Pressure-Induced Staging Transition in KC_{24}

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With use of diamond-anvil x-ray techniques a reversible, first-order phase transition has been observed from Stage-2 KC_{24}, in both single-crystal and highly oriented pyrolytic graphite forms, to a Stage-3 structure of KC_{24} at ~2 kbar and 300 K. Coexistence of Stage-2 and -3 sequences is observed over the pressure range 2–12 kbar. The transition is accompanied by a 2×2 superlattice ordering of the potassium layers. The results are in qualitative agreement with a recent theory in which staging is driven by long-range elastic interactions.

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The phenomenon of "staging",[1] or the formation of ordered sequences of host and intercalant layers, is the most fundamental feature of graphite intercalation compounds. Theoretical studies have attempted to explain the formation and equilibrium of "pure"[2] ordered stages in terms of electrostatic effects[3] for saturated Stage-1 compounds, and as the consequence of long-range elastic interactions[4] within the host structure for unsaturated, higher-stage compounds. However, the process of staging is not yet well understood.

In this Letter we report the results of high-pressure x-ray scattering experiments which show that, in KC_{24}, the staging equilibrium is very sensitive to elastic deformations of the sample; so much so, in fact, that a staging transition can be induced isothermally under modest hydrostatic pressures. These are the first experiments to probe the microscopic evolution of a staging transition under controlled conditions of stoichiometry and equilibrium.

Natural graphite single crystals[5] and flakes of highly oriented pyrolytic graphite (HOPG) were intercalated with potassium to Stage 2 [see Fig. 1(a) inset], by the method of Hérold.[6] The sample, either single crystal or HOPG, was then transferred under degassed mineral oil to a Bassett[7] diamond-anvil cell. The mineral oil provides a medium for transmitting true hydrostatic pressure to the sample, which had typical dimensions $0.35 \times 0.35 \times 0.05$ mm^3. Pressure was measured to an accuracy of ± 0.5 kbar using the ruby R_1 fluorescence technique.[8] It was confirmed by x-ray techniques that the samples were not degraded by this pressure medium for periods of several weeks.[9] The high-pressure cell was mounted on a Picker four-circle diffractometer and irradiated with Mo $K\alpha$ x rays from a 12-kW

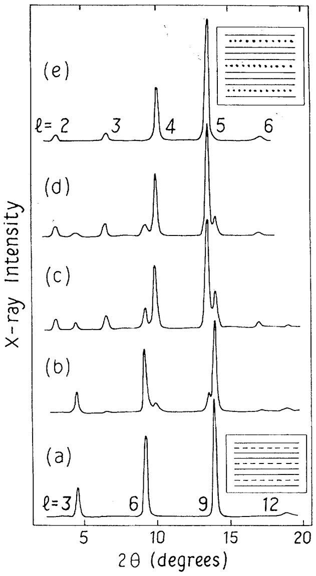

FIG. 1. Room-temperature $00l$ profiles for HOPG KC_{24}. (a) ambient pressure, (b) 2.5 kbar, (c) 4.0 kbar, (d) 5.5 kbar, and (e) 6.5 kbar. Insets: (a) Stage-2 stacking (intercalant planes indicated by broken lines). (e) Stage-3 stacking.

rotating-anode generator. Further experimental details are given in Ref. 9.

Figure 1 shows a sequence of 00l diffraction profiles as a function of increasing pressure for an HOPG sample of KC_{24}. This particular scattering geometry probes the layer stacking arrangement along the c axis. At a pressure of approximately 2.5 kbar [Fig. 1(b)], several new peaks appear, and with increasing pressure these can be seen to grow at the expense of the Stage-2 peaks. At pressures of approximately 6.5 kbar [Fig. 1(e)] and above, the 00l profile can be identified as that of a *pure Stage-3* stacking sequence. Coexistence of Stage-2 and -3 sequences [see Fig. 2(a)] marks the staging transition as being of first order. The transition is hysteretic and reversible. Thus the potassium intercalant is not being squeezed out of the sample but is redistributing within the host layers to form a Stage-3 structure. If the pressure is held constant in the coexistence region, for example at 3 kbar, it is observed that the fraction of Stage 3 increases slowly with time. This is consistent with the recent calculations of Safran and Hamann[4] which show that coherency strains between islands of differing stage tend to drive a mixed-stage sample to a pure stage.

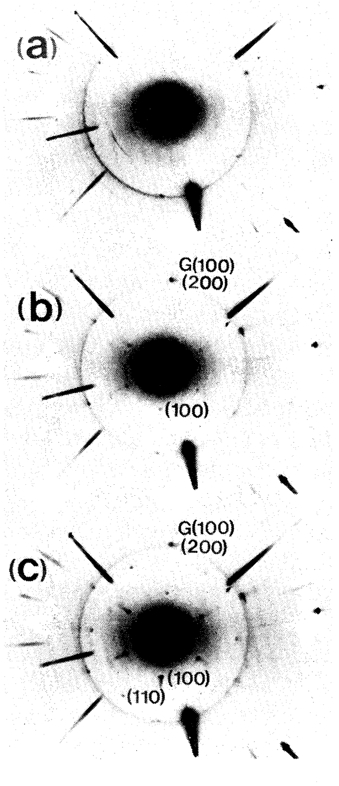

FIG. 2. X-ray oscillation photographs of KC_{24} single crystals at (a) 1 kbar, (b) 4 kbar, and (c) 11 kbar. The intense streaks are x-ray reflections from the diamond anvils and the diffraction ring is from the Be-Cu gasket of the pressure cell. Reflections G(100) contain contributions from both host and K atoms. Other indices indicate potassium superlattice reflections.

The structure of the K layer in KC_{24} is disordered[10] at ambient pressure and temperature with the K atoms either registered[11] or unregistered[12] with respect to the centers of the carbon-layer hexagons. The mean *layer* stoichiometry is KC_{12}, which holds for all stages, $n \geq 2$.[1] A transformation from Stage-2 to Stage-3 stacking, assuming no expulsion of K from the sample, implies that the local areal density of K atoms must increase by a factor of $\frac{3}{2}$ to maintain the overall stoichiometry; i.e., the local layer stoichiometry becomes KC_8 in the high-pressure Stage-3 phase! The layer stoichiometry KC_8 is suggestive of the 2×2 potassium superlattice structure observed in the Stage-1 K, Rb, and Cs intercalates.[1] Indeed, our x-ray diffraction patterns (Fig. 2) of single crystals of KC_{24} clearly reveal the appearance of such superlattice reflections at high pressures. The in-plane linewidth of these superlattice peaks, measured with a diffractometer, indicates that at high pressure the potassium layer gains long-range order limited by defects in the graphite host layers.

Comparison of calculated structure factors for the various possible Stage-3 stacking sequences with measured $h0l$ intensities for single crystals of KC_{24} reveals that the most probable c-axis stacking sequence is $A\alpha ABA\alpha AB\ldots$, where A and B refer to carbon planes and α to the ordered intercalant planes. However, an analysis[13] of the widths of the single-crystal $10l$ reflections along c^* (shown for different pressures in Fig. 3) indicates that the coherency of the stacking sequence extends over only ~ 40 Å in the pure Stage-3 KC_{24} phase at 11 kbar. The distance 40 Å is comparable to the mean spacing between carbon-layer stacking faults previously observed in Stage-2 KC_{24} (Ref. 14) and CsC_{24} (Ref. 15) at ambient pressure. It is interesting to note that the $10l$ profile (Fig. 3) is very broad in the coexistence region. From this width it can be inferred that the stacking coherence length falls to approximately 20 Å at 4 kbar, indicating a very large density of stacking faults (~ one per unit cell) as one might expect in a mixed-stage sample.

Consider now some details of the pressure-induced staging transition which are related to the

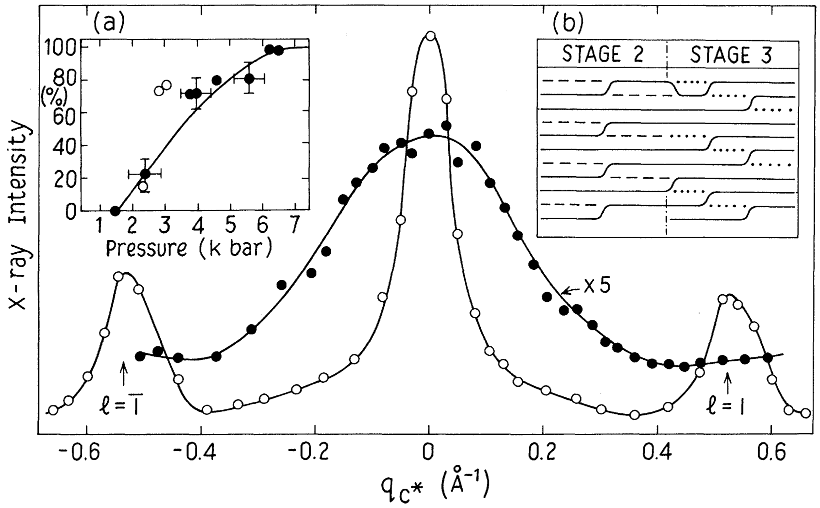

FIG. 3. X-ray intensity as a function of diffraction wavevector, q_{c^*}, along the $10l$ reciprocal-lattice row of single-crystal KC$_{24}$ at 4 kbar (closed circles) and 11 kbar (open circles). (The $10l$ scan at ambient pressure is indistinguishable from background.) Insets: (a) Percentage of Stage-3 phase in an HOPG sample of KC$_{24}$, as a function of pressure, taken as the ratio of Stage-3 peak intensity, $I_{l=4}$, to $I_{l=4}+I_{l=6}$ (Stage 2) intensity. First run, closed circles; second run, open circles. (b) Deformation model for graphite layers during staging transition.

deformation of the graphite host. In the elastic interaction theory of Safran and Hamann[4] mentioned above, which pertains to Stage-2 and higher compounds, small local deformations of the carbon layers are created by the presence of intercalant atoms. These deformations are predicted to behave like elastic "dipoles" interacting repulsively for intercalant atoms in different layers but attractively for those in the same layer. The resulting agglomeration of the intercalant species into islands within each layer is calculated[4] to lower the free energy of the sample and the interaction of these islands with each other and with the graphite host leads to the observed formation of pure, staged sequences. If this model is applied to the present experiment, the principal effect of the pressure is to increase the local deformation around each intercalant atom. The attractive intralayer force between dipoles would thus be increased, promoting the observed higher local density of intercalant atoms. A uniaxial pressure along c would have had the same effect as a hydrostatic pressure since the major component of the deformation is along this "soft" direction.[9]

A representation of the microscopic deformations leading to the transformation to the Stage-3 phase, based on the domain model of Daumas and Hérold,[16] is shown in Fig. 3, inset (b). We emphasize a crucial feature of this model: In order for such a staging transition to proceed it is necessary to assume[16] that every interlayer space contains an equal number of intercalant atoms which are distributed inhomogeneously rather than uniformly as in the simple "empty layer" configurations depicted in the insets of Fig. 1. Such a constraint leads naturally to the picture described above where islands of intercalant atoms are formed, separated by kinks in the carbon layers of the higher stage compounds.

The kinks depicted in Fig. 3, inset (b), can be thought of as the result of slippage of neighboring carbon layers relative to each other as the intercalant atoms redistribute to form a particular stage. We might therefore expect the staging mechanism to be rather sensitive to the *shear deformation* properties of the host. It is known that dislocations are very mobile in the basal planes of the graphite structure,[17] and the variation in dislocation density from one type of sample to another is also known to have marked effects on the basal-plane shear moduli.[17] For example, the shear modulus C_{44} is found to be typically an order of magnitude smaller in HOPG than in single crystals, even though all other elastic constants are effectively sample insensitive.[18] We have observed a similar sample dependence in our high-pressure measurements: Two sets of measurements similar to those shown in Fig. 1, made on single crystals rather than HOPG, show that the coexistence of Stages 2 and 3 persists up to at least 12 kbar as compared with ~ 6 kbar in HOPG KC_{24}. The slippage of neighboring carbon layers in the host and the consequent formation of Stage-3 islands is thus inhibited in single-crystal samples. We believe that this is a consequence of the sample dependence of dislocation densities and mobilities mentioned above. As further evidence that the staging transition is sensitive to the presence of defects in the host structure we have observed that the pressure range of the coexistence region in HOPG samples becomes narrower on pressure cycling through the transition several times; see Fig. 3, inset (a).

In conclusion, our experiments demonstrate that applied pressure is a very important variable for the study of the staging mechanism in intercalation compounds. It is likely that high-pressure techniques will reveal further interesting order-disorder effects and structural phase transitions in the graphite intercalates.

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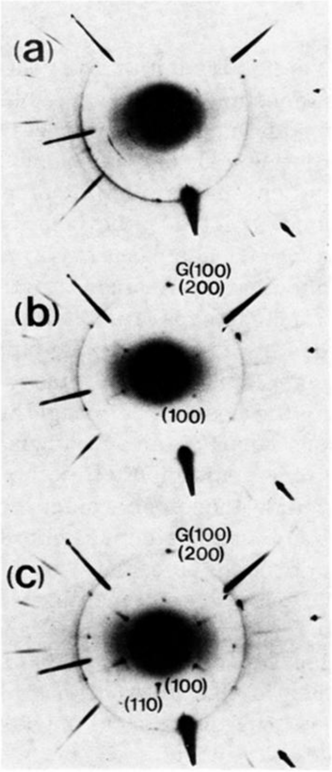

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