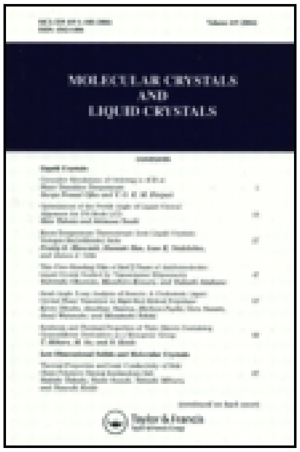

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electronic Structure and Charge Transfer Mechanism of Bromine-Graphite Intercalation Compound

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Version of record first published: 04 Oct 2006

To cite this article: Shin;ichi Higai, Seiji Mizuno, Shugo Suzuki & Kenji Nakao (1998): Electronic Structure and Charge Transfer Mechanism of Bromine-Graphite Intercalation Compound, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 267-272

To link to this article: http://dx.doi.org/10.1080/10587259808045347

Mol. Cryst. Liq. Cryst., 1998, Vol. 310, pp. 267–272
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Electronic Structure and Charge Transfer Mechanism of Bromine-Graphite Intercalation Compound

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We have studied the electronic structure of bromine-graphite intercalation compound from first principles for the first time, and proposed a new charge transfer mechanism. The Br_2 molecule intercalated between graphite layers is transformed into tribromide Br_3 with the open shell electronic structure. Then the charge of graphite π bands is transferred to the singly occupied molecular orbital (SOMO) of Br_3, so that the π bands form hole Fermi surfaces. Since the charge transfer to SOMO is incomplete, the SOMO band also forms a hole Fermi surface.

Keywords: graphite intercalation compound; bromine; Br-GIC; electronic structure; charge transfer

INTRODUCTION

Bromine-graphite intercalation compound (Br-GIC) is well-known as a typical acceptor-type GIC (AGIC), and a considerable number of studies have so far been made on it. However, the details of the charge transfer between graphite and intercalated Br and the band structure are still not clarified[1]. In general, its electronic properties have been understood based on a simple picture, as schematically shown in Fig.1. When the Br_2 molecule is intercalated between graphite layers, the charge of graphite π bands is transferred to the lowest unoccupied molecular orbital (LUMO) of Br_2, because its LUMO level is thought to be lower than the Fermi level (E_F) of graphite. Since this charge transfer is complete, the LUMO band exists below E_F

and only the π bands form hole Fermi surfaces (FSs). Nevertheless, experimentally estimated values of charge transfer per Br atom (f_{Br}), which widely range from 0.01[2] to 0.25[3], are much smaller than unity. Such small values of f_{Br} suggest the existence of the FS originating from Br, and are inconsistent with the generally accepted picture.

In the present work, we carry out the first principle calculations on Br-GIC for the first time, in order to determine theoretically the electronic structure and to examine the charge transfer mechanism.

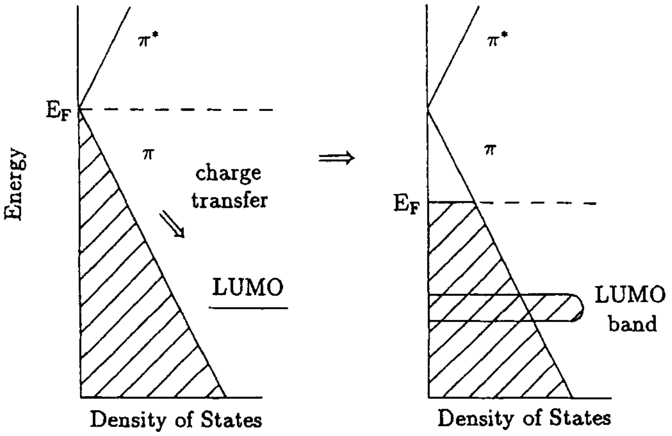

FIGURE 1 Generally accepted schematic picture for charge transfer and band structure of Br-GIC.

RESULTS AND DISCUSSION

In the present study, we adopt the linear combination of atomic orbitals method[4] using the numerical double basis set[5,6] based on the local density functional scheme[7,8,9].

The crystal structure analysis for Br-GIC provides the in-plane ($\sqrt{3} \times \sqrt{13}$) structure for the stage-2 compound. However, the sublattice structure of Br has not been completely established. Up to the present, two structural models have been proposed. In one model, its sublattice is composed of Br_2 molecules[10], and in another model, Br is in a long-chain polymeric form[11].

First of all, we carried out the band structure calculations for these two structural models (stage-2). Resulting band structures are shown in Fig.2. For both models, the lowest unoccupied band of Br is not lower than E_F

of graphite, i.e., no charge transfer from graphite to Br occurs. This result shows that Br-GIC does not become AGIC, if this compound has either of the proposed sublattice structure. Since this is inconsistent with the fact that Br-GIC is classified as AGIC, we can not support either of sublattice structures in these two models.

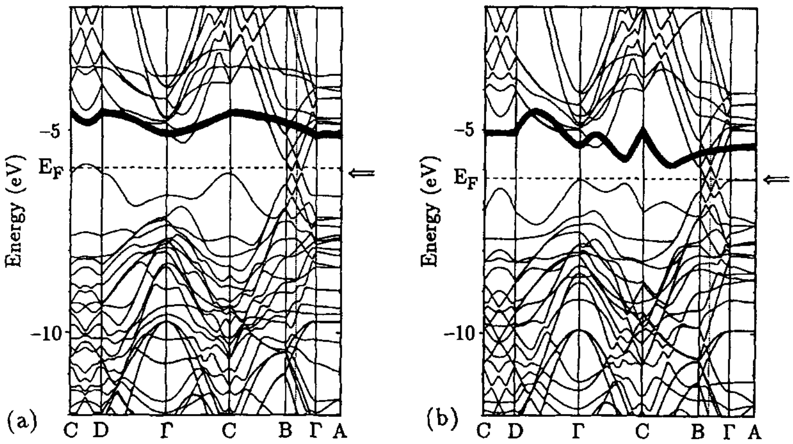

FIGURE 2 Band structures for two structural models (stage-2): (a) the sublattice is composed of Br_2 molecules; (b) long-chained polybromide. The lowest unoccupied band of Br and E_F of graphite are represented by a thick solid line and an arrow, respectively.

Here, we consider tribromide Br_3 as the sublattice unit of Br-GIC. The Br_3 molecule has the open shell electronic structure, and its singly occupied molecular orbital (SOMO) level (-7.3 eV) characterized as $4p\pi^*$ is lower than E_F of graphite (-6.1 eV), as obtained in our calculation. Hence it is expected that the charge of graphite π bands is transferred to SOMO of Br_3, provided that Br exists as Br_3 in Br-GIC. Then, we construct a new structural model whose sublattice is made up of Br_3 unit, assuming that intercalated Br_2 is transformed into Br_3. This structural model is illustrated in Fig.3.

The band structure calculated for this model (stage-2) is presented in Fig.4. As expected, charge transfer occurs to SOMO of Br_3, and the π bands form hole FSs. However, contrary to the general picture for Br-GIC, charge transfer to SOMO is incomplete, i.e., the SOMO band also forms a hole FS.

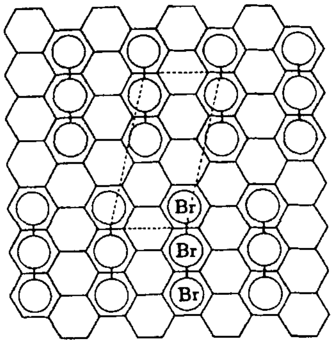

FIGURE 3 Top view of the structural model with Br_3 sublattice unit. The in-plane ($\sqrt{3} \times \sqrt{13}$) unit cell is represented by dashed lines.

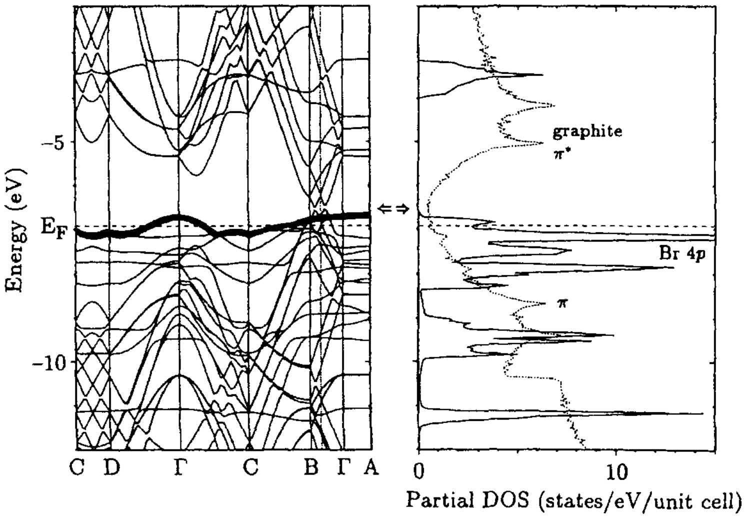

FIGURE 4 Band structure and corresponding partial density of states for the structural model (stage-2) shown in Fig.3. The SOMO band of Br_3 is represented by a thick solid line.

Several experimental results can be explained in terms of our model and results. The assumption that Br exists as Br_2 molecule in Br-GIC is mainly based on the fact that the Raman frequency 242 cm^{-1} attributed to Br_2 stretch mode was observed[12]. However, there remains a question about this. Erbil *et al.* explained that this frequency is shifted down from 320 cm^{-1} for gaseous Br_2 and 295 cm^{-1} for solid Br_2 by charge transfer to Br_2 [13]. On the other hand, Ghosh and Chung claimed that the frequency 242

cm^{-1} obtained from Br-GIC is rather close to 249 cm^{-1} observed in Br_3 compound[11]. Matsuzaki *et al.* investigated the pressure dependence of the Raman frequency of Br-GIC[14]. In their results, as pressure is applied, a broad peak at 240 cm^{-1} disappears, and sharp peaks appear at 266, 292, and 300 cm^{-1}. Since these frequencies are close to those of Br_2 molecule, there is a possibility of the transformation of Br_3 into Br_2 by pressure.

From our calculation, the value of f_{Br} is obtained as 0.03. Because of such a small value of f_{Br}, the SOMO band forms the hole FS. Experimentally obtained values of f_{Br} are also small, and these suggest the existence of the FS originating from Br. However, the mobility of its hole carrier is low because of the small dispersion of the SOMO band, as shown in Fig.4, and the scattering by the defect of Br sublattice. Therefore, it is possible that the band originating from Br has not been observed in experiments.

Our results also suggest the existence of the charge density waves in Br-GIC. From Fig.4, the FS of Br_3 SOMO band is found to be one-dimensionally open in the B-Γ direction. The nesting vectors are obtained as $\boldsymbol{Q}_1=0.295\boldsymbol{a}^*$ and $\boldsymbol{Q}_2=0.749\boldsymbol{a}^*$, where $\boldsymbol{a}^*$ is the in-plane reciprocal unit vector of graphite. Batallan *et al.* supposed the FSs of Br-GIC from the de Haas-van Alphen orbits and the nesting vectors[15]. In their proposition, the outline of FSs is one-dimensional, and the nesting vectors are $\boldsymbol{Q}_1=0.225\boldsymbol{a}^*$ and $\boldsymbol{Q}_2=0.76\boldsymbol{a}^*$. These are much close to our results.

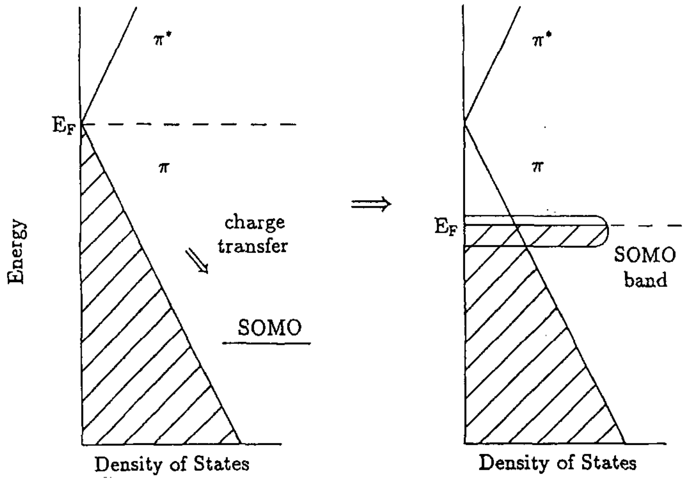

FIGURE 5 New schematic picture for Br-GIC.

CONCLUSION

In the present paper, we showed from our results that both of sublattice structures proposed in the past are not relevant. Furthermore, we also showed that the general picture for charge transfer and band structure of Br-GIC has to be modified. As the final conclusion, a new picture is schematically presented in Fig.5. Intercalated Br_2 is transformed into Br_3, then charge transfer to SOMO of Br_3 occurs. This charge transfer is incomplete, and both the π bands and the SOMO band form hole FSs.

ACKNOWLEDGEMENT

We would like to thank T. Yamashita, T. Enoki, K. Matsubara, and K. Sugihara for helpful discussions. We are also grateful to S. Matsuzaki and S. Tanuma for providing useful information.

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