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Kinetics of staging transitions: A neutron diffraction study of pressure-quenched potassium-intercalated graphite

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Computer simulations of constant-density staging transitions induced by quenching from high temperature show interesting kinetic effects, but on a very short time scale. We performed analogous pressure quenches from zero to 10–15 kbar at 300 K in an attempt to slow down transient processes and reveal the time dependence. However, we found no time-dependent effects for 2 min $< t <$ 5 days. The 300 K P-induced transitions are much faster than the corresponding high-T transitions during intercalation, suggesting that the constant-density process is nucleation controlled rather than diffusion limited. A dilute sample shows the same high-P phases after fast or slow pressurization, while KC_{24} shows much more disorder when quenched, including some stage-4 cells which do not occur in the "adiabatic" case. We suggest that the unique quenching behavior of the stage-2 phase is related to the discommensuration-domain in-plane structure.

Staging in layer intercalates, particularly graphite, continues to attract a lot of attention. Staging represents a prototypical one-dimensional lattice, the thermodynamics and kinetics of which are determined, in principle, by simple electrostatic and elastic interactions, but which may be complicated in practice by competition between these interactions,[1] in-plane[2] and out-of-plane[3] finite-size effects, pinning by domains or discommensurations,[4] etc. Experimental efforts have focused recently on the evolution of different stage sequences versus intercalate concentration,[5] high-resolution x-ray results[6] showing departures from the coexistence of equilibrium phases expected from simple theory.[7] Other workers have quantified the one-dimensional disorder in long-period stage sequences and found a correlation between temperature-dependent staging disorder and an in-plane order-disorder transition in which the areal density changes by an amount consistent with the change in the fraction of occupied galleries.[8] Also, the connection between the intercalate/graphite in-plane commensurability and the stability of particular stages has been studied as a function of hydrostatic pressure;[9] one finds that indeed, some stable stages or mixtures do correspond to in-plane commensurability for all occupied galleries, while in other cases well-ordered pure stages or mixtures occur with no apparent connection to stoichiometries dictated by simple in-plane commensurate lattices.

One of the last frontiers is the question of dynamic behavior: How does an intercalation compound get from one stage to another in response to an abrupt change in temperature, pressure, or chemical potential? The Daumas-Herold domain model[2] was proposed to explain the apparent rapidity with which stage transformations occur; otherwise one has to envisage complete emptying of the appropriate galleries and filling of the correct ensemble of previously empty ones, requiring lateral atomic diffusion paths of the order of the sample dimensions. Physicochemical kinetic studies of Br-graphite[10] and Ag-TiS_2 (Ref. 11) intercalation confirm the original work of Hooley[12] by showing that, in response to an increase in chemical potential, new atoms enter the sample through edges normal to the layers and diffuse parallel to the layers, and that equilibrium stage-1 regions grow out of stage-2 intermediate precursors.[11] The well-defined geometries of these experiments are amenable to modeling[13] and computer simulations.[14] In contrast, staging transitions at constant density[15] are likely to begin randomly throughout the sample, so the kinetics could be nucleation or diffusion limited[16] and both processes must be included in modeling. Domain growth and domain-wall "friction" or "viscosity" might be expected to play a major role in the kinetics of both kinds of staging transition. To the extent that staging transitions are associated with in-plane melting,[17] the staging kinetics will reflect the kinetics of in-plane ordering[18] to some degree.

Several kinetic calculations and Monte Carlo simulations have recently appeared.[13,14,16] The first to provide a "real-time" scale[13] predicts that transitions from stage n to n' occur via long-lived intermediate phases, the time scale being of order 10^{-4} sec for either a quench from high T at fixed concentration or a step change in chemical potential corresponding to usual intercalation conditions. Effects on this time scale might be resolvable with linear detectors and synchrotron radiation. Alternatively, to the extent that thermally activated diffusion processes control the kinetics of staging transitions, the kinetic response to hydrostatic pressure at ambient temperature should be conveniently slower than a quench from high T. Furthermore, the connection between pressure- and temperature-induced quasiequilibrium staging transitions obeys a simple thermodynamic relation,[19] so the model of Ref. 13 should apply equally well to pressure-quench experiments. We describe here the results of such experiments on potassium-graphite intercalation compounds, for which the quasiequilibrium staging phase diagram versus pressure and concentration has been extensively studied.[9]

The experiments consisted of comparing neutron diffraction $(00L)$ profiles for fast and slow pressurizations of two different samples prepared from about 200 mg of highly oriented pyrolytic graphite. At ambient pressure these were pure stage-2 and stage-4 compounds, with compositions determined from weight uptake of $KC_{23.1\pm0.6}$ and $KC_{41.2\pm1.5}$, respectively. Apparatus and sample mounting are described elsewhere.[9] A pressure quench from ambient pressure to 10–15 kbar takes about 5 sec, but another 2 min are required to align the sample before starting the first scan (there is some movement of the free-floating sample in the pressure cell upon applying the hydrostatic load). The time evolution was followed by repeating short scans (about 8 min) covering the (001) reflections of the expected P-induced stages. Long scans were also recorded in order to perform Hendricks-Teller fits as a measure of staging disorder[8,9] for comparison with equilibrium data.

The stage-4 sample was first pressurized slowly to 15 kbar in small increments, exhibiting a continuous evolution of the stage-5 phase up to 8 kbar and then transforming abruptly at 8.5 kbar to a 15/85 ratio of the stage-5 phase to the stage-6 phase which remained stable up to 15 kbar.[20] The pressure was then released and the sample transformed back to pure stage 4. Quenching to 11 kbar yielded the same mixed stage-$(5+6)$ spectrum with slightly more staging disorder. The kinetics of the basic staging transition in this sample is evidently faster than our 2 min dead time.

On the other hand, stage-2 KC_{23} showed important differences between quenching and slow pressurization. This particular sample was characterized as 99% pure stage 2 at 1 atm from the Hendricks-Teller fit shown in Fig. 1(a). Similar samples transform with slow pressurization to a nearly pure stage-3 phase (95 vol%) plus a small but sharp stage-2 remnant, the transition occurring in two abrupt steps at 3.5 and 6.5 kbar.[9] This sample was first quenched to 10.5 kbar, resulting immediately (<2 min) in the broad profile shown in Fig. 1(b) which indicates qualitatively the presence of the stage-2, -3, and -4 phases. This profile exhibited essentially no time dependence after the quench, only a slight sharpening of some peaks. The Hendricks-Teller fit reveals a 34% stage-2 component which is only 20%–30% broader than at 1 atm, plus a strongly mixed phase of the stage-3 (39%) and -4 (27%) phases. We emphasize that the stage-2 and -3 phases are the only equilibrium phases at this pressure, so the appearance of the stage-4 phase is directly connected to the quenching. After several hours at 10.5 kbar with no detectable change, we quenched further to 15 kbar which resulted in only small changes in relative amounts and correlation parameters—31%, 41%, and 28% of stages 2, 3, and 4, respectively. No further changes occurred in 5 days. The unique stage mixture induced by quenching in this sample was completely reversible and exactly repeatable. In other words, as soon as the pressure was released (after quenching or slow pressurizing), the original stage-2 phase immediately recovered; upon requenching it returned to the same mixed phase.

Furthermore, quenching had no permanent effect on the sample, since a slow pressurization after the quench experiments produced the expected equilibrium phases, 88% stage 3 plus 12% stage 2 as shown in Fig. 1(c). Finally, the order of fast and slow pressurization is unimportant since a quench after the equilibrium run gave the same profile as Fig. 1(b). This unusual kinetically formed nonequilibrium phase mixture is stable against further increases in pressure, is formed very rapidly (<2 min) after quenching, and shows no evolution thereafter on a time scale of days. There is also considerably more stage disorder compared to that after slow pressurization, but this is difficult to quantify because of the presence of the "third phase," i.e., stage-4 cells.

In their calculation of the mass-conserving transition induced by a quench from high to low temperature, Hawrylak and Subbaswamy[13] showed that the staging transition occurs via an intermediate metastable phase which could persist for long times. It is tempting to associate the nonequilibrium mixed phase in quenched KC_{23} with this theoretical result, but the absence of a similar long-lived nonequilibrium intermediate phase in quenched KC_{41} suggests that this behavior is unique to the more concentrated compound. While similar quenching experiments were not performed on the stage-3 phase, we expect the kinetic behavior to be comparable to that of the stage-4 phase since the quasiequilibrium behavior is comparable, both showing a progression of single-step transitions from stage n to stage $n+1$ to stage $n+2$ with increasing pressure. The unique kinetic behavior of the stage-2 phase is thus very likely connected to its

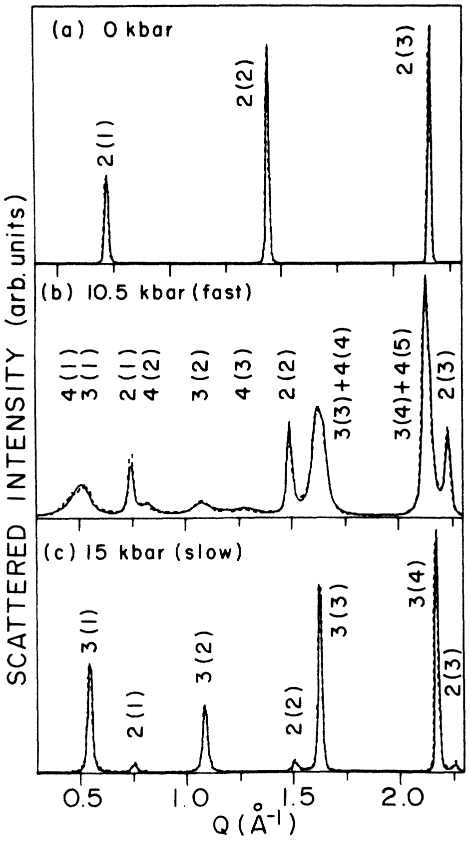

FIG. 1. Neutron (00L) diffraction profiles (dotted curves) of $KC_{23.1}$ and fits to the Hendricks-Teller model (solid curves) which accounts for partially disordered staging, as described in Ref. 9. Each peak is labeled by $n(m)$ which denotes the (00m) reflection from a perfect stage n. (a) Before pressurizing: The fit parameters indicate 99% stage-2 unit cells with 0.9% and 0.1% stage-1 and stage-3 cells, respectively, distributed almost at random throughout the majority stage-2 phase (3 adjustable parameters). (b) Quenched to 10.5 kbar: The fit is a superposition of two independent three-cell line shapes (stage-2, -3, and -4 cells), but with different correlations. The fractions of the three cells are comparable (see text), a result which is insensitive to the details of the model (this one giving by far the best fit, with 7 adjustable parameters). (c) Pressurized slowly in small increments to 15 kbar: three-parameter fit indicates almost perfect phase separation between the stage-2 phase (9%) and a phase consisting of stage 3 (88%) with random stage-2 impurities (3%). In equilibrium, 10.5 and 15 kbar are equivalent; the most important consequence of quenching is to increase the fractions of stage-2 and -4 cells at the expense of stage 3.

unique quasiequilibrium behavior, namely, a two-step transition from stage 2 to mostly stage 3. Even the 34% relative amount of the stage-2 phase in quenched KC_{23} seems to coincide with the 30%–40% found in the plateau between the two anomalies in slow-pressurization experiments. A possible origin of this peculiar behavior, in quenching as well as in equilibrium, might be the formation of "incommensurate" in-plane ordered structures which are only stable over a narrow range in equilibrium (e.g., 3.5–6.5 kbar) but which are frozen in by quenching to higher pressures. Such structures would probably consist of locally commensurate islands surrounded by domain walls or discommensurations,[4] which could interact with Daumas-Herold domains during the process of a staging transition. Thus, the pressure quenching of KC_{23} would freeze in a metastable nonequilibrium state in which domains of denser islands, bounded by discommensurations, are pinned either by intrinsic defects, Daumas-Herold domain walls, or c-axis interactions. Similar effects would not occur in more dilute compounds because the c-axis interactions are on average weaker and because the equilibrium in-plane ordered phases are closer to commensurate.[8] This scenario is consistent with the simpler equilibrium behavior of dilute compounds at high pressure[9] and low temperature.[8] None of the existing kinetic theories take in-plane ordering into account.

This line of reasoning can also explain the differences between dilute stage-2 K and Li GIC's. The Li analog of KC_{24} is LiC_{16}, which transforms in one step at low T or high P to a mixture of dense ordered stage-2 and -3 phases, both of which exhibit a commensurate $\sqrt{3}\times\sqrt{3}$ in-plane superlattice.[19] In the Li case the kinetics are very slow, of the order of days for either experiment, perhaps because of an unusually low atomic jump diffusivity associated with a very strong corrugation potential from the graphite hexagonal network relative to the heavy alkali-metal atoms.[21] Of greater significance is the fact that Li is most likely commensurate in both ordered and disordered phases, again due to the strong corrugation potential. In the present context we would therefore argue that the absence of incommensurate phases in LiC_{16} at any T or P explains why quenching to low T or high P fails to produce nonequilibrium intermediate phases analogous to the highly disordered mixture (including a stage-4 phase) which we observe in pressure-quenched KC_{23}. The existence of the low-T incommensurate structure in KC_{24} may in turn explain why this compound does not undergo a low-T staging transition analogous to the LiC_{16} case.[22]

The observed kinetics in our mass-conserving transitions is substantially faster than the kinetics of the same staging transitions versus concentration at much higher temperatures,[5] suggesting that random nucleation plays an important role in the present case. This is consistent with the proposal that pressure-induced staging transitions are driven by in-plane densification,[23] a process which is expected to nucleate randomly.

In summary, (1) pressure-induced staging transitions in KC_{23} and KC_{41} go to completion at 300 K in less than 2 min, and (2) nonequilibrium phases are induced by quenching in KC_{23} but not KC_{41}. The formation of a nonequilibrium stage-4 phase in the quenched stage-2 phase may be related to the two-step quasiequilibrium behavior, both observations possibly indicating the importance of in-plane discommensurations to the thermodynamics and kinetics of staging.

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