

Origin of simple staging in graphite intercalation compounds

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We present a simple model of staging in graphite intercalation compounds. Unlike previous theoretical studies, finite- T calculations based on our model yield the staged structures which are observed experimentally. Certain choices of model parameters result in more complex structures such as those predicted recently by Safran. The model provides physical guidelines for identifying materials in which the latter structures may be realized. Rich and varied phase diagrams are predicted.

It has been known for many years that when other chemical species are intercalated between the layers of carbon atoms forming a graphite crystal, staged structures are formed. These are periodic arrangements of graphite and intercalant layers in which the period consists of one layer of intercalant followed by n layers of graphite. We will refer to these structures as *simple stages*. Current theoretical work^{1,2} suggests that staging occurs because of electrostatic repulsion between different intercalant layers. Recently, Safran² showed that, assuming such an interlayer repulsion and an intralayer attraction between intercalant atoms, the intercalant layers can form periodic structures. However, instead of the simple stages which have been observed experimentally, the finite temperature calculations predicted more complex structures.³ The question why only the simple stages have been observed in nature remains unresolved. Moreover, many of even the most basic features of the phase diagrams associated with staging have yet to be determined either experimentally or theoretically.

In this Communication we show how the difficulties encountered by the previous theoretical studies of staging can be overcome in a simple and intuitively appealing way. Our calculations yield the observed simple staging for a wide variety of intercalants including the alkali metals and aromatic molecules. We

also suggest possible candidates for more complex staged structures. A rich variety of phase diagrams depending on the host and intercalant species may be expected for the latter class of systems.

Our model of graphite intercalation compounds is a generalization of that of Safran.² The intercalant is represented by a lattice gas with N_0 allowed sites per intercalant layer and an intralayer interaction energy $-\epsilon$ between occupied nearest-neighbor intercalant sites. The interaction energy between an occupied intercalant site and the adjacent graphite layers is $-\delta$. It is also assumed that an energy γ per intercalant site must be supplied to separate the adjacent graphite layers in order to admit the intercalant. We consider the graphite layers to be completely rigid⁴ so that for a partly occupied intercalant layer this separation energy equals $N_0\gamma$, independent of the fraction of intercalant sites which are occupied. Following Safran and Hamann,^{1,2} we assume a power-law repulsion $V_{ij} = V_0|x_{ij}|^{-\alpha}\eta_{ij}$ between intercalant layers i and j , where x_{ij} is the separation between layers i and j . We consider both "infinite range" potentials² where $\eta_{ij} = 1$ for all i and j , and "strongly screened" potentials where $\eta_{ij} = 1$ if there is no occupied intercalant layer between i and j and $\eta_{ij} = 0$ otherwise.

In the Bragg-Williams approximation⁵ the energy of the system is

$$E(\{N_i\}) = \sum_i (-\epsilon z N_i^2 / 2N_0 - \delta N_i + \theta_i \gamma N_0) + \sum_{i < j} V_{ij} N_i N_j / N_0,$$

where N_i is the number of occupied sites in layer i , and z is the in-plane coordination number; $\theta_i = 0$ if $N_i = 0$, $\theta_i = 1$ if $N_i \neq 0$. For a given configuration $\{N_i\}$ the free energy obtained from the grand canonical partition function is then

$$\phi = E(\{N_i\}) - \mu \sum_i N_i - kT \sum_i [N_0 \ln N_0 - N_i \ln N_i - (N_0 - N_i) \ln (N_0 - N_i)].$$

In the present work our main objective was to investigate the nature and stability of the low period structures at finite temperatures. Thus in deciding which structure minimizes the free energy for given μ and T we examined all possible structures in which the period consists of 1, 2, or 3 intercalant layers,

which can be either partly or completely filled, or empty. For periods of four and five layers, selected structures corresponding to self-consistent solutions to the minimization problem were examined. For periods ≥ 6 we considered only simple staging.

While a detailed identification between specific

values of the parameters entering the model and individual intercalation compounds is difficult, certain broad trends are apparent. For example, in graphite intercalation compounds the in-plane interaction ϵ can range from being strongly attractive for transition-metal chloride intercalants, to being weak and perhaps even repulsive for alkali metals and aromatic molecules. Similarly, γ and δ depend on the host and intercalant species.⁶ Notice that δ can be absorbed into the chemical potential in the free energy ϕ so that while it has a role in determining the values of the chemical potential at which the various stages are stable it does not influence the density-temperature phase diagrams which we present here. The electrostatic parameters V_{ij} should be sensitive to the amount of charge transfer per intercalant site. However, it is reasonable that V_{ij} should be less than γ for reasons of stability.

In describing the structures which we found, we will use the term "stage (n/m) compound" to mean a periodic structure in which the period consists of n graphite layers and m partly filled intercalant layers. Stage ($n/1$) = stage (n) will then refer to the simple stages which have been observed experimentally. By a stage (n/m)* compound we will mean a period n structure in which all n intercalant layers are occupied but the intercalant density in $n-m$ of the layers is markedly smaller than in the others at the lower temperatures.

In the limiting case $\gamma = 0$ our model reduces to that of Safran.² We shall begin the discussion of our results by considering this limit. In Fig. 1(a) we show the phase diagram for $\gamma = 0$ and "infinite range" repulsive interlayer interactions. In this case all of the stage (n/m)* structures with $n > m$ occur in the phase diagram. For example, the period-5 structures ($5/1$)*, ($5/2$)*, ($5/3$)*, and ($5/4$)* are all found. However, the experimentally observed simple staging does not appear at all at finite temperatures, except for stage 1. Safran and Hamann have argued that because of electrostatic screening such an infinite range potential may not be appropriate.¹ In fact, for equally occupied intercalant planes they found that the repulsion is negligible beyond the nearest-neighbor occupied intercalant layers. In order to study the effect which such a cutoff could have on the phase diagram we considered the "strongly screened" potential described above. Our results for $\gamma = 0$ are shown in Fig. 1(b). Simple staging is found at $T = 0$, but only stages (1) and (2)* are stable for finite T . The results in Fig. 1 are for the repulsive potentials $V_{ij} = (\frac{1}{6})z\epsilon|x_{ij}|^{-5}\eta_{ij}$ where x_{ij} is measured in units of the c -axis spacing of graphite. The qualitative behavior shown is not sensitive to the exponent or to the magnitude of the prefactor. Presumably, for unequally filled intercalant layers a situation in between the strong screening and infinite-range-potential limits is realized. However, in view of the above results

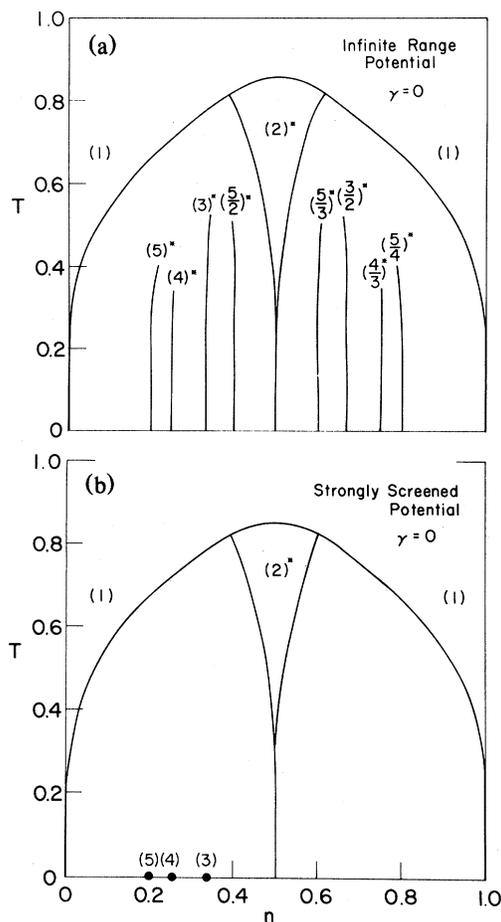


FIG. 1. Temperature-density phase diagrams for $\gamma = 0$. T in units of ϵ/k ; n is the filling coefficient relative to complete filling of all of the intercalant sites. $n = \sum_i N_i / \sum_i N_0$. The areas labeled stages (1) and (2)* and the lines labeled (n/m)* (which represent narrow areas) are single-phase regions. Only phases with period ≤ 5 are shown.

it seems very unlikely that an improved repulsive potential V_{ij} would by itself be capable of explaining the simple staging observed experimentally at finite T .

In real systems, however, γ can never actually be zero, and as noted above, for many intercalants the in-plane interaction is so weak that γ can be comparable with $z\epsilon$. For example, consider the case of graphite-cesium. For this material, Salzano and Aronson measured the energy required to separate the graphite planes to be 1.23 kcal/mole of carbon, in good agreement with estimates of the interlayer bonding energy of graphite.⁶ For the compounds $C_{8n}Cs$ this yields $\gamma = 9.84$ kcal/mole of intercalant. ϵ is more difficult to estimate, but we note that the cohesive energy of pristine cesium (18.8 kcal/mole) should be larger than $\frac{1}{2}z\epsilon$ (the in-plane interaction energy between Cs atoms in the intercalate) because

of the charge transfer which reduces the screening between the positive Cs ions in the intercalate compared with the metal. This yields $z\epsilon/\gamma < 4$.

The effect of such large values of γ on the phase diagram is dramatic: In Fig. 2 we show the case $\gamma = z\epsilon$; the values of the other parameters are as in Fig. 1. Again we consider both infinite range and strongly screened potentials. In both cases we found that the in-plane densities of all of the *occupied* intercalant layers are approximately equal (within 3%) so that there are no $(n/m)^*$ structures, in contrast with the $\gamma = 0$ limit. Given this, the premise of Safran and Hamann¹ about equal filling of the occupied intercalant layers should apply so that the strongly screened potential is the appropriate one to use for real systems in this situation. Thus it is especially gratifying that our phase diagram for the strong screening case consists entirely of *simple* stages at all temperatures! It should also be noted that all of the

predicted phase transitions in Fig. 2 are first order. Again the qualitative aspects of the phase diagram are not sensitive to the values of the parameters used. For infinite-range-potentials the phase diagram contains all of the simple stages, but all other (n/m) structures occur as well. For $z\epsilon/\gamma = 4$ (our upper bound for Cs graphite), the phase diagrams obtained are similar to those in Fig. 2.

For some intercalants such as the transition-metal chlorides, the in-plane attraction ϵ can be quite strong and $z\epsilon/\gamma$ is expected to be large. At sufficiently large values of $z\epsilon/\gamma$ there is a crossover between the radically different phase diagram topologies represented in Figs. 1 and 2. In this crossover regime we find a profusion of dissimilar phase diagrams with intricate topologies which depend sensitively on the parameters entering the model. A survey of these phase diagrams will be presented elsewhere. In Fig. 3 we show just one such intermediate

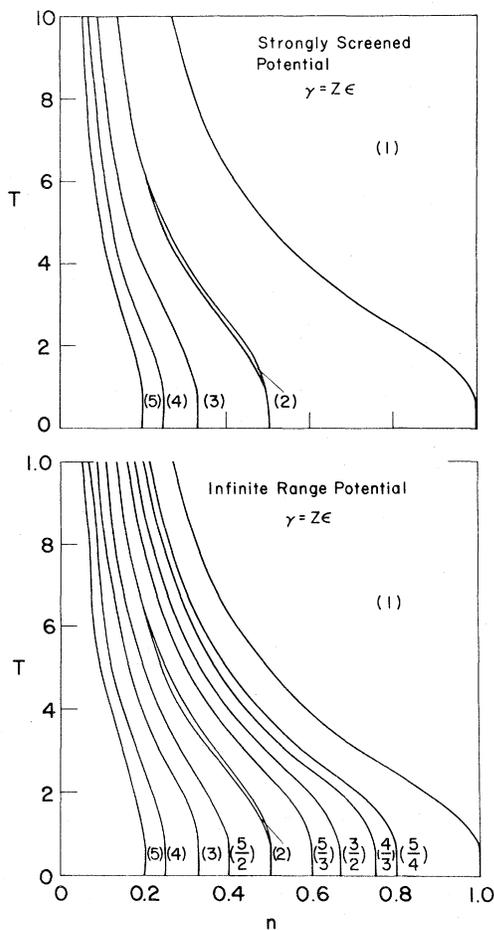


FIG. 2. Temperature-density phase diagrams for $\gamma = z\epsilon$. Notation as in Fig. 1. The area labeled stage (1), the narrow loop labeled stage (2), and the lines (n/m) are single-phase regions.

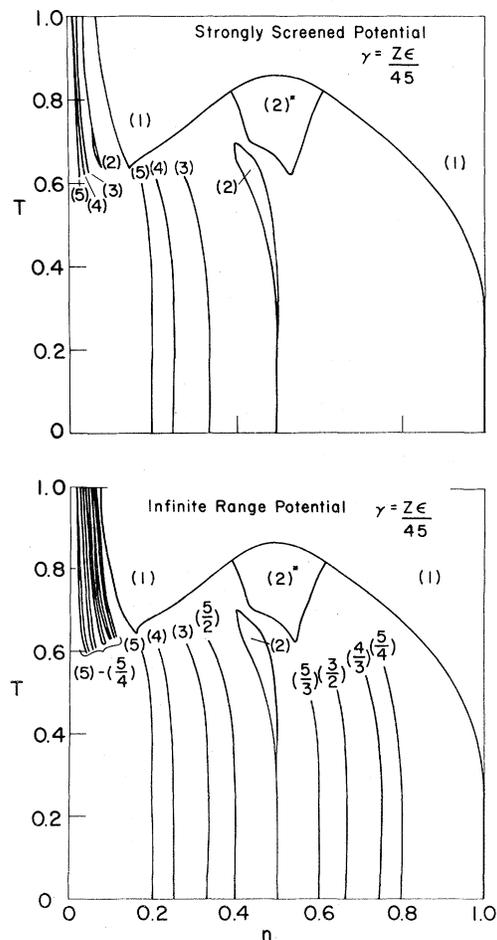


FIG. 3. Temperature-density phase diagrams for $\gamma = z\epsilon/45$. Notation as in Figs. 1 and 2. The lines in upper left corners represent low-density staged phases.

situation corresponding to $z\epsilon/\gamma = 45$, the other parameters being chosen as in Figs. 1 and 2. Perhaps the most striking new feature of Fig. 3 is the occurrence of a high-density stage (2), a low-density stage (2), and a stage-(2)* phase at the same temperature in different parts of the phase diagram. In fact, it is possible for the stage-(2) and stage-(2)* phases to coexist in equilibrium with each other. This behavior is found both for the strongly screened and the infinite-range interlayer interactions. On the basis of the calculated in-plane densities, we expect that the strongly screened potential should still be a better approximation than the infinite-range potential under these conditions. Thus even for such a large value of $z\epsilon/\gamma$ the simple stages predominate in the phase diagram, although some more complex structures, namely, stage (2)*, are beginning to appear.

In conclusion, we have shown that the separation energy γ plays a decisive role in the physics of the

staging process and is crucial for the formation of the simple stages which are observed in nature. This quantity has no analog in the modulated magnetic structures (e.g., CeSb)⁷ which have been the subject of considerable recent theoretical interest⁸ and have served as a model for previous theoretical studies of the staging phenomenon.

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¹S. A. Safran and D. R. Hamann, *Phys. Rev. B* **23**, 565 (1981); **22**, 606 (1980).

²S. A. Safran, *Phys. Rev. Lett.* **44**, 937 (1980).

³An improved calculation including elastic effects yielded similar complex structures. See J. R. Dahn, D. C. Dahn, and R. R. Haering, *Solid State Commun.*, **42**, 179 (1982).

⁴We expect this rigidity assumption to be good except at very low in-plane intercalant densities or in the presence of gross inhomogeneities such as intercalant islands.

⁵The appropriateness of using a mean-field approximation to treat the in-plane interactions in the theory of staging has been discussed by Safran (Ref. 2).

⁶Some idea of the relative strengths of the interactions involved in ϵ , γ , and δ may be obtained by comparing the

corresponding force constants used to fit phonon spectra to lattice-dynamics calculations. See A. Magerl and H. Zabel, *Phys. Rev. Lett.* **46**, 444 (1981); and G. Dresselhaus, R. Al-Jishi, J. D. Axe, C. F. Majkrzak, L. Passell, and S. K. Satija, *Solid State Commun.* **40**, 229 (1981). More direct values for some of the parameters can be obtained from thermodynamic data. See F. J. Salzano and S. Aronson, *J. Chem. Phys.* **44**, 4320 (1966).

⁷J. Rossat Mignod, P. Burlet, J. Villain, H. Bartholin, Wang Tseng-Si, D. Florence, and O. Vogt, *Phys. Rev. B* **16**, 440 (1977).

⁸See P. Bak, *Phys. Rev. Lett.* **46**, 791 (1981), and references therein.