

# Electronic structures of HOPG and stage-2 IBr-GIC studied by angle resolved photoemission

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## Abstract

Angle resolved photoemission spectra (ARPES) of host HOPG and IBr-GIC have been measured at 16 K using  $h\nu = 122$  eV. Both HOPG and IBr-GIC show clear dispersions of upper  $\pi$  band and  $\sigma$  bands derived from C 2s and 2p electrons. The intensity plot of ARPES spectra shows the overlap of the dispersion curves along the  $\Gamma$ M and  $\Gamma$ K directions due to the in-plane mosaic structure of HOPG. Based on the Johnson-Dresselhaus band model, the dispersion curves of the  $\pi$  bands of HOPG and IBr-GIC are reproduced over full Brillouin zone. We shall discuss an important role of interactions between C-C atoms in the neighboring layers in the stage-2 structure.

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## 1. Introduction

Intercalation of IBr molecules into van der Waals (vdW) gaps of graphite forms an acceptor graphite intercalation compound, IBr-GIC. Based on the Blinowskii-Rigaux (BR) band model [1], the variation of the valence  $\pi$  bands around the K point near the Fermi energy  $E_F$  were discussed and controversial values of  $E_F$  were evaluated using different band parameters; from Hall effect [2,3],  $E_F = 0.55$  eV using the hole concentration of  $8 \times 10^{-20} \text{ cm}^{-3}$  with band parameters  $\gamma_0 = 3.16$  eV and  $\gamma_1 = 0.38$  eV, while from the de Haas-van Alphen (dHvA) effect [4],  $E_F = 0.79$  eV using the dHvA frequencies of  $f_1 = 455$  T and  $f_2 = 1106$  T with  $\gamma_0 = 2.40$  eV and  $\gamma_1 = 0.328$  eV. However, much less is known about electronic states of IBr-GIC over full Brillouin zone (BZ). To our knowledge, there are a few photoemission spectroscopic studies using angle integrated mode on the electronic structure of acceptor GICs, such as  $\text{AuCl}_3$ -GIC [5],

which show the shift of valence bands to lower binding energy side but give no information about band dispersion and guest electronic states. In the present study, we have measured angle resolved photoemission spectra (ARPES) of host graphite and IBr-GIC to obtain dispersion curves of their valence bands, and discuss variation in the electronic states upon IBr guest intercalation.

## 2. Experimental

Mosaic crystals of highly oriented pyrolytic graphite (HOPG) flakes were employed as a host material. IBr molecules were intercalated by using a two-bulb method with  $105^\circ\text{C}$  for IBr-GIC [2]. Chemical composition of IBr-GIC was determined to be  $\text{C}_{18(1)}\text{IBr}$  from the mass variation before and after the intercalation. Lattice constants of HOPG were  $a_0 = 2.46(1) \text{ \AA}$  and  $c_0 = 6.71(1) \text{ \AA}$ . Repeat distance along the  $c$ -direction of IBr-GIC,  $I_c$ , was determined

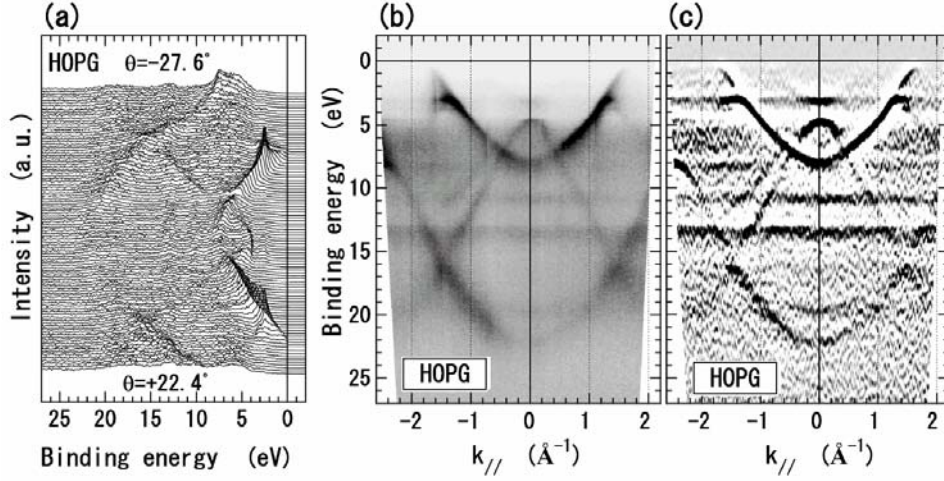


Fig. 1. (a) EDC curves, (b) intensity plot, and (c) second derivative intensity plot of ARPES spectra for HOPG at 16 K using  $h\nu = 122$  eV.

to be  $10.56(1)$  Å, indicating stage-2 structure.

The ARPES measurements at 16 K were carried out at the undulator beam line BL-1, installed at Hiroshima Synchrotron Radiation Center (HSRC), Hiroshima University [6]. Incident photon energy of 122 eV was employed, and the total energy and angular resolutions were set to 50-100 meV and  $\pm 0.4^\circ$ , respectively. Samples were cleaved in the atmosphere and transported to analyzer chamber ( $P < 1 \times 10^{-10}$  Torr). The value of binding energy  $E_B$  was defined to  $E_F$ , which was calibrated by Fermi edge of an evaporated Au film.

### 3. Results and discussion

ARPES results of HOPG are shown in Fig. 1. In

the energy distribution curves (EDCs) of HOPG [Fig. 1(a)], feature peaks are observed at  $E_B = 4.8, 8.0,$  and  $22.0$  eV at the  $\Gamma$  point ( $\theta = 0^\circ$ ), and the peak positions change remarkably with  $\theta$ . Their dispersions can be visualized more clearly by plotting the photoemission intensities and their second derivative values as functions of  $E_B$  and parallel momentum  $k_{\parallel}$ , where  $\hbar k_{\parallel} = (2mE_{\text{kin}})^{1/2} \sin\theta$  with the mass  $m$  and a kinetic energy  $E_{\text{kin}}$  of emitted photoelectron [Figs. 1(b) and 1(c)]. By comparing with the band dispersions calculated by the first principal methods [7,8], two branches with minima at  $\Gamma$  point are assigned to the  $\pi$  bands and  $\sigma_1$  one, and other two branches with a maximum at  $\Gamma$  point are to  $\sigma_2$  and  $\sigma_3$  bands of graphite. As pointed out by the previous ARPES results [9], since a perpendicular momentum of

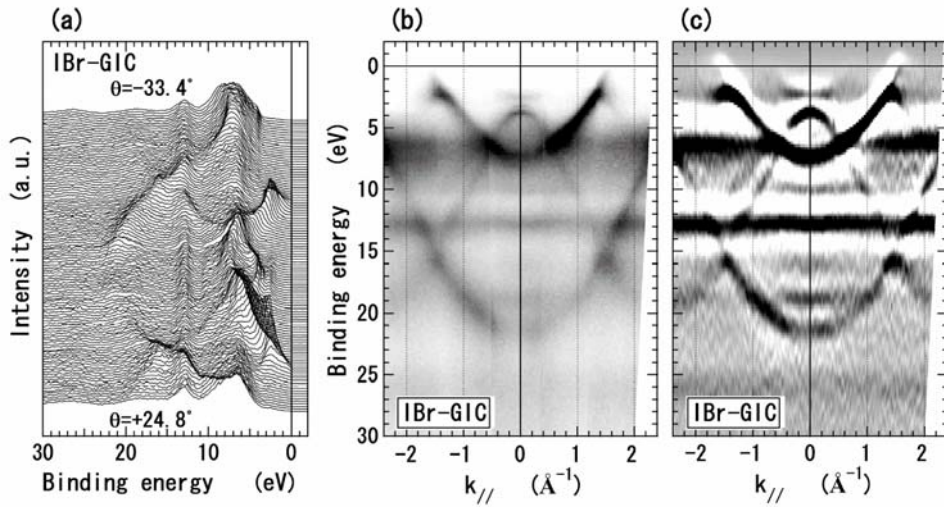


Fig. 2. (a) EDC curves, (b) intensity plot, and (c) second derivative intensity plot of ARPES spectra for IBr-GIC at 16 K using  $h\nu = 122$  eV.

photoelectron varies as a function of  $h\nu$ , the positions and PES intensities of  $\pi$  bands change remarkably with  $h\nu$  because of large sinusoidal dispersions of  $\pi$  bands along the  $\Gamma A$  direction. Furthermore,  $\pi$  bands show a clear splitting for  $k_{\parallel} > 1.2 \text{ \AA}^{-1}$  into two branches, one shows a maximum at  $k_{\parallel} = k_M (= 1.474 \text{ \AA}^{-1})$ , and another goes to cross the Fermi level at  $k_{\parallel} = k_K (= 1.703 \text{ \AA}^{-1})$ , indicating the superposition of the dispersion curves along the  $\Gamma M$  and  $\Gamma K$  directions due to the mosaic structure of HOPG. PES intensities of the  $\pi$  bands show remarkably asymmetric properties around the M and K points; the intensities in the second BZ is much lower than that in the first BZ due to photoemission structural factor, in which the waves from different C sites interfere positively in the first BZ but negatively beyond the K point [10]. Furthermore, flat branches are located at  $E_B = 3.2, 8.2, 11.0, 13.5,$  and  $19.5 \text{ eV}$ , although their photoemission intensities are rather small. These non-dispersive

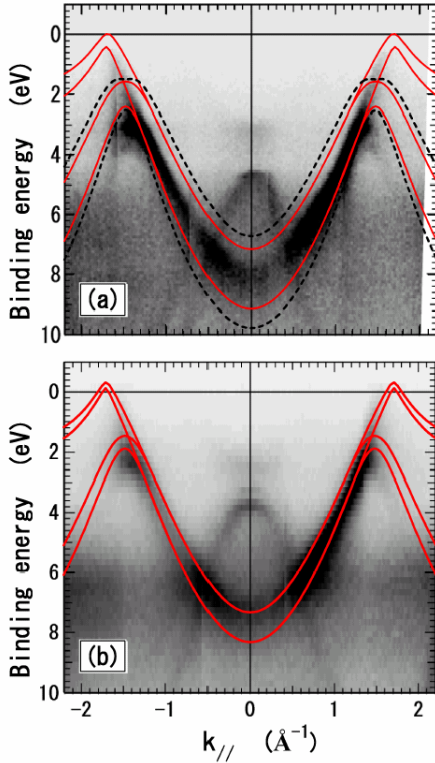


Fig. 3. (a) Band dispersions of the  $\pi$  bands along the  $\Gamma M$  and  $\Gamma K$  directions for graphite calculated by JD model and (b) those along the  $\Gamma M$  and  $\Gamma K$  directions for stage-2 IBr-GIC. Dashed and solid lines for graphite indicate the results calculated with the reported parameters [6] and those with the new fitted parameters in the present work, respectively. Solid lines are the dispersion curves for stage-2 IBr-GIC calculated using the same parameters for graphite and Fermi energy shift of  $0.4 \text{ eV}$ .

Table 1

The values of SWMcC band parameters  $\gamma_0$ - $\gamma_5$ ,  $\Delta$ ,  $-E_F$ , and coordination number  $z$  used to calculate the  $\pi$  band dispersions of HOPG and stage-2 IBr-GIC using JD band model, in units of eV, together with the reported results using BR band model.

	HOPG			Stage2 IBr-GIC			
	$z$	JD [13]	Present	$z$	Present	BR[2]	BR[4]
$\gamma_0$	3	2.41	2.457	3	2.457	3.16	2.40
$\gamma_1$	2	0.27	0.26	2	0.26	0.38	0.328
$\gamma_2$	2	-0.022	-0.015	0	-	-	-
$\gamma_3$	6	0.14	0.071	3	0.071	0	0
$\gamma_4$	6	0.074	0.037	3	0.037	0	0
$\gamma_5$	2	0.0065	0.0035	0	-	-	-
$\Delta$	-	0.0074	0.030	-	0.030	-	-
$-E_F$	-	0	0	-	-0.40	-0.55	-0.79

branches are also observed for single-crystalline Kish graphite flakes, and disappear by a heat treatment above  $800 \text{ }^\circ\text{C}$  before measurements, suggesting that they may be due to some localized states of any molecules produced by bond breaking when cleaved or atoms adsorbed on the graphite surface after cleavage in the atmosphere. No further reference is given in the present paper.

Fig. 2 illustrates ARPES results of IBr-GIC. At the first glance, the overall behaviors are similar to the results of the host HOPG (Fig. 1). Dispersionless branches are also observed at  $E_B \sim 2.6, 13.0$  and  $19.0 \text{ eV}$ . These results are consistent with the facts that photoionization cross sections of Br  $4s$ , Br  $4p$ , I  $5s$  and I  $5p$  electrons are much smaller than those of C  $2s$  and C  $2p$  ones at  $h\nu = 122 \text{ eV}$  [11]. With examining closely, however, variation upon intercalation of IBr guests can be seen. The  $\sigma_1$ ,  $\sigma_2$  and  $\sigma_3$  bands shift by  $0.4(1) \text{ eV}$  to the lower  $E_B$  side. Also  $\pi$  bands show such a shift but the dispersion curves become broader and their curves seem to be modified a little by IBr intercalation. The observed shift value is smaller than the reported values,  $0.55 \text{ eV}$  [2] and  $0.79 \text{ eV}$  [4]. Furthermore, a new flat branch appears at  $E_B = 26 \text{ eV}$  and it is attributed to I  $5s$  and/or Br  $4s$  states. Broad contributions are observed at  $E_B = 4\sim 10 \text{ eV}$  and they may be attributed to I  $5p$  and/or Br  $4p$  states. Partial density-of-states of I  $5p$  and Br  $4p$  electrons in the valence band have been investigated at BL-7 of HSRC and will be reported elsewhere [12].

Now, we shall discuss dispersions of  $\pi$  bands of HOPG and IBr-GIC over full BZ based on the ARPES data. As is well known,

Slonczewski-Weiss-McClure (SWMcC) model is useful for the fitting restricted near the K point. Johnson-Dresselhaus (JD) band model is useful for full zone fitting of the  $\pi$  band dispersions. The details of the respective Hamiltonians and relations between SWMcC and JD parameters are found in Ref. 13. Here we employ the JD model to make full zone fitting to the  $\pi$  band dispersions obtained experimentally. With the reported values of JD parameters [13], at first, we calculated dispersion curves along the  $\Gamma M$  direction for graphite; the calculated results are shown by dashed lines in Fig. 3(a). For the sake of comparing with parameters used in other models, SWMcC parameters evaluated from the JD parameters are listed in Table 1, together with coordination number  $z$  for respective interactions. In this case, the difference between the upper and lower  $\pi$  bands at the  $\Gamma$  point is 3.1 eV (dashed lines), much larger than the experimental data [9]. Using slightly modified parameters [Table 1], the experimental dispersions of HOPG can be reproduced over full BZ to locate at the center of upper and lower  $\pi$  bands, as indicated by solid lines. For stage-2 GIC, we have calculated the band dispersions with the same values of  $\gamma_0$ - $\gamma_5$  obtained for host graphite [Table 1] but different coordination numbers for stage-2;  $z = 0$  for  $\gamma_2$  and  $\gamma_5$ , and  $z = 3$  for  $\gamma_3$  and  $\gamma_4$ , half of those for graphite, which leads to a decrease of the  $\pi$  band splitting, since the interactions  $\gamma_3$  and  $\gamma_4$  between C-C atoms in the neighboring layers play an important role to determine the binding energies of the  $\pi$  bands. With shifting by  $E_F = 0.40(1)$  eV, furthermore, the experimental dispersion curve of the  $\pi$  band are successfully reproduced, as indicated by solid lines in Fig. 3(b). Thus, variation of  $\pi$  bands upon intercalation observed by ARPES measurements can be understood based on the JD band model with almost unchanged band parameters, which is the direct evidence that some charge transfer from host C layers to IBr guests is dominant in this acceptor GIC, and there is no need to consider any drastic change of the interaction parameters between C atoms upon intercalation.

#### 4. Conclusions

ARPES measurements of host HOPG and

IBr-GIC using  $h\nu = 122$  eV show clear dispersions of  $\pi$  and  $\sigma$  bands derived from C 2s and 2p electrons, which are overlapped along the  $\Gamma M$  and  $\Gamma K$  directions due to the in-plane mosaic structure of HOPG. Full zone fitting of  $\pi$  bands based on the JD band model confirms the energy shift of stage-2 IBr-GIC by 0.4 eV from the graphite, in agreement with variation in  $\sigma$  bands. Upon intercalation, the interaction strengths between neighboring C-C atoms remain almost unchanged, but the decreases of their coordination numbers change the magnitude of the  $\pi$  band splitting. Two and three dimensional mapping of hole and electron pockets of kish graphite and GICs using ARPES measurements will give us direct information about Fermi surfaces comparable to dHvA oscillations.

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#### References

- [1] J. Blinowski, *et al.*, J. Phys. **41** (1980) 47.
- [2] K. Kobayashi, *et al.*, J. Phys. Soc. Jpn. **68** (1999) 2006.
- [3] M. Barati, *et al.*, J. Phys.: Condens. Matter **11** (1999) 5569.
- [4] E. Tchernier, *et al.*, J. Phys.: Condens. Matter **9** (1997) 8221.
- [5] T. Ishii, *et al.*, J. Phys. Soc. Jpn. **66** (1997) 3424.
- [6] K. Shimada, *et al.*, Nucl. Instrum. Methods A **467-468** (2001) 517.
- [7] R. C. Tatar and S. Rabii, Phys. Rev. B **25** (1982) 4126.
- [8] J.-C. Charlier, *et al.*, Phys. Rev. B **43** (1991) 4579.
- [9] T. Kihlgren, *et al.*, Phys. Rev. B **66** (2002) 235422.
- [10] H. Nishimoto *et al.*, J. Phys.: Condens. Matter **8** (1996) 2715.
- [11] J.-J. Yeh, Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters, Gordon and Breach, New York, 1993.
- [12] S. Negishi *et al.*, J. Phys. Chem. Solids, 2006 (this issue).
- [13] L.G. Johnson and G. Dresselhaus, Phys. Rev. B **7** (1973) 2275.