Pinned Incommensurate Structure of Cesium Intercalated Graphite

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An inhibition of long-range three-dimensional order at low temperatures in nearly commensurate Cs-graphite (stages 2 and 3) is reported. We interpret this as the result of a competition between local in-plane ordering at domain walls and interlayer interactions which in stage 3 favor a simple hcp intercalant stacking. Computer modeling shows evidence for two stable rotated domain-wall configurations.

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Systems with competing interactions exhibit a rich variety of phases in which the physical behavior is dominated by topological features such as domain walls.[1] Graphite intercalation compounds (GIC's) are emerging as ideal systems for the experimental study of such effects.[2,3] In particular, through the usual mechanism of staging, GIC's offer the opportunity to investigate the role of three-dimensional (3D) interactions of various strengths.

In this paper we present x-ray scattering results on stage-2 and stage-3 single-crystal cesium GIC's. As we shall see, these two stages[4] represent respectively strong and weak interlayer coupling regimes for incommensurate Cs-GIC and we will find it useful to contrast the results on each stage throughout the paper. Our experiments give new insights into the competing forces which result in unexpected structural properties, in particular an inhibition of long-range three-dimensional ordering at low temperatures. The effects reported here may have been masked in previous studies[5,6] of heavy-alkali-metal GIC's which were based on HOPG, a polycrystalline form of graphite which has a considerably larger stacking-fault density than natural graphite crystals.

In addition, this paper will directly address the nature of the intercalant structure since this is central to the understanding of the low-temperature Cs stacking disorder. Our results also allow, for the first time, a detailed examination of the domain-wall structure; hexagonal systems, of which these GIC's are examples, are currently the subject of much theoretical debate and are not nearly so well studied as the uniaxial (stripe) case.[1]

Briefly, the experimental details are as follows. A graphite crystal was mounted in the center of a thin evacuated glass bulb of diameter ~ 30 mm and intercalated to the desired stage by the usual two-zone method.[7] The sample was sealed off and placed in a closed-cycle He cryostat mounted on an offset four-circle diffractometer. The x-ray source was a 12-kW Mo rotating-anode generator fitted with a graphite monochromator.

As is well known, the alkali atoms in stage $n=2,3$ GIC's exist in a fluid phase at ambient temperature with no correlation between layers.[8] The fluid interacts appreciably with the neighboring carbon substrate causing the halos of diffuse scattering to be periodically repeated about the graphite reciprocal-lattice positions. On cooling below $T=180$ K, the intercalant layer orders substantially in-plane so that one can identify distinct Cs(10.0) peaks located approximately 15° from the graphite (10.0) direction. Information regarding the 3D correlations between layers of intercalant can be obtained from a scan of reciprocal space in the direction perpendicular to Cs(10.0) or Cs(11.0). As cooling proceeds, the intercalant continues to order in-plane; however, until ~ 169 K (for stage $n=2$) or 138 K (for stage $n=3$), there is little or no correlation between intercalant layers, as seen in Fig. 1. Somewhat below the temperatures given, the c-axis correlations improve dramatically so that by 162 K ($n=2$) and 130 K ($n=3$) the peak full width at half maximum along c^* is ≤ 0.025 Å^{-1} *for both stages.* This corresponds to an intercalant-stacking correlation length of 250 Å with the Cs layers stacked in an $\alpha\beta\alpha\beta$ (hcp) sequence; interestingly, this value is

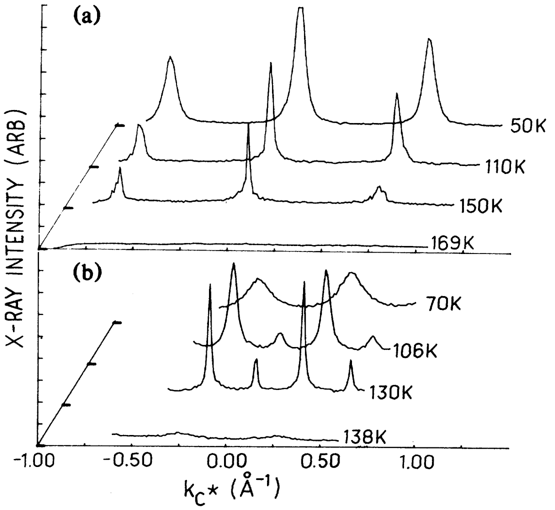

FIG. 1. c^* scans for single-crystal cesium-graphite samples at various temperatures: (a) stage 2, Cs(11.l); (b) stage 3, Cs(10.l).

slightly larger than that for the graphite-layer stacking (~ 220 Å for the single-crystal samples and temperature independent down to $T = 10$ K). At 160 K stage-2 samples transform from the hcp sequence to nominally fcc ($\alpha\beta\gamma$) stacking. The details will be discussed in a longer paper.

On further cooling, interesting and unexpected behavior occurs (see Fig. 1): *The c^* scans begin to broaden,* the effect in stage 3 being much more pronounced than in stage 2. By $T = 50$ K the full widths at half maximum are 0.07 and 0.13 Å^{-1}, for stages 2 and 3, respectively. The latter figure corresponds to only ~ 50-Å stacking coherence. The intercalant-stacking disorder persists to the lowest temperature of measurement, $T = 10$ K. In all cases the samples were cooled very slowly over a period of several days to minimize quenching effects. The effect is completely reversible and without hysteresis.

To understand the loss of stacking coherence at low temperature it is necessary to discuss the in-plane intercalant structure. Figure 2 shows a composite intensity contour map for stage-2 and stage-3 samples at $T = 10$ K. From symmetry considerations, each 30° segment contains all of the in-plane diffraction information. The essential features are as follows: In addition to the principal Cs and graphite peaks there exist a number of "modulation" satellites which can be described in terms of linear combinations of graphite and Cs wave vectors. Through the comparison of the $T = 10$ K diffraction patterns for stages 2 and 3 it is seen that many more higher-order modulation peaks are resolved in stage 2. Also, the diffuse scattering (which is found to be uncorrelated between layers) is much more pronounced in stage 3. These results imply that stage-2 samples achieve much better in-plane ordering than stage-3 samples.

Combination of the observations for in-plane ordering and out-of-plane disordering leads us to propose the following interpretation. As the fluid phase cools and becomes progressively more ordered, regions of intercalant atoms start to register with the graphite layers. At temperatures above ~ 160 K, the Cs ions diffuse with ease[9] and the modulations of the intercalant are rather weak. Thus, a simple hcp stacking of the intercalant is possible in this temperature range.[10] However, as the temperature is lowered, in-plane modulations of the intercalant become more pronounced so that a domain-wall picture is valid. Now the strong interactions of the Cs ions with the graphite layers promote the correlation of nearly commensurate domains in adjacent layers. Through a combination of elastic and electrostatic forces the interlayer interactions in stage 2 are sufficiently strong to form well ordered "columns" of registry along the c axis.

At very low temperatures, atoms on the boundaries of the domains attempt to order on their respective sublattices but are frustrated by the interlayer interactions which in stage 3 try to maintain the simple hcp stacking. Thus, in-plane ordering can only be improved with associated sacrifices in the interlayer

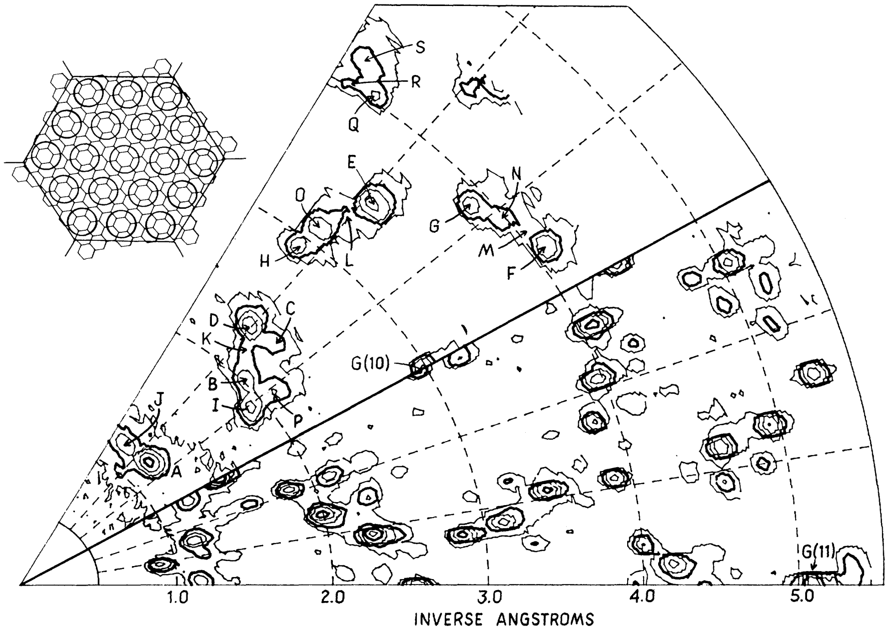

FIG. 2. In-plane diffraction patterns for Cs-graphite at $T = 10$ K. Lower 30° segment: stage 2; upper segment: state 3. The relative intensities of labeled peaks are given in Table I. Inset: domain model for incommensurate Cs-graphite with interaction parameters $A/C = -200$, $B = 0.61$ Å^{-1}. Cs ionic diameter drawn to scale.

correlations; it is this competition which accounts for the progressive c^*-peak broadening seen in Fig. 1. The stacking disordering in stage 2 is rather subtle; however, in stage 3 the interlayer interaction is much weaker and the ordering at domain walls in the basal plane has a much more drastic effect on the 3D structure.

To justify our use of a domain model, which has been considered somewhat controversial, we present here a zero-temperature calculation of the x-ray scattering intensities for comparison with the measured diffraction pattern shown in Fig. 2. We take a domain consisting of nineteen atoms, corresponding to the minimum free-energy curve of Naiki and Yamada,[11] the size being determined from the first-order modulation-satellite wave vector. An interaction between the substrate and the intercalant ions of the form

$$C\{\cos(2\pi x)+\cos(2\pi y)+\cos[2\pi(x+y)]\}$$

is assumed[12] together with a repulsive Cs-Cs interaction, $A\exp(-Br_{ij})$; contributions up to next nearest neighbor are included.

We use periodic boundary conditions and the potential energy of the Cs layer is minimized by allowing the intercalant ions to displace with respect to the lattice of graphite hexagon centers, which is assumed to be rigid. The calculation represents a significant improvement over previous models[2,11,13,14] that assumed complete registry of the intercalant ions. The results of the energy minimization are shown in Fig. 2 (inset). Two important aspects are immediately apparent: First, the intercalants are close to registered positions but there is a noticable *rotation* around the center of the domain which shifts the Cs ions slightly off the hexagon centers at the domain walls. We find two closely spaced stable minima associated with the rotation; both are shown superposed in Fig. 2. Second, the (heavy) domain walls are parallel, modulo the small rotation just mentioned, to the $\sqrt{7}$ translation vectors corresponding to the commensurate superlattice[2] in the heavy-alkali-metal GIC's. This finding is consistent with an earlier theoretical conjecture for asymmetric overlayers which are strongly coupled to the substrate.[15]

Table I shows a comparison of the measured intensities for stage 3 at $T=10$ K with those calculated from the Fourier transform of the model shown in Fig. 2 with the usual corrections for the x-ray beam polarization and a small Debye-Waller factor. The effects of weak interlayer correlations are taken care of by integration of the intensity over one c^* cycle in reciprocal space. The agreement achieved by the simple two-parameter (A/C and B) fit to the model is very encouraging. We find that the distribution of satellite intensities is quite sensitive to the small displacements of the Cs ions that we have derived from the model; for example, allowing the atoms to relax to their nearest hexagon centers considerably worsens the agreement shown in Table I.

In conclusion, we find evidence that domain-wall effects lead to a competition between in-plane and out-of-plane ordering in weakly incommensurate Cs-GIC's, which results in a pinned[16] three-dimensional structure at low temperature. Interlayer coupling drives the structure almost to order in stage 2 but is too weak to do so in stage 3. We would therefore characterize the latter structure as quasi two dimensional. In this connection we point out that the alkali-metal GIC's are complementary to rare-gas monolayers[17] for the study of hexagonal-domain phenomena. In particular, the domain walls seem to be well defined (essentially one atomic spacing wide) and the low-temperature regime, where one might hope to distinguish entropic effects from thermal fluctuations, is easily accessible.

On a broader front, our results have important general implications for achieving three-dimensional crys-

TABLE I. Comparison of measured and calculated x-ray intensities for stage-3 sample. A through C are principle Cs peaks and the remainder are modulation satellites. See Fig. 2 for peak assignments.

Peak	I_{meas}	I_{calc}	Peak	I_{meas}	I_{calc}
A	1.00	1.00	J	0.21	0.21
B	0.22	0.29	K	0.08	0.07
C	0.09	0.14	L	<0.05	0.02
			M	<0.05	0.02
D	0.68	0.64	N	0.12	0.09
E	0.72	0.58	O	0.26	0.28
F	0.49	0.41	P	0.14	0.13
G	0.35	0.30	Q	0.16	0.16
H	0.30	0.30	R	0.06	0.06
I	0.51	0.48	S	0.10	0.17

talline order in any system showing discommensurations. For example, artificial superlattices often have slight lattice-parameter mismatches and may therefore be expected to develop misfit dislocations analogous to the domain walls discussed here.

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