bottom of the conduction bands as compared to a hexagonal structure (D_{3d}¹). The lattice relaxation of the iodine atoms around a vacant site on the atomic plane of bismuth is found to play an important role on the conduction band bottom. It is proved that the rhombohedral BiI₃ is an indirect semiconductor, while the hexagonal BiI₃ has a direct band gap.

1. Introduction

Bismuth tri-iodide (BiI₃) is known as a layered semiconductor exhibiting optical properties characteristic of a layered structure [1–8]. This wide-band-gap material, whose constituents are heavy atoms, is a candidate for use as a room-temperature gamma-ray detector or an x-ray digital imaging sensor [9, 10]. Recently interesting work on optical functions of BiI₃ has been reported by Jellison *et al* [6] and Sobolev *et al* [7]. The best-known theoretical work on BiI₃ is the calculation of the electronic band structure performed by Schlüter *et al* [8]. They succeeded in obtaining the band structure of the hexagonal BiI₃ crystal by adopting the empirical pseudopotential method [11]. There are two structures of the BiI₃ crystal as listed in Wyckoff's book [12]. One is a hypothetical structure having the hexagonal structure (space group D_{3d}¹ symmetry), and the other is a realistic structure whose primitive unit cell is rhombohedral (C_{3i}² symmetry). These structures differ from each other in the periodicity of the arrangement of the layers: the rhombohedral structure has three-layered packing while the hexagonal structure has one-layered packing. The band structure obtained by Schlüter *et al* indicates that hexagonal BiI₃ is a direct semiconductor, while experimental results of optical measurements indicate that its transition type is indirect. For instance, Krylova *et al* [1] measured the absorption and luminescence spectra of BiI₃ crystals in the temperature range of 1.6–77 K and found phonon-assisted indirect transitions. Their observations suggest an

indirect band gap of 2.009 eV (16 205 cm⁻¹). A similar result was also reported by Kaifu and Komatsu [3], who observed that the edge absorption spectrum of BiI₃ consists of phonon steps of the indirect exciton with a transition energy of 2.0081 eV. Therefore, there is a discrepancy between theoretical and experimental results for the electronic structure of the BiI₃ crystal. In the present work, we have investigated whether this discrepancy is likely to be caused by a difference in the crystal structure. For this purpose, we have performed electronic band structure calculations for both the hexagonal and the rhombohedral structures using the total-energy pseudopotential method [13]. This would be the most suitable one for comparing the results to those in the pioneering work of Schlüter *et al* [8] based on the empirical pseudopotential method [8]. The present work is the first to report the electronic band structures for rhombohedral BiI₃ crystals along with the optimized crystal structures by performing first-principles calculations.

2. Calculation

The total-energy pseudopotential calculations [13] were performed using an OSAKA2000 [14] program package which was slightly modified for our purpose. The program includes the code TSPACE [15], which enables us to treat the space group, and the conjugate gradient method is implemented for optimized calculations. The physical scheme of the program is as follows. The first-principles

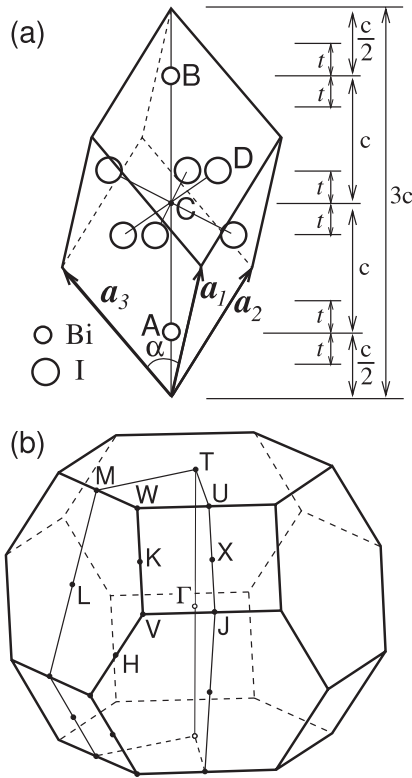


Figure 1. (a) Rhombohedral primitive cell of a BiI_3 crystal with C_{3i}^2 symmetry, and (b) the corresponding Brillouin zone. The rhombohedral cell is defined by the lattice constant a_0 and the angle α between the three translational vectors, \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 , and includes not only two bismuth atoms (sites A and B) and six iodine atoms (the representative site D) but also a vacant site (site C) at the center of the cell. This is considered to be a three-layer packing structure in which one layer has the thickness c . The sites of the iodine atoms are a distance t away from the C site along the main axis.

norm-conserving pseudopotentials are of the Troullier–Martins type [16], and the nonlocal parts are expressed in the Kleinman–Bylander form [17]. For the local density approximation (LDA) to the exchange–correlation energy, the Ceperley–Alder expression [18] is used. The Monkhorst–Pack mesh [19] is employed for Brillouin zone sampling.

The cutoff energies used in the plane wave expansions are 33.4–37.6 Ryd (about 7400–8000 waves) for the hexagonal structures and 41.6–43.7 Ryd (about 10000 waves) for the rhombohedral structures. Accurate calculations for the rhombohedral structures with C_{3i}^2 symmetry needed more plane waves than those for the hexagonal structures with D_{3d}^1 symmetry. The k sampling for evaluation of the total energy is $8 \times 8 \times 8$ in all the present calculations for both hexagonal and rhombohedral structures.

Our calculations were carried out in order to determine stable structures for hexagonal and rhombohedral BiI_3 lattices within the theoretical framework. Optimization of the crystal structures was carried out using two methods: the first allows only a change in the lattice parameters, and the second allows the displacement of atoms in the cell in addition to the change in the lattice parameters. The spin–orbit effect is neglected in these calculations.

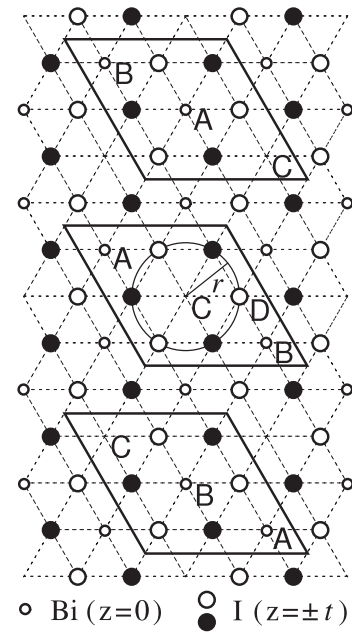


Figure 2. Illustration of the atomic arrangement, viewed along the c -axis, for one of three layers constituting a BiI_3 crystal. Each of the three layers consists of three atomic planes: one basis plane of bismuth atoms, and two iodine planes above and below it. The three layers, which have the same atomic arrangement, are horizontally shifted with respect to each other so that a difference appears in the sequence of A, B and C sites along the c -axis.

3. Results and discussion

In this section, we prioritize the discussion of crystal structures obtained in the present study, followed by a discussion of the electronic band structure.

3.1. Crystal structure

First, we organize the crystal structures of BiI_3 already established before presenting the results of the optimized structures obtained from the total-energy calculations in this study. For this purpose, we introduce a useful description that can be applied to both the hexagonal and rhombohedral lattices within the same framework. After that, the calculated results will be shown and discussed.

The hexagonal lattice is defined by two lattice constants a and c . The rhombohedral lattice is defined by a lattice constant a_0 and the shear angle α between any two of the primitive translation vectors illustrated in figure 1(a). These structures are linked to each other by the relation $a = a_0\sqrt{3}\beta$ and $c = a_0\sqrt{1-\beta^2}$, where $\beta \equiv \frac{2}{\sqrt{3}}\sin(\frac{\alpha}{2}) = 1/\sqrt{1+3(c/a)^2}$. For the BiI_3 crystal, the primitive unit cell of either the hexagonal or the rhombohedral structure contains two bismuth atoms and six iodine atoms.

The crystal structure of BiI_3 , of which primitive cell is shown in figure 1(a), is considered to be a layered one made up of three layers which intersect the so-called c -axis (the direction $\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3$) perpendicularly at bismuth sites A, B and C (nominally vacant site). Each of the three layers is composed of three atomic planes (I–Bi–I planes), as shown in figure 2,

Table 1. Hexagonal structures of BiI_3 were investigated in the present study. The first structure in this list is a model structure introduced by Schlüter *et al* in [8]. The second is a structure from [12]. The other two are optimized structures determined by means of the present calculations. The bismuth site of $(a/\sqrt{3}, -\pi/6, 0)$ is invariant even for OLS structure. For details, see the text.

Structure	Lattice parameters		Iodine site			ℓ (Å)
	a (Å)	c (Å)	$(r,$	$\theta,$	$t)$	
Ideal	7.50	6.90	$a/3$	0	$c/4$	3.0374
Wyckoff	7.50	6.90	$0.333a$	0.000	$0.264c$	3.0912
OL	7.4269	6.6936	$0.333a$	0.000	$0.264c$	3.0396
OLS	7.3138	6.5028	$0.3212a$	0.0000	$0.2748c$	2.9515

Table 2. Rhombohedral structures of BiI_3 investigated in the present study. The bismuth site of $(0, 0, c)$ in the cell shown in figure 1 is invariant even for OLS structure. For details, see the text.

Structure	Lattice parameters		Hexagonal ^a		Iodine site			ℓ (Å)
	a_0 (Å)	α	a (Å)	c (Å)	$(r,$	$\theta,$	$t)$	
Wyckoff	8.13	$54^\circ 50'$	7.4871	6.8856	$0.333a$	0.000	$0.264c$	3.0855
OL	7.9978	55.07°	7.3947	6.7629	$0.333a$	0.000	$0.264c$	3.0416
OLS	7.7881	56.17°	7.3255	6.5338	$0.3259a$	0.613°	$0.2765c$	2.9940

^a Conversion of rhombohedral lattice parameters into hexagonal ones is carried out using the relationships mentioned in the text.

and the successive layers are shifted horizontally. Without this horizontal shift, the rhombohedral structure is reduced to be a hexagonal one having one-layered packing [8], where the C site would lie in a straight line along the c -axis as well as the A and B sites. Throughout the present work, the C site on the bismuth atomic plane is taken as the origin, and we express representative positions of iodine (D) and bismuth (B) atoms by the cylindrical coordinate (r, θ, z) . For example, the D site in figures 1 and 2 is represented by (r, θ, t) , the B site in figure 1(a) by $(0, 0, c)$ and the B site in the middle rhomboid in figure 2 by $(a/\sqrt{3}, -\pi/6, 0)$. We note that the A site of $(0, 0, -c)$ and B site $(0, 0, c)$ in figure 1(a) are, respectively, equivalent to the A $(a/\sqrt{3}, 5\pi/6, 0)$ and B $(a/\sqrt{3}, -\pi/6, 0)$ sites in the middle rhomboid in figure 2. θ denotes the angle measured from a primitive translation vector of the hexagonal lattice plane. r and t are invariant for the symmetry operation of C_3 , and only a change of sign of t is added for the D_3 symmetry operation. The positions of six iodine and two bismuth atoms in the primitive unit cell are determined by the lattice parameters (a, c) and the iodine site (r, θ, t) , and the bismuth site. This description for a single layer is common to the hexagonal and the rhombohedral structures of the BiI_3 crystal and enables us to discuss the BiI_3 structure without bothering about the choice of the primitive translation vectors or the unit cell. We use the hexagonal lattice constants a and c and the iodine atom position (r, θ, t) for both the hexagonal and rhombohedral structures. The nearest distance ℓ between the C site and the iodine site is given by $\ell = \sqrt{t^2 + r^2}$.

Next, we apply our representation to the structures investigated in the previous and present works: the iodine atom position of $r = a/3$, $t = c/4$ and $\theta = 0$ for the ideal structure of the hexagonal structure employed by Schlüter *et al* [8] mentioned above, and $t = 0.264c$ while maintaining $r = 0.333a \simeq a/3$ and $\theta = 0$ for the rhombohedral structure listed in Wyckoff's book [12].

The hexagonal structures studied in the present work are listed in table 1. The 'Ideal' structure is a model structure used by Schlüter *et al* [8]. In this structure, iodine atoms are located at geometrically *right* positions ($r = a/3$, $\theta = 0$, $t = c/4$). The second structure in the table is the 'Wyckoff' structure. What we call the Wyckoff structure indicates the rhombohedral structure mentioned in his book [12], and it is therefore necessary to comment on the hexagonal Wyckoff structure. This structure is defined by the use of hexagonal lattice constants and the iodine position in the rhombohedral structure. According to Wyckoff, the realistic position of iodine atoms has a larger component perpendicular to the layers ($t > c/4$), which is probably due to layer-layer interaction. The third, 'OL' structure, implies an optimized structure obtained by taking the iodine site of Wyckoff structure. The other structure, which we call 'OLS', has been obtained by optimizing both the lattice parameters and the iodine site. The rhombohedral structures studied in the present work are listed in table 2. Both the OL and OLS structures are optimized structures in the present work.

We can now discuss our results which were obtained from the optimization procedure. It is well known that optimization of the crystal structure diminishes the lattice constants in the first-principles calculations. Such a tendency is also seen in our optimized structures of OL and OLS listed in tables 1 and 2. We focus our attention on the iodine site because its position has an effect on the electronic band structure of BiI_3 , as discussed later. It is to be noted that the iodine site in the OLS structures is different from that in the other structures in tables 1 and 2. In the hexagonal OLS structure, iodine atoms are displaced: r changes to $0.321a$ ($< a/3$), and $t = 0.275c$ ($> 0.264c > c/4$). For the iodine site in the rhombohedral OLS structure, not only do r and t change into $r = 0.326a$ and $t = 0.276c$ but the other component θ also changes from zero to $\theta = 0.6^\circ$. The displacement of iodine atoms can be interpreted as being a distortion of the iodine lattice.

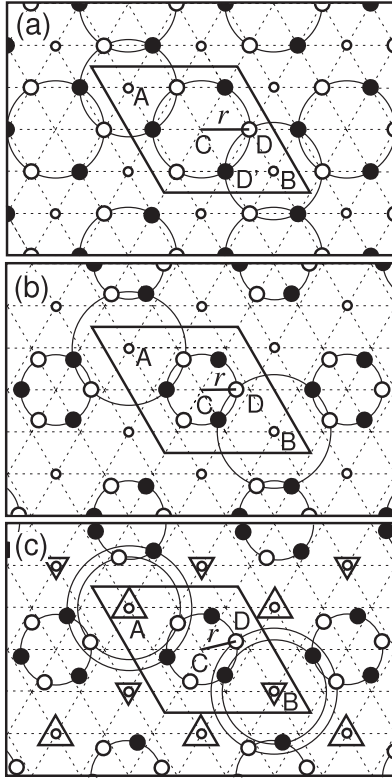


Figure 3. Three schematic structures classified by the iodine site: (a) geometrically ideal structure in which the iodine site is indifferent to either the bismuth site or the C site ($r = a/3$, $\theta = 0$), (b) structure involving displacement of iodine atoms toward the C site within the layer ($r < a/3$, $\theta = 0$), and (c) structure involving displacement of iodine atoms toward the C sites in the upper and lower layers as well as the displacement of type (b) within the layer ($r < a/3$, $\theta > 0$). Case (c) is specific to the rhombohedral BiI_3 structure. See the text for details. Bismuth and iodine atoms are represented by the same symbols as in figure 2. Triangles in (c) represent the C sites in neighboring layers. The large ones are vacancies in the upper layer, while the smaller ones are vacancies in the lower layer. The displacement of iodine atoms in (b) and (c) is exaggerated for the sake of clarity.

The three types of iodine sites are illustrated in figure 3 shown with exaggeration for the changes in r and θ except for the t component which is perpendicular to the layers. In this figure, the hexagonal structures in table 1 are classified into two types (a) and (b), while the rhombohedral structures in table 2 are classified into (a) and (c) types. The hexagonal OLS and rhombohedral OLS structures correspond to (b) and (c), respectively. As a consequence of the displacement of the iodine atoms, the distance between the C site and the neighboring iodine atoms differs from the Bi–I bond length. In particular, for the rhombohedral OLS structure with $\theta \neq 0$, the Bi–I bond has two different lengths $d_{(\pm)} = \sqrt{t^2 + s_{(\pm)}^2}$, where $s_{(\pm)} = \sqrt{(\frac{a}{\sqrt{3}})^2 + r^2 - 2(\frac{a}{\sqrt{3}})r \cos(\frac{\pi}{6} \pm \theta)}$, represented by two concentric circles around the bismuth atom site in figure 3(c). For instance, the Bi–I bond length in the hexagonal OLS structure is $d = 3.0595 \text{ \AA}$ ($> \ell = 2.9515 \text{ \AA}$), and in the rhombohedral OLS structure it is $d_{(+)} = 3.0422 \text{ \AA}$ and $d_{(-)} = 3.0775 \text{ \AA}$, which are greater than $\ell = 2.9940 \text{ \AA}$. It is

not surprising that the iodine site has rotational displacement around the C site in a layer, if the layer–layer interaction is taken into account. The displacement of θ is caused by the presence of the upper and lower layers with different phases in the rhombohedral structure. Using simple geometry, it can be seen that the lengths $\Delta_{(\pm)}$ of the interlayer I–I bonds are expressed by $\Delta_{(-)} = \sqrt{(c - 2t)^2 + 2(s_{(-)})^2 + r^2 - \frac{a^2}{6}}$ and $\Delta_{(+)} = \sqrt{(c - 2t)^2 + s_{(+)}^2}$ for the range of $-\pi/6 \leq \theta \leq \pi/6$. $\Delta_{(-)}$ ($\Delta_{(+)}$) shows a monotonic decrease (increase) with increasing θ . That is, the value of θ is considered to be determined by the bond lengths $\Delta_{(\pm)}$, which reflect the strength of the layer–layer interaction. The values of $\Delta_{(-)}$ and $\Delta_{(+)}$ in the rhombohedral OLS structure are 3.7450 and 3.8389 \AA , while they are 3.7735 and 3.8246 \AA when $\theta = 0$. An iodine atom has one bond with length $\Delta_{(-)}$ and two bonds with length $\Delta_{(+)}$.

Consequently, the rotational displacement of iodine atoms is specific to the rhombohedral BiI_3 structure, which forms three-layer packing, and reflects the interlayer interaction that mainly originates from interactions between iodine atoms belonging to separate successive layers, while the displacement of r is due to the intralayer interaction originating mainly from Bi–I bonds. We believe that the above interpretation is reasonable, though the change in θ for the rhombohedral OLS structure is as small as $\sim 0.6^\circ$. The fact that BiI_3 has a rhombohedral structure rather than a hexagonal structure suggests that the three-layer packing structure is preferred to compensate for local nonuniformity of the atomic density due to the C site through the relaxation of iodine atoms around it.

Finally, let us compare our OLS structure with available experimental data obtained by means of x-ray diffraction. The experimental data of BiI_3 reported by Trotter and Zobel [20] can be converted into $a = 7.516 \text{ \AA}$, $c = 6.906 \text{ \AA}$ and ($r = 0.3313a$, $\theta = 1.223^\circ$, $t = 0.2585c$) in our expression. The value of θ is twice as large as ours of 0.6° . r is also larger than our result, while t is smaller than ours. However, their disagreement is within a few per cent of the magnitude.

3.2. Electronic band structure

We have calculated the electronic band structures for all the crystal structures discussed in the preceding section. The results are summarized in table 3. The electronic band structure of the rhombohedral BiI_3 crystal is shown in figure 4 along with that of the hexagonal crystal.

With regard to the hexagonal structure of BiI_3 , there is a well known electronic band structure reported by Schlüter *et al* [8], who studied it using the empirical pseudopotential method more than 30 years ago. Our calculation, based on the first-principles pseudopotential method, agrees well with their result except for the value of the band gap, which is underestimated in the LDA calculations.

As shown in table 3, the rhombohedral structures have an indirect band gap while the hexagonal structures have a direct band gap. It is seen that the gap is made from A–A points for the hexagonal structures and from slightly different points on the path between Γ and T for the rhombohedral structures of Wyckoff and OL. Other candidates for the point

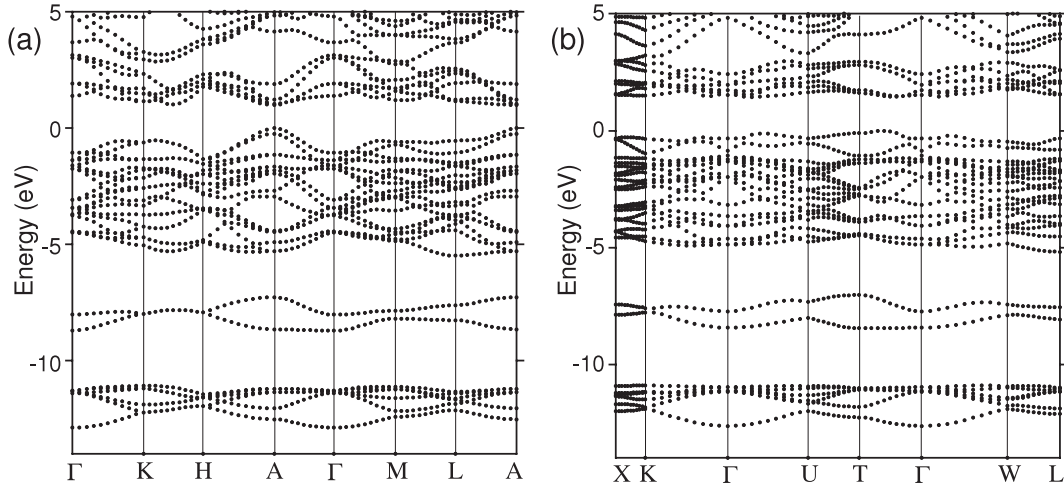


Figure 4. Electronic band structures of the optimized structures of BiI_3 : (a) the hexagonal OLS structure and (b) the rhombohedral OLS structure. The path in reciprocal space for the hexagonal structure is that used in [8], and that for the rhombohedral structure is chosen in the first Brillouin zone drawn in figure 1(b). The valence band top is taken as the zero of the energy.

Table 3. Characteristics of electronic band structures for the crystal structures listed in tables 1 and 2. The top of the valence bands (VT) and the bottom of the conduction bands (CB), represented by the high-symmetry points, determine the energy gap E_g and the transition type. SD indicates a measure of the flatness for TBV and BBC. For details, see the text.

Structure	E_g (eV)	VT	CB	Type	SD (eV)	
					TBV	BBC
Hexagonal structure						
Ideal	1.3775	A	A	Direct	0.2210	0.1708
Wyckoff	1.3468	A	A	Direct	0.2531	0.1673
OL	1.1404	A	A	Direct	0.2854	0.1887
OLS	1.0011	A	A	Direct	0.3113	0.1870
Rhombohedral structure						
Wyckoff	1.6652	$0.7\bar{\Gamma}\bar{T}$	$0.5\bar{\Gamma}\bar{T}$	Indirect	0.1129	0.0949
OL	1.5929	$0.7\bar{\Gamma}\bar{T}$	$0.5\bar{\Gamma}\bar{T}$	Indirect	0.1245	0.1036
OLS	1.4392	$0.6\bar{\Gamma}\bar{T}$	$0.3\bar{\Gamma}\bar{U}$	Indirect	0.1330	0.0941

of the conduction band bottom appear in OLS structures. The points are observed in figures 5 and 6, e.g. $0.5\bar{K}\bar{H}$ (1.0155 eV) for the hexagonal structure and $0.3\bar{\Gamma}\bar{U}$ (1.4392 eV) for the rhombohedral structure. Here, the expression $x\bar{A}\bar{B}$ represents the \bar{k} point between the high-symmetry points A and B shown in figure 1(b): $\bar{k} = (1-x)\bar{A} + x\bar{B}$, and the value in parentheses is the energy of the bottom band of the conduction bands measured from the valence band top. In the case of the rhombohedral OLS structure, the conduction band bottom shifts from the point $0.5\bar{\Gamma}\bar{T}$ (1.4680 eV) to the point $0.3\bar{\Gamma}\bar{U}$, while there are two other candidates, $0.2\bar{\Gamma}\bar{W}$ (1.4532 eV) and $0.2\bar{\Gamma}\bar{K}$ (1.4771 eV). The present results thus indicate that the rhombohedral BiI_3 structure can be an indirect band-gap semiconductor, while the hexagonal structure is not so. Both the valence band top and the conduction band bottom are basically located in the same direction in the Brillouin zone for both rhombohedral and hexagonal structures, since the T point

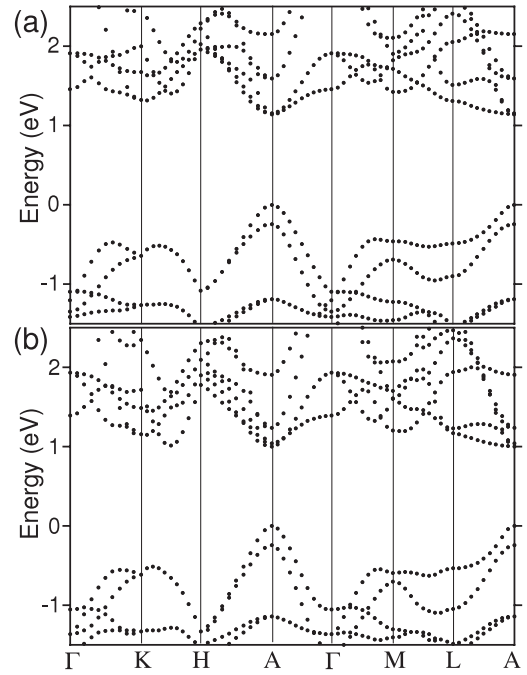


Figure 5. Electronic bands near the band gap of the hexagonal BiI_3 structure: (a) OL structure and (b) OLS structure listed in table 1. The valence band top is taken as the zero of the energy.

for the rhombohedral structure corresponds to the A point for the hexagonal. It should be noted that the conduction band bottom of the rhombohedral OLS structure is shifted from the Γ -T direction to the Γ -U direction by the displacement of iodine atoms.

Here, we focus our attention on the top band of the valence bands (TBV) and the bottom band of the conduction bands (BBC), which form the band gap, to discuss the result mentioned above. Some characteristics of the bands can be pointed out. Figures 5 and 6 show enlarged views of the bands

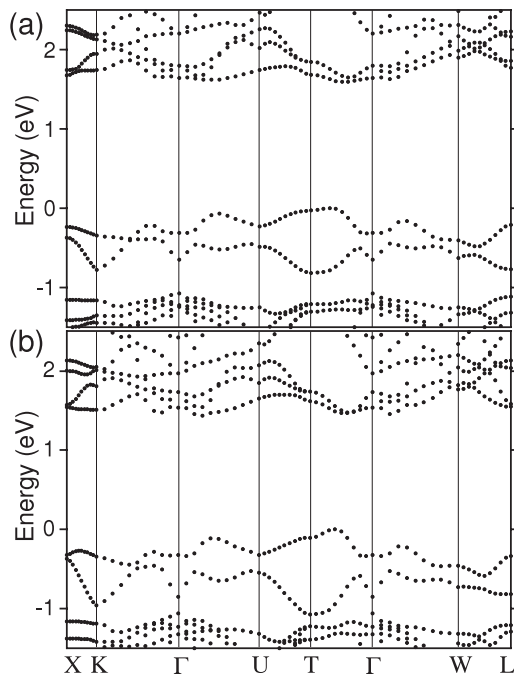


Figure 6. Electronic bands near the band gap of the rhombohedral BiI_3 structure: (a) OL structure and (b) OLS structure listed in table 2. The valence band top is taken as the zero of the energy.

near the gap for the hexagonal and rhombohedral structures respectively. The band structure for the OL structure in each figure shows a representative profile of the structures that have the iodine site of $r = a/3$. It can be seen that the bands (TBV and BBC) near the gap for the rhombohedral structures are flatter than those for the hexagonal structures. In order to quantitatively estimate the flatness of the bands, we evaluated the standard deviation (SD) of an electronic band, and this value is shown in table 3. The SD is the deviation from the mean value of a whole band curve along the paths shown in figure 4. From the comparison, the SD for the rhombohedral structures is half that for the hexagonal structures with regard to either BBC or TBV, and there is a tendency for BBC to be flatter than TBV for any structure. It follows that BBC for the rhombohedral structures is the flattest band, followed by TBV for the rhombohedral structure, BBC for the hexagonal structure, and finally TBV for the hexagonal structure, in decreasing order of the flatness of the bands. This feature of the bands near the band gap has an influence on the transition type of the rhombohedral and hexagonal structures. Namely, the rhombohedral structures have such a flat BBC that a slight change in the profile of BBC due to the displacement of the iodine site brings about a relocation of the conduction band bottom, while the conduction band bottom of the hexagonal structures is stable enough to remain at the same position in spite of the displacement of the iodine site. Therefore, we cannot rule out a possibility that the spin-orbit interaction, which is not considered here, induces a shift in the position of the conduction band bottom in the rhombohedral structure. Nevertheless, we believe that this will not affect our conclusion concerning a direct or indirect band gap.

Finally, we should mention a possible reason for the flatness of the electronic bands in the rhombohedral BiI_3 crystal. It would arise from the nature of a molecular crystal. The molecularity, which is inherent in the BiI_3 crystal, is stronger in the rhombohedral structure than in the hexagonal structure because the vacancies are distributed three dimensionally in the rhombohedral structure, in contrast to the two-dimensional distribution in the hexagonal structure.

4. Conclusion

We have for the first time performed electronic band structure calculations for the BiI_3 semiconducting crystal using the first-principles pseudopotential method, and resolved the disagreement between experimental and theoretical results relating to a direct or indirect band gap. It is found that the BiI_3 crystal has an indirect band gap only when its crystal structure is treated as a three-layer packing structure. In the crystal structure obtained from the optimization procedure for the rhombohedral structure, the relaxation of iodine atoms takes place around a vacant site on the atomic plane of bismuth.

Acknowledgments

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