PHYSICAL REVIEW B VOLUME 31, NUMBER 8 15 APRIL 1985

Domain model of stage order and disorder in intercalation compounds

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(Received 30 November 1984)

A theoretical model of staging is presented which takes account of the domain structure of intercalation compounds. The model is able to treat stage order and disorder in a unified way. The staging phase transitions in which the stage index of the intercalation compound changes are predicted to proceed via stage-disordered states. If the domains are finite and can be considered to be independent, then the staging transitions are predicted to be continuous. The model is applied to the case of typical donor and acceptor graphite intercalation compounds. Other systems are also discussed. A model-independent scaling rule is proposed relating stage disorder to domain size, stage, temperature, in-plane density, and charge transfer, and a fundamental limit is set on the period of well-staged structures. The relationship between the present model and previous theories of staging is discussed. The implications of recent staging experiments are also considered.

I. INTRODUCTION

When a quest species is intercalated into a layered host material such as graphite, the resulting sequence of quest and host layers can be ordered[1] or disordered.[1-12] The period of the ordered structures consists of a layer of the guest species followed by n layers of host for a stage-n compound. The ordered structures have been extensively studied experimentally[1] and, in the past few years, following the pioneering work of Safran[13] and of Safran and Hamann,[14] theoretical models[10,13-17] of them have been developed. However, none of the theoretical models has been able to treat stage disorder, which has remained a poorly understood, although frequently observed, phenomenon. Some interesting unresolved questions are the following: What is the basic physics governing stage disorder? Should stage order-disorder phase transitions occur, and, if so, what should they be like? Does stage disorder play an important role in the staging phase transitions in which the stage index n of an intercalation compound changes? It is the purpose of this article to formulate a single theory describing both stage order and stage disorder and to address the above questions.[18]

A basic assumption which is implicit in the previous theoretical models of staging[10,13-17] is that the intercalate layers in the intercalation compound are continuous over macroscopic distances, occupying the entire galleries between selected pairs of host layers. However, there is persuasive experimental evidence that this is not the case in reality, and that, in fact, the intercalate between a pair of host layers is divided into separate islands. The most often quoted island size is of the order of 100 Å, but very much larger (up to 10 000 Å) and smaller islands have also been reported.[4,19-24] Physically, it is reasonable that the intercalants between a pair of host layers should cluster into islands, since, as has been shown by Safran and Hamann,[25] and by Ohnishi and Sugano,[26] the elastic deformation of the host by the guest atoms leads to a long-ranged attractive effective in-plane interaction between the intercalants. On the other hand, Kirczenow[27] and Hawrylak and Subbaswamy[28] have shown that the shorter-ranged elastic interactions between intercalant islands are such as to tend to stabilize the islands between a pair of host layers against agglomeration into a continuous intercalant layer, at least for small intercalant species. Much of the work on islands in intercalation compounds was stimulated by a suggestion by Daumas and Hérold[29] that islands should play a central role in the kinetics of intercalation and of the staging phase transitions.

In the model put forward by Daumas and Hérold,[29] the intercalation compound consists of microscopic domains, such that within any domain the intercalate layers are continuous and, together with the host layers, form a well-ordered (staged) sequence, but in adjacent domains the intercalate layers lie between different pairs of host layers. Thus a macroscopic intercalated crystal can be stage n almost everywhere, and, at the same time, globally there can be equal numbers of intercalants between every neighboring pair of host layers. This makes it possible for a phase transition in which the stage index changes to occur by the movement of microscopic islands of intercalant atoms between adjacent domains, without the need to empty of intercalate entire galleries between pairs of host layers throughout the crystal and to fill others. The consequences for staging kinetics are quite dramatic, and the Daumas-Hérold model is widely accepted as the only reasonable explanation for the results of a broad range of experiments.[1,21,30-34] It should be noted, however, that there has been as yet no direct experimental observation of a Daumas-Hérold domain boundary.

In this paper, a mathematical model of staging based on the Daumas-Hérold view of intercalation is presented. It is shown that stage disorder is an inherent property of the Daumas-Hérold domain model, or indeed of any model in which the intercalants form into finite islands. The phase transitions in which the stage index changes are found to proceed via stage-disordered states, the width of the transition increasing with stage index.

An important consideration is that of domain size, i.e., of the in-plane dimensions of the intercalant islands. In the Daumas-Hérold model, the reason for the existence of the islands is not thermodynamic but rather a consequence of the layered topology of the host and of intercalation kinetics, i.e., the Daumas-Hérold domains, in common with domain structures observed experimentally in many other physical systems, are a *nonequilibrium* phenomenon. This view is supported by the fact that a very wide range of domain sizes is reported experimentally, the domain size apparently being determined more by sample preparation and history than by ambient conditions.[1,4,19–24] Thus it would be incorrect to calculate the domain size from considerations of equilibrium thermodynamics, and we shall instead take it to be a variable parameter in the theory, which is to be measured experimentally whenever the theory is to be compared with experiment.

In the present calculations the elastic interactions between the intercalant layers in different domains are neglected. Such an approximation can only be made if the neighboring domains contain similar overall amounts of intercalant so that there are no long-range elastic strains present. If it is assumed that domain-domain interactions can be neglected, it follows that the staging phase transitions in which the stage index changes are continuous for any finite domain size. This remains true if correlations between the intercalate layers in different domains are included approximately in the theory by replacing the domain size by any larger but still finite effective domain size which reflects these correlations. Since the domains themselves are nonequilibrium entities, it would seem doubtful that correlations between them could lead to an effective domain size very much larger than the actual domain size.

However, the problem of including domain-domain interactions properly in a theory of stage disorder is a very delicate one. For example, in a naive thermodynamic treatment these interactions would cause all of the domains to merge into a single domain as the sample is cooled to low temperatures. This behavior would be grossly unphysical since it would require intercalants to pass through various host layers, violating the topology of the system and the basic concepts underlying the Daumas-Hérold model. If one attempts to treat domain-domain interactions in a simple mean-field theory, for example, by assuming the domain-domain interaction energy to be just a function of the degree of stage disorder, it is easy to arrive at a prediction that the staging phase transitions should not be continuous but first order, with an abrupt jump in the properties of the system and in the distribution of staging packages which make up the stage-disordered state. Such a prediction, however, cannot be relied upon since mean-field theories do not always correctly predict the nature, or even the existence, of a phase transition, particularly for low dimensionalities. In the present case, the prediction of such a theory of domain-domain interactions is qualitatively the same whether there are only two finite interacting domains in the system or infinitely many. We know that the prediction of a first-order transition occurring for the case of only two finite domains interacting with each other is incorrect, since such a system is still, in fact, one-dimensional. Thus such arguments cannot supply definite answers about the nature of staging phase transitions.

More generally, it is difficult to devise a treatment containing domain-domain interactions which would include stage disorder, do justice to the nonequilibrium nature of the Daumas-Hérold domains, and, at the same time, be tractable.[35,36] However, if the domain size is assumed to be given, if the domains are considered to be at least metastable entities, and if domain-domain interactions can be neglected, then it seems reasonable to apply equilibrium thermodynamics to the problem of stage disorder within a domain. This view will be adopted here. Whether a good approximation to quasiequilibrium is attained in this sense in a given system can only be established experimentally, and the relevant experiments are only now beginning to be done. The limited experimental data which are currently available appear to be consistent with this theoretical approach.

II. THE MODEL AND FREE ENERGY

As was noted above, all of the previous theoretical treatments of staging were devised for the case of infinite Daumas-Hérold domains. The extension to the case of a finite domain is the simplest for the staging model proposed by Millman *et al.*[5] In that model, the energy of the system for a given configuration of intercalant layers $\{N_j\}$ is

$$E(\{N_j\}) = \sum_j (-\varepsilon z N_j^2/2N_0 - \delta N_j + \theta_j \gamma N_0) + \tfrac{1}{2} \sum_{\substack{i,j \\ i\neq j}} V_{ij} N_i N_j / N_0 \; . \tag{1}$$

In the present paper, $E(\{N_j\})$ will be the energy of a Daumas-Hérold domain. Then N_0 will be the number of lattice-gas sites available to intercalants in any gallery between a pair of host layers within the domain; it specifies the in-plane size of the domain. N_j is the number of intercalants present in gallery j in the domain. $-\varepsilon$ is the nearest-neighbor in-plane interaction energy between intercalants and z the in-plane coordination number. V_{ij} is the repulsive interaction between layers i and j which is responsible for staging.[13,14] δ represents the chemical interaction between the intercalant and the host. γ is the energy per lattice-gas site which is required to separate the host layers sufficiently to admit the intercalants.

Following Ref. 15, it will be assumed that (a) $V_{ij}=0$ if there is any occupied intercalant layer between layers i and j (the strong-screening assumption), and (b) that the host layers can be treated as if they were perfectly rigid *within any domain,* although, of course, the layers must bend at the domain boundary. The strong-screening assumption (a) is supported by the calculation of Safran and Hamann.[14] The idealization of perfect rigidity (b) means that $\theta_i=0$ if $N_i=0$, and that $\theta_i=1$ if $N_i>0$. The applicability of the idealization (b) has been checked theoretically[15] by relaxing it in a number of calculations using an improved phenomenological form of the energy suggested by Dahn *et al.*,[10] and it appears to be good for most graphite intercalation compounds, except at very high temperatures.[15] Departures from the idealization of perfect rigidity are characterized in the calculations by the appearance at high temperatures of intercalants in the nominally empty galleries in the staged intercalation compounds. That this has *not* been observed experimentally lends further support to the use of idealization (b).

Safran[13] and subsequent authors[10,15–17] took the free energy for configuration $\{N_j\}$ to be of the form

$$\phi(\{N_j\})=E(\{N_j\})-\mu\sum_j N_j -kT\sum_j[N_0\ln N_0-N_j\ln N_j -(N_0-N_j)\ln(N_0-N_j)]\ , \quad (2)$$

where the quantity δ in (1) is usually absorbed into the chemical potential μ in (2). The use of the simple Bragg-Williams form for the in-plane entropy in (2) is usually justified on the basis that, experimentally, stage ordering occurs in a wide variety of compounds and appears insensitive to the details of the in-plane order or lack thereof. The correctness of this point of view for the problem of stage disorder will be demonstrated explicitly in Sec. III. However, recently it has been argued by DiVincenzo *et al.*,[37] on the basis of a comparison between theory and experiment in the (p,T) plane for Li-graphite, that the above simple in-plane entropy may actually be a reasonably good approximation for some real systems.

Since in the previous calculations[10,13,15–17] only perfectly periodic structures were being considered (i.e., structures in which N_i is a periodic function of the layer i), the free energy $\phi(\{N_j\})$ was calculated for various such structures, and the structure $\{N_j\}$ which yielded the lowest value of $\phi(\{N_j\})$ for given μ and T was taken to be the equilibrium state for those conditions. Here we are interested in stage-disordered as well as stage-ordered states and such a procedure is not acceptable. The free energy Φ, which should be used to treat the more general problem, can be constructed from the restricted configurational free energies $\phi(\{N_j\})$ as follows.

Within the same approximations on the in-plane properties which yielded (1) and (2), the canonical partition function restricted to those microscopic states which occur in the configuration $\{N_j\}$ can be written as

$$Z(\{N_j\},T)=\exp\left[-\left[\phi(\{N_j\})+\mu\sum_j N_j\right]\Big/kT\right]\ . \quad (3)$$

We require the unrestricted grand-canonical partition function

$$Q(\mu,T)=\sum_{\{N_j\}}Z(\{N_j\},T)e^{\mu\sum_j N_j/kT} =\sum_{\{N_j\}}e^{-\phi(\{N_j\})/kT}\ , \quad (4)$$

where the sum is taken over all configurations of layers, both periodic and nonperiodic.

Let ν_i be the number of packages each consisting of i host layers sandwiched between a pair of intercalate layers in any configuration $\{N_j\}$. I will refer to such a sandwich with i host layers as "a stage-i unit." Then,

$$Q(\mu,T)=\sum_{\{\nu_i\}}\sum_{\{N_j\}}{}' e^{-\phi(\{N_j\})/kT}\ , \quad (5)$$

where the prime indicates that the sum over $\{N_j\}$ is now restricted to those configurations belonging to the distribution $\{\nu_i\}$ of packages being indexed in the first sum in (5). The equilibrium distribution $\{\nu_i\}$ is the one for which the term

$$\tilde{Q}(\{\nu_i\})=\sum_{\{N_j\}}{}' e^{-\phi(\{N_j\})/kT} \quad (6)$$

in the sum (5) is maximized. In evaluating the sum in (6) for the purpose of comparing its value for different distributions $\{\nu_i\}$, one can, as is usual in statistical mechanics, consider only the largest terms. In this case, this means finding, for each arrangement of *occupied* layers consistent with the distribution $\{\nu_i\}$, the values of the layer occupation numbers $\{\hat{N}_j\}$ which maximize $e^{-\phi(\{N_j\})/kT}$, and retaining only those maximal terms in the sum (6). In general, this is still a very difficult coupled problem to solve, since the most probable value of the number of intercalants $\hat{N}_j$ in a given layer j depends on the *locations* and *occupations* of its two neighboring layers via the interlayer repulsion term $\frac{1}{2}\sum_{ij}V_{ij}N_iN_j/N_0$ in the energy (1). The most probable occupations of these neighboring layers depend on their neighbors, etc.

The problem can be simplified considerably and solutions of the model obtained which are exact in a number of experimentally realizable limiting situations if one considers the case where the rigidity energy $\theta_j\gamma N_0$ in (1) is comparable in magnitude with the in-plane interaction energy $-\varepsilon z\hat{N}_j^2/2N_0$ and where the interlayer repulsion energy $V_{ij}\hat{N}_i\hat{N}_j/N_0$ is smaller. I will refer to this case as "the GIC case" since it appears to be characteristic of many graphite intercation compounds (GIC's).[15] Under these conditions, if the assumption of "strong screening" and the idealization of perfect rigidity are made, Millman *et al.*[15] showed that the periodic structures which are found to be stable in their (infinite-domain) model are the simple stages which are observed experimentally under normal conditions. They also found that the in-plane density depends rather weakly on stage at constant temperature. When, in the GIC case, the strong-screening condition was relaxed, and complex stages (where the period contains more than one intercalant layer) appeared in the phase diagram, the in-plane densities of the occupied inequivalent intercalant layers were found to differ from each other by only a few percent.[15]

Thus, in the GIC case, it would seem to be a good approximation to replace each nonzero N_j in (6) by an average value N characteristic of the distribution $\{\nu_i\}$. This is instead of using $\{\hat{N}_j\}$, where each $\hat{N}_j$ depends on the particular stacking of filled and empty layers being considered, as discussed above. If this "mean-field" approximation on the in-plane density is made, then the configurational free energy ϕ depends only on the distribution $\{\nu_i\}$ of staging packages and *not* on how these packages are arranged in the stack. The restricted free energy of the important configurations contributing to the sum (6) can then be written as

$$\phi(\{\hat{N}_j\})\simeq\phi(\{\nu_i\},N)$$
$$=\left[\sum_i \nu_i\right](-\varepsilon z N^2/2N_0+\gamma N_0-\mu N)+\sum_i u_i\nu_i N^2/N_0-kT\left[\sum_i \nu_i\right][N_0\ln N_0-N\ln N-(N_0-N)\ln(N_0-N)]\ , \tag{7}$$

where $u_i=V_{j,j+i}$, strong screening being assumed. Thus, in order to find the equilibrium distribution of stage-i units, $\{\nu_i\}$, and the filling N of an occupied intercalate layer, we must maximize the function

$$\frac{\left[\sum_i \nu_i\right]!}{\prod_i \nu_i!}e^{-\phi(\{\nu_i\},N)/kT}\ , \tag{8}$$

where the combinatorial prefactor is the number of different arrangements of staging units which can be made out of the distribution $\{\nu_i\}$. Equivalently, one can minimize the free energy

$$\Phi=\phi(\{\nu_i\},N)-kT\left[\left[\sum_i \nu_i\right]\ln\left[\sum_j \nu_j\right]-\sum_i(\nu_i\ln\nu_i)\right] \tag{9}$$

at constant μ and T with respect to the distribution $\{\nu_i\}$ and N, subject to the constraint that the number of host layers,

$$\nu_H=\sum_i i\nu_i\ , \tag{10}$$

is held constant.

It should be noted that the last term in (9) represents the entropy due to stage disorder, while the remaining term $\phi(\{\nu_i\},N)$ is essentially the same as the free energy of a particular configuration $\phi(\{N_j\})$.

While $\phi(\{\nu_i\},N)$ is proportional to the domain size N_0, the entropy due to stage disorder is independent of N_0, so that for very large domain sizes, stage disorder might, at first, appear to become negligible, justifying the earlier calculations in which stage disorder was ignored. This is true for low stages for most values of the chemical potential. It will be shown, however, that for any finite domain size N_0 and nonzero temperature, for a sufficiently high stage index n, stage disorder dominates. In addition, for any finite domain size, for those values of μ and T at which the phase transitions between the different stages occur, the system is also stage disordered.

As has already been mentioned, the approximation made above by replacing $\hat{N}_j$ by a single value N in all layers is expected to be a good one in the "GIC case." Indeed, it is *exact* in those situations in which the expectation value of the in-plane density $\hat{N}_j$ becomes the same in all occupied layers. One such case is the *low-temperature limit,* where the filling of every occupied intercalant layer tends to N_0, the maximum possible occupation of the layer allowed in the lattice-gas model. Another such case is *the high-stage limit,* where the occupied layers are very far apart, so that the interlayer repulsion energy is very small and the filling of every layer is determined almost entirely by the in-plane free energy. Another case is the *limit of high temperatures,* where the in-plane density is determined primarily by the in-plane entropy.

In those cases where the approximate free energy Φ is applicable (i.e., the in-plane density is the same in all intercalant layers), every stacking arrangement of the host and intercalant layers which is consistent with a given distribution $\{\nu_i\}$ has the same configurational free energy $\phi(\{N_j\})$. Therefore the arrangement of the various staging units in the disordered stack is predicted to be completely random. Where the approximation begins to break down, the stacking of the staging units will become correlated. Such correlations can be detected experimentally in x-ray- or neutron-scattering experiments and can thus provide a direct experimental check on the applicability of the approximation to any given experimental system.

Situations in which the approximate free energy Φ is inadequate are discussed in Sec. VI.

III. ANALYSIS OF THE FREE ENERGY: MODEL-INDEPENDENT SCALING RULE FOR STAGE DISORDER

For any given μ and T we would like to find the distribution $\{\nu_i\}$ of stage-i units in the intercalation domain and the filling N of the occupied guest layers which minimize the free energy Φ [Eq. (9)] subject to the physical constraint that the number of host layers $\nu_H=\sum_i i\nu_i$ is held fixed. The solution to this problem satisfies, for all i, the equation

$$\frac{\partial}{\partial\nu_i}\left[\Phi+\Psi\sum_j j\nu_j\right]=0\ , \tag{11}$$

where Ψ is a Lagrange multiplier. Direct evaluation of (11) yields that the frequency (or fraction) of stage-i units, f_i, defined by

$$f_i=\hat{\nu}_i\Big/\sum_j\hat{\nu}_j\ , \tag{12}$$

where $\{\hat{\nu}_j\}$ is a solution of (11), is given by

$$f_i=\exp(c_i)\ , \tag{13}$$

where

$$c_i=N_0\ln N_0-N\ln N-(N_0-N)\ln(N_0-N)-i\beta\Psi$$
$$+\beta(\mu N+\varepsilon z N^2/2N_0-\gamma N_0-u_iN^2/N_0) \tag{14}$$

and $\beta=1/kT$.

The normalization condition $\sum_i f_i=1$, which follows from (12), then yields, from (13), the result

$$\sum_i\exp(c_i)=1 \tag{15}$$

We now obtain an explicit expression for f_i in the case where the frequency of stage-i units is a sufficiently smoothly varying function of i that i can be treated as a continuous variable. (In practice, this means that $\tilde{i}$, the value of the stage index i at which ν_i and f_i are the largest, needs to be sufficiently large.) Then,

$$\left[\frac{\partial f_i}{\partial i}\right]_{i=\tilde{i}} = \left[\frac{\partial c_i}{\partial i}\right]_{i=\tilde{i}} = 0 \tag{16}$$

and

$$c_i \simeq c_{\tilde{i}} + \tfrac{1}{2}(i-\tilde{i})^2 \left[\frac{\partial^2 c_i}{\partial i^2}\right]_{i=\tilde{i}} . \tag{17}$$

From (14) and (16) it follows that

$$\Psi = -\frac{N^2}{N_0}\left[\frac{\partial u_i}{\partial i}\right]_{i=\tilde{i}} , \tag{18}$$

while, from (14) and (17),

$$f_i \simeq f_{\tilde{i}} \exp\{-[(i-\tilde{i})/\sigma]^2/2\} , \tag{19}$$

where

$$\sigma^2 = kT \Big/ \left[N_0 x^2 \frac{\partial^2 u_i}{\partial i^2}\right]_{i=\tilde{i}} , \tag{20}$$

and

$$x = N/N_0 \tag{21}$$

is the filling coefficient of the occupied layers. If, as is usually done, we assume a power-law form

$$u_i = v_0 i^{-\alpha} , \tag{22}$$

we find

$$\sigma^2 = kT\tilde{i}^{\alpha+2}/[N_0 x^2 v_0 \alpha(\alpha+1)] . \tag{23}$$

Equations (19)—(23) mean that the distribution of staging units in the disordered structure is approximately Gaussian and peaked at the dominant staging unit $\tilde{i}$. σ is the width of the distribution and is a measure of the stage disorder. From (23) we see that the degree of stage disorder should increase strongly with increasing stage $\tilde{i}$. It should increase with temperature and decrease with increasing domain size N_0 and in-plane density x. If, following Safran and Hamann,[14] we attribute the repulsive interlayer interaction responsible for staging to the charge transfer, then v_0 is a measure of the magnitude of the charge transfer so that stage disorder should increase with decreasing charge transfer.

The derivation which was given for expressions (20) and (23) for the degree of stage disorder turns out to be remarkably model independent. First, one should note that the in-plane interaction energy ε and the cohesion between the host layers, γ, do not enter the expressions (19)—(23) describing stage disorder. Their effect is felt only indirectly through the influence which they have on the equilibrium in-plane density x and the dominant stage $\tilde{i}$. Indeed, it is easy to verify that the derivation of the results (19)—(23) proceeds exactly as above, and that the expressions for the stage disorder are unchanged if, instead of taking ε and γ to be constants, we allow them to be arbitrary functions of the in-plane density. [It is required, however, that the values taken by ε and γ at the *equilibrium value of the in-plane density* be sufficiently large compared to the interlayer repulsion at stage $\tilde{i}$ that the derivation of the free energy Φ in Sec. II, and, in particular, the condition (7) that $\phi(\{\hat{N}_j\}) \simeq \phi(\{\nu_i\},N)$, be satisfied. As was explained in Sec. II, this will always be true if $\tilde{i}$ is sufficiently large.] A particular model where γ depends on the in-plane density was first put forward by Dahn *et al.*[10] and their form for γ is widely used. An in-plane interaction energy ε which depends on the in-plane density was recently used by DiVincenzo *et al.*[17] to model the effect of corrugation potentials on the phase diagram of graphite-Li. Similarly, the simple Bragg-Williams form for the *in-plane* entropy appearing in the free energy (7) can be replaced by an arbitrary function without altering the results (19)—(23) for the stage disorder.[38] More generally, the entire *in-plane* free energy appearing in $\phi(\{\nu_i\},N)$ in Eq. (7) [i.e., the entire expression (7) for $\phi(\{\nu_i\},N)$, excluding the interlayer repulsion term and leaving the normalization factors $\sum_i \nu_i$ unchanged] can be replaced by any general form for the in-plane free energy. The argument proceeds unchanged and the results (19)—(23) again follow.

This shows that stage disorder should not be influenced significantly by such things as the in-plane order of the intercalants or lack of in-plane order, or whether the intercalant layers are commensurate or incommensurate with the host. All such things should manifest themselves in the stage disorder only indirectly through their influence on the in-plane density x, and on the dominant stage $\tilde{i}$, both experimentally measurable quantities.

This high degree of model independence of the scaling rules (20) and (23) for stage disorder makes their experimental verification a matter of considerable interest. In addition to furnishing a good means of testing the present theory of stage disorder experimentally, the scaling rules also provide a novel and sensitive way of measuring the interlayer repulsion energy u_i, which is responsible for staging. Thus we have a promising new method for experimentally probing the mechanism of staging itself, without having to be concerned with complications involving the in-plane free energy which make it difficult to deduce detailed information about the staging mechanism from measurements of intercalation phase diagrams.

While the above derivation was made for high dominant stages $\tilde{i}$, comparison with the exact numerical calculations of the distribution $\{f_i\}$ described below shows that the same qualitative trends in the degree of stage disorder are found also for the case of low stages. Indeed, if suitably interpreted, the same expressions for σ continue to be a good quantitative predictor of some important aspects of stage disorder, even for low values of $\tilde{i}$.

IV. NUMERICAL METHOD

The key to the problem of finding an efficient numerical procedure for calculating the equilibrium distribution of staging packages $\{f_i\}$ and the equilibrium in-plane density x for any choice of μ and T is contained in the results (13) and (14). These results state that *for any fixed value of the in-plane density* the entire distribution $\{f_i\}$ of stage-i units which minimizes the free energy Φ subject to the constraint (10) is given by a function which becomes explicitly known as soon as the parameter Ψ is determined. Thus we begin with some trial value of the in-plane density, $x=N/N_0$, and, for that value, we solve Eqs. (14) and (15) numerically for Ψ. Then we can insert this value of Ψ into (13) and (14) to find the distribution $\{f_i\}$ which minimizes Φ subject to the constraint (10) *and* subject to the constraint that the in-plane density be equal to our trial choice of x. We then can use our calculated distribution $\{f_i\}$ to calculate the free energy per layer of host Φ/ν_H directly from (7), (9), and (10). Since Ψ has already been calculated, this last step can be simplified if one realizes that this extremal value of Φ/ν_H is given by

$$(\Phi/\nu_H)_{\min}=-\Psi \,, \tag{24}$$

which is easily proved from (11). This process is repeated for different trial choices of x until the value of x (and hence the distribution $\{f_i\}$) which minimizes the free energy per host layer is found.

V. NUMERICAL RESULTS FOR LOW STAGES

We now need to consider whether the present theory yields a significant amount of stage disorder for the low stages which are studied experimentally, for realistic values of the model parameters. We begin with the case of K-graphite.

It is clear from the discussion in Sec. III that stage disorder should be very sensitive to the interlayer repulsion u_i. Thus it is important to have as realistic an estimate of this energy as is possible. Safran and Hamann[14] have argued that if the interlayer repulsion is caused by the charge transfer which occurs between the guest and host layers, then, for high stage numbers i,

$$u_i \sim v_0 i^{-\alpha} \,, \tag{22}$$

with an asymptotic value $\alpha \sim 5$. However, this asymptotic result is not approached until i becomes very large,[14] $\gtrsim 200$, and is well outside of the regime in which experiments are done ($1 \leq i \lesssim 15$). For the low stages the stage dependence is much weaker. Thus, while the power-law form (22) of the repulsion has been widely applied in modeling staging theoretically, exponents $\alpha=2$ and $\alpha=4$ have usually been used.[13,15–17] To obtain more realistic values, one can estimate u_i from the ranges of chemical potential $\Delta\mu(j)$ in which the various stages j are stable experimentally. The procedure for doing this has been discussed by Safran and Hamann.[14]

Fitting the form (22) to the chemical-potential data of Nishitani *et al.*[39] for stages 1–7 of K-graphite in this way yields $\alpha \sim 1$ and $v_0 \sim 0.3$ eV, in agreement with the earlier fits[14] to the experimental data of Salzano and Aronson[40] for the alkali-metal intercalates. Thus we use these values of α and v_0 in the numerical calculation of stage disorder in K-graphite. We take $\gamma=1$ eV, which corresponds approximately to the cleavage energy of graphite measured by Salzano and Aronson.[40] ε is more difficult to estimate, but since $z\varepsilon$ is expected to be comparable to γ,[15] we set $z\varepsilon=1$ eV. Here one should note that, as explained in Sec. III, stage disorder is not sensitive to γ or ε, provided that these quantities are sufficiently large that the "GIC case" applies. (Direct numerical calculations have been carried out within the present model, confirming that this result obtained analytically for high stages in Sec. III also holds for low stages.)

The numerical results calculated using this choice of γ, $z\varepsilon$, v_0, and α for K-graphite for $kT=0.03$ eV (about room temperature) and $N_0=300$ (domains with an in-plane dimension of about 100 Å) are shown in Fig. 1(a). The fraction f_i of stage-i units in the domain is plotted for each i against chemical potential. $\tilde{\mu}=\mu-\mu_\infty$, where μ_∞ is the threshold for intercalation for infinite domain size, i.e., μ_∞ is the chemical potential below which there is no intercalant present in an equilibrium sample with infinite domains.

For large values of μ, $f_1=1$ and $f_i=0$ for $i>1$, i.e., the system is a pure stage 1. In a very narrow range of chemical-potential values near $\tilde{\mu}=0.45$ eV, f_1 decreases continuously with decreasing μ from 1 to 0, while f_2 increases from 0 to 1, i.e., at high values of μ the system is nearly pure stage 1, but near $\tilde{\mu}=0.45$ eV randomly placed stage-2 packages begin to appear in the domain. The proportion of stage-2 packages in this microscopic mixture grows continuously with decreasing μ, while the proportion of stage-1 packages decreases until the domain becomes nearly pure stage 2. This transition is very sharp, the domain changing from 95% stage 1 to 95% stage 2 in an interval of chemical potential $\Delta\mu \simeq 0.001$ eV. The change from 99.9% stage 1 to 99.9% stage 2 occurs within an interval $\Delta\mu \simeq 0.002$ eV. For chemical-potential values further from the value at the center of the transition, the proportion of the minority staging unit continues to decrease rapidly, the stage-1 and -2 phases becoming "pure" to within the numerical accuracy of the present calculation. As μ decreases further, similar continuous

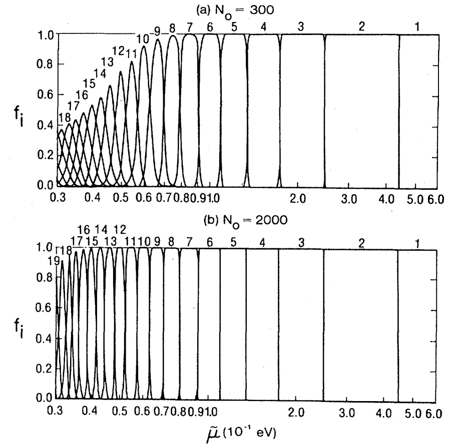

FIG. 1. Stage disorder in K-graphite. Fraction f_i of stage-i units vs $\tilde{\mu}=\mu-\mu_\infty$. μ_∞ is the lowest μ at which intercalation occurs for infinite domains. $\gamma=z\varepsilon=1$ eV, $v_0=0.3$ eV, $\alpha=1$, and $kT=0.03$ eV. The curve giving the fraction of stage i in the domain is labeled by its value of i.

transitions occur from stage 2 to 3, 3 to 4, 4 to 5, 5 to 6, and 6 to 7, but with increasing stage the region of chemical potential in which the transition (and the stage disorder) occur becomes broader relative to the region occupied by the pure stages. For stage $i > 7$ pure stages no longer exist and the domain is always a disordered mixture of two or more different staging units. Eventually (beyond stage 16), no single staging unit makes up even half of the distribution for any value of μ, more and more different staging units contributing to the mixture.

The results for a larger domain size ($N_0 = 2000$) are shown in Fig. 1(b). As one might expect from the analytic results for the degree of stage disorder obtained in Sec. III, the stage disorder is less for the larger domain size. The staging transitions are still continuous, but narrower than in Fig. 1(a), and pure stages can exist for higher values of the stage index, up to approximately $i = 14$. These results again show the sensitivity of stage disorder to domain size, and clearly demonstrate that it is essential to measure the in-plane dimensions of the intercalant islands in any systematic experimental study of stage disorder.

The effect of a smaller charge transfer ($v_0 = 0.06$ eV) typical of graphite intercalated with acceptors is shown for the low stages in Fig. 2, for $N_0 = 300$. At $kT = 0.03$ eV the results are similar to those in Fig. 1(a), but the transitions are relatively broader, and the stage disorder more prominent, in qualitative agreement with the predictions of the scaling rule of Sec. III. This may explain why stage disorder is more often seen experimentally, and seen for lower stages, in acceptor than donor graphite intercalation compounds.[1-4] However, a careful, systematic experimental study comparing stage disorder in different compounds *and taking proper account of the variation in domain size* from compound to compound and from sample to sample is clearly needed to check this idea.

As can be seen from Figs. 2(a)—2(d), the degree of disorder increases, the transitions broaden, and the highest attainable pure stage decreases with increasing T. At $kT = 1.0$ eV [Fig. 2(c)] even a pure stage 2 does not occur. In intercalated graphite this temperature is unrealistic, but in $\mathrm{Li}_x\mathrm{TiS}_2$ the scale of energies is lower, and behavior consistent with that shown in Fig. 2(c) has been reported,[10-12] a pure stage 1 being observed at high chemical potentials, but only a stage-disordered stage 2 occurring at lower μ. $\mathrm{Li}_x\mathrm{NbSe}_2$—where well-ordered stages 1 and 2 but only a disordered stage 3 have been observed[10]—may be a case intermediate between Figs. 2(b) and 2(c). At still higher T [Fig. 2(d)], even an "imperfect" stage 2 is not present and $f_1 \geq f_2$ for all μ.

The above results show that stage disorder should play an important role in the Daumas-Hérold domain model for realistic domain sizes and reasonable choices of the model parameters. However, stage disorder should be very sensitive to the interlayer repulsion u_i, while our choice of the form $u_i \sim v_0 i^{-\alpha}$ with $\alpha = 1$ was based on experimental data whose accuracy is limited and which are available only for low stages. Given that theoretically the exponent α is expected to increase with increasing stage, it is of interest to examine the effect a higher exponent α on stage disorder. In Fig. 3(a) the results are presented for the case $\alpha = 4$, all of the other parameters being the same

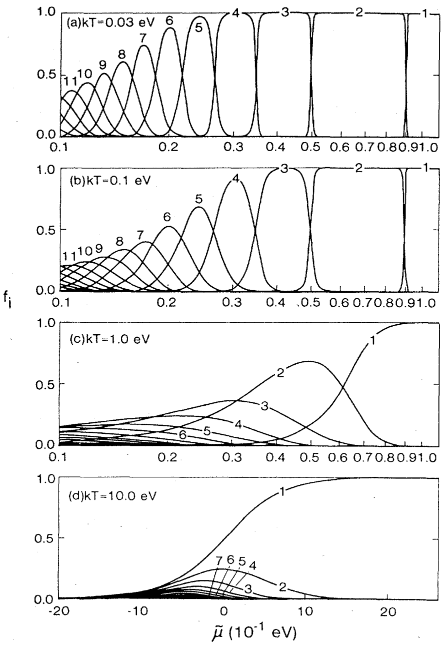

FIG. 2. Stage disorder for acceptorlike charge transfer. $\gamma = z\varepsilon = 1$ eV, $v_0 = 0.06$ eV, $\alpha = 1$, and $N_0 = 300$. Notation as in Fig. 1.

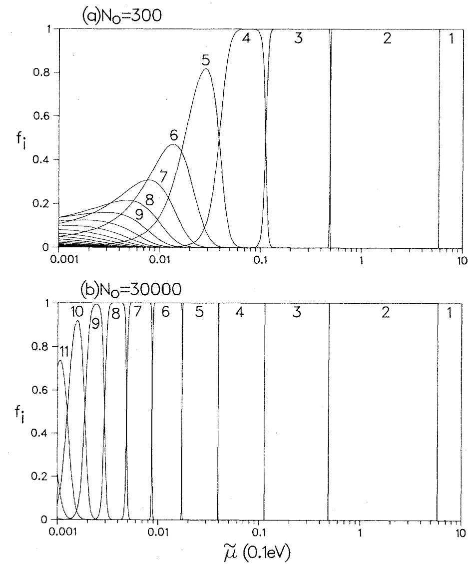

FIG. 3. Stage disorder for a strongly-stage-dependent interlayer repulsion energy. $\gamma = z\varepsilon = 1$ eV, $v_0 = 0.3$ eV, $\alpha = 4$, and $kT = 0.03$ eV. Notation as in Fig. 1.

as in Fig. 1(a). The main qualitative difference between these two cases is that the degree of stage disorder increases much more rapidly with increasing stage for $\alpha=4$ than for $\alpha=1$, in agreement with the predictions of the scaling rule obtained in Sec. III. Also, from Fig. 3(b), where the results are shown for $\alpha=4$ and $N_0=30\,000$ [a domain with in-plane dimensions 10 times larger than those for Fig. 3(a)], it is clear that for higher values of the exponent α, stage disorder is important at moderate values of the stage index i, even for quite large domain sizes.

VI. LIMITS TO THE VALIDITY OF Φ

In the preceding examples, γ and $z\varepsilon$ are comparable with each other and larger than v_0, so that the arguments given in Sec. II, which lead to the approximate free energy Φ [Eqs. (7) and (9)] of the stage-disordered system, should apply. It is of interest, however, also to consider the physics of what happens when these arguments begin to break down. To this end let us consider the case in which $z\varepsilon=1$ eV, $v_0=0.3$ eV, $N_0=300$, $kT=0.12$ eV, $\alpha=1$, and $\gamma=0.2$ eV. Here we have chosen $\gamma<v_0$ and a moderately high temperature. The results of minimizing the approximate free energy Φ using the same procedure as before are shown in Fig. 4. The main qualitative difference between this and the previous results is that Φ now has two different local minima (characterized by different distributions $\{v_i\}$ and in-plane densities x) in the region of the stage-1—to—stage-2 transition, and the transition is no longer continuous. A greatly expanded view of the hysteresis loop showing only the values taken by f_1 in this region ($f_2 \simeq 1-f_1$) is shown in the panel at the right of the figure. This discontinuous behavior is not physical, since the model which is being used is a one-dimensional one. It reflects an inadequacy of the approximate free energy Φ. To correct this difficulty it is necessary to construct a more accurate free energy in which the in-plane density in a particular intercalant layer is allowed to depend on the local environment in which that layer occurs, i.e., on the location of the neighboring intercalant layers. A complete solution to this problem is beyond the scope of the present paper; some comments, however, are in order:

(1) If such a more accurate free energy is constructed, then the in-plane density will no longer be constrained to be the same in all of the intercalant layers. Thus thermodynamic states will be allowed in which spatial fluctuations occur in the domain during the stage-1—to—stage-2 transition. Some parts of the domain will resemble the state characteristic of one of the local minima of the approximate free energy Φ, while others will resemble the state at the other local minimum. As is generally the case with one-dimensional models, these fluctuations will cause the stage-1—to—stage-2 transition to become continuous. What effect domain-domain interactions would have on such a situation is not clear at present. However, it would appear that the likelihood of them resulting in a first-order transition is higher in this case than in the situations considered in Sec. V.

(2) As was explained in Sec. II, the approximate free energy Φ should become exact in the high-stage limit. This is in agreement with the results shown in Fig. 4, where the unphysical discontinuous behavior is found only for the stage-1—to—stage-2 transition. The higher transitions are all continuous as expected. Also in agreement with the discussion in Sec. II, the numerical calculations based on the approximate free energy Φ yield a continuous stage-1—to—stage-2 transition at low temperatures where all of the occupied intercalant layers become completely filled in the lattice-gas model and, thus, equally occupied.

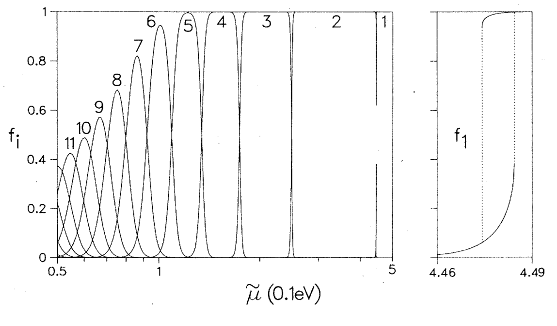

FIG. 4. Stage disorder calculated from the approximate free energy Φ for $\varepsilon z=1$ eV, $\gamma=0.2$ eV, $v_0=0.3$ eV, $kT=0.12$ eV, $\alpha=1$, and $N_0=300$. The panel to the right-hand side of the figure shows the hysteresis loop for the fraction of stage 1 in the stage-1—to—stage-2 transition in more detail. The discontinuous behavior in the stage-1—to—stage-2 transition is due to an inadequacy of the free energy Φ and is not expected to occur in an improved theory.

VII. SCALING FOR LOW STAGES

The expressions (20) and (23) for σ, which were derived for the high-stage limit, continue to provide a useful scaling rule for the degree of stage disorder even for low stages *if* we reinterpret σ to be a measure of the *relative* prominence on a chemical potential scale (as in Figs. 1—4) of the disordered- and pure-stage regions at stage $\tilde{i}$.

The present low-stage numerical calculations show that the degree of stage disorder increases with increasing temperature and stage index, and with decreasing domain size, in-plane density, and charge transfer, in agreement with this interpretation of σ. This agreement is not merely qualitative, but can provide useful quantitative results as well. For example, we can use it to obtain a quantitatively reliable expression for the limit to pure staging: A comparison of the numerical results shown in Figs. 1—4 with the form (23) for σ shows that in all cases pure stages cease to be found when σ exceeds the value 0.29. Indeed, inserting this value for σ into (23) yields $\tilde{i}=8$, 15, 4.7, 3.1, 1.2, 0.4, 4.1, 8.9, and 5.0 for the cases of Figs. 1(a), 1(b), 2(a), 2(b), 2(c), 2(d), 3(a), 3(b), and 4, respectively, predicting very accurately the stage beyond which pure staging ceases to be possible. A value of $\tilde{i}<1$ should be interpreted at 1 since a pure stage 1 can always be produced by choosing a sufficiently high value of μ.

VIII. RECENT EXPERIMENTS

Although observations of stage disorder have been reported for many years,[1] systematic experimental studies of it have only recently begun. One reason for this delay appears to have been the sensitivity of this phenomenon to sample preparation, which was not understood, and which in the present theory is explained by the dependence of stage disorder on domain size. Here I will comment on some of the recent experiments and briefly discuss their relevance to the present theory.

A central issue which needs to be addressed experimentally is whether the entropy associated with stage disorder actually is the determining factor which drives this phenomenon, as is assumed in this paper. Dahn and Haering[12] have recently reported a thermodynamic study of the voltage characteristics of Li/Li_xTiS_2 electrochemical cells which may provide a part of the answer to this question. They interpreted structure in their curves of $(\partial V/\partial T)_{x,p}$ as a function of concentration as being due to the entropy associated with stage disorder in the intercalation compound Li_xTiS_2. They also correlated these thermodynamic measurements with their earlier structural x-ray work.[10] This is a very promising approach which should be followed up with more detailed studies and extended also to other materials.

Another experiment which may be relevant to the problem of the entropy associated with stage disorder was reported by Fuerst *et al.*[5,6] These authors observed that the degree of stage disorder in a microscopic mixture of stage-7 and -8 units in a K-graphite sample decreased with decreasing temperature in a way which could be interpreted as being driven by the entropy of stage disorder. However, a very recent study by Heiney *et al.*[7] suggests a possible alternative driving mechanism for this phenomenon, in terms of an in-plane phase transition which occurs with decreasing temperature and involves a reduction of the in-plane density with a corresponding increase in the number of galleries occupied by the intercalant. A more complete experimental and theoretical understanding of this phenomenon would be of real interest.

Another experimental approach to the question of stage disorder is to measure the distribution of staging units $\{f_i\}$ as a function of the thermodynamic variables as the system goes through a succession of different stages. A number of such measurements have been reported, principally focusing on the K-graphite system, with varying results. The most recent such studies have been by Nishitani *et al.*[39] and by Misenheimer and Zabel.[8] The former authors[39] did not observe any stage disorder occurring during the sequence of transitions from stage 1 to stage 7. However, the latter[8] report admixtures of stage-$(n\pm1)$ packages in every nominally stage-$(n>2)$ compound through stage 5, the stage disorder increasing in the vicinity of the staging phase transitions, particularly for the higher stages, as predicted by the present theory. Both of these sets of observations, as well as the work of Fuerst *et al.*[5,6] and Heiney *et al.*[7] on K-graphite are consistent with the present theory and with each other if one assumes different Daumas-Hérold domain sizes in the samples of different groups. A large domain size would make the staging transitions very sharp and stage disorder difficult to detect, explaining the results of Nishitani *et al.*,[39] while a smaller domain size would account for the observation of stage disorder by the other groups.[5-8] This further emphasizes the need for reliable measurements of domain sizes in experimental studies of stage disorder.[41] However, differing levels of instrumental resolution and sample homogeneity[42] in the different experiments may also have contributed to the different amounts of stage disorder which could be detected.

Another aspect which requires further experimental and theoretical study is whether the staging phase transitions are first order or continuous. The present theory, based on noninteracting domains, and the other considerations explained in the Introduction, tend to favor continuous transitions; however, a definite theoretical answer to this question is yet to be given. Experimentally, first-order transitions have usually been reported, in agreement with the predictions of the previous theories which did not allow for finite-domain-size effects or stage disorder. However, the kinetics of staging are notoriously sluggish, and sample homogeneity is difficult to achieve and also difficult to check experimentally. Thus the apparent coexistence of two different staged phases in the same sample and/or hysteresis cannot be considered as adequate evidence of a first-order phase transition, as has often been assumed in the past. The extreme sharpness of the staging transitions predicted in Sec. V for the case of low stages and large domains makes it particularly difficult to distinguish between first-order and continuous transitions in the presence of any sample inhomogeneities. Misenheimer and Zabel[8] have reported observing discontinuous changes in the distribution $\{\nu_i\}$ of staging units which occur during the transitions between the different stages in K-graphite. These discontinuities could be "miscibility gaps" caused by domain-domain interactions driving the staging transitions first order. However, the observations could equally well be explained by the presence of sample inhomogeneities due to slow kinetics.[42] Thus the question as to whether staging phase transitions are continuous or first order is likely to remain controversial for some time. It is possible that answers to this question may be easier to obtain by studying intercalation compounds of transition-metal dichalcogenides such as Ag_xTiS_2 (Ref. 9) or Li_xTis_2 (Refs. 10—12) using powder samples in which the intercalation kinetics is less difficult than in single-crystal graphite or in highly oriented pyrolytic graphite, or by using the electrointercalation technique in which the chemical potential is easier to control than in the two-zone vapor-transport technique used to intercalate graphite.

Another interesting approach to the problem of stage disorder is suggested by the recent high-pressure experiments on staging. As was first pointed out by Clarke *et al.*,[30,32] a reversible transition from a lower to the next-higher stage can be achieved by the application of pressure to the sample. This change is accompanied by a change in the in-plane density of the intercalant as well as by an increase in the number of dislocations. The latter observation is clearly in concordance with the Daumas-Hérold view of the role which dislocations should play in staging phase transitions, and may provide a way of varying the domain size experimentally in a relatively predictable manner. It is to be expected in view of the increase in the number of dislocations (or domains) that stage disorder should be particularly pronounced during these phase transitions. Indeed, Fuerst *et al.*[31] have recently reported observing an intermediate-stage ($\frac{3}{2}$) phase occurring in a stage-1—to—stage-2 pressure-induced transition. This phase nominally consists of an alternating sequence of stage-1 and -2 units, but the observed structure was highly disordered, with the probability of an error occurring at any unit being 20%. This implies that the probability of two complete perfect unit cells of the stage-$\frac{3}{2}$ structure occurring one after the other is only 50%. Therefore, given the present lack of any theoretical basis for the existence of the *unscreened* interlayer repulsion required for fractional stages to be stable,[15,16] it is necessary to consider the possibility that correlated stage disorder due to finite domain size (and not fractional staging) may be the correct explanation of this phenomenon.

ACKNOWLEDGMENTS

I would like to thank K. K. Bardhan, R. Barrie, J. R. Dahn, R. Frindt, C. Niccolini, and S. E. Ulloa for discussions and H. Zabel for his comments. This work was supported by the Natural Sciences and Engineering Research Council of Canada and by the U.S. Department of Energy.

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[1] For a comprehensive review of intercalation, see M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981).

[2] T. Sasa, Y. Takahashi, and T. Mukaibo, Carbon **9**, 407 (1971).

[3] W. Metz and D. Hohlwein, Carbon **13**, 87 (1975).

[4] J. M. Thomas, G. R. Millward, R. F. Schlögl, and H. P. Boehm, Mater. Res. Bull. **15**, 671 (1980).

[5] C. D. Fuers, T. C. Koch, J. E. Fischer, J. A. Axe, J. B. Hastings, and D. B. McWhan, in Vol. 20 of *Materials Research Society Symposium Proceedings,* edited by M. S. Dresselhaus, G. Dresselhaus, J. E. Fischer, and M. J. Moran (North-Holland, New York, 1983), p. 39.

[6] J. E. Fischer, C. D. Fuerst, and K. C. Woo, Synth. Met. **7**, 1 (1983).

[7] P. A. Heiney, M. E. Huster, V. B. Cajipe, and J. E. Fischer, in Proceedings of the Materials Research Society Fall Meeting, Boston, 1984 (unpublished).

[8] M. E. Misenheimer and H. Zabel, in Proceedings of the Materials Research Sociey Fall Meeting, Boston, 1984 (unpublished).

[9] K. K. Bardhan, G. Kirczenow, and J. C. Irwin, J. Phys. C (to be published).

[10] J. R. Dahn, D. C. Dahn, and R. R. Haering, Solid State Commun. **42**, 179 (1982).

[11] J. R. Dahn and R. R. Haering, Solid State Commun. **40**, 245 (1981).

[12] J. R. Dahn and R. R. Haering, Can. J. Phys. **61**, 1093 (1983).

[13] S. A. Safran, Phys. Rev. Lett. **44**, 937 (1980).

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

[15] S. E. Millman and G. Kirczenow, Phys. Rev. B **26**, 2310 (1982); **28**, 3482 (1983), S. E. Millman, G. Kirczenow, and D. Solenberger, J. Phys. C **15**, L1269 (1982).

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

[17] D. P. DiVincenzo, Ph.D. thesis, University of Pennsylvania, 1983; D. P. DiVincenzo and T. C. Koch (unpublished).

[18] A preliminary account of some of the present results has already been published [G. Kirczenow, Phys. Rev. Lett. **52**, 437 (1984)].

[19] S. Flandrois, J. M. Masson, J. C. Rouillon, J. Gaultier, and C. Hauw, Synth. Met. **3**, 1 (1981).

[20] F. Baron, S. Flandrois, C. Hauw, and J. Gaultier, Solid State Commun. **42**, 759 (1982).

[21] D. Kaluarachchi and R. F. Frindt, Phys. Rev. B **28**, 3663 (1983); Phys. Rev. B (to be published).

[22] A. N. Berker, N. Kambe, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. Lett. **49**, 249 (1982).

[23] G. Timp, M. S. Dresselhaus, P. C. Eklund, and Y. Iye, Phys. Rev. B **26**, 2323 (1982).

[24] A. R. Kortan, A. Erbil, R. J. Birgeneau, and M. S. Dresselhaus, Phys. Rev. Lett. **49**, 1427 (1982).

[25] S. A. Safran and D. Hamann, Phys. Rev. Lett. **42**, 1410 (1979); Physica (Utrecht) **99B**, 469 (1980); S. A. Safran, Synth. Met. **2**, 1 (1980).

[26] S. Ohnishi and S. Sugano, Solid State Comun. **36**, 823 (1980).

[27] G. Kirczenow, Phys. Rev. Lett. **49**, 1853 (1982).

[28] P. Hawrylak and K. R. Subbaswamy, Solid State Commun. **51**, 787 (1984).

[29] N. Daumas and A. Hérold, C. R. Acad. Sci. **268**, 373 (1969).

[30] R. Clarke, N. Wada, and S. A. Solin, Phys. Rev. Lett. **44**, 1616 (1980).

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

[32] R. Clarke and C. Uher, Adv. Phys. (to be published).

[33] M. B. Dowell and D. S. Badorrek, Carbon **16**, 241 (1978).

[34] G. Schoppen, H. Meyer-Spasche, L. Siemsglüss, and W. Metz, Mater. Sci. Eng. **31**, 115 (1977).

[35] Recently, G. Forgacs and G. Uimin [Phys. Rev. Lett. **52**, 633 (1984)] have proposed an interesting alternative theory of staging transitions which includes domain-domain interactions in an approximate way. In their theory, the phase transitions occur by rotation of the domain walls through a succession of angles relative to the *c* axis in response to changes in the chemical potential. They predict that complex ordered intermediate structures resembling fractional stages should occur during all staging transitions, first appearing at the domain boundaries and then spreading through the crystal. Their theory, however, does not allow for any stage disorder in the system, all of their intercalant islands moving *coherently* as the domain wall rotates.

[36] Another approach to the problem of domain structures in intercalation physics has been studied by P. Hawrylak and K. R. Subbaswamy (unpublished), who solved numerically the time evolution of the kinetic equations describing phase transitions in a small segment of a staged intercalation compound using a Landau-Ginzburg approximation.

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

[38] An interesting related result which has been confirmed numerically during the present study is that a high degree of stage disorder is possible even at such low temperatures that the filling of the occupied intercalant layers is virtually complete and the in-plane entropy is effectively zero. Thus, it is possible for the entropy due to stage disorder, to completely dominate the thermodynamics of the staged system at low temperatures for suitable ranges of values of the chemical potential.

[39] R. Nishitani, Y. Uno, and H. Suematsu, Phys. Rev. B **27**, 6572 (1983); see also R. Nishitani, Y. Uno, and H. Suematsu, in Summary Report of Special Distinguished Research Project, Ministry of Education, Science and Culture of Japan, edited by S. Tanuma and H. Kamimura (March 1984), pp. 25—34 (unpublished).

[40] F. J. Salzano and S. Aronson, J. Chem. Phys. **44**, 4320 (1966).

[41] It should be noted, however, that an attempt by Misenheimer and Zabel (Ref. 8) to measure the domain size in their samples from the width of the x-ray lines yielded a remarkably large estimate. The significance of this result is not yet clear. It may possibly be interpreted as an indication that the exponent α in the interlayer repulsion energy increases rapidly with stage already at quite low values of the stage index. (Compare the results of Figs. 1 and 3.)

[42] It was first pointed out by J. G. Hooley, W. P. Garby, and J. Valentin [Carbon 3, 7 (1965)] that the elastic properties of the layered host material strongly favor the development of inhomogeneities during intercalation. Their argument was that it costs less elastic energy to open the microscopic "crack" needed to insert intercalant atoms between two host layers if one of these host layers is a bounding layer of the stack which makes up the sample than if the two host layers are in the middle of the stack. Thus intercalation should begin at the bounding layers of the sample and then work through towards the interior layers. One would then expect that in a staging phase transition in which the stage index decreases from stage n to stage $n-1$, the transition will happen first in the exterior layers and then proceed into the interior of the sample. The present theory would then imply that during this transition the interior part of the sample would be stage n and the exterior part stage $n-1$, and that there should be a band of stage disorder in between. For low stages n and large domains, the transition is sharp, so that this band of stage disorder would occupy only a small portion of the sample and would be difficult to detect. Thus the phase transition would very closely resemble a first-order transition experimentally. For high stages, however, the region occupied by stage disorder would be much larger. For example, for stages $n>8$ for the conditions shown in Fig. 1(a), *only stage-disordered states can occur,* so that the entire sample would be stage disordered. At intermediate stages n, the stage disorder would occupy a substantial part of the sample, but there would be pure stage-n and -$(n-1)$ regions as well. A sophisticated analysis of the x-ray data for this inhomogeneous intermediate situation would not be easy to carry out, but nevertheless may prove to be the most practical approach for determining the order of staging phase transitions experimentally, since achieving a high degree of sample homogeneity during a staging transition may well be even more difficult.