Search and realization of novel electronic properties of surfaces and interfaces and of nanostructures

Takeshi INAOKA

Department of Physics and Earth Sciences, Faculty of Science, University of the Ryukyus, 1 Senbaru, Nishihara, Okinawa 903-0213

Advances in supercomputers have made it possible to calculate the electronic structure of organic crystals composed of large molecules. Using the van-der-Waals density functional theory, we have been investigating the electronic structure of x-form phthalocyanine (Pc) crystals doped with iodine (I) atomic chains. The Pc is a planar π-conjugated macrocyclic molecule which can include an atom of various species at its center position, such as Si or Li, as mentioned below. The x-form crystal is constituted of a square-lattice arrangement of molecular chains with double period and with molecular planes normal to the stacking direction. Doped I atoms form atomic chains between these molecular chains.

We employ the program package 'Vienna Ab initio Simulation Package' (VASP) [1-4] on system B (ohtaka).

(I) x-SiPcI crystals

In last year's study [5], we found that the SiPc chains act to form equally spaced I atomic chains, while the I atoms try to create trimerized chains. These effects compete with each other, but the trimerization effect is larger. The trimerized I atomic chains are not metallic . However, since the distance between neighboring trimers is not so large compared to the bond length of the trimer, application of uniaxial compression in the stacking direction could create equally spaced I chains and thereby conduction bands. In this study, with a gradual increase in uniaxial compressive strain, we perform structural optimization and trace changes in the electronic structure. Since SiPc molecules are stacked with double period, and I atomic chains are trimerized, we assume an x-form SiPcI crystal with 6-fold period in the stacking direction.

In the stable structure, the lattice constant c_0 of the unit cell in the c-axis direction is 19.12 Å, the bond length of each trimer is 3.00 Å, and the distance between adjacent trimers is 3.55 Å. In order to apply uniaxial compressive strain in the stacking direction, we gradually decrease c_0, and perform structural optimization at each c_0 value. In this process, the bond distance of the trimer almost remains unchanged, but the distance between neighboring trimers decreases, and at c_0=18.00Å, the I atomic chains are equally spaced at 3.00Å. Figure 1 shows the electron density distribution (a) before and (b) after application of uniaxial compressive strain. The compressive strain changes the distribution localized in each trimer to that extending over the entire I chain.

Our band analysis along this process clearly shows how the Peierls gap associated with the trimerized I chains gradually reduces and finally closes above the Fermi level E_F. When I atoms are equally spaced, the structure becomes doubly periodic in the stacking direction. Analysis of band dispersion shows that a band with extremely strong dispersion originating from the p_z orbitals of the I

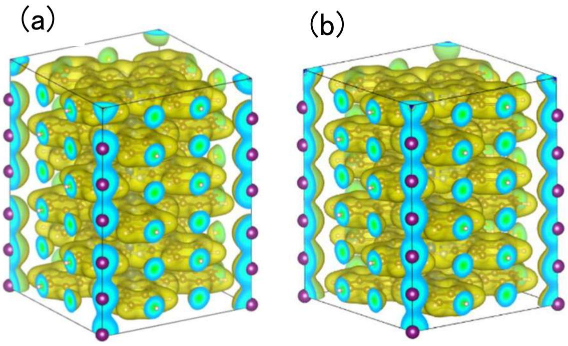

Fig.1 Electron density distribution of x-SiPcI crystals (a) before and (b) after uniaxial compression is applied. This compression changes trimerized I chains to equally spaced ones.

atoms crosses E_F, indicating that the conduction band is formed by uniaxial compressive strain. The effective mass ratio and the one-dimensional electron density are m^*/m_0=0.11 and n_{1D}=1.00 $\times 10^7$/cm, respectively. From the strain dependence of the total energy, the uniaxial compressive stress required for formation of conduction bands is estimated to be about 1.6 GPa.

(II) x-LiPcI crystals

Teruya et al. showed that Mott insulators of x-LiPc can be converted to metals of x-LiPcI and vice versa by chemical I doping and dedoping [6]. Here, we describe the progress of our theoretical study of x-LiPcI crystals.

Figure 2 exhibits the band dispersions on the Γ-Z line in the stacking direction in the Brillouin zone. The dispersive bands near and above E_F originate from p_z-orbital overlapping between neighboring stacked molecular planes. The double period in the stacking direction is reflected in the band structure. A pair of bands b193 and b194 with strong dispersion are formed by band folding at the Z point, and b193 crosses E_F, which indicates that this is a metallic band. Without I doping, the Fermi level E_F comes just at the band folding point of b193 and b194 at the Z point. As stated in last year's report as

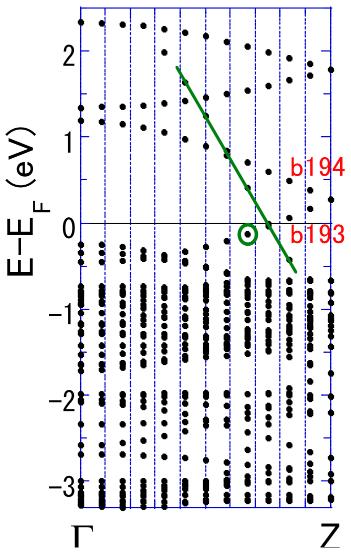

Fig. 2 Band dispersions of x-LiPcI crystal on the Γ-Z line.

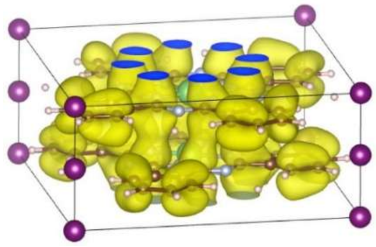

Fig. 3 Electron density distribution (isosurfaces) of the state circled green in Fig. 2.

for a single x-LiPc chain, each of these two degenerate states at the band folding point is occupied by an unpaired electron. This corresponds to the appearance of Mott insulators in x-LiPc. On I doping, since I atomic chains receive electrons from x-LiPc molecular chains, the Fermi level E_F shifts down from the band folding point, and the band b193 becomes metallic. Figure 3 exhibits the electron density distribution of the state on b193 just below E_F circled green in Fig. 2. We can see the p_z orbital overlap between the neighboring stacked molecules at each position of C atoms nearest to the center Li atom. This overlap contributes to electrical conductivity in the stacking direction.

If we consider equally spaced I chains, we have a metallic band originating from I atomic chains, as lined green in Fig. 2. However, Raman spectroscopy analysis indicates that the I chains are in a pentameric arrangement as I_5^-. If we consider ten-fold periodicity in the stacking direction and perform structural optimization, we would find that pentamerized chains are more stable than equally spaced chains, and that the resulting band of I chains is not metallic.

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