Electronic and Structural Investigations of Fe-Phthalocyanine Crystals*  

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In order to understand the effects of the polymorphism to the electronic structures of the Fe-phthalocyanine (FePc) crystals, we have performed first-principles calculations by using full-potential linearized augmented plane-wave method based on constraint density functional theory. From the total energy calculations for the electronic configurations of the $^3\text{A}_2g$ and $^3\text{E}_g$ states, by varying the crystal parameters of a tilt angle of the molecular plane with respect to the molecular stacking direction and a distance between the neighboring inter-molecular planes, we find that the structural polymorphism plays an important role in determining the ground state electronic configurations. [DOI: 10.1380/ejssnt.2014.221]

Keywords: Density functional theory; Crystallization; Iron; Nitrogen atom; Carbon; Hydrogen atom

I. INTRODUCTION

Fe-phthalocyanine (FePc), which is one of planar organic molecules with an Fe ion located at the center with a $D_{4h}$ site symmetry, has a variety of electric, optical, and magnetic properties with high chemical and physical stability. Generally, the properties of the FePc are known to be governed by the electronic structure, so-called multiplet (or electronic configuration) that arises from the electronic structure, so-called multiplet (or electronic configuration). The ground state is the $^2\text{A}_2g$ state for the $^3\text{E}_g$ state for the $^2\text{B}_2g$ and $^3\text{A}_2g$ states [3, 4].

In condensed forms, further, two polymorphic crystal structures of $\alpha$- and $\beta$-forms were experimentally reported, which behave as ferromagnetism and paramagnetism, respectively. The observed crystal structures, shown in Fig. 1(a) and (b), are characterized by the tilt angles of the molecular plane with respect to the perpendicular to the molecular stacking direction (b-axis in Fig. 1), where the distance between the nearest neighbor Fe ions along the b-axis is shorter than that between the Fe ions perpendicular to the b-axis (i.e., $\alpha$- and c-axis) by a factor of about four [11]. The observed crystal structures of the FePc molecule, simple picture of the structural polymorphism may be obtained as our present purpose, although the investigations treating the three-dimensional periodicity in the $\alpha$- and $\beta$-crystals are mainly characterized by the orientation of the molecules with respect to the molecular stacking direction (b-axis in Fig. 1), where the distance between the nearest neighbor Fe ions along the b-axis is shorter than that between the Fe ions perpendicular to the b-axis (i.e., $\alpha$- and c-axis) of 14.4 Å, which is illustrated by the tilt angle ($\theta$) of the molecular plane with respect to the molecular stacking direction and the distance (z) between the neighboring inter-molecular planes. The internal atomic positions in the FePc molecule [Fig. 1(c)] were assumed to be that given by experiments [12]. With such one-dimensional chain model, a simple picture of the structural polymorphism may be obtained as our present purpose, although the investigations treating the three-dimensional periodicity in the $\alpha$- and $\beta$-forms would be necessary for a quantitative agreement to experiments.

Calculations were carried out by the FLAPW method [13, 14] within the generalized gradient approximation (GGA) [15] for exchange correlation. The electronic structures were treated within constraint density functional theory, where a set of constraint field (Lagrange multiplier parameters), $\mu_n$, is introduced in order to constraint density-matrix, i.e. the d-orbitals occupation numbers, for the designed electronic configuration [16]. We here considered two electronic configurations, the $^3\text{A}_2g$ and $^3\text{E}_g$ states, which were reported in experiments [1–

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FIG. 1: (a) and (b) Structures of two polymorphic crystals of α- and β-forms. (c) Structure of a single Fephthalocyanine (FePc) molecule; an Fe$^{2+}$ ($d^6$) ion has a $D_{4h}$ symmetry. (d) Chain structure of the FePc employed in the present work, which are characterized by a columnar stacking of the planar molecule with the inter-molecular distance $z$ and a tilt angle $\theta$ with respect to the molecular stacking direction. Circles in (a), (b) and (d) represent the Fe$^{2+}$ ions at the center of the molecules.

For simplicity, we use the term symbols within $D_{4h}$ symmetry throughout the present paper. The LAPW basis sets with cutoffs of $|k + G| \leq 3.6$ a.u.$^{-1}$ and muffin-tin (MT) sphere radii of 2.3 a.u. for Fe, 1.2 a.u. for N and C, 0.8 a.u. for H were used, and lattice harmonic with angular momenta up to $l = 8$ for Fe, 6 for N and C, 4 for H are employed to expand the charge and spin densities.

III. RESULTS AND DISCUSSION

The relative stability between the $^3A_{2g}$ and $^3E_g$ states, by varying the tilt angle ($\theta$) and the inter-molecular distance ($z$) for the chain structure of the FePc are shown in Fig. 2, where closed squares (opened diamonds) indicate that the total energy of the $^3A_{2g}$ state is lower (higher) than that of the $^3E_g$ state. In the region for $z$ from $\sim 3$ Å to $\sim 8$ Å and $\theta$ over 5° (inside the hatched area in the figure), the ground state results in the $^3E_g$ state, but in the other region the ground state remains to be the $^3A_{2g}$ state as in the free-standing single FePc molecule [16]. Thus, the stability of the electronic configurations strongly depends on the tilt angle and the inter-molecular distance. For the crystal with the α-form, which is characterized by 26.5° of $\theta$ and 3.79 Å of $z$, the predicted $^3E_g$ ground state agrees with experiments [3, 4], although that for the β-form with $\theta = 44.8^\circ$ and $z = 4.80$ Å disagrees with experiments [5, 6]; further considerations including the interaction between the chains may be needed since the ions of the molecules at the neighbor chain becomes close to the Fe ions.

In order to understand the effect of the structural polymorphism to the electron configurations, the densities of states (DOS) for the $^3A_{2g}$ state at ($\theta, z$) = (0°, 3.79 Å) and the $^3E_g$ state at (26.5°, 3.39 Å) are shown in Fig. 3 (a) and (b), respectively. For the $^3A_{2g}$ state, due to the hybridization of the Fe $d$-orbitals between the adjacent Fe ions.

FIG. 2: Relative stability of the electronic configurations by varying the tilt angle $\theta$ and the inter-molecular distance $z$ for the chain structure [Fig 1 (d)]. Closed squares (outside the hatched area) and opened diamonds (inside) indicate that the total energy of the $^3A_{2g}$ state is lower and higher than that of the $^3E_g$, respectively. A dashed line represents the phase boundary.

FIG. 3: Density of states of $d$-orbitals in (a) $^3A_{2g}$ and (b) $^3E_g$ states. Solid black, red, green, and dashed purple lines represent $d_{xz}$, $d_{x^2-y^2}$, $d_{xy}$, and $d_{z^2}$ states, respectively. Negative and positive energies indicate occupied and unoccupied orbitals.

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
molecules along the chain axis, the \(d_{xz}(yz)\) and \(d_{z^2}\) orbitals have large dispersions along the chain axis. The DOS in the majority-spin bands at the \(E_F\) is zero but the metallic feature arising from the minority-spin \(d_{z^2}\) bands appears, which behaves like a half-metal. The electron charge density [Fig. 4 (a)], which are calculated by eigenvectors from \(E_F\) to \(-0.54\) eV below \(E_F\), spreads out along the chain axis due to the hybridization between the Fe \(d_{z^2}\) orbitals of the adjacent molecules. Thus, the hybridization pushes the bonding \(d_{z^2}\) state down to the lower energy below \(E_F\), which causes the \(3A_{2g}\) state to be energetically favorable.

For the \(3E_g\) state at \((26.5^\circ, 3.39\ \text{Å})\), the \(d_{xz}(yz)\) and \(d_{z^2}\) orbitals have large dispersions along the chain axis, and a small energy gap in the minority-spin \(d_{xz}(yz)\) bands appears, which behaves as a semiconductor. The charge density of the \(3E_g\) state [Fig. 4 (b)], which calculated with eigenvectors from \(E_F\) to \(-0.82\) eV below \(E_F\), spreads out along the chain axis. In contrast to the \(3A_{2g}\) state, the hybridization mainly comes from the \(d_{xz}(yz)\) orbitals between the adjacent molecules. The \(d_{xz}(yz)\) states further hybridize to the \(N\ p_z\) orbitals on the same molecular plane. Thus, the hybridization pushes the bonding \(d_{xz}(yz)\) state down to the lower energy below \(E_F\), which causes the \(3E_g\) state to be the ground state.

IV. CONCLUSION

We have performed the first-principles calculations to discuss the role of the polymorphism to the electronic configurations for the FePc crystals by using the FLAPW method based on the constraint density functional theory. We found that the stability of the electronic configurations strongly depends on the tilt angle of molecule and inter-molecular distance. The calculated DOS and charge density suggest that the ground states are governed by the hybridization between the Fe \(d\)-orbitals of the adjacent molecules.

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