## VOLUME 24, NUMBER 12

## Pressure-induced anomalies in the *c*-axis resistivity of potassium-intercalated graphite

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Sharp anomalies are observed in the 300-K pressure-dependent c-axis resistance of stage 1-4 potassium-intercalated graphite. Extrapolating from previous x-ray-diffraction results, we speculate that the anomalies are dominated by transitions to higher pure stage with denser K packing, and that mixed-stage behavior accounts for precursor effects which we observe at pressures below the anomalies.

Structural phase transitions may be induced in graphite intercalation compounds by variations in temperature,<sup>1</sup> chemical potential,<sup>2</sup> or hydrostatic pressure. The first example of the latter was discovered by Clarke, Wada, and Solin<sup>3</sup> (CWS). They found that  $KC_{24}$  transforms at 300 K from a stage 2 compound with disordered K layers at ambient pressure (layer stoichiometry  $KC_{12\times 2}$ )<sup>4</sup> to a stage 3 structure with a commensurate 2 × 2 K layer superlattice ( $KC_{8\times 3}$ ) at 7 kbar.

In this Communication we report the observation of sharp, dramatic anomalies in the 300-K c-axis resistance  $R_c(P)$  of stages 1-5 potassium compounds. These are preceded in stages 1-3 by monotonic precursor effects whose magnitudes in  $R_c$  are comparable to those of the sharp anomalies. Both the anomalies and the precursor effects are much larger than would be expected from the influence of compressibility on  $R_c$  (i.e., variable wave function overlap at constant crystal structure), suggesting that phase transitions are implicated. We therefore propose a speculative interpretation of the  $R_c(P)$ behavior in which the monotonic precursor effects are associated with mixed stage behavior and the sharp anomalies signal the achievement of pure, higher stages. Our proposal is qualitatively but not quantitatively consistent with CWS as regards the pressures at which various transitions occur. This discrepancy may be related to the use of different pressure media, as discussed below.

Standard dc 4-probe measurements were carried out with spring contacts in a Teflon cell pressurized by a conventional piston-cylinder device. The pressure medium was a 50:50 mixture of pentaneisopentane, for which  $R_c(P)$  of pure graphite is monotonic and in agreement with previous reports.<sup>5</sup> The pressure scale is accurate to  $\pm 5\%$  and reproducible to  $\pm 2\%$ . Highly oriented pyrolytic graphite (HOPG) measured in mineral oil gave spurious anomalies in  $R_c(P)$  as well as nonreproducible  $R_c(P)$  curves, due perhaps to the oil freezing at 7 kbar and 300 K. Samples  $5 \times 5 \times 0.2 \text{ mm}^3$  were prepared from HOPG by the usual 2 bulb technique and characterized before and after measurement by (001) x-ray diffraction and  $R_c$ . Most of the data reported here are typical of repeated runs on multiple samples.

The data are presented in Figs. 1 and 2 as relative resistance  $R/R_0$  versus pressure. The odd stages KC<sub>8</sub>, KC<sub>36</sub>, and KC<sub>60</sub> show similar qualitative behavior (Fig. 1). For KC<sub>8</sub>  $R/R_0$  increases slowly at first, while for KC<sub>36</sub> and KC<sub>60</sub> there is an initial decrease. KC<sub>36</sub> alone exhibits a large monotonic increase in  $R_c$  just below the anomaly. All three com-



FIG. 1. Relative change in *c*-axis resistance vs hydrostatic pressure for KC<sub>8</sub>, KC<sub>36</sub>, and KC<sub>60</sub>. Each horizontal division equals 25% change; the origins are displaced for clarity.

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FIG. 2. Relative change in c-axis resistance hydrostatic pressure for  $KC_{24}$  and  $KC_{48}$ .

pounds show sharp increases in  $R/R_0$  at higher pressures: KC<sub>8</sub> at 15 kbar ( $\Delta R/R_0 = 60\%$ ), KC<sub>36</sub> and KC<sub>60</sub> both with maximum slope at 10 kbar (225% and 10%, respectively). The even stages KC<sub>24</sub> and KC<sub>48</sub> behave quite differently (Fig. 2), both showing marked changes starting within the first kbar.  $R/R_0$ for KC<sub>24</sub> starts decreasing, drops abruptly at 3.5 kbar and levels off at 30% of its original value, then jumps at 7.5 kbar. Careful examination of repeated runs on two KC<sub>48</sub> samples indicate the presence of reproducible anomalies at 7.9 and 10 kbar which follow a large precursive increase in  $R_c$  with increasing P.

Lacking diffraction data other than CWS, our interpretation of the  $R_c(P)$  data is necessarily speculative. The two known pressure-induced structural changes are expected to produce competing effects on  $R_c$ : a stage increase should increase  $R_c$  by reducing the spatial overlap between screened "metallic sandwiches,"<sup>6</sup> while the in-plane densification would be expected to reduce  $R_c$  because more charge per unit area is available for interlayer conduction. The relative contributions at a particular transition will determine whether the net effect on  $R_c$  is an increase or decrease. The effect of stage changes at constant  $KC_{12}$  in-plane density can be seen in the solid line of Fig. 3, which shows that at P = 0, the resistivity for  $KC_{12n}$  increases exponentially with stage. This behavior asymptotes to the graphite value at  $n \sim 6$ . Referring to Fig. 2, we attribute the 0-4-kbar region of KC<sub>24</sub> to the KC<sub>12×2</sub>  $\rightarrow$  KC<sub>8×3</sub> transition observed by CWS, in which the initial strong monotonic de-



FIG. 3. Correlations between c-axis resistivity and stage, with in-plane intercalant density as parameter. Data points represented by n in KC<sub>n</sub> denote plateau regions below and above the anomalies, assuming the layer stoichiometry rules discussed in the text.

crease represents mixed stage 2+3 behavior and the sharp anomaly at 3.5 kbar signals the achievement of pure (dense) stage 3. CWS find the end point of this transition at 6.5 rather than 3.5 kbar, which we suggest is due to the use of different pressure fluids. Indeed there are no features in the CWS data to suggest an  $R_c$  anomaly at 3.5 kbar. Here the densification wins out over the stage change since we observe a net decrease in  $R_c$ . The  $R_c$  value in the KC<sub>8×3</sub> plateau region 5-7 kbar gives us one point on a new line representing  $R_c$  versus stage at constant KC<sub>8</sub> inplane density. Two other points on this new (dashed) line are  $KC_8$  at P = 0 and the first anomaly in KC<sub>48</sub> at 7.9 kbar, which we suggest is the end point of the  $KC_{12\times4} \rightarrow KC_{8\times6}$  transition by analogy to  $RbC_{48}$ .<sup>7</sup> Note that here, in contrast to the  $KC_{12\times 2} \rightarrow KC_{8\times 3}$  transition, the stage increase dominates the densification to give a large net  $R_c$  increase, as would be expected from adding two graphite spacings to the intersandwich distance rather than one.

We now suggest an extrapolation from CWS to explain the remaining anomalies. The second  $KC_{24}$  anomaly at 7.5 kbar is tentatively identified as a combined stage change and further densification:  $KC_{8\times3} \rightarrow KC_{6\times4}$ . Similarly in Fig. 1 we suggest  $KC_{12\times3} \rightarrow KC_{6\times6}$  and  $KC_{12\times5} \rightarrow KC_{6\times10}$ , both at 10 kbar; and from Fig. 2, the second  $KC_{48}$  anomaly at 10 kbar is attributed to  $KC_{8\times6} \rightarrow KC_{6\times8}$ . The implication is that the odd stages at P = 0 ( $KC_{36}$ ,  $KC_{60}$ )

skip over the KC<sub>8</sub> in-plane structure, which would require phase separation. These four transitions define a third (dotted) line on Fig. 3 for  $KC_6$  layer stoichiometry, the lowest two points of which follow the exponential trend while the stage 8 and 10 points are well within the asymptotic limit. Note that the  $KC_{60}$  anomaly is the smallest, as would be expected since  $R_c$  at the end point of the transition (stage 10) is so close to the HOPG value. Conversely, the  $KC_{36}$ anomaly is the largest, consistent with adding three graphite layers to the repeat unit within the exponential regime. The sequence of KC<sub>24</sub> anomalies is a threefold drop followed by a twofold rise, consistent with the 33% increase in in-plane density overwhelming the stage increase at the  $KC_{12 \times 2} \rightarrow KC_{8 \times 3}$  transition whereas the 25% in-plane density increase is overcome by the stage change when KC<sub>8×3</sub> goes to KC<sub>6 × 4</sub>.

The implied existence of  $\sqrt{3} \times \sqrt{3}$  K layers at high pressure is speculative and must be confirmed by diffraction studies. In support of this speculation is the observation of  $\sqrt{3} \times \sqrt{3}$  contributions to the electron diffractograms of some high-stage alkali compounds at 1 atm.<sup>8</sup> An interpretation of the KC<sub>8</sub> anomaly in similar terms is problematic, since it would imply a superdense  $2 \times 1$  or  $1 \times 1$  in-plane superlattice. Thus we omit the KC<sub>8</sub> plateau above 15 kbar from the summary Fig. 3.

The systematics of the pressure locations of the various anomalies support the interpretation presented above. The transformation from the "open"  $KC_{12}$  to close-packed  $KC_8$  layer stoichiometry begins essentially at P = 0, since the large initial  $R_c$  changes in  $KC_{24}$  and  $KC_{48}$  with increasing P are more likely precursor effects related to mixed stage behavior

rather than compressibility effects. By contrast, transitions ending in the denser  $KC_6$  layer phase would require more strain and thus would be expected to occur at higher *P*, which is consistent with the data. The unexplained  $KC_8$  transition occurs at even higher pressure, either because it starts from a close-packed structure or because it ends in a superdense structure.

CWS observe macroscopic mixed stages over some pressure range for all compounds with  $n \ge 2$ , which we identify with the broad precursor effects to the sharp anomalies in KC<sub>24</sub>, KC<sub>36</sub>, and KC<sub>48</sub>. Furthermore, CWS observed no x-ray changes in KC<sub>8</sub> up to 12 kbar, and indeed our  $R_c(P)$  curve for KC<sub>8</sub> is essentially flat to 15 kbar.

Despite the obvious need for confirming diffraction studies, the high degree of internal consistency between our model and the various experimental observations gives us confidence in its validity. In addition to agreeing with the CWS result that even stages transform to higher stages consistent with the overall stoichiometry, we further conclude that odd stages also transform eventually to pure higher stages under the same constraint, in the process skipping over intermediate in-plane densities which would require phase separation. The strictness with which phase transitions follow simple arithmetic rules suggests that, contrary to existing model calculations,<sup>9</sup> the inplane intercalant density is intimately involved in staging.

We gratefully acknowledge the experimental assistance of A. Denenstein. This work was supported by the NSF MRL Program, Contract No. DMR 7923647.

<sup>4</sup>Notation:  $KC_{s \times t}$  means stage t with in-plane density s car-

bons per potassium.

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