

X-ray observation of a $\sqrt{3} \times \sqrt{3}$ superlattice in KC_8 at high pressure

J. M. Bloch

*Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
and National Synchrotron Light Source, Brookhaven National Laboratory,
Upton, New York 11727**

H. Katz,[†] D. Moses,[‡] V. B. Cajipe,[§] and J. E. Fischer**

*Laboratory for Research on the Structure of Matter, University of Pennsylvania,
Philadelphia, Pennsylvania 19104
(Received 17 December 1984)*

A single-crystal x-ray study under pressure reveals a phase transition from an in-plane 2×2 commensurate potassium superstructure to a new $\sqrt{3} \times \sqrt{3}$ commensurate superstructure. This is the first such transition to be observed; it is related to the recently discovered staging transition of KC_8 under pressure. In addition, we observe this staging transition to occur more slowly and at much lower pressures than in the reported neutron-scattering experiment on highly oriented pyrolytic graphite samples.

Layer intercalates are quasi-two-dimensional impurity-host systems whose gross structures are defined by the (ordered) sequence of host layers and intercalant monolayers (i.e., the stage), by the in-plane registry of the intercalant within the monolayer (the in-plane structure), and by the relative lateral displacements of the impurity and host two-dimensional lattices (stacking). The phase transitions associated with the staging phenomenon in donor-intercalated graphite have received much attention recently. The stage of an intercalated compound is known to be strongly affected by temperature, pressure, and chemical potential. It has been demonstrated that at lower temperature¹ and high pressure,² intercalated compounds tend to form denser packing in the layers, maintaining stoichiometry by reducing the number of filled galleries (i.e., increasing the stage). The temperature- and chemical-potential-driven phase transitions were modeled by mean-field free-energy expansions,³⁻⁶ and the pressure-induced transitions were described by an extension of these models.⁴ The temperature and pressure phase diagrams in Ref. 4 clearly indicate the preference to higher stage upon reducing temperature or applying pressure at constant concentration. A relation between the temperature-driven and the pressure-induced phase transitions was proposed recently,¹ and was shown to fit the LiC_{16} phase-transition data.⁵

For a transition to a higher stage to occur, the in-plane density of the initial stage must be less than maximal so that it can accommodate more intercalant after the transition. For example, in the case of KC_{24} , Clarke, Wada, and Solin² found the transition $\text{KC}_{12 \times 2} \rightarrow \text{KC}_{8 \times 3}$ at 6 kbar and 300 K, in which the ambient dilute-disordered stage 2 transformed into dense-ordered stage 3. In all the cases where a phase transition under pressure was detected, the low-density phase of the compound was in-plane disordered, while the high-pressure ordered phase exhibited the "ordinary" density characteristic of stage-1 compounds at 1 bar (2×2 superstructure for K, Cs, or Rb, and $\sqrt{3} \times \sqrt{3}$ for Li graphite). First-stage K, Rb, and Cs compounds which already exhibit the registered 2×2 superstructure were reported not to undergo a similar phase transition at pressures of up to 12 kbar, and it was therefore assumed that these ions cannot form a closer packing. However, the resistivity of KC_8 under pressure showed a discontinuity at about 14

kbar,⁶ and it was suggested that this was related to a staging transition. This assumption has been verified by a neutron-diffraction experiment on highly oriented pyrolytic graphite (HOPG) KC_8 .⁷ These authors reported two sequential phase transitions at about 15 and 19 kbar. In the intermediate region they found a mixture of stage 1 and a new phase with a repeat distance corresponding to stage $\frac{3}{2}$ (i.e., $\text{CKCCK} \dots$ layer sequence). The latter disappears at the second transition, and a stage-2 phase appears. The in-plane structure or stacking reflections could not be detected, as they were working on HOPG, which spreads these reflections in cylinders in reciprocal space, because of the relatively low scattering factor of potassium for neutrons, and because of the weak modulation along C^* associated with stacking imperfections.

We report here the results of x-ray diffraction experiments on single crystal KC_8 from ambient pressure up to 30 kbar. Natural graphite single crystals of typical size of $0.2 \times 0.2 \times 0.05 \text{ mm}^3$ were intercalated with potassium to first stage by the two-bulb method.⁸ The samples were then transferred under a 50:50 mixture of degassed and potassium-purified pentane-isopentane to a Bassett diamond anvil cell. The pentane-isopentane provides a hydrostatic medium up to 80 kbar at 300 K. The pressure was measured using the standard ruby R_1 fluorescence technique. The pressure was determined to better than ± 0.5 kbar, using a double-grating spectrometer. It has been confirmed, using x-ray technique and monitoring pure potassium, that the pressure medium did not react with the sample for periods of months (see also Refs. 6 and 7). The high-pressure cell was mounted as needed on a precession camera, oscillation camera, or on a Picker 4-circle diffractometer. We used a fine-focused sealed Mo tube at 45 kV and 20 mA. At ambient pressure, precession photographs revealed the expected diffraction patterns for $Fddd$ space group [the previously reported KC_8 structure with a 2×2 potassium superstructure, Fig. 1(a)]. When the pressure was raised to about 10 kbar, a second set of reflections associated with $\sqrt{3} \times \sqrt{3}$ superstructure emerged. The intensity of these reflections increased gradually with pressure, relative to the intensity of the 2×2 superlattice [Fig. 1(b)]. The appearance of the new $\sqrt{3} \times \sqrt{3}$ superstructure was accompanied by a pronounced increase in the diffuse scatter-

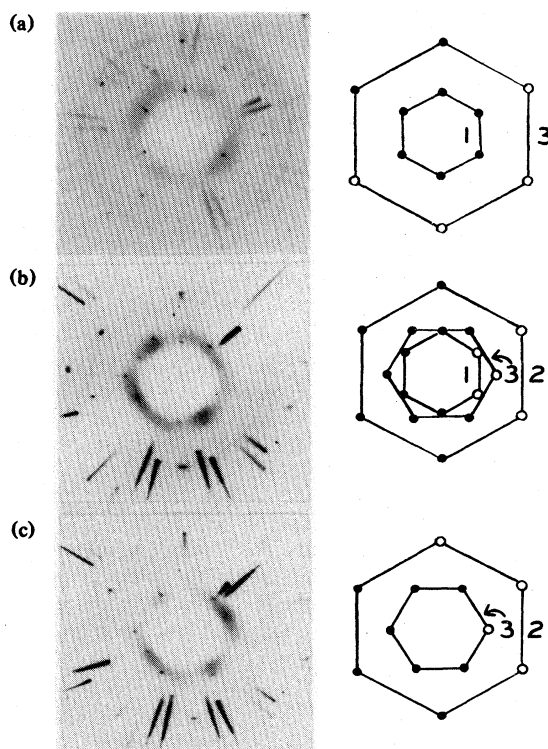


FIG. 1. X-ray oscillation pictures of KC_8 single crystal in a diamond anvil pressure cell. The intense streaks are diffractions from the diamond anvils. The diffraction rings are from the beryllium filters (a) at about 1 kbar, (b) at 11 kbar, (c) at 23 kbar. The reflections from the sample are indicated on the diagram on the right of the picture. The diffraction on hexagon 2 corresponds to reflections from graphite and potassium. The diffraction spots on hexagon 1 correspond to the 2×2 superstructure. The spots on hexagon 3 correspond to the $\sqrt{3} \times \sqrt{3}$ in-plane structure. Closed circles indicate observed reflections. All the possible reflections on this diagram were confirmed using a 4-circle diffractometer.

ing, which formed circular broad lobes. Upon further increase of the pressure, the 2×2 superstructure faded gradually, and at about 26 kbar disappeared completely, while the high-pressure $\sqrt{3} \times \sqrt{3}$ superstructure intensified [Fig. 1(c)]. In the coexistence regime of the two phases, the $\sqrt{3} \times \sqrt{3}$ reflections intensified slowly with time, over a period of several days at constant pressure. A similar effect was also reported in KC_{24} .²

Scans were performed along the c^* directions of the graphite lattice ($10l$), ($11l$), along the 2×2 superstructure positions ($\frac{1}{2}0l$), ($\frac{1}{2}\frac{1}{2}l$), along the $\sqrt{3} \times \sqrt{3}$ superstructure positions ($\frac{1}{3}\frac{1}{3}l$), ($\frac{2}{3}\frac{2}{3}l$), as well as along all the other equivalent positions. The results were very hysteretic, but reproducible. The experiments were performed on three different samples, and the results were consistent with variations of the onset pressures of about ± 3 kbar. These variations were mainly attributed to time effects, which seem to play a major role in these processes (see below).

The results can be summarized as follows.

(1) The ambient-pressure 2×2 superstructure phase disappears completely about 29 kbar [Fig. 1(c)]. It reappears only when the pressure is completely released. Even

then, the phase-transition cycle introduces a high concentration of stacking faults, which produces an unresolved pattern along c^* . The high pressure $\sqrt{3} \times \sqrt{3}$ superstructure phase shows three-dimensional order with a high occurrence of stacking faults (unresolved pattern of the reflection profile along c^*). It disappears completely only upon releasing the pressure. The rocking curves of both reflections in the basal plane reveal relatively sharp structure with a spread of 4° centered around the 2×2 and $\sqrt{3} \times \sqrt{3}$ superstructures, respectively. The widths of these profiles were pressure independent. This indicates that the commensurate-to-commensurate in-plane phase transitions is of the first order.⁹

(2) The modulation of the intensity profile of the graphite ($10l$) and ($11l$) reflections along c^* is about 0.4 \AA^{-1} wide and is almost pressure independent, corresponding to a c -axis correlation of about 15 Å. A rocking curve in the basal plane through the rod line showed a slightly narrower profile than the superstructure reflections (3° spread). A similar value was found for other graphite reflections. This implies at least five times better long-range order in the basal plane than in the c direction, and suggests a high occurrence of stacking faults (every 3–5 layers).

(3) Consequently, the repeat distance extracted from these profiles in the c^* direction is not exactly consistent with stages 1, 2, or $\frac{3}{2}$. This is not surprising, as it is well known that stacking faults not only broaden the lines but are also responsible for the distortion of the reflection maxima from their expected positions.¹⁰

(4) The similar widths of ($10l$) and ($11l$) reflections along c^* indicate that the stacking disorder is more complicated than just a random mixture of the familiar stacking disorder $ABAB \rightarrow ABCABC$ in which two carbon layers, A and B , in graphite or intercalants with stage $n > 1$, are known to form.¹¹ As noted by Franklin¹¹ both ABC and AB structures have a (110) and a (111) reflection, so that a simple disorder between them would have left the width of these reflections unbroadened. However, the ($10l$) reflections appear at different l values for the two different stacking sequences, and in a random sequence of the two stacking orders, considerable broadening of the reflections profiles is expected. The complicated stacking sequence of this compound is actually not unexpected. The high-pressure phase has, as we showed, a $\sqrt{3} \times \sqrt{3}$ in-plane superstructure. This unusual situation combines two different elements of lateral displacement: an AB stacking translation between two adjacent carbon layers, and three (α, β, γ) possible arrangements of the $\sqrt{3} \times \sqrt{3}$ K intercalant. The total number of independent lateral displacements can be shown to be 9 for stage $\frac{3}{2}$. A full account of the line-shape analysis induced by these stacking faults should follow a scheme similar to the one outlined in Ref. 9, and is beyond the scope of this paper. However, the variety of possible stacking faults makes it probably an important factor in the phase transition (but see the following).

For the detection of the ($00l$) reflections, a sample was mounted on its edge in the pressure cell. The pressure was then raised to 5.2 kbar. An ($00l$) scan revealed the correct KC_8 c -axis repeat distance 5.28 Å. The sample was then left in the cell for 2.5 months under pressure. The pressure dropped to 4.2 kbar during this time. A second ($00l$) scan at this pressure revealed a profile very similar to the one earlier reported to appear at about 15 kbar (the intermediate

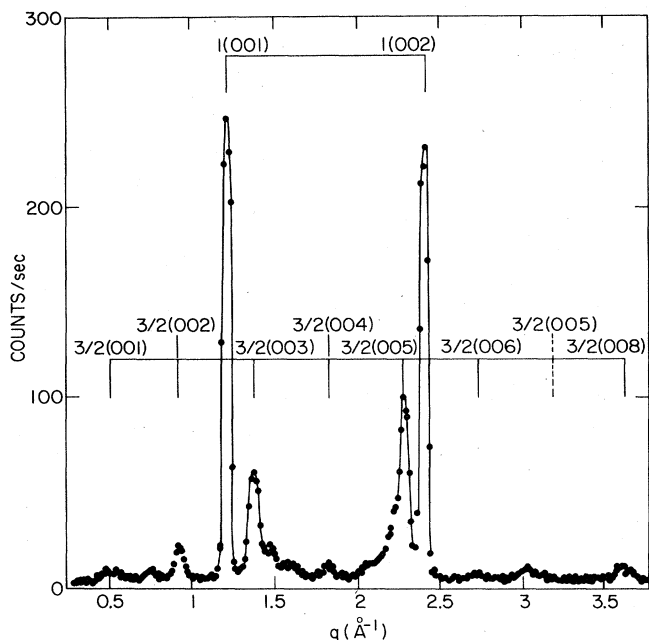


FIG. 2. (00*l*) scan of KC_8 at 4.2 kbar. Two sets of peaks were predominantly detected. (In addition, some fainter peaks also show up, possibly of another phase.) The repeat distance of one set was identical to that of stage 1 KC_8 . The other sequence of peaks was very similar to the one obtained at 15 kbar, using neutron scattering, which was identified as stage $\frac{3}{2}$ (Ref. 10).

pressure in Ref. 7). The reflections can be identified as belonging predominantly to two phases, one to stage $\frac{3}{2}$ and the other to stage 1 (Fig. 2). A second (00*l*) scan at 28 kbar revealed a completely different intensity profile with broad bands instead of narrow Bragg reflections. Even after three weeks at that pressure not much change was seen, and this spectrum has been left unresolved.

Aside from the definite high pressure $\sqrt{3} \times \sqrt{3}$ structure demonstrated by our experiment, four other observations should be noted: (i) the highly frequent occurrence of stacking faults, (ii) the wide range of pressures in which the two in-plane structures coexist (10–23 kbar), (iii) the long time scale that the system needs to achieve equilibrium, and

(iv) the large hysteresis of the transition pressure (to reobtain the low pressure in-plane structure, the pressure must be practically released, as was the case with all other high pressure experiments on KC_8).^{6,7} Bak and Domany¹² first noted the importance of stacking faults in the phase transitions of intercalated compounds. They pointed out that these compounds are physical realizations of one-dimensional randomness of the type introduced for the Ising model by McCoy and Wu.¹³ They concluded that the effect of this randomness is to smear the first-order transition temperature. As the transition temperature and transition pressure are related by the Clausius-Clapeyron equation,¹ this will also induce spread in the transition pressure in our experiment. Therefore, it seems reasonable that the high concentration of stacking faults is responsible for the coexistence of two in-plane densities over a large range of pressure, and we are observing a first-order smeared transition of the McCoy-Wu type.

We do not have, however, a consistently good explanation for the time effects involved in the experiment, nor for the probably associated hysteresis effect. The in-plane data suggest time-dependent effects of the order of days or weeks, and this has also been observed in some other high-pressure experiments on single crystals.² Our observation of the intermediate pressure phase ($1 + \frac{3}{2}$) after three months at about 5 kbar (but on only one sample) suggests a very long relaxation time. On the other hand, neutron and resistivity data^{6,7} consistently show a sharp transition at 15 kbar to this phase on HOPG samples with no more than several hours of relaxation. In all experiments, however, the pressure must be completely released to reobtain the low-pressure phase. This may indicate a lower-pressure transition than the one obtained by the experiment, and therefore a much longer relaxation time. This is an open question that can be resolved by a high-pressure experiment at higher temperatures, where the kinetics are more rapid.

One of us (J.M.B.) wishes to acknowledge E. Domany of the Weizmann Institute, Israel, for pointing out the relevance of Ref. 11 and the McCoy-Wu process to this problem. This work was supported by the Department of Energy Contract No. DEAC-02-80ER10600, and by the NSF Materials Research Program DMR 82-16718, and in part by Department of Energy Contract No. DEAC-02-76CH00016, and a grant from Exxon Corporation.

*Present address.

[†]Present address: Fox Chase Medical Center, Philadelphia, PA 19111.

[‡]Present address: Institute for Organic Polymers, University of California, Santa Barbara, Santa Barbara, CA 93106.

[§]Also Physics Department.

^{**}Also Materials Science and Engineering Department.

¹D. P. DiVincenzo, C. D. Fuerst, and J. E. Fischer, *Phys. Rev. B* **29**, 1115 (1984).

²R. Clarke, N. Wada, and S. A. Solin, *Phys. Rev. Lett.* **44**, 1616 (1980); N. Wada, *Phys. Rev. B* **24**, 1065 (1981).

³S. A. Safran, *Phys. Rev. Lett.* **44**, 927 (1980); S. A. Safran and D. R. Hamann, *Phys. Rev. B* **22**, 606 (1980); S. E. Millman and G. Kirczenow, *ibid.* **26**, 2310 (1982); J. R. Dahn, D. B. Dahn,

and R. R. Haering, *Solid State Commun.* **42**, 179 (1982).

⁴P. Hawrylak and K. R. Subbaswamy, *Phys. Rev. B* **28**, 4851 (1983).

⁵A change in the relative temperature of the graphite and the intercalant corresponds to a change in the relative concentration *x* on a phase diagram, and therefore it does not represent a scan along a constant-*x* vertical line. It is therefore not contradictory to the previous statements to find higher stages at higher temperatures in experiments such as by R. Nishitani, Y. Uno, and H. Suematsu, *Phys. Rev. B* **27**, 6572 (1983); and M. E. Misenheimer and H. Zabel, *ibid.* **27**, 1443 (1983).

⁶C. D. Fuerst, D. Moses, and J. E. Fischer, *Phys. Rev. B* **24**, 7971 (1981).

⁷C. D. Fuerst, J. E. Fischer, J. D. Axe, J. B. Hastings, and D. B. McWhan, *Phys. Rev. Lett.* **50**, 357 (1983).

⁸A. Herold, *Mater. Sci. Eng.* **31**, 1 (1977).

⁹We observed reflections from the ruby crystal, in the same run, which were several times narrower than the superstructure reciprocal basal-plane reflections, and the width of the superstructure spots were clearly not resolution limited. The accuracy of the position of the superstructure spots was limited to about 0.06 \AA^{-1} and we did not detect deviation from registry. We also have not detected satellite reflections, and therefore conclude that, to

the accuracy of this experiment, the superstructure is commensurate with the lattice.

¹⁰D. E. Moncton, F. J. DiSalvo, J. D. Axe, L. J. Sham, and Bruce R. Patton, *Phys. Rev. B* **14**, 3432 (1976); J. B. Hastings, W. D. Ellenson, and J. E. Fischer, *Phys. Rev. Lett.* **42**, 1552 (1979).

¹¹R. E. Franklin, *Acta Crystallogr.* **4**, 253 (1951).

¹²Per Bak and Eytan Domany, *Phys. Rev. B* **29**, 1320 (1981).

¹³B. M. McCoy and T. T. Wu, *Phys. Rev. Lett.* **23**, 383 (1968).

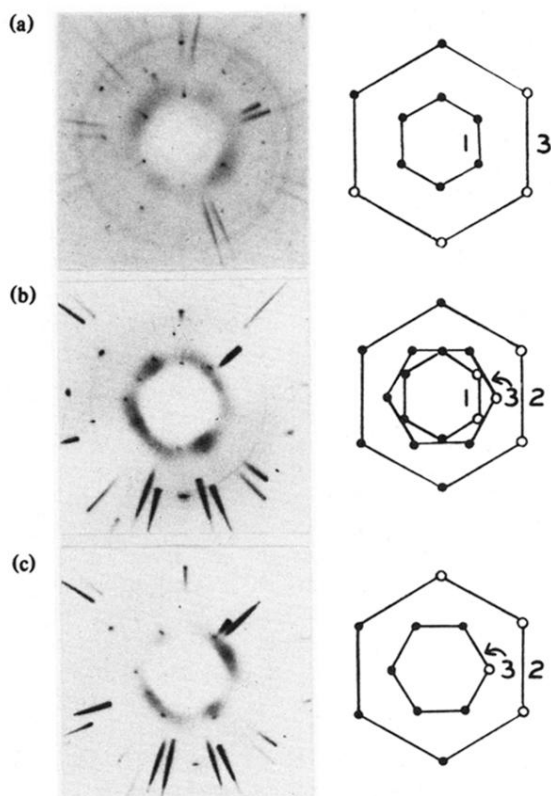


FIG. 1. X-ray oscillation pictures of KC_8 single crystal in a diamond anvil pressure cell. The intense streaks are diffractions from the diamond anvils. The diffraction rings are from the beryllium filters (a) at about 1 kbar, (b) at 11 kbar, (c) at 23 kbar. The reflections from the sample are indicated on the diagram on the right of the picture. The diffraction on hexagon 2 corresponds to reflections from graphite and potassium. The diffraction spots on hexagon 1 correspond to the 2×2 superstructure. The spots on hexagon 3 correspond to the $\sqrt{3} \times \sqrt{3}$ in-plane structure. Closed circles indicate observed reflections. All the possible reflections on this diagram were confirmed using a 4-circle diffractometer.