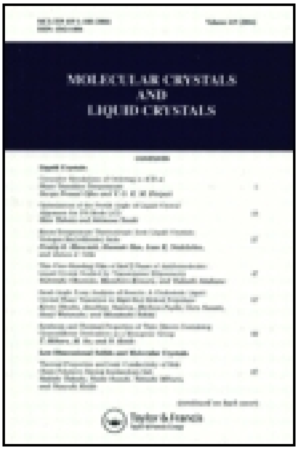

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Band Structure of Homocatenated Indium Polymer

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The electronic structure of linear homocatenated indium (In) polymer has been studied by tight-binding band calculations with the extended Hückel approximation. The polymer was found to have semiconducting behavior with a direct gap. The highest occupied crystal orbital (HOCO) of the polymer are formed by σ-bonding between neighboring p orbitals of In atoms, whose σ-electrons were well delocalized along the main chain. The possible presence of σ-conjugation in the chains can result in $\sigma-\sigma^*$ interband transitions, as in the case of polysilane, which is formed by group 14 elements.

Keywords: band structure; group 13 elements; linear homocatenated chain

1. INTRODUCTION

A number of studies have focused on linear homocatenated inorganic and metallic compounds as prototypes of one-dimensional conducting materials. Among such studied compounds, homocatenated polymers containing group 14 elements, such as polysilanes, have been synthesized and found to exhibit ultra-violet absorption caused by σ electrons delocalized along the main chain [1]. Recent studies have focused on well-defined linear homocatenated compounds formed by group 13 elements. Among such studies, Ref. [2] has observed that donor-stabilized Ga_3I_5 compounds possess a linear structure, in which the central Ga atom is combined with two Ga atoms, an I atom, and trimethylphosphine (PMe_3) that provides an electron pair to the central Ga atom [2]. In another recent study, a linear homocatenated indium compound In_6 consisting of indium iodide and protonated N-xylyl β-diketiminate was synthesized [3]. This compound exhibited ultra-violet absorption

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due to the σ-conjugation of the In–In bond. In the above-mentioned study, the authors discussed the possibility of fabricating linear chains of $(\mathrm{InIL})_n$ (where L is a ligand such as $\mathrm{PMe_3}$) in which the In atom could fulfil the octet requirement through five electrons of indium (In) atoms, one I atoms and two of P atoms, in a similar manner as that in the case of the central Ga atom of $\mathrm{Ga_3I_5}$. We are interested in investigating the electronic structures of a linear homocatenated In polymer. In this study, we developed an infinite model of the homocatenated In compound and examined its band structure, total density of states (TDOS), projected DOS (PDOS), and crystal orbital overlap population (COOP) of the In-In bond of the polymer chain.

2. CALCULATION METHOD

The extended Hückel approximation was used for the tight-binding band calculation of the linear homocatenated chains. In this calculation, both π-type and σ-type electrons were accounted for using the YAeHMOP program [4], and the valence eigenfunctions listed in Table 1 were employed as the basis. The atomic parameters (H_{ii} = orbital energy, ζ = Slater exponent) listed in Table 1 were used for the approximation. Slater exponent ζ determined the Slater-type orbitals of the atomic orbitals for the extended Hückel approximation as follows:

$$\Phi_{\mathrm{nlm}}(r,\theta,\phi) = \mathrm{N}\, r^{\mathrm{n}-1} \exp(-\zeta r) Y_{\mathrm{lm}}(\theta,\phi).$$

In a modified Wolfsberg–Helmholz formula, the off-diagonal matrix elements H_{ij} can be evaluated as follows:

$$H_{\mathrm{ij}} = 1/2KS_{\mathrm{ij}}(H_{\mathrm{ii}} + H_{\mathrm{jj}}),$$

TABLE 1 Parameters for H, C, P, In and I Atoms

Atom	Orbital	H_{ii} (eV)	ζ
H	1s	−13.60	1.3000
C	2s	−21.40	1.6250
	2p	−11.40	1.6250
P	3s	−18.60	1.7500
	3p	−14.40	1.3000
In	5s	−12.60	1.9030
	5p	−6.19	1.6770
I	5s	−18.00	2.6790
	5p	−12.70	2.3220

$$K = k + \Delta^2 + \Delta^4(1 - k); \quad k = 1.75,$$

$$\Delta = (H_{\mathrm{ii}} - H_{\mathrm{jj}})/(H_{\mathrm{ii}} + H_{\mathrm{jj}}),$$

where i, j lavel is the atomic orbitals, and S_{ij} is the overlap matrix between the Slater-type orbitals of the atomic orbitals.

In this band calculation, 20 representative wave vectors (k) at regular intervals between 0 and π/a (a is the unit cell length) were selected. Neighboring unit cells as far as the fifth nearest unit cell were considered.

First, we examined the orbital phases using a simple model in which we have considered linear In chain without side groups, as shown in Fig. 1(a). Subsequently, we calculated the band structure of a kinked In chain (Fig. 1(b)) without side groups. Finally, we modeled an In polymer (Fig. 1(c)) whose In atom fulfiled the octet requirement thorough atoms of the side groups of PMe_3 and I. In order to calculate the band structure of the model, it was necessary to determine the chemical structure of a unit cell of the In polymer. However, since an infinite chain of In complexes has not yet been synthesized, the calculations in this study were mainly based on the chemical structures of In_6 compounds [3]. Furthermore, it was assumed that the geometrical structure of the unit cell of the In polymer corresponded to a trans-form, as shown in Fig. 1(c). The bond lengths of In–In, In–I, In–P, and C–P were determined to be 2.80 Å, 2.60 Å, 2.60 Å, and 1.85 Å, respectively. These bond lengths are determined, respectively, from reference of the lengths of the In–In bond [3], the In–I bond [5], the In–P bond [6], and the C−P bond [7]. From reference [3], the angle of In–In–In was found to be 140°; this value was used in our model in the case of both the kinked In chain and the In polymer. The crystal structures of the ligands had some bond angles and dihedral angles whose values were distorted from those given in the

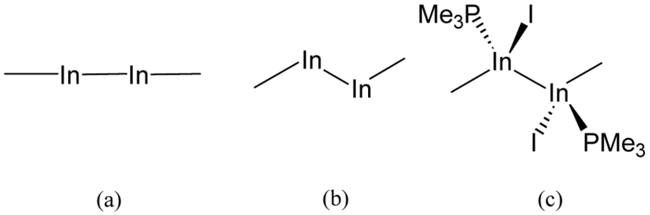


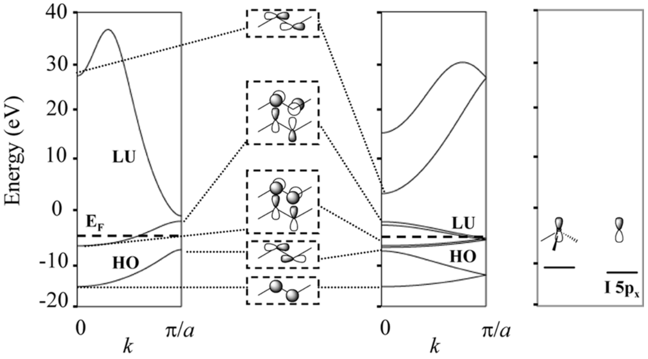
FIGURE 1 Chemical structures of (a) linear In chain, (b) kinked In chain, and (c) In polymer.

reference due to the inhibition of the steric hindrance of PMe_3. In such cases, typical values of bond length, bond angle, and dihedral angle mentioned in the references were used to determine the chemical structures [7].

3. RESULTS AND DISCUSSION

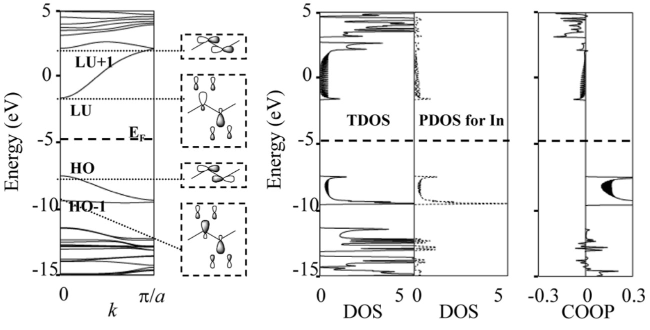
First, we examined the band structure of the linear In chain (Fig. 1(a)). In a review, Hoffmann [8] suggests the band structure of a linear, bare carbon chain. As in the case of the carbon chain, two bands of In $5p_x$/$5p_y$ orbitals (where the z axis is parallel to the main chain) become almost degenerate at energy levels near -7 eV, which cross the Fermi level. It was assumed that there was a relatively strong $5s-5p_z$ interaction in the direction parallel to the main In chain. Therefore, the two bands formed by 5 s and $5p_z$ orbitals would forbid the crossing and repel each other inside the Brillouin zone. As a result, the two bands formed by $5s-5p_z$ mixing appeared at energy levels from -15 eV to -8 eV and 5 eV to 35 eV. These two bands became the HO and LU bands.

As shown in Fig. 1(b), since the polymeric kinked structure contained two In atoms in its unit cell, its band structure showed almost folding relationship with the linear structure of the In chain. However, unlike the bond length in a carbon chain, the bond length of In–In is much considerably longer than that of the kinked carbon chain. Therefore, the two bands of the In $5p_x$/$5p_y$ orbitals (where the xz plane is



(a) (b) (c)

FIGURE 2 Band structure of (a) linear In chain, (b) kinked In chain, and (c) energy levels of PMe_3 and I atom. Their orbital phases are also described.



(a) (b) (c)

FIGURE 3 (a) Band structure, (b) TDOS, PDOS for In atom, and (c) COOP for In–In bond of In polymer. The orbital phases are also described.

formed by three neighboring In atoms) were almost degenerate. The Femi level was at the energy level of −6.44 eV, at which the four bands were almost degenerated.

PMe_3 possessed the energy level of the highest occupied molecular orbital (HOMO) at −11.4 eV. The HOMO mainly consisted of a P $2p_x$ orbital that was perpendicular to the plane formed by three H atoms. The HOMO of the I atom was formed by I 5p orbitals and was located at the energy level of −12.7 eV. It could be assumed that In $5p_x/5p_y$ orbitals interacted with the abovementioned orbitals of the PMe_3 and I atoms.

Next, we analyzed the band structure of the In polymer. The In polymer exhibited a semiconducting behavior with a direct band gap of approximately 6 eV. The bandwidth of the HO band was relatively broad. Further, the PDOS for an In atom showed the great contribution to the crystal orbitals (COs) of the HO band. The band structure of the In polymer was formed by that of the kinked In chain, the molecular orbitals of PMe_3 and atomic orbitals of I. The highest occupied crystal orbital (HOCO) showed σ-bonding between neighbouring In 5p orbitals, which had almost no interaction with the orbitals of the PMe_3 and I atom, as in the case of polysilane [9]. Further, the COOP of In–In bond also showed the bonding character of the HO band. The lowest unoccupied CO (LUCO) and the next HOCO (HOCO-1) were formed by the interaction of the In $5p_x$ band of the kinked In chain with HOMOs of both PMe_3 and the I atom. Since the degeneracy of the In $5p_x/5p_y$ orbitals was lost due to these interactions, In $5p_x$ possessed a big lobe to mix with orbitals of the PMe_3 and I atoms. The LUCOs were formed by antibonding between In $5p_x$ (+5s) orbital and either the P $2p_x$ or the I $5p_x$ orbital. From the COOP of In–In bond, we assumed that the LUCO would show a weak antibonding character between the In-In bond due to the antibonding of the neighboring In 5s orbitals. On the other hand, the HOCO-1 showed a bonding character between In $5p_x$ (+5s) orbitals and either the P $2p_x$ or the I $5p_x$ orbital. The bonding character of the In–In bond was attributed to the bonding character of the neighboring In 5s orbitals. The next LUCO (LUCO +1) showed the antibonding character of the In $5p_z$ orbitals, which was attributed to In 5s and $5p_z$ orbitals not overlapping with each other.

CONCLUSION

We examined the band structures of In polymers. The In polymer exhibited semiconducting behavior with a direct gap. It was found that I atom and PMe_3 afforded the stability of the In–In bond. The COOP of In–In bond also suggests the possibility of the stable In main chain. The broad bandwidth of the HO band and the HOCO suggested that the polymer possessed the σ-conjugation formed by In 5p orbitals, as in the case of linear homocatenated chains formed by group 14 elements.

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