Ternary Graphite Intercalation Compound $KCsC_{16}$: An Ideal Layered Heterostructure

B. R. York, S. K. Hark, and S. A. Solin
Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824

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An ideal ternary heterostructure graphite intercalation compound, $KCsC_{16}$, which exhibits a stage-1 c-axis stacking sequence, ...CKCCsCKCCs..., has been prepared. The stage, stacking sequence, and $(2\times2)R0°$ in-plane structure have been confirmed by high-resolution x-ray diffraction studies which reveal a c-axis correlation range of ~ 350 Å. The structure factor and widths of the $(00l)$ reflections calculated on the basis of the proposed stacking sequence are in excellent agreement with experimental observations.

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Heavy-alkali-metal ternary graphite intercalation compounds (GIC's), which were first synthesized more than a decade[1] ago using powdered graphite, have become the focus of considerable recent interest[2,3] in part because they represent potential model systems with which to study the structural properties of binary alloys in two dimensions. The ternary GIC's prepared to date have always been planar solid solutions $(A_xB_{1-x})_m C_{s\times n}$, where n/m is the stage corresponding to the number of carbon layers separating nearest layers of intercalate ions, and $1/s$ is the areal number density of intercalate atoms relative to carbon atoms.[4]

We report in this Letter the first successful preparation of a ternary heterostructure GIC. The general form of such a compound can be stoichiometrically represented by the notation $(A_m C_{s\times n})_l (B_{m'} C_{s'\times n'})_{l'}$, where $m(m')$, $s(s')$, and $n(n')$ retain the definitions inferred above and $l(l')$ corresponds to the number of times the corresponding bracketed unit repeats in the minimum size c-axis stacking unit which defines the structure. The ternary GIC which we have prepared, $(KC_{8\times1})_1(CsC_{8\times1})_1$ or equivalently $KCsC_{16}$, is the simplest such structure and can be represented by the repeat sequence ...CKCCsCKCCs.... It is an ideal heterostructure because the potassium and cesium layers are commensurate with (i.e., epitaxial to) the carbon layer; the carbon, potassium, and cesium layers are atomically flat; there is no interdiffusion at the layer interfaces; and the stacked layers exhibit long-range order in both the c-axis and the a-axis directions. To our knowledge, such an ideal manmade heterostructure has not to date been prepared by use of sophisticated techniques such as molecular beam epitaxy.[5]

Samples were prepared in Pyrex with highly ordered pyrolytic graphite (HOPG) ($\sim 5\times10\times0.5$ mm^3) by a sequential intercalation procedure. A well-ordered pure stage-2 CsC_{24} compound[6] was first obtained.[7] The sample was then rapidly transferred in a glove box (≤ 0.5 ppm O_2) to another Pyrex tube containing pure potassium metal. The tube was evacuated and sealed off in the usual manner. The tube was uniformly heated to 70 °C and the CsC_{24} sample was immersed in liquid potassium. Periodically, to facilitate x-ray examination, the sample tube was placed in a centrifuge which was housed in an oven at 70 °C, the excess liquid potassium was spun off, and the tube was quenched in air to room temperature. The diffraction patterns reported here were recorded using a 12-kW Rigaku rotating-anode x-ray source, a molybdenum target, and a Huber Model No. 430-440-512 four-circle diffractometer equipped with a vertically bent graphite monochromator. The maximum resolution of this instrument was measured with use of the (400) reflection of single-crystal germanium and found to be 0.003 Å^{-1}.

Figure 1 shows the $(00l)$ x-ray diffraction patterns of the CsC_{24} starting material, after immersion and quenching for two hours, two days, and 12 days. The small diffuse background noticeable in Fig. 1 is due to the Pyrex envelope. The patterns of Fig. 1 have been indexed with the notation $(n/m)\mathcal{I}(00l)$, where n/m is the stage and l is the order of the c-axis reflection. The symbol $\mathcal{I}$ denotes the intercalate species. Thus $\mathcal{I} = K$, Cs, or H, where H represents the heterostructure $KCsC_{16}$. As can be seen from Fig. 1, the monophase KC_{24} evolved to a three-phase system containing CsC_{24}, KC_{24}, and CsC_8; then to another three-phase system containing the $KCsC_{16}$ heterostructure, KC_8, and KC_{24}; and finally to a two-phase system of KC_8 and $KCsC_{16}$.

In Fig. 2 we show a plot of the wave vector, q, versus the order of the reflections shown in Fig. 1(c). For a properly identified stacking structure such a plot should yield a straight line passing

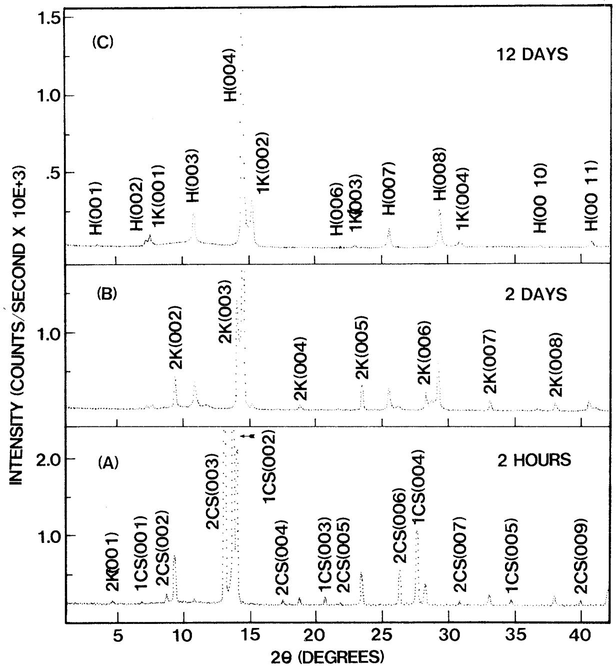

FIG. 1. (00l) diffraction patterns of stage-2 CsC_{24} after immersion in liquid potassium. The reflections labeled $H(00l)$ correspond to the heterostructure $KCsC_{16}$. Those labeled $n\mathcal{I}(00l)$ correspond to a stage-n binary GIC intercalated with species $\mathcal{I}$. The diffraction patterns were acquired with Mo $K\alpha$ radiation. Reflections which appear in more than one trace have been labeled only once. The ordinates of curves A and B have been truncated for presentation.

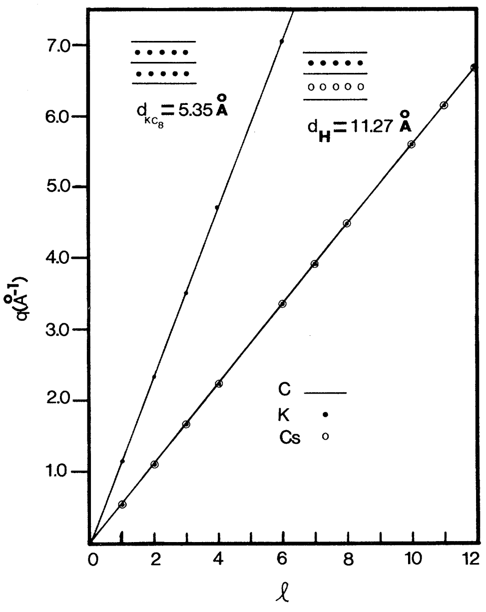

FIG. 2. A plot of the wave vector vs the order of the corresponding (00l) reflection for the KC_8 (dots) and $KCsC_{16}$ (circled dots) components of Fig. 1(c). The basal spacings d_H and d_{KC_8} indicated were determined from the slopes of the straight (solid) lines which are least-squares fits to the data.

through the origin and with a slope $2\pi/d$, where d is the minimum distance along the c axis (or sandwich thickness) which defines the stacking sequence.[6] From Fig. 2 we find $d_{KC_8} = 5.35$ Å. Similarly, from our measurements of CsC_8 we find that $d_{CsC_8} = 5.94$ Å. Thus, to within experimental error, $d_H = d_{KC_8} + d_{CsC_8}$ as would be expected for the stacking sequence ...CKCCsCK....

To further confirm the heterostructure stacking sequence of $KCsC_{16}$, we have calculated the (00l) x-ray intensity distribution $I(q)$ vs q from the following equation[8]:

$$I(q)\propto\left|\sum_j f_j(q)\exp\left[-W_j\left(\frac{q}{4\pi}\right)^2\right]\exp[-i(d_H\bar{z}_j)\cdot(q\hat{z})]\right|^2\left[\sum_l N^2\exp\left(-\frac{(q-q_l)^2}{\Gamma^2/4\ln 2}\right)\right]L_p(q). \qquad (1)$$

Here $L_p(q)$ is the combined Lorentz-polarization factor; $\hat{z}$ is a unit vector; $\bar{z}_j$ is the distance of the jth layer from the origin of the c-axis cell; $f_j(q)$, $j = C, Cs, K$, are the q-dependent form factors[9]; and the reciprocal lattice vectors are $\vec{q}_l = (2\pi/d_H)l\hat{z}$. The appropriate values of W_j, the Debye-Waller factor, have been obtained from measurements of KC_8 and CsC_8.[10] The square-bracketed term in Eq. (1) is the Gaussian approximation to the Bragg scattering term.[8] The full width at half maximum of each reflection is $\Gamma = 4(1.4)/Nd_H$. Here N is the number of cells of length d_H that are correlated along the c axis, the correlation range of which is Nd_H.

In Fig. 3 we have plotted $I(q)$, derived from Fig. 1(c), and the theoretical diffraction pattern of Eq. (1) obtained with $N = 31$ and a Γ corrected for the instrument resolution. With the exception of the (001) peak, the experimental and theoretical curves of Fig. 3 are in excellent agreement. The discrepancy at low angle arises from the fact that at grazing incidence [$\theta = 1.3°$ for the (001) reflection] the effective sample cross section is only a small fraction of the incident beam cross section. For our sample configuration this geometrically induced cross section mismatch is absent for $\theta > 9°$ and has only a marginal effect on reflections which occur in the range $3° \leq \theta \leq 9°$.

The value of N used to compute $I(q)$ was in fact

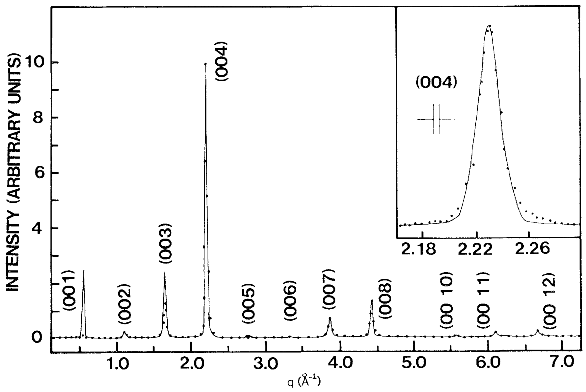

FIG. 3. The intensity of the (00*l*) diffraction pattern of $KCsC_{16}$ vs q. The solid line is the calculated pattern [see text, Eq. (1)]. The dots correspond to experimental results and are obtained from Fig. 1(c) after correction for the measured glass envelope background, subtraction of the stage-1 KC_8 pattern, and normalization to the theoretical curve at (004). The inset shows a high-resolution scan of the (004) reflection (vertical bars indicate the instrument resolution, 0.0045 $Å^{-1}$).

deduced from the high-resolution x-ray scan shown in the inset of Fig. 3. From a Gaussian fit to the observed (004) heterostructure reflection we find, taking account of the instrument resolution of 0.0045 $Å^{-1}$, a c-axis correlation range of ~ 350 Å. The corresponding correlation range for the KC_8 component of our sample was found from the (002) reflection to be ~ 260 Å. We also found that the width of the (00*l*) reflections of $KCsC_{16}$ were, to within experimental error, independent of q as expected when N is large.[8] This q independence of the linewidth indicates that the staging of the heterostructure is "pure" over the ~ 350-Å correlation range with little or no statistical admixture of other stacking sequences (e.g., pristine HOPG or KC_8) as was recently found in pressure-induced fractional stages of KC_8.[4]

The observation of phase-separated KC_8 and $KCsC_{16}$ in the saturated compound which we have prepared is quantitatively consistent with two conditions which appear to govern the intercalation process during the initial period (0 to ~ 15 days) of intercalation, and at the immersion temperature of 70 °C: (1) No cesium is expelled from the sample, and (2) potassium does not alloy with the Cs present in the sample. We have carried out a neutron activation analysis of the residual potassium used for immersion of CsC_{24} and find no cesium in excess of the impurity amount, ≤ 50 ppm, present in our potassium. Thus, the neutron activation analysis results support condition (1). Condition (2) is supported by the fact that intralayer Cs in CsC_{24} does not form a solid solution with potassium, but densifies to CsC_8 during the early stages of exposure [see Fig. 1(a)].

Conditions (1) and (2) above, together with our x-ray results, indicate that immersion intercalation of CsC_{24} by potassium is initially controlled by the reaction

$$CsC_{24} + 2K \rightarrow KCsC_{16} + KC_8, \qquad (2)$$

the right-hand side of which is a saturated nonequilibrium state which appears to be metastable when the sample is cleansed of liquid potassium and quenched to room temperature. If the intercalation process was allowed to proceed to completion with the sample immersed in liquid potassium, the equilibrium product would probably be a ternary solid solution $K_xCs_{1-x}C_8$. But there is evidence that such compounds are ultimately unstable[11] and further evolve into a phase-separated system composed of a ternary solid solution, KC_8, and/or CsC_8.[3] Note, however, that the ternary solid solution and binary GIC components cited above would yield (00*l*) diffraction patterns which are easily distinguished from those of the $KCsC_{16}$ heterostructure.

Using Eq. (2) we calculate that the ratio of the peak intensity of $H(004)$ to 1K(002) should be 7.2. The corresponding observed ratio [see Fig. 1(c)] is 5.4, in good agreement with theory. In principle an alternative metastable saturated heterostructure of the form $(KC_8)_2(CsC_8)_1$ or equivalently K_2CsC_{24} with the stacking sequence ...CKCKCCsCKCKCCs... could be generated by the admixture of CsC_{24} and potassium. Apparently such a structure has a higher free energy than the admixture of the higher-symmetry components $KCsC_{16}$ and KC_8.

The in-plane diffraction patterns of our ternary heterostructure $KCsC_{16}$ have been carefully measured and confirm that both the potassium and the cesium layers form $(2 \times 2)R0°$ (Ref. 6) commensurate superlattices with respect to the graphite host. We find no evidence for any other in-plane structure. We do, however, find a slight expansion of the a-axis lattice parameter of the host material from 2.46 Å in the pristine form to 2.47 Å when intercalated.

While KC_8 does make a contribution to the $(2 \times 2)R0°$ in-plane diffraction pattern, we calculate on the basis of Eq. (2) that the contribution would be down by a factor of 17 for the (100) and (110) reflections compared to the contribution from $KCsC_{16}$. These two reflections contain no carbon layer contributions.[6] Therefore, we are confident that the $KCsC_{16}$ does indeed exhibit a $(2\times 2)R0°$ in-plane superlattice structure. As a final note on this point, Raman scattering studies carried out on $KCsC_{16}$ (Ref. 12) yield the unique spectra characteristic of an ordered $(2\times 2)R0°$ superlattice.[13]

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