PHYSICAL REVIEW B VOLUME 30, NUMBER 12 15 DECEMBER 1984

Theoretical phase diagram for Li-intercalated graphite

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(Received 18 June 1984)

A mean-field model for the phase diagram of Li-intercalated graphite is presented. Recent observations indicate that different Li graphite compounds occur with the same stage but with different, nearly commensurate in-plane Li densities. This phenomenon, which is a consequence of the corrugation potential of the host graphite lattice, is accounted for approximately in the present model by a small modification of the effective in-plane alkali-alkali potential. The resulting calculated phase diagram agrees well with experiment. The stability of the dilute stage-two phase is identified as a consequence of the high entropy of the compound. The dense stage-two compound has low entropy and decomposes at much lower temperature. A comparison of the present model with previous models is given, and the extension to other alkali-metal compounds is considered.

Recent work has shown that as thermodynamic conditions (temperature, pressure, chemical potential) are varied, different graphite intercalation compounds can occur with the same stage[1] but with distinct in-plane structures. As a consequence, staging transformations, which involve a change in the intercalant ordering normal to the host graphite planes, are frequently accompanied by modifications of the in-plane structure of the intercalant layers. This was originally shown for the compound KC_{24}, which undergoes[2] a transformation under pressure from a stage-two compound with a dilute, disordered in-plane structure to a stage-three compound with dense commensurate 2×2 K layers. Since then a variety of transformations under pressure involving a simultaneous change of stage and in-plane density have been reported.[3–5] In every case, it is found that the in-plane density never varies continuously, but is observed to change by discrete jumps. In some cases these in-plane structures are ordered, in others disordered, but usually the in-plane concentration is observed to be near a commensurate value. Recently such a transformation involving a change of both stage and in-plane density has been seen as a function of temperature at ambient pressure in Li-intercalated graphite.[4,5] This work provides the first reasonably complete experimental picture of the concentration-temperature phase diagram of a graphite intercalation compound; this phase diagram is reproduced[5] as Fig. 1. (Measurements of a similar sort have appeared recently for K-intercalated graphite.[6]) As expected from earlier theory,[7–9] this phase diagram displays a complete sequence of integral stages at low temperature, as well as a universal transformation at high temperature to stage one for any concentration. While many theories have been advanced by now to explain such observations,[10–13] none of them have predicted a phase diagram with the behavior displayed by Fig. 1. Particularly lacking is an explanation for the two distinct forms of stage two, dense (2′ in the figure) and dilute (2) (Ref. 14). In this paper we present a very simple modification of existing theories that incorporates the physical effects of the host corrugation potential, which tends to favor commensurate intercalant concentrations. This modified theory predicts a phase diagram which is in reasonable quantitative agreement with Fig. 1 and provides a simple physical explanation for the general form of the stage-two region of the phase diagram. The

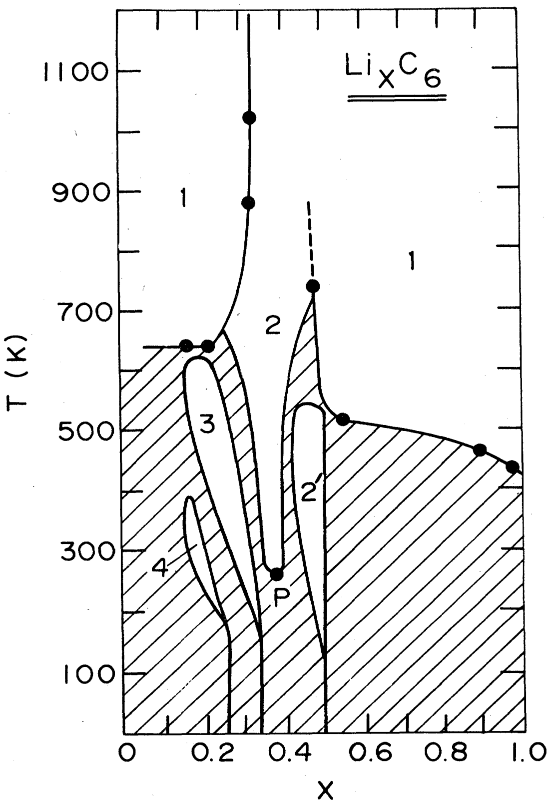

FIG. 1. The experimentally determined concentration-temperature phase diagram for Li-intercalated graphite (Ref. 4). 2 denotes a dilute stage two, 2′ a dense stage 2.

model also provides an explanation of the driving force for the occurrence of simultaneous changes of stage and in-plane density.

Safran[7] has proposed the model which is the basis of most subsequent theoretical work on the phase diagram of graphite intercalation compounds, including the theory presented here. It is a mean-field description in terms of σ_i, the average concentration of intercalant in layer i. He showed that stable staging resulted if the energy were assumed to have the form

$$E[\sigma_i]=\sum_i U[\sigma_i]+\tfrac{1}{2}\sum_{i,j} V_{ij}\sigma_i\sigma_j , \tag{1a}$$

$$U[\sigma]=-U_0\sigma^2 , \tag{1b}$$

with attractive in-plane interactions ($U_0>0$) and repulsive out-of-plane interactions ($V_{ij}>0$). In this equation the sums run over the intercalant layers i and j, and the in-plane density is constrained to lie between 0 (no intercalants) and 1 (the saturation value). The results of a Thomas-Fermi screening study[15] indicate that the out-of-plane interaction V_{ij} should have a long-ranged, power-law form

$$V_{ij}=V_0\frac{1}{|i-j|^{\alpha}} ,\quad \alpha=4 . \tag{2}$$

The phase diagram in Safran's model is constructed using a mean-field free-energy expression:

$$F=\sum_i E[\sigma_i]-\mu\sum_i \sigma_i-TS , \tag{3a}$$

$$S=-k\sum_i[(1-\sigma_i)\ln(1-\sigma_i)+\sigma_i\ln\sigma_i] . \tag{3b}$$

Here T is temperature, μ is the intercalant chemical potential, and k is the Boltzmann constant. The entropy S is approximated by the entropy of a non-interacting lattice gas, i.e., k times the logarithm of the number of ways that $\sigma_i \times N$ particles can be distributed over N lattice sites, divided by N. Attempts to go beyond this mean-field theory and include more realistic fluctuation and interaction effects have only just begun;[16] however, a previous comparison of mean-field theory with experiment in the (p,T) plane for Li graphite[4] indicates that Eq. (3b) actually gives a reasonably accurate value for the entropy of the intercalated system.

The concentration-temperature (x-T) phase diagram predicted by the model of Eqs. (1)—(3) has many of the general features of the experimental phase diagram, Fig. 1. The model gives a complete sequence of integral stages (as well as fractional stages[17]) at zero temperature, and with simple entropic arguments it accounts for the observation that all stages transform to disordered stage one at high temperature. It also correctly predicts that among the higher stage compounds ($n>1$), stage two is the most stable and undergoes the transformation to stage one at the highest temperature, although the predicted difference between the stage-two and stage-three transformation temperatures is smaller than in the experiment. The Safran model also possesses an artificial symmetry between σ and $1-\sigma$; if all σ_i are replaced by $1-\sigma_i$ and μ is replaced by $\mu+2U_0-\sum_j V_{0j}$, then the free energy remains invariant up to a trivial constant. This implies that the upper boundary of the phase diagram (below the stage-one region) is symmetric about $x=0.5$ in the Safran model.

The real system clearly does not possess this symmetry. Theoretical studies which followed Safran focused on removing this artificial symmetry by the inclusion of various additional terms in the free energy. These include C-plane—C-plane elastic interactions in various forms,[10,11] and in-plane potentials $U[\sigma]$ which depend on the thickness of the carbon-intercalant-carbon sandwich.[12,13] Other theoretical efforts[9] have focused on the removal of fractional stages from the phase diagram by the use of the "strong screening" approximation in which V_{ij} is cut off at nearest neighbor. (However, fractional stages have recently been observed experimentally at high pressure.[3]) A wide range of parameters has been studied, and many model phase diagrams have been produced. However, for the most part these were done before the availability of comprehensive data such as that presented in Fig. 1. While some of the published phase diagrams bear some resemblance to Fig. 1, none of them predict the crucial

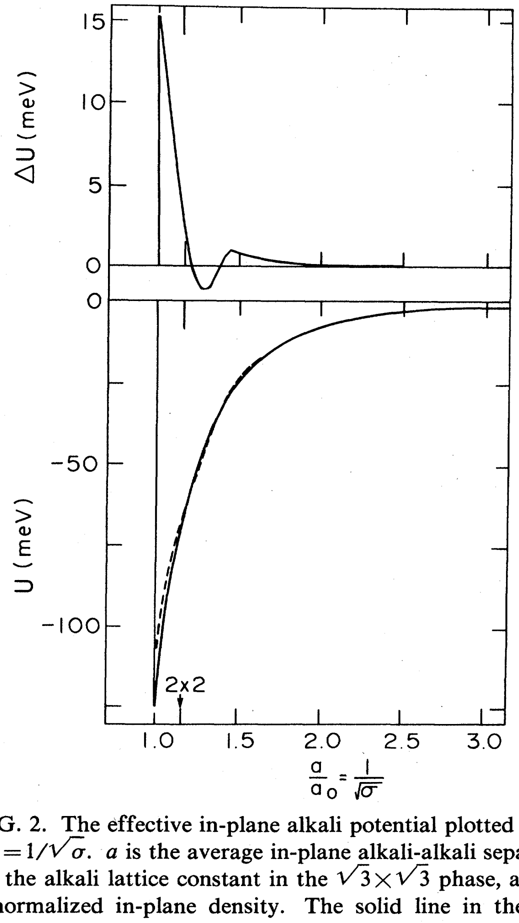

FIG. 2. The effective in-plane alkali potential plotted against $a/a_0=1/\sqrt{\sigma}$. a is the average in-plane alkali-alkali separation, a_0 is the alkali lattice constant in the $\sqrt{3}\times\sqrt{3}$ phase, and σ is the normalized in-plane density. The solid line in the lower panel is $U[\sigma]$ in the original model proposed by Safran (Refs. 6 and 7) and the dashed line is the modified $U[\sigma]$ used here [Eq.(4)]. The difference between them, ΔU (shown in the upper panel), is quite small. The important feature of ΔU is the pronounced dip near the 2×2 lattice separation (arrow).

feature of the occurrence of two distinct stage-two compounds with different in-plane densities. It would seem that the additional terms which have been added previously to the Safran free energy do not contain the physics of this aspect of the stage-two region of the Li graphite phase diagram.

We believe that these two different stage-two Li graphite compounds with different in-plane densities occur because of the strong corrugation energy felt by Li ions in the graphite host.[18,19] By "the corrugation energy" we mean the difference in energy between a Li atom sitting above the center of a carbon hexagon (the preferred position) and over a C—C bond. Our calculations indicate that this energy is in the neighborhood of 1 eV for Li, but only ≈ 0.1 eV for the heavy alkali-metal compounds.[18–20] As discussed in Ref. 19, corrugations in the Li compound are much stronger because of the smaller lattice constant in Li graphite as compared with the heavier alkali-metal compounds. Commensurate states, for which all of the intercalant atoms are able to sit at hexagon centers, are favored (at least locally) by a large corrugation energy. For stage-two Li graphite, it is clear that this causes the commensurate $\sqrt{3}\times\sqrt{3}$ concentration to be favored, resulting in the dense 2′ phase. We suggest that this strong corrugation energy also causes there to be a second favored concentration in the vicinity of the commensurate 2×2 layer concentration, leading to the dilute 2 phase. Although the layers in the 2 compound are observed to be disordered, the average separation between the Li atoms is in the right neighborhood to permit a *local* 2×2 commensurability between the intercalant and the host.

It is clear that a correct treatment of this idea within statistical mechanics would need to go beyond the mean-field model described above, perhaps to a lattice-gas,[21] renormalization group,[22] or Landau-Ginzburg-Wilson[16] approach. Still, there is an approximate way to incorporate the effect of different preferred commensurate concentrations into the Safran model: we propose modifying the effective in-plane potential $U[\sigma]$, which in its original form [Eq. (1b)] favors only the saturated in-plane density $\sigma=1$, so that an intermediate in-plane density σ_0 is also favored. Our modified $U[\sigma]$ is shown in Fig. 2, which illustrates the original Safran form of $U[\sigma]$ (plotted as a function of the interparticle separation a, normalized to the $\sqrt{3}\times\sqrt{3}$ separation a_0) and the modified form (dotted line) which we use to obtain the theoretical phase diagram discussed below. The differences between them appear to be quite small; however, these small modifications result in physically important modifications of the phase diagram. As the difference curve ΔU shows, the primary modification which we have introduced is a small drop near the 2×2 commensurate concentration, which causes the new $U[\sigma]$ to have a small concave-up region in this concentration range.

The actual functional form which we have used to generate the curve of Fig. 2 is

$$U[\sigma]=-U_0\sigma_i^2+E_0\left[\frac{1}{e^{-(\sigma-\sigma_0)/\alpha}+1}-\frac{(\sigma-\sigma_0+3\beta)^2}{2\beta^2}\Theta(\sigma-\sigma_0+3\beta)e^{-(\sigma-\sigma_0+3\beta)/\alpha}\right]. \tag{4}$$

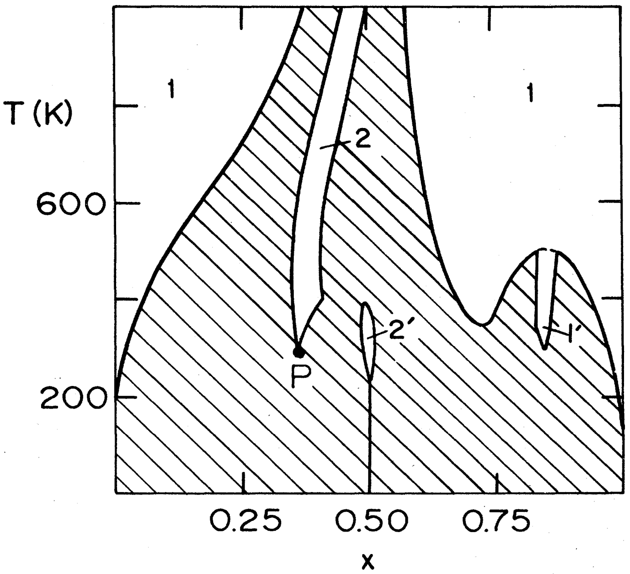

FIG. 3. The concentration-temperature phase diagram as determined theoretically by the present model. Note the overall agreement with Fig. 1, especially with respect to the general behavior of the 2 and 2′ phases.

Here $\Theta(x)$ is the step function: $\Theta(x)=1$, $x>0$; $\Theta(x)=0$, $x<0$. We retain in the first term the original σ^2 form of the Safran model. The second term is chosen to provide a depression in ΔU at a chosen concentration (σ_0) with a chosen width (α) and depth (E_0) with some freedom in the shape of the depression (β). No significance should be attached to the arbitrary functional form used for ΔU in Eq. (4). It is purely phenomenological, and no attempt has been made to derive it from more fundamental energy calculations. Still, with the choice of parameters $\alpha=0.11$, $\beta=0.11$, $V_0=0.02$ eV, $E_0=0.02$ eV, $U_0=0.125$ eV, and $\sigma_0=0.8$ we obtain a temperature-concentration phase diagram (Fig. 3) which is in reasonable quantitative agreement with experiment, Fig. 1. This diagram is computed by a numerical search for the absolute minimum of the free energy F [Eq. (3a)] in the space of σ_i's with the restriction $0<\sigma_i^{\min}<1$. This minimization is performed separately for each of a finely spaced set of values of chemical potential μ and temperature T. Since we have searched only for stage-one and -two phases, the searching space is two dimensional. The results are plotted in the plane T, $x\equiv(1/n)\sum_i\sigma_i^{\min}$, where n is the stage. (Note that our numerical approach is distinct from that of most previous authors, who proceed by solving the non-linear equations $\partial F/\partial\sigma_i=0$ by iteration.) Except for the modification to $U[\sigma]$ in Eq. (4), we have used the original free-energy expression of Safran, without any of the terms which have been added by other workers (strong screening, elastic interaction, sandwich-thickness dependent $U[\sigma]$). Still, like the experiment our model displays the skewing of the upper phase boundary to low values of x and the especially high stability of stage two relative to the other stages. The overall temperature scale in our model is also in reasonable agreement with experiment.

The point of particular interest is that we correctly predict the presence and general behavior of the two distinct stage-two phases. Their overall structure actually has a simple explanation within the present model. The high in-plane entropy of the dilute, disordered 2 phase causes it to remain stable up to very high temperature, up to and beyond the 750-K decomposition point. Conversely, the 2′ phase, being fully ordered, has low entropy; it therefore decomposes at rather low temperature ($\approx$400—500 K in both theory and experiment) into a mixture of high-entropy phases 2 and disordered stage 1. Another important feature of the phase diagram is that although the low-entropy phase 2 is (and must be) stable down to $T=0$ K, the high-entropy 2′ phase has a lowest point of stability (denoted P in Figs. 1 and 3) at $T_P\approx250$ K (Ref. 23). Below this temperature, the 2 phase is observed[5] to decompose into a mixture of low-entropy phases 2′ and dense stage 3. The point P has been studied in detail for Li graphite in an earlier publication,[4] where it was shown that the linear increase of T_P with applied pressure provides the most direct check to date of the validity of the mean-field entropy approximation of Eq. (3). In the present work, we find that were it not for the finite entropy of the 2 phase, T_P would be required to be equal to 0 K. Even for a finite-entropy phase it is possible to drive T_P to zero by a modification of the parameters in $U[\sigma]$ (an increase of E_0 or a decrease of α or β); this apparently happens in the K, Rb, and Cs compounds, in which the dilute stage-two phases are stable down to at least 90 K, and possibly down to absolute zero.[24] Another difference between the heavy alkali-metal compounds and the Li compound is that in the former a 2′ phase does not seem to occur at all at zero pressure, although it has been seen at elevated pressure.[4]

Of course, the model we have described here does not correctly describe all of the features of the Li graphite phase diagram. The small region denoted 1′ in Fig. 3 corresponds to a phase consisting of alternating dense ($\sigma_i\approx0.75$) and dilute ($\sigma_i\approx1.00$) layers. This is not seen experimentally, and it is likely to be simply an artifact of our model, which does not include any mismatch penalties (which must surely exist in nature) for neighboring layers of different periodicities. A more general criticism which has been raised is that while the model we use assumes thermodynamic equilibrium, the experimental observations may be of kinetically limited, metastable states because of the very long atomic relaxation times in the graphite intercalation compounds.[20,25] In the experiments shown in Fig. 1 (Refs. 4 and 5) considerable care was taken to equilibrate the samples. However, the possibility that the experiments are kinetically limited still exists in the Li graphite system and seems a certainty in measurements on other graphite intercalation compounds.[25,26] A greater theoretical effort directed at the non-equilibrium aspects of these phenomena would seem to be in order.

To conclude, we have constructed a modified mean-field model for phase transformations in graphite intercalation compounds. This model accounts for the observation that staging transformations are frequently accompanied by changes of in-plane density. We have been guided by the observation that the corrugation potential of the graphite host causes certain *discrete* in-plane densities (those which are commensurate) to occur. We have constructed a phenomenological model in which these discrete densities are favored. Our model thus differs from previous theories constructed to explain changes of in-plane density under pressure,[12,13] which assume that a *continuous* range of in-plane densities is permitted. Our model provides a realistic description of the experimental (x,T) phase diagram for Li graphite. In particular, it correctly predicts the presence of two distinct stage-two compounds: a dilute, disordered, high-entropy phase which is stable up to very high temperature but not down to absolute zero, and a dense, ordered, low-entropy phase which is stable at $T=0$ but which decomposes into high-entropy phases at relatively low temperature. Other contributions to the mean-field model which have been suggested by previous workers (strong screening, elastic effects) are undoubtedly important in a comprehensive description of the intercalate phase diagram, but they apparently are not relevant for a correct description of the 2 and 2′ phases in Li graphite.

We thank Professor E. J. Mele for many useful discussions, and we are particularly grateful for Professor J. E. Fischer's careful reading of this manuscript. Most of the work described here was performed at the University of Pennsylvania, where it was supported by the National Science Foundation—Materials Research Laboratory Program under Grant No. DMR-82-16718.

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