Pressure-Induced Staging Transitions in KC_8: Observation of a Fractional Stage

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An elastic neutron-scattering study of the "saturated" graphite compound KC_8 under hydrostatic pressure up to 20 kbar reveals two reversible staging transitions which require an increase of K in-plane density relative to the usual 2×2 superlattice. Between 15 and 19 kbar a mixture of integral stage-1 ($\ldots CM\ldots$) and fractional stage-$\frac{3}{2}$ ($\ldots CMCCM\ldots$) stacking sequences is observed. The fractional staging confirms theoretical predictions of its existence in systems with long-range interlayer repulsion.

Staging in layer intercalates refers to the formation of ordered periodic sequences of filled and empty gaps between adjacent host layers.[1-3] Recent experimental[4,5] and theoretical[6] work has focused on staging transitions in graphite intercalation compounds versus T, P, and intercalant concentration, x, and on the equilibrium (T,x) phase diagram. The stacking sequence of intercalant and host layers is defined by a stage, n/m, where m and n denote the number of guest and host layers per repeat unit, respectively. In K-intercalated graphite a phase of a given stage, n/m, with a K areal particle density $1/s$ relative to a graphite layer can be concisely represented as $K_m C_{s \times n}$. To date only integral $(m = 1)$ stages have been reported. Fractional stages $(m > 1)$ with two or more intercalant layers per repeat unit are predicted to occur at low T if their interlayer repulsion is long ranged.[3,6]

Pressure-induced staging transitions in graphite intercalants have been observed,[4] for example, stage 2 to stage 3, $KC_{12 \times 2} \rightarrow KC_{8 \times 3}$ at ~ 7 kbar. In this Letter we report the observation of a fractional stage, occurring as one of the phases present in KC_8 under hydrostatic pressure. The neutron-scattering studies presented here elucidate the structural origins of the pressure-induced anomalies in the c-axis resistivity of KC_8 (15 kbar), RbC_8, and CsC_8 (20 kbar) observed previously.[7]

Samples were prepared from ~ 100-mg pieces of highly oriented pyrolytic graphite, intercalated by the two-zone vapor phase technique. They were transferred under argon into an aluminum capsule containing the pressure-transmitting fluid, 1:1 pentane/isopentane, which remains fluid in the pressure range studied. The capsule was loaded into a piston-cylinder pressure cell which has been described elsewhere.[8] Detailed measurements were made as a function of increasing pressure only because frictional effects within the cell as the pressure is decreased lead to uncertainties in the pressure scale; however, qualitative measurements made with decreasing pressure showed that all transitions were reversible but with possible slight hysteresis. The pressure scale is based on earlier measurements with this cell[8] and agrees with the compressibility of KC_8 to $\pm 10\%$.[9] Neutron-scattering measurements were done at 300 K at the Brookhaven National Laboratory High Flux Beam Reactor with three-axis spectrometers with pyrolytic graphite monochromators and filter, 14-meV neutrons, and 20-40-40-20 collimation.

Figures 1(a) and 1(b) show the $(00l)$ scans of the two mixed-stage regions observed at 16 and 19 kbar, respectively. The (001) and (002) reflections from stage 1 persist up to 20 kbar but with reduced intensity. The five new reflections in Fig. 1(a) are indexed as $l = 1$ through 5 with a repeat distance 13.61 Å which we attribute to the fractional stage $\frac{3}{2}$ (repeat sequence $CMCCM$, where C refers to a carbon layer and M an alkali layer). At higher P, Fig. 1(b), the stage-$\frac{3}{2}$ re-
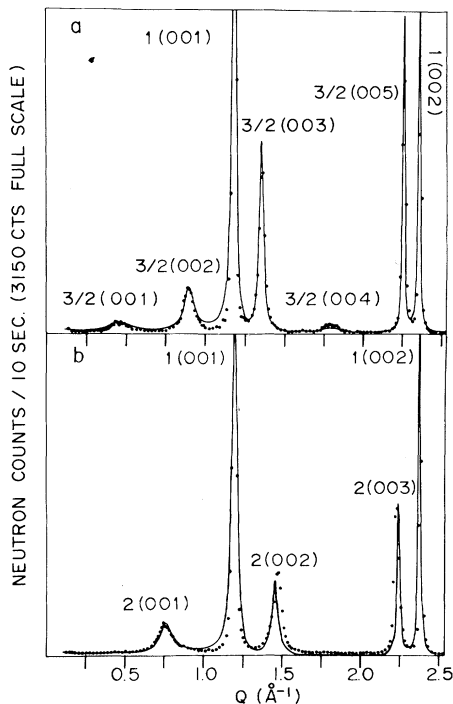
FIG. 1. Elastic neutron scattering in the $(00l)$ geometry from KC_8 at (a) 15 kbar and (b) 19 kbar hydrostatic pressure. Solid lines are model profiles accounting for disorder in the layer sequences (see text). In (a) we observe five reflections from a fractional stage-$\frac{3}{2}$ phase, i.e., a $CMMCM\ldots$ sequence.

flections are replaced by peaks which index as stage 2 with an 8.35-Å repeat distance. The widths of the peaks in Fig. 1 are not resolution limited but show a pronounced and nonmonotonic variation with Q [e.g., the (001) stage-$\frac{3}{2}$ peak is ~ 4 times broader than (005)]. This broadening was shown to result from a finite concentration of staging defects within the individual phases, which can be simply modeled by stochastic disordering of an appropriately chosen two-component layer sequence.[10] For example, the stage-1 $(00l)$ profiles are well represented at both pressures shown in Fig. 1 by a random dispersion of 4% graphite layers into the stage-1 matrix. The stage-$\frac{3}{2}$ profiles are approximately reproduced by a 50:50 mixture of stage-1 (CM) and stage-2 (CCM) components with probability 0.80 that they occur in the correct alternating sequence for stage $\frac{3}{2}$. Similar analysis of the 19-kbar data, Fig. 1(b), is consistent with macroscopically separated phases of (slightly) disordered stages 1 and 2. For the quantitative comparisons of Fig. 1 it was also necessary to apply a Q-dependent correction resulting from the fact that the sample
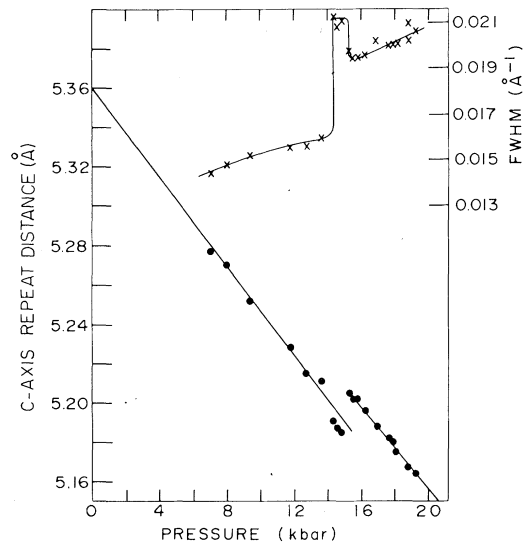

FIG. 2. Stage-1 c-axis repeat distance and FWHM vs pressure, derived from Gaussian fits to the (001) reflection. The straight lines through the d-spacing data are least-squares fits. The instrumental resolution is ~ 0.051 Å^{-1}.

mosaic spread ($\sim 8°$ and weakly pressure dependent) exceeded the vertical resolution of the spectrometer.[11]

Figure 2 shows the pressure dependences of the c-axis repeat distance and full width at half maximum (FWHM) derived from Gaussian fits to the stage-1 (001) peak. The initial Hooke's-law region extends to 14 kbar and the FWHM increases slightly with increasing P, consistent with previous results.[4] At 14 kbar the FWHM increases discontinuously, accompanied by a small decrease in integrated intensity (top panel of Fig. 3). These observations indicate onset of disorder in the stage-1 sequence which we attribute to the pressure-induced appearance of graphite layers in the initially ordered stage-1 structure. The loss in intensity is accompanied by a slight increase in the diffuse background. The new values of FWHM and intensity required about an hour to stabilize, after which no measurable changes were observed for the next 6 h. This change, like all the changes to be discussed, is fully reversible. We therefore attribute the existence of graphite layers to a densification within the K layers to a value greater than that of the 2×2 structure leaving behind intercalant-free regions, rather than to the loss of K from the sample. The physical origin of this condensation is the PdV term in the free energy, since the intercalant-free regions collapse along c. However, a ran-

domly nucleated densification has an excess free energy which can be reduced by intraplanar migration leading to staged sequences.[2]

Raising P to 15 kbar induces further changes which take several hours to stabilize. The discontinuous increase in the stage-1 c-axis repeat distance from 5.19 to 5.21 Å (Fig. 2) indicates a further change in the character of the K layer. The slight drop in FWHM (Fig. 2) suggests improved ordering of the stage-1 sequence. The stage-1 intensity drops to 35% of its initial value as the stage-$\frac{3}{2}$ intensity increases abruptly from zero to its maximum value (Fig. 3). Once established, the mixture of stage-1 and stage-$\frac{3}{2}$ phases was stable for at least 6 h and presumably indefinitely. These observations, along with the analysis of Fig. 1(a), suggest a narrow P range, 14–15 kbar, where disordered stage 1 is observed prior to a transition producing a rather well-ordered two-phase region.

With reference to Fig. 3(b), the loss of stage-$\frac{3}{2}$ intensity above 16 kbar presages a second staging transition which occurs at 19 kbar where the fractional stage, $\frac{3}{2}$, is replaced by integral stage 2. The stage-1 phase is unaffected by the second
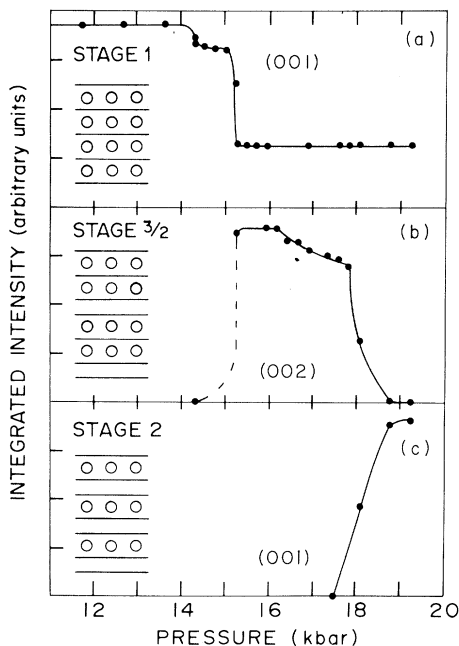
transition since its c-axis repeat distance, FWHM (Fig. 2) and intensity [Fig. 3(a)] are unchanged. The mixture of stage-1 and -2 phases persists to at least 20 kbar, the limit of our experiment.

All the data are consistent with the following sequence of transitions: (1) partial in-plane densification of stage-1 KC_8 to a "superdense" stage-1 KC_6 at 15 kbar, leaving behind intercalant-free regions and KC_8 regions which order into stage $\frac{3}{2}$ with $s = 8$, i.e., $K_2C_{8\times3}$; (2) densification of the K layers in stage $\frac{3}{2}$ to $s = 6$, providing additional intercalant-free regions which then restage as $KC_{6\times2}$. As in previous work the stable phases are dictated by the mass-density conservation within each K layer.[4] As the scattering power of the $(00l)$ reflections is dominated by C atoms and since we could not observe $(hk0)$ or (hkl) reflections from the K sublattice at high P (because of low intensity resulting from a combination of cylindrical averaging of the scattering from highly oriented pyrolytic graphite and the presumed weak c-axis correlations among K layers) we are thus unable to directly determine the in-plane arrangement of K atoms from the neutron measurements. However, Bloch et al.,[12] using the oscillation x-ray technique on KC_8 single crystals in a diamond-anvil cell, observed a progression from pure 2×2 to mixed 2×2 plus $\sqrt{3} \times \sqrt{3}$ to pure $\sqrt{3} \times \sqrt{3}$ in-plane structures with increasing P. The discontinuous increase in stage-1 c-axis repeat distance at 15 kbar is consistent with the $KC_8 \rightarrow KC_6$ transition, the 8% decrease in compressibility correlating with the increased in-plane density.[13] The KC_6 c-axis repeat distance extrapolated to $P = 0$ is 5.365 Å, 0.1 Å greater than that of the known compound BaC_6. We note that in-plane structures with $s = 6$ have previously been observed for heavy alkali-graphite compounds via low-energy electron diffraction[14] and electron diffraction.[15]

Our reversible sequence ($6KC_{8\times1} \rightarrow 4KC_{6\times1} + K_2C_{8\times3} \rightarrow 4KC_{6\times1} + 2KC_{6\times2}$) is perhaps the simplest set of mass-conserving transformations. Other transformations exist that would also be consistent with our results. One interesting possibility would be replacing the $...MCMCC...$ sequence by $...MCM^*CC...$, where M and M^* are layers with $s = 6$ and $s = 8$ areal densities.[6] Detailed diffraction measurements of hkl reflections could distinguish among these possibilities. It is also interesting that in the progression from stage 1 to stage 1 + stage 2 the direct transformation $3KC_8 \rightarrow K_3C_{6\times4}$, i.e., to a pure stage $\frac{4}{3}$, is not observed. In the model of Bak and Bruinsma[16]

FIG. 3. Integrated intensity vs pressure for the phases observed in KC_8 up to 20 kbar. Note that the disappearance of stage $\frac{3}{2}$ at 19 kbar leaves stage 1 unaffected but coincides with the emergence of stage 2. The solid and dashed curves are guides to the eye and the peak indices are indicated in the figure.

stage $\frac{4}{3}$ has a narrower stability range than stage $\frac{3}{2}$.

The observation of fractional-stage graphite compounds is consistent with some theoretical predictions[3,6,16] and supports the view that the interlayer interaction is effective at very long range in establishing ordered sequences.[2,6] More realistic calculations including commensurability potentials[17] that stabilize discrete areal densities will clearly be necessary to model these results. As in the pressure measurements on KC_{24},[4] in order for the transition from stage $\frac{3}{2}$ to stage 2 to proceed it is necessary that every interlayer space contain an equal number of intercalant atoms which are distributed in domains[18] rather than the simplified picture of Fig. 3. However, in contrast to the KC_{24} studies where the pressure-induced staging transitions were observed in a low-P in-plane disordered phase,[4] all the phases in KC_8 up to 20 kbar show ordered in-plane structures.[12] Finally, we have observed a similar stage-1→ stage-1+ stage-$\frac{3}{2}$ transformation in RbC_8 at $P = 20$ kbar, the same pressure as the anomaly in the c-axis resistivity.[7] Other fractional stages might also be pressure induced in dilute compounds, as suggested by the multiplicity of observed resistance anomalies.[7]

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