

Long range ordering in the graphite intercalation compounds

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Abstract

Graphite surfaces treated with NaOH, LaCl₃ and CeCl₃ aqueous solutions were studied by scanning tunneling microscopy. These metals in the compounds are known to have poor lattice matching with graphite. In the presence of low densities of intercalants, which are not enough to form a stage structure, the existence of large periodic superstructures was confirmed. Since the observed structures could not be interpreted by Moiré pattern hypothesis, they might be directly related to the intercalant arrangement. The obtained results directly show the importance of long-range interactions for the understanding of the graphite intercalation compound structures as predicted by theoretical studies.

Keywords: AFM, STM, Graphite and related compounds, Single crystal surface

1. Introduction

Graphite intercalation compounds (GICs) have attracted considerable attention because graphite can be intercalated by a wide variety of atoms and the resulting compounds show characteristic properties different from those of the host graphite. According to X-ray diffraction measurements, GICs show periodic stacking structures. When intercalated materials, i.e., intercalants, exist between every *n* and *n*+1 layer of the host graphite, the structure is called a stage-*n*-type structure. In addition, intercalants form ordered superstructures in-plane. In general, when the chemical potential is lowered, the distance between intercalants increases, i.e., structures with larger in-plane lattices and higher stages are formed.

Alkali-metal GICs (AM-GICs) have been studied widely because of simplicity of analysis. When the intercalants are Li and K, stage-1 structures with $\sqrt{3}\times\sqrt{3}$ in-plane structures are formed [1]. However, for Na-GICs, only high stage (*n*=6, 8) structures with $\sqrt{3}\times\sqrt{3}$ and 2×2 in-plane structures are formed [2]. The high-stage structure appearing in the Na-GIC is explained by the difficulty of intercalation of Na atoms because of their weak interaction with C in graphite [3]. However, since $\sqrt{3}\times\sqrt{3}$ in-plane structure is formed in the 8-stage structure, Na seems to be easily intercalated in-plane, which may suppress the formation of lower stage structures. These results indicate that the formation of GIC structures is governed by the balance of some related interactions. Theoretically, the importance of the long-range interactions due to elastic strain has been pointed out in addition to electrostatic interactions [4,5]. In order to clarify these points, we studied GICs with very low densities

of intercalants by scanning tunneling microscopy (STM).

2. Experimental

Samples were prepared by dipping highly oriented pyrolytic graphite (HOPG) into NaOH, LaCl₃ and CeCl₃ aqueous solutions. After drying the sample in air, they were measured by X-ray diffraction (XRD), X-ray photoemission spectroscopy (XPS) and STM. STM images were taken in air at room temperature using a Pt/Ir tip. All STM images reported here were taken in the constant-height mode. From the results of XPS measurements, we confirmed the existence of intercalants. However, since X-ray diffraction patterns related to the stage structures were not observed, intercalants were confirmed to be present in small amount.

3. Results and discussion

Fig. 1 shows STM images of the HOPG treated with (a), (b) NaOH, (c) LaCl₃ and (d) CeCl₃. We can see large periodic superstructures with lattice constants of (a) 1.7nm, (b) 9.1nm, (c) 1.5nm and (d) 5nm. Similar superstructures are known to be observed on clean graphite surface, and are known to be well interpreted by the Moiré pattern hypothesis [6,7]. Since Moiré patterns are formed by the lattice mismatch between the top layer and underlying graphite layers, the symmetry of Moiré patterns must reflect that of the host material, i.e., a threefold symmetry for graphite. However, as shown in Figs. 1(a) to 1(d), the observed superstructures in Figs. 1(c) and 1(d) have twofold symmetry, which is not reflected by the Moiré pattern. For the structures in Figs. 1(a)

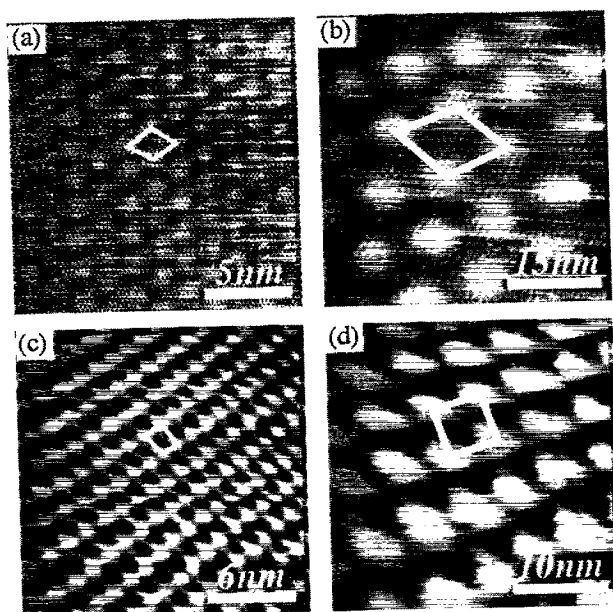


Fig. 1. STM images of the HOPG surface treated with (a), (b) NaOH ((a) $V_s = -20\text{mV}$, $I_s = 1.9\text{nA}$, (b) $V_s = 30\text{mV}$, $I_s = 0.7\text{nA}$), (c) LaCl_3 ($V_s = 19\text{mV}$, $I_s = 1.8\text{nA}$), and (d) CeCl_3 ($V_s = 15\text{mV}$, $I_s = 2.3\text{nA}$).

and 1(b), there existed mismatch from the theoretical calculation based on the Moiré analysis [8]. These results suggest the existence of some other mechanism for the formation of the large superstructures observed.

As mentioned above, theoretically, the importance of elastic interactions has been pointed out in addition to the electrostatic ones [4,5]. Na, La, and Ce are elements that usually have poor lattice matching with graphite. In this case, the interactions between intercalant layers may be stronger than those in-plane, resulting in the dense structure for higher stages, as shown in Fig. 2(a). In fact, Eu, which forms stage-1 GIC with $\sqrt{3} \times \sqrt{3}$ in-plane structure as shown in Fig. 2(b) [9], exhibits a good lattice matching with graphite. For GICs such as Rb-GIC, large lattice in-plane superstructures with the stage-1 structure are reported to be formed as shown in Fig. 2(c) [10]. Their formation is explained by mechanisms such as the charge density wave; however, the balance of long-range interactions may also apply in this cases.

4. Conclusion

On the graphite surfaces treated with NaOH, LaCl_3 and CeCl_3 solutions, large periodic superstructures were observed by STM. The observed structure could not be interpreted by Moiré pattern hypothesis, suggesting the structure to be directly related to the intercalant arrangement. The obtained results directly show the importance of long range interactions for the understanding of the GIC structures as predicted by theoretical studies.

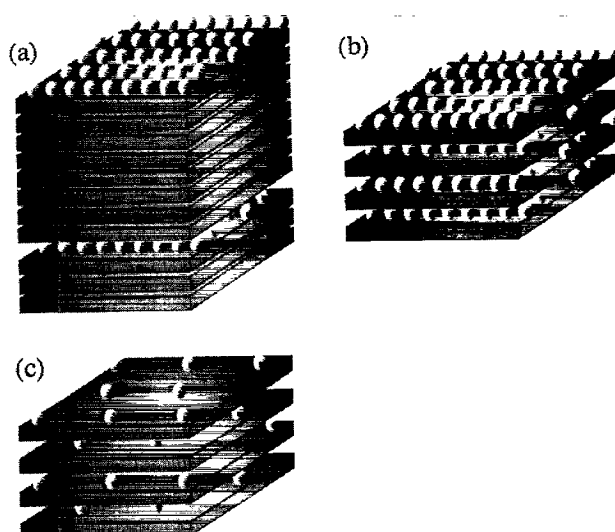


Fig. 2. Structures of GICs: (a) dense in-plane with high-stage, (b) dense in-plane with low-stage, and (c) large lattice in-plane with low stage.

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References

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- [1] H. P. Lang, R. Wiesendanger, V. Thommen-Geiser and H. -J. Güntherodt, *Phys. Rev. B* **45** (1992) 1829.
 - [2] K. Miyake, Y. Aiso, M. Komiyama and H. Shigekawa, *Scanning Micro.*, **8** (1994) 459.
 - [3] D. P. DiVincenzo and E. J. Mele, *Phys. Rev. B* **32** (1985) 2538.
 - [4] S. A. Safran and D. R. Hamann, *Phys. Rev. Lett.*, **42** (1979) 1410.
 - [5] S. A. Safran and D. R. Hamann, *Phys. Rev. B* **22** (1980) 606.
 - [6] M. Kuwabara, D. R. Clarke and D. A. Smith, *Appl. Phys. Lett.*, **56** (1990) 2396.
 - [7] J. Xhie, K. Sattler, M. Ge and N. Venkateswaran, *Phys. Rev. B* **47** (1993) 15835.
 - [8] K. Miyake, K. Akutsu, T. Yamada, K. Hata and H. Shigekawa, *Ultramicroscopy*, **73** (1998) 185.
 - [9] M. E. Makrini, D. Guerard, P. Lagrange and A. Herold, *Physica*, **99B** (1980) 481.
 - [10] D. Anselmetti, V. Geiser, D. Brodbeck, G. Overney, R. Wiesendanger and H. -J. Güntherodt, *Synth. Met.*, **38** (1990) 157.