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Experimental phase diagram of lithium-intercalated graphite

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First-order transitions to dilute stage 1 from stages 2–4 and from mixed stages are observed in Li-graphite compounds in the range 430–1020 K. The resulting (T,x) phase boundary agrees generally with predictions by Safran and others except for a sharp peak of very stable stage-2 compositions around $x \sim 0.4$. The commensurability energy does not contribute to this peak since both low-T and high-T phases are disordered.

A unique feature of intercalated layer crystals is the phenomenon of staging,[1] whereby the foreign atoms occupy a periodic sequence of van der Waals gaps in the host crystal (every nth gap in a stage-n compound). The stability of long-period coherent structures has been attributed to long-range electrostatic or elastic ("coherency strain") repulsion among intercalant layers.[2] Safran[3] pioneered the calculation of (T,x) phase diagrams for layered intercalates (x is the concentration expressed as a fraction of the saturation value). At low T, compositions which do not correspond to pure stages are predicted to macroscopically phase-separate into mixed stages, as observed in graphite compounds at 300 K. Safran's simple two-body model predicts a high-T transition $T_c(x)$ at which any compound with $x < 1$ transforms *at constant x* to a stage-1 sequence by reducing the in-plane density.[3] The existence of the dilute stage-1 phase at high T is insensitive to the details of the Hamiltonian, but the phase boundaries reflect the inclusion of additional interactions, screening, etc.[4,5] We have observed transitions to dilute pure stage 1 in Li-graphite compounds with $0.16 < x < 0.99$, using x-ray and neutron diffraction (the latter performed at the Oak Ridge High Flux Isotope Reactor). These are plotted as the solid dots in Fig. 1, which shows a narrow peak of extremely stable stage-2 compositions ranging from $x = 0.3$ to 0.5, a feature which is not accounted for by any of the model calculations.[3–5] The peak appears to be superposed on a weaker x dependence of T_c skewed in favor of dilute compounds, as predicted when elastic guest-host interactions are included.[4] This is the first systematic study of the concentration dependence of T_c and thus provides experimental input to the (T,x) staging phase diagram of a prototyp-

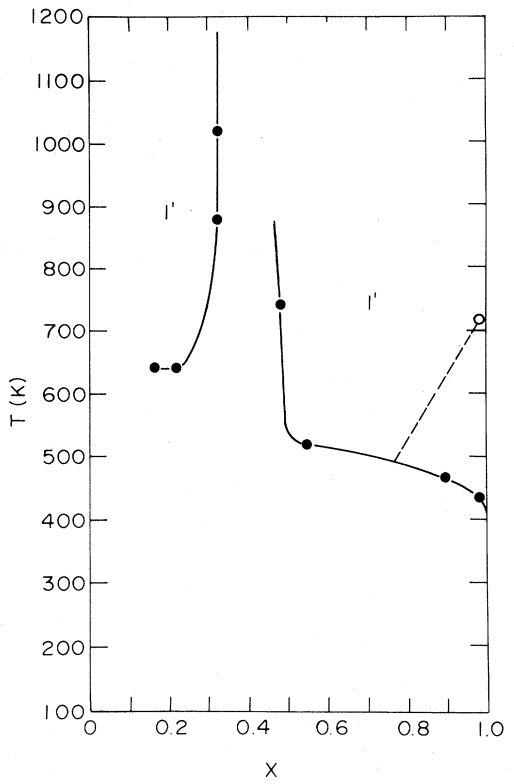

FIG. 1. Experimental upper phase boundary for Li-graphite compounds. Solid dots represent phase-transition temperatures (from x-ray or neutron diffraction) above which only stage 1 is present. Except near $x = 1$ there is a corresponding loss of in-plane order; the $x = 0.99$ sample is three-dimensionally ordered pure stage 1 from 433 to 715 K (open circle from Ref. 11).

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ical system.[6] We present here an account of how Fig. 1 was obtained, deferring for a longer article a discussion of the phase boundaries of higher stages, detailed analysis of the transitions, etc.

We screened several intercalants by looking for evidence of the stage-2 → stage-1 transition with differential scanning calorimetry. Li-graphite compounds showed such evidence at accessible temperatures whereas KC_{24} and CsC_{24} did not. An advantage of the Li-graphite system is the existence at 300 K of two different stage-2 compositions LiC_{12} and LiC_{18}, which permits the study of in-plane density effects at constant stage.[7] We label these stages 2 and 2′, respectively, where the unprimed integer denotes an ordered commensurate in-plane structure while the primed integer indicates a (generally) less-dense structure with no long-range order. The model calculations do not consider in-plane order or lack thereof, the predicted structures being delineated only by the sequence of occupied gaps. Another advantage is the low Li vapor pressure such that our samples, sealed in thin stainless-steel containers, could be run at high T without deintercalation. (We included excess metal alloy in the containers to maintain equilibrium vapor pressure, a precaution which was probably superfluous—see below.)

Unfortunately Li intercalation compounds transform irreversibly to lithium carbide Li_2C_2 above 750 K (Ref. 8); we turned this to our advantage in some cases. Visible quantities of Li or Li-Na alloy are often incorporated in macroscopic cracks during liquid-phase synthesis,[9] which complicates the determination of x. Thus chemical analyses[9] of stage 2′ samples range from $LiC_{14.5}$ to LiC_{18} while x-ray photoelectron spectroscopy (XPS) core-level intensities[10] give $LiC_{18\pm1}$. We adopt the latter value as being consistent with the blue color, relative to the pink and gold of LiC_{12} and LiC_6, respectively. The presence of alloy in intimate contact with the compound also raises concern that x may vary during a high-T run. We find, however, that the diffracted intensities of the low-T phases are quite reproducible after repeated cycling (except when Li_2C_2 is formed), probably because the time scale of the experiment is short compared to the intercalation time and/or because the compound is in equilibrium with the alloy from which it was grown. Thus we neglect the possible presence of free metal in determining x. Most of our samples were mixed phase at 300 K. The relative amounts of the various phases present in a given sample were estimated from (00l) diffraction intensities in most cases, the exception being mixtures of stages 2 and 2′ which were analyzed via their different carbon-layer stacking sequences.[7] Equivalent homogeneous-phase x values were obtained by assigning $x = 1.0$, 0.5, and 0.33 to pure stages 1, 2, and 2′, respectively. We estimate the error in x to be ± 0.02 via this procedure. Single-phase samples of stages higher than 2 were assumed to follow the dilute $LiC_{9\times n}$ sequence at 300 K: LiC_{27} stage 3′, LiC_{36} stage 4′, etc. The pale gray colors are consistent with smaller Li content than blue LiC_{18}, etc. From Fig. 1, $T_c(x)$ is either relatively flat or sharply peaked in different regions of x. Thus our approximate x determination is adequate over most of the range while extraordinary efforts would have to be made to resolve different x values near 0.4 corresponding to different T_c's.

The solid dots in Fig. 1 denote the temperatures at which pure stage-1 (00l) diffractograms are first observed upon heating samples of various x. These transitions are all first order, exhibiting ~10-K hysteresis. Above 433 K the $x = 0.99$ sample is pure three-dimensionally ordered stage 1, presumably with Li vacancies because the low-T phase contains 2 vol% stage 2. Upon further heating to 715 K the three-dimensional Li order disappears[11] (open circle), implying the existence of a second boundary between ordered and disordered pure stage-1 phases (dashed line), the former supporting a significant vacancy concentration at high T by analogy to Cs_xC_8.[12] A similar sample transforms to pure stage 1 at $T_c(0.90) = 467$ K, establishing the weak x dependence of the boundary near $x = 1$.

Mixed stage samples near $x = 0.5$ show complex behavior upon heating. Figure 2 shows the normalized T dependence of Li(100) and representative (00l) peak intensities for $x = 0.55$ (stage 2 + 10% stage 1 at 300 K). The stage 2 (004) drops abruptly at 495 K to 40% of its initial strength, levels off, and then disappears between 510 and 520 K. Mirroring this two-step behavior is the growth of stage-1 (002) intensity which is attributed to dilute disordered stage 1′ above 520 K since the Li(100) is gone. Between 495 and 510 K, (10l) neutron scans show stage-1 periodicity so the ordered Li comes from stage 1 while the remaining stage 2 must be disordered. To confirm this, we recorded a ($\sqrt{3}$0l) scan (carbon row) and found a mixture of A-A (stage 1) and

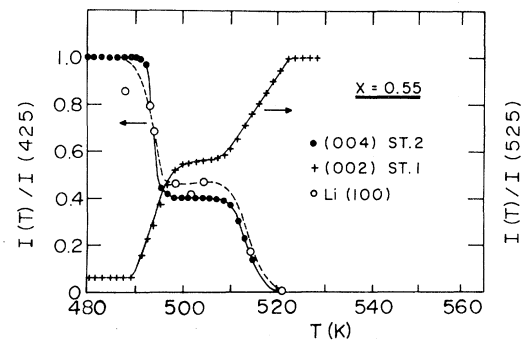

FIG. 2. Staging transitions for a sample with $x = 0.55$. Normalized peak intensity vs T for stage 2 (004), stage 1 (002) from x rays, and in-plane Li(100) from neutrons.

AB/BA (stage 2′) stacking.[7] We take the midpoint of the upper transition as $T_c(0.55) \simeq 515$ K. The data in Fig. 2 were obtained by monitoring a peak after each step change in T, stabilization generally occurring in less than 1 h. Both transitions are fully reversible.[13]

Dramatically different behavior occurs in a slightly different sample, stage 2 with 5% stage 2′ at 300 K whence $x = 0.49$. These coexist until 503 K where the stage 2 begins to disappear and stage 1 emerges. The coexisting $1 + 2'$ transform at 533 K to $1' + 2'$ as the last of the Li(100) disappears. This (third) mixed-phase region continues up to $T_c(0.49) = 733$ K where the 2′ disappears. Holding the sample at 750 K leads to gradual formation of Li_2C_2, leaving behind a lamellar compound with reduced x value. This process increases T_c noticeably, confirming the large negative dT_c/dx through the point (743 K, 0.49).

X-ray studies of three "LiC_{18}" samples showed very different behavior upon heating, suggesting slight differences in x and a steep phase boundary. One such sample transformed completely to Li_2C_2 at 1150 K without showing any staging transitions en route. The other two passed through narrow $1' + 2'$ mixed-phase regions and then transformed to pure 1′ at 875 and 1020 K upon first heating. Reversibility was confirmed for the former by working quickly as the Li_2C_2 formed. The attendant reduction in x *decreased* T_c, indicating a large *positive* dT_c/dx. We identify the transition as $1' + 2' \rightarrow 1'$ since a $(10l)$ neutron scan of LiC_{18} at 773 K confirms that the Li is disordered below and above T_c. Thus we can rule out the commensurability energy as a contributing factor to the unusually high stability of stage 2 at $x = 0.33$. The $(00l)$ linewidths are the same above and below the phase boundary. Finally, pure stages 3′ and 4′ ($x = 0.22$ and 0.16, respectively) both transform to pure stage 1′ at 640 K so the exact x values are not critical. Neither sample exhibited stage-2′ reflections at any T. These two samples establish the weakly asymmetric "background" which underlies the strong peak in Fig. 1.

The gross features of the experimental phase diagram accord well with Safran's original predictions[3]; only dilute stage 1′ is stable above some concentration-dependent temperature, and the most stable concentration for higher stages is nearer $x = 0.5$ than 0 or 1. An Ising Hamiltonian with two-body interactions[3] thus provides a reasonable basis for treating the statistical mechanics of staging. The upper boundary in Safran's model is symmetric about $x = 0.5$; our data are better reproduced by including an elastic guest-host interaction which breaks the symmetry.[4] The most surprising aspect is the sharp peak between $x = 0.33$ and 0.49; stage 2′ at some x is apparently stable to at least 1150 K. None of the proposed modifications to the theory account for this dramatic effect. The possibility of a second-order transition near the stability limit[3–5] can only be tested on materials with lower T_c.

In Safran's model the T scale depends only on U_0, the in-plane two-body attractive interaction. On this basis one would therefore expect similar T_c's for Li intercalated into different hosts. At 300 K Li_xTiS_2 $(0 < x < 1)$ is stage 1′ at all x,[14] a situation which obtains in graphite only above 1150 K if at all. Since the main features of the simple model appear to be borne out by our results, one is tempted to reconcile this discrepancy in the simplest terms possible. For example, an attractive guest-host interaction, stronger for graphite than for TiS_2, could be incorporated into U_0 as an indirect contribution to the Li-Li in-plane attraction.[15] On the other hand, the sharp peak in our phase diagram could be unique to graphite, in which case the T_c scales for Li_xTiS_2 and Li_xC_6 may differ by less than a factor of 2. Similar low-T experiments on Li_xTiS_2 would clearly be of great interest.

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[15]This would also imply a short-range indirect (host-mediated) interlayer attraction competing with the long-range repulsion which stabilizes pure stages. We suggested an interlayer attraction in Ref. 7 to explain the unusual $\alpha AA\,\alpha AA$ stacking sequence of LiC_{12}.