Relaxed incommensurate structure of the intercalant layer in higher-stage graphite intercalation compounds

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(Received 29 December 1981)

It is shown that the general features of the x-ray data for higher-stage alkali-metal graphite intercalation compounds can be accounted for by a conceptually simple structure for the intercalant layer. This structure combines registry with the tendency of the intercalant ions to form close-packed incommensurate structures. The dependence on stoichiometry of the orientation of the intercalant lattice relative to the graphite lattice is accurately predicted.

The structure of the intercalant layer in higher-stage alkali-metal graphite intercalation compounds (GIC's), particularly at low temperatures, has remained a controversial subject. For potassium-intercalated graphite (K-GIC) at high temperatures, there is evidence[1,2] that the intercalant layer has an incommensurate close-packed (icp) or liquidlike structure with little reference to the graphite lattice other than the occurrence of a preferred orientation. At liquid-nitrogen temperatures the x-ray diffraction patterns change,[1,3] with rings of modulation satellites appearing around each of the graphite reflections; it is this structure that must be explained. One interpretation[3] proposes a deformation of the graphite lattice by a rigid icp K lattice. The idea of a rigid K lattice was motivated by the persistence of the K Bragg reflections, although the higher-order peaks are considerably weakened. However, the K ions are separated by ~ 6 Å, compared to 4.53 Å in the metal, and the expected weakness of the K-K repulsion at these separations suggests instead registered structures, in which K ions occupy sites above (or below) the centers of the graphite hexagons. A registered structure based on a 9×9 unit cell in the plane has been proposed,[4] but it cannot, for example, accommodate the observed variation in stoichiometry. This paper describes a general, physically motivated registered structure that accounts for the basic features of the x-ray data and that, moreover, accurately predicts the relationship between stoichiometry and the orientation of the intercalant layer. The proposed structure, therefore, can serve as a starting point for a detailed understanding of the structure of these compounds.

It has long been known that the intercalant layers in stage-1 heavy alkali-metal GIC's (MC_8) form a close-packed (cp) 2×2 registered structure. In the higher-stage compounds of approximate stoichiometry MC_{12n}, n being the stage, the in-plane density is lower. Although there is no cp registered structure, it is nevertheless plausible that the intercalant ions do register at sufficiently low temperatures. The ideal stoichiometry allows other simple periodic registered structures,[5] none of which is at all consistent with the x-ray data.

Another kind of registered structure frequently considerd is the random lattice gas (rlg); its failure to account for experiment has led some to rule out the hypothesis of registry. The rlg structure is typically[2,6] generated by randomly selecting lattice sites to be occupied, subject to the minimum M-M spearation (found[7] in MC_8) of $2a$, where a is the graphite lattice constant. For an infinite two-dimensional (2D) lattice this random filling yields a stoichiometry of $MC_{13.5n}$,[6] which is inconsistent with experiment. However, this filling technique may be appropriate to chemisorption but hardly to intercalation, where the ions must, at least initially, be mobile. If the ions in a filled array become mobile, more sites become available for occupation, allowing the density to increase. Although the problem with stoichiometry may be thus avoided, the substantial disagreement between the rlg model and the x-ray data remains.[2]

The rlg model assumes only a hard-core repulsion at separations less than $2a$ for the M-M interaction. However, in the liquidlike intercalant structures observed at high temperature the M-M separation of ~ 6 Å (or $2.5a$) indicates a repulsive M-M interaction at greater distances. Thus any model of the low-temperature structure should include this repulsion along with the graphite-intercalant interaction.

This is accomplished in Ref. 3 by a perfect icp intercalant layer, with the graphite layers "rumpling" in order to accommodate the intercalant. But because the M lattice can be expected to deform more easily than the relatively stiff graphite lattice, a registered structure seems more realistic. Ideally, such a structure would be generated via a Monte Carlo calculation of a lattice-gas model combining both the $2a$ minimum separation and the long-range repulsive interaction. The difficulty of using long-range interactions in a lattice-gas calculation being obvious, one may settle for generating a minimum-energy structure. This is done by superimposing the icp intercalant array on the triangular lattice of hexagon centers, and by allowing the M ions to "relax" to the nearest lattice sites. The details of the resulting relaxed close-packed (rcp) structure depend on θ, the orientation of the rows of ions in the cp array relative to the rows of graphite-determined lattice sites. The rcp structure calculated for $\theta = 0.12$ rad and an intercalant lattice constant of $2.35a$ is shown in Fig. 1(a).

Each ion in the rcp structure still has six first-neighbor ions, now at distances of $2a$, $\sqrt{7}a$, or $3a$. As θ increases from 0 the number of $\sqrt{7}a$ first distances increases, at the expense of the $2a$ and $3a$ distances; at large enough θ first distances of $\sqrt{3}a$ occur. Other experiments[7] show that M-M separations of $\sqrt{3}a$ are not forbidden, and thus these large values of θ are physically not allowed. Figure 2
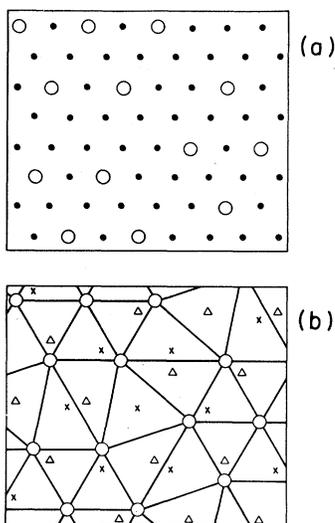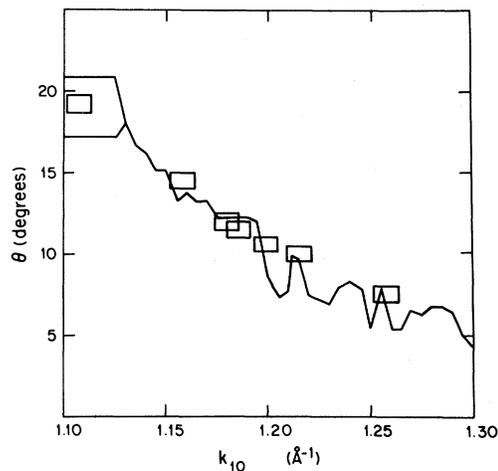
FIG. 2. θ as a function of k, the magnitude of the scattering vector of the principal peak (inversely proportional to the intercalant density). The curve was calculated, as described in the text, for a circular array of 30 diameter lattice sites. The curve splits at low k values because in that region no separations of $2a$ occur. The rectangles are experimental values of k and θ. From left to right: a ($\sqrt{7} \times \sqrt{7}$) Rb structure (Ref. 9); Cs (Ref. 1); Rb (Ref. 10); stage-3 K (Ref. 3); Rb (Ref. 11); Rb (Ref. 12); and stage-2 K (Ref. 3).

shows a plot of θ_{max} as a function of stoichiometry, where θ_{max} is the maximum θ for which no $\sqrt{3}a$ distances occur; also shown are data for a variety of alkali-metal GIC's. The good agreement with data implies that for all these compounds the orientation maximizes the proportion of $\sqrt{7}a$ distances while satisfying the requirement of $2a$ minimum separation. This may be because, although most of the charge transferred from the M ion undoubtedly goes to the ion's 12 nearest-neighbor C atoms, a significant fraction is also estimated[8] to be transferred to its 12 next-nearest C neighbors; two M ions separated by $\sqrt{7}a$ share none of their next-nearest C neighbors.

For stage-2 Cs-GIC the intercalant has a significantly lower in-plane density. The rcp structure then consists of hexagonal domains of ($\sqrt{7} \times \sqrt{7}$) structure, similar to what is proposed in Ref. 12, but with the domain size depending on θ and increasing as θ increases towards the orientation of the perfect ($\sqrt{7} \times \sqrt{7}$) superlattice. This may be compared with the claim[12] that the angle θ observed in the x-ray data does not correspond to an orientation of the Cs lattice in real space but instead results only from the domain size, and also with the claim that domain sizes can explain the orientations of those GIC's with higher intercalant density, in

FIG. 1. (a) Portion of the rcp structure described in the text. Small dots represent graphite-determined lattice sites, and open circles represent intercalant ions. (b) Locations of the M ions in the α (open circles), β ($\times$'s), and γ (triangles) planes, for the stage-2 $/A\alpha AB\beta BC\gamma C/A$ stacking sequence.
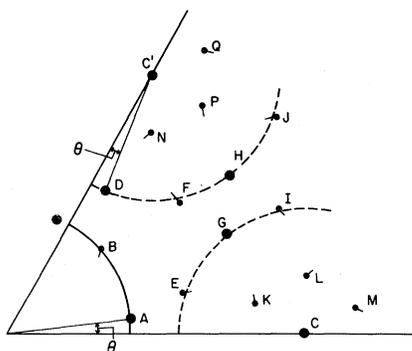
FIG. 3. Fourier transform of the two-dimensional structure of Fig. 1. The peaks are identified in Table I. If θ is increased peaks A, D, G, and H will move counterclockwise along their circles; the other peaks will move along the indicated arcs.

which the $(\sqrt{7}\times\sqrt{7})$ "domains" would involve only two or three M atoms.

To test the rcp structures against experiment, their Fourier transforms can be compared with the $(hk0)$ reflections from the single-crystal x-ray data for K-GIC.[3] The transform of the rcp structure of Fig. 1 is shown in Fig. 3. As is the case when the intercalant is assumed to modulate the graphite structure, there is exact agreement between the experimental and the calculated scattering vectors, except that experimentally orientations of $+\theta$ and $-\theta$ occur with equal probability and one observes twice as many peaks. Note that the graphite reflec-

tions occur, as a result of the ions occupying sites in a graphite-determined lattice. The pattern for the icp structure is also present, and the higher-order spots are weak, as is seen in the single-crystal data. Because the vectors of the icp reciprocal lattice are unchanged the in-plane intercalant density is easily inferred from the K(10) peak, the principal peak. The additional peaks are modulation-induced "satellites," the sums of vectors from the graphite and the icp patterns. A different value of θ does not cause a simple rotation of the pattern about the origin. Instead, each satellite peak will rotate about the graphite spot on which it is centered, as is indicated in Fig. 3, and the magnitude of its scattering vector will change.

FIG. 4. The cylindrically averaged Fourier transform for the array of Fig. 1: (a) the two-dimensional structure only, (b) the stage-2 $/A\alpha AB\beta BC\gamma C/A$ structure, (c) the stage-3 $/A\alpha ABA\beta ABA\gamma AB/A$ structure, and (d) the $/A\alpha ABaBCaC/$ structure; (e) is the stage-2 K-GIC data of Ref. 2. The letters identify each peak with the reflections in Fig. 3.

TABLE I. Identification of peaks in the Fourier transforms of relaxed close-packed structures.

Peak	Identification	Stage 2	Stage 3	α-α
A	K(10)			x
B	K($\bar{2}$1)$\times$C(10)		x	
C	C(10)		x	
D	K(0$\bar{1}$)$\times$C(01)	x		
E	K(1$\bar{2}$)$\times$C(01)		x	
F	K(11)	x	x	x
G	K($\bar{1}$1)$\times$C(10)			
H	K(1$\bar{1}$)$\times$C(01)			
I	K($\bar{1}\,\bar{1}$)$\times$C(11)	x	x	x
J	K($\bar{1}$2)$\times$C(10)		x	
K	K(20)			x
L	K(2$\bar{2}$)$\times$C(01)	x		
M	K(0$\bar{2}$)$\times$C(11)			x
N	K($\bar{2}$2)$\times$C(10)	x		
P	K($\bar{2}$0)$\times$C(11)			x
Q	K(0$\bar{2}$)$\times$C(01)	x		

It is known that the ordering transition also brings about (faulted) three-dimensional (3D) order, with the c-axis stacking sequence of the K and the C layers in stage-2 K-GIC of $/A\alpha AB\beta BC\gamma C/A$, where ABA is the normal graphite stacking sequence and $\alpha\beta\gamma$ refers to the fcc stacking of the K layers. Figure 1(b) shows a 3D rcp structure generated by first stacking the K layers and then relaxing them onto the appropriately rotated graphite lattices; this causes some reflections to move out of the $(hk0)$ plane. The stage-2 structure, the stage-3 $(/A\alpha AB\beta ABA\gamma AB/A)$ structure, and an α-α stacking sequence were considered. The reflections in Fig. 3 are identified in Table I, which also indicates which peaks occur in each of the 3D calculations.

The exact mapping between the scattering vectors of the calculated peaks and the peaks observed in the single-crystal data has been noted above. To check the relative intensities, however, the cylindrically averaged Fourier transform[2] may be compared with x-ray data taken on samples of intercalated highly oriented pyrolytic graphite (HOPG). HOPG consists of microcrystallites of graphite with the c axes well aligned, but with random orientations of the in-plane lattices; x-ray data on this material therefore resemble powder data, except that the averaging is done in only two dimensions. Figure 4 shows the cylindrically averaged transforms of the rcp structures mentioned above with the HOPG data for stage-2 K-GIC.[3] The obvious discrepancy between the stage-2 calculation and the data is due to stacking faults: All peaks that occur in the data but not in the calculations are known experimentally to be out-of-plane. Stacking faults can be included in a model only by introducing additional parameters,[3] but that results in a loss of determinism. While the HOPG data thus do not allow a careful test of this model, a future comparison of calculated (hkl) peaks with data for nonzero l could overcome the problem of stacking faults.

In summary, the relaxed close-packed structure proposed here for the intercalant layer in higher-stage alkali-metal graphite intercalation compounds at low temperatures accounts well for the general features of the x-ray diffraction data. This simple model, in contrast to the model of Ref. 3, gives a physically motivated explanation for both the existence, and the dependence on stoichiometry, of preferred orientations of the intercalant layer in K-, Rb-, and Cs-GIC's. The $(\sqrt{7}\times\sqrt{7})$ domains proposed elsewhere[12] for the Cs-GIC occur naturally for that stoichiometry, and the predicted orientation of the Cs lattice agrees with experiment. Although a detailed comparison with the measured x-ray intensities is made impractical by the occurrence of stacking faults, the general agreement suggests that the rcp structure may provide a good first-order model of the intercalant layer, to which small displacements of the intercalant ions, or small distortions of the graphite lattice, might be added.

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