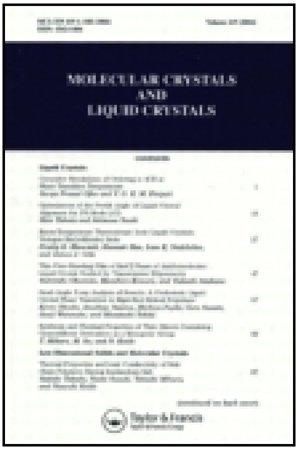

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Charge Transfer Mechanism and Electronic States of Acceptor-Type Graphite Intercalation Compounds

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Version of record first published: 24 Sep 2006

To cite this article: Shin'ichi Higai, Seiji Mizuno, Shugo Suzuki & Kenji Nakao (2000): Charge Transfer Mechanism and Electronic States of Acceptor-Type Graphite Intercalation Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 149-154

To link to this article: http://dx.doi.org/10.1080/10587250008025458

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 149-154
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Charge Transfer Mechanism and Electronic States of Acceptor-Type Graphite Intercalation Compounds

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A new model for the charge transfer mechanism and electronic states of the acceptor-type graphite intercalation compounds is proposed. The essential points of this model are the following two. One is the transformation of the molecular intercalate into another molecular form with the open shell electronic state. The other is the existence of the Fermi surface originated in the intercalate due to the incomplete charge transfer to its singly occupied molecular orbital.

Keywords: graphite intercalation compound; acceptor-type; arsenic-fluoride; charge transfer mechanism; electronic state; first-principles calculation

INTRODUCTION

In general, the charge transfer (CT) mechanism and electronic states of the acceptor-type graphite intercalation compounds (A-GIC's) have been understood based on a simple model, which is schematically shown in Fig. 1(a). In this model, CT to the lowest unoccupied molecular orbital (LUMO) of the intercalated molecule is complete, so that only the π bands of host graphite form the hole Fermi surfaces (FS's) and contribute to the electric conduction. However, details of the CT mechanism and electronic states of A-GIC's are still unclarified[1]. Furthermore, there are some serious problems in this model. The most serious one is the inevitable existence of FS originated in the intercalate. For A-GIC's, the amounts of CT estimated

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from various experiments are much smaller than unity[2], which implies the participation of the incompletely filled intercalate bands to the conduction states. In order to reveal their details and to examine the above model, we have performed the first-principles calculation. Firstly, we have taken up the bromine GIC on behalf of the halogen GIC's. Then we have shown that the general model is not appropriate for this compound, and proposed a new one[3], which is given in Fig. 1(b). The essential points of our model are the following two. One is the transformation of the intercalated molecule (Br_2) into the different molecular form with the open shell electronic state (Br_3). The other is the existence of FS originated in the intercalate due to the incomplete CT to its singly occupied molecular orbital (SOMO). Next,

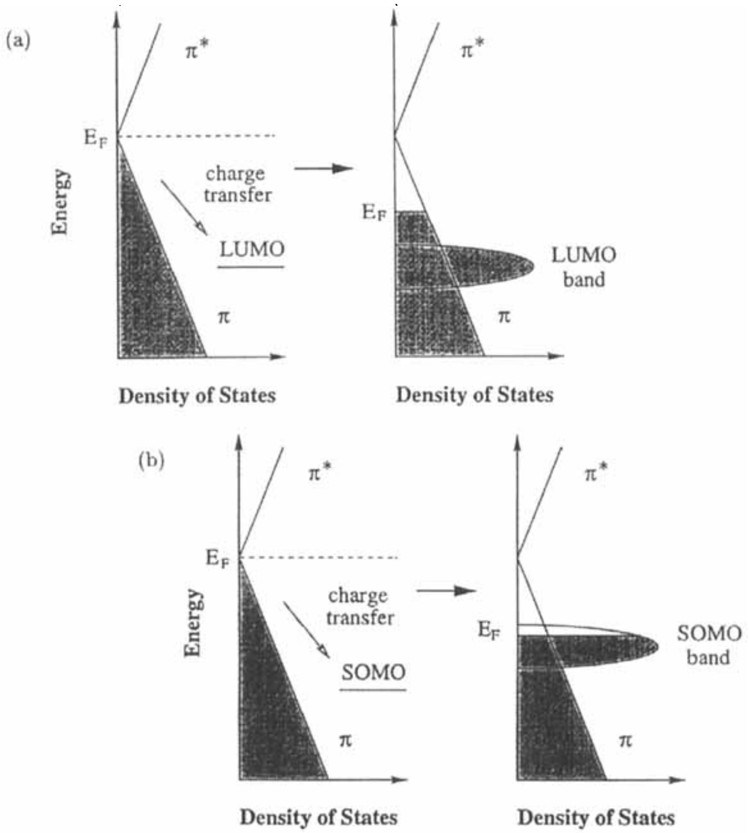

FIGURE 1 (a) The generally accepted model for the charge transfer mechanism and electronic states of A-GIC's. (b) A new model.

we have taken up the arsenic-fluoride (AsF)-GIC because of the following reasons. For the Lewis-acid GIC's including AsF-GIC, a unique CT mechanism has been shown[4], which is called the disproportionation and described as

$$3\ \mathrm{AsF_5} + 2\ \mathrm{e^-} \longrightarrow \mathrm{AsF_3} + 2\ \mathrm{AsF_6^-}.$$

This is essentially identical to our model in the point that the intercalated molecule transforms into that with the open shell electronic state. In addition, as an acceptor of electron, AsF_6 is stronger compared with Br_3, which reflects the depth of their SOMO levels. Therefore, if FS originated in AsF_6 would exist, this is also possible for the other A-GIC's. In the present paper, we give the result for AsF-GIC, and show that our model is also held for this compound.

STRUCTURAL MODELS

The structure of the intercalate in AsF-GIC has so far been unclarified. Thus we had to construct the structural models based on the experimental results[2,5]. For the stage-1 compound, the chemical formula is obtained as C_8AsF_5, and the c-axis repeat distance is 8.10 Å. There are two possibilities for the states of the intercalated AsF_3, AsF_5, and AsF_6. One is the case

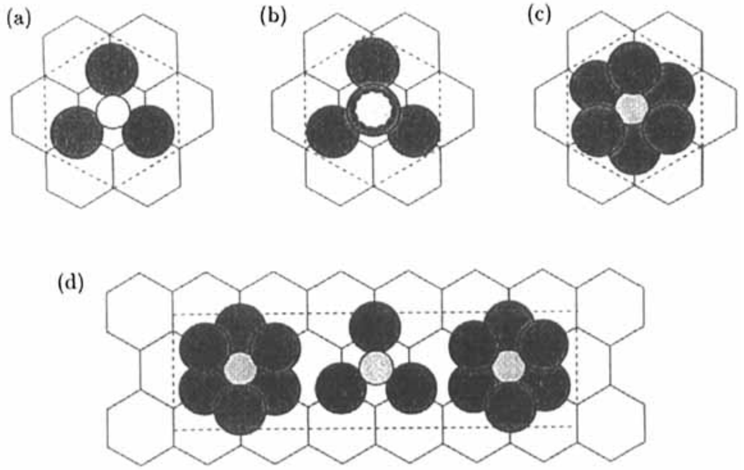

FIGURE 2 The top views of the structural models; (a) C_8AsF_3, (b) C_8AsF_5, (c) C_8AsF_6, and (d) $C_{24}AsF_3(AsF_6)_2$. Dashed lines indicate a unit cell. The hexagonal net gives graphite. Light and dark shaded circles show the As and F atoms, respectively.

that each of them forms domains, and the other is the case that they co-exist. For the former case, we put them in the in-plane (2×2)R0° unit cell individually as shown in Figs. 2(a)-(c). On the other hand, for the latter case, we put one AsF_3 and two AsF_6 in the $(6\times\sqrt{3})R(0°,30°)$ unit cell as Fig. 2(d), in which the disproportionation is complete. For their molecular structures, those of the isolated molecules have been tentatively used.

RESULTS AND DISCUSSION

In the present calculation, we have adopted the linear combination of atomic orbitals method using the numerical multiple basis set[6] based on the local density functional formalism[7].

First of all, in order to prospect CT between AsF_3, AsF_5, AsF_6 and graphite, we have calculated their electronic states individually. The results are given in Table I. For AsF_3 and AsF_5, the LUMO levels identified as the As 4*p*-state are higher than the Fermi level (E_F) of two-dimensional graphite, while the highest occupied molecular orbital (HOMO) levels (F 2*p*) are lower, so that no CT is expected. On the other hand, a large CT is expected for AsF_6, because its SOMO level (F 2*p*) is much lower.

TABLE I The LUMO and HOMO levels of AsF_3 and AsF_5 and the SOMO level of AsF_6 relative to E_F of two-dimensional graphite.

	AsF_3	AsF_5		AsF_6
LUMO (eV)	+5.1	+2.8	SOMO (eV)	-5.1
HOMO (eV)	-1.8	-4.3		

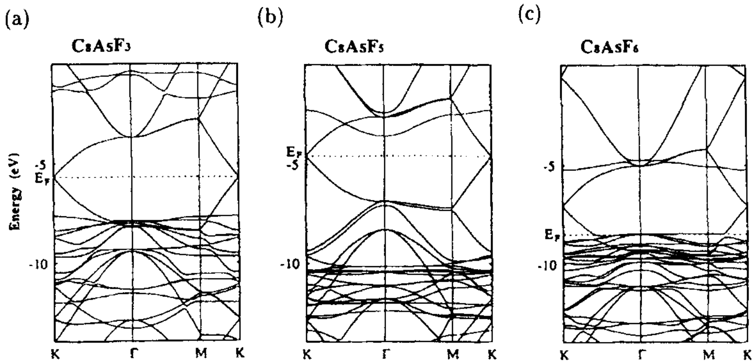

FIGURE 3 The electronic band structures for the structural models; (a) C_8AsF_3, (b) C_8AsF_5, and (c) C_8AsF_6. Dashed lines indicate E_F.

Then, we have calculated the electronic band structures for the structural models C_8AsF_3, C_8AsF_5, and C_8AsF_6, which are presented in Fig. 3(a), (b), and (c), respectively. As expected, no CT occurs between AsF_3, AsF_5 and graphite, because their LUMO bands are higher than E_F of graphite, while the HOMO bands are lower. On the other hand, CT takes place to the SOMO of AsF_6. As a result, the π band of graphite forms the hole FS. However, CT to SOMO is incomplete, so that the SOMO band with a very small dispersion also forms the electron FS. The amount of CT has been estimated as 0.30 per AsF_6.

Next, the band structure for the structural model $C_{24}AsF_3(AsF_6)_2$ has been calculated, which is given with corresponding partial density of states (DOS) in Fig. 4. Only AsF_6 takes charge from graphite, and AsF_3 stays neutral. Consequently, the graphite π-bands and two SOMO bands of AsF_6 form the hole and electron FS's, respectively. The amount of CT has been estimated as 0.53 per AsF_6, and also given as 0.35 per AsF_5.

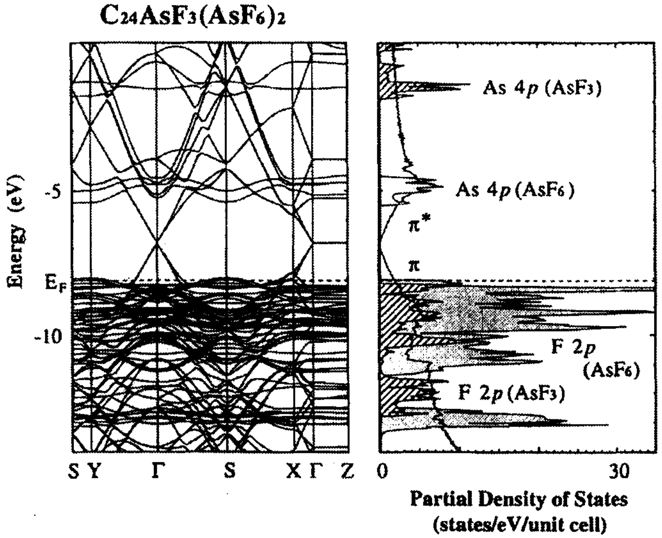

FIGURE 4 The band structure and corresponding partial DOS for the structural model $C_{24}AsF_3(AsF_6)_2$. The partial DOS's of AsF_3, AsF_6, and graphite are presented by hatched, shaded, and unshaded parts, respectively.

Rachdi et al.[8] have estimated the amount of CT from the Shubnikov-de Haas oscillation for AsF-GIC (stage-1), which has been obtained as 0.34 per AsF_5. Since this value is much smaller than 2/3, which is for the case that CT to AsF_6 is complete, the existence of FS originated in the intercalate is suggested. However, the mobility of the carrier originated in the intercalate band may be very small due to the small dispersion of the SOMO band and defects in the intercalate layer, which can make difficult to observe it.

In our calculation, the structures of the intercalates have not been optimized. It has also been found that the appearance of the SOMO band and amount of CT are sensitive to the structure of AsF_6. Therefore, more information for their structures is needed for the quantitative discussion. Furthermore, it is also difficult to conclude only from our results whether the intercalates form domains or coexist.

It is not novel case for the alkali-metal ternary GIC's, which are the donor-type GIC's, that the acceptors of electron form FS's together with the antibonding π^*-bands of graphite. For the potassium-oxygen-GIC[9], it has been shown that the O $2p$-band forms the hole FS, and for the sodium-hydrogen-GIC[10], the H $1s$-band also forms it.

CONCLUSION

We have shown that our new model for the CT mechanism and electronic states of A-GIC's is also held for AsF-GIC. Lastly, we conclude that it is necessary to consider the existence of FS's originated in the intercalates in investigating the electronic states of A-GIC's.

Acknowledgments

We would like to thank T. Yamashita, T. Enoki, K. Matsubara, K. Sugihara, W. R. Datars, and A. Ziatdinov for useful information and helpful discussions.

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