Stage Order, Disorder, and Phase Transitions in Intercalation Compounds

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A theoretical study of intercalation predicts stage-changing phase transitions to be continuous and to proceed via stage-disordered states. Detailed results are presented for typical donor and acceptor graphite intercalation compounds. Other systems are also discussed. A scaling rule relating stage disorder to domain size, stage, temperature, in-plane density, and charge transfer is proposed. A fundamental limit is set on the period of well staged structures. Experimental implications are discussed.

When a guest species is intercalated into a layered host material such as graphite, the resulting sequence of guest and host layers can be ordered[1] or disordered.[1-5] 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. Stages $1 \le n \le 15$ are usually reported. This remarkable case of high-period one-dimensional ordering has attracted a great deal of attention. However, little is known about the associated order-disorder phase transitions.[6] The phase transitions in which the stage index n of the intercalation compound changes are also not well understood, although a number of elegant experiments[1,7] support the view of Daumas and Hérold[8] (DH) that the staged structures consist of microscopic domains, each domain being ordered in the above sense, but in different domains the guest layers occupy galleries between different pairs of host layers. Thus the change of stage can take place by the movement of rafts of guest atoms from one domain to another. The purpose of this Letter is to present a theoretical study which shows how both stage disorder and the above phase transitions can be understood within the DH picture. The phase transitions in which the stage index changes are shown to be continuous and proceed via stage-disordered states. Detailed results are presented for typical donor and acceptor graphite intercalation compounds. A simple scaling rule governing state disorder is proposed, and a limit is set on the period of staged structures. The present calculations explain much of the available qualitative experimental data relating to stage disorder and should provide a focus for more quantitative experimental work.

Following Safran[9] and others,[4,10] the guest atoms are treated as a lattice gas with attractive intralayer interactions and repulsive electrostatic interlayer interactions. Within this model the free energy of a $single$ $domain$ with state disorder can be written approximately as

$$\varphi = \left(\sum_i \nu_i\right)\left(- \epsilon Z N^2/2N_0 + \gamma N_0 - \mu N\right) + \sum_i u_i \nu_i N^2/N_0$$

$$- kT\left\{\left(\sum_i \nu_i\right)[N_0 \ln N_0 - N \ln N - (N_0 - N)\ln(N_0 - N)] + \left(\sum_i \nu_i\right)\ln\left(\sum_j \nu_j\right) - \sum_i (\nu_i \ln \nu_i)\right\}, \qquad (1)$$

where ν_i is the number of "stage-i units" (sandwiches consisting of a pair of guest layers separated by i host layers) in the domain, $- \epsilon$ is the nearest-neighbor in-plane interaction energy between intercalants, N_0 is the number of lattice-gas sites per intercalant layer, N is the number of intercalants in an occupied layer, and Z is the in-plane coordination number. γN_0 is the energy required to separate a pair of host layers sufficiently to admit the intercalants if one assumes rigid host layers[10] $within$ a $domain$. $u_i N^2/N_0$ is the electrostatic repulsion between a pair of intercalate layers separated by i host layers. The interaction between a pair of intercalate layers is assumed to be screened out by any intervening intercalate layer.[10,11] The last two terms in the curly braces are the entropy due to stage disorder.

In (1) the elastic interactions between intercalate layers in different domains have been omitted. However, if the distribution $\{\nu_i\}$ is the same in all domains then there are no long-range elastic strains present, and the main effect of the elastic interactions[12] is to introduce possible correlations between the positions of the intercalate layers in different domains. This can be accounted for by redefining N_0 to be a function of an appropriate correlation length instead of simply the domain size. Since reported intercalate island sizes vary widely, from less than 100 to 10 000 Å and more,[1,7,13] and appear to depend on sample

preparation more than on ambient conditions, N_0 will be treated as a given parameter.[14]

A further simplification made in (1) is to assume that the in-plane density $x = N/N_0$ is the same in every occupied intercalant layer. This is in fact a mean-field approximation. It is expected to be accurate if $Z\epsilon$ and γ are comparable and u_i is smaller, which appears to be true for most graphite intercalation compounds.[10] Under these conditions, previous calculations have shown that the in-plane density in any intercalate layer is not very sensitive to the location of the neighboring intercalate layers.[10] The approximation becomes *exact* (i) at low temperatures where all occupied layers are completely filled, (ii) in the high-stage limit where $u_i \to 0$, and (iii) in the high-temperature limit.

The equilibrium distribution $\{\nu_i\}$ and value of N are those which minimize φ subject to the constraint that the number of host layers $(\sum_i i \nu_i)$ is held fixed. To establish whether stage disorder should be important in real systems, consider the case of graphite-K. Fitting the form[9] $u_i = V_0 i^{-\alpha}$ to the chemical-potential data of Nishitani, Uno, and Suematsu[15] for stages 1–7 yields $\alpha \simeq 1$, $V_0 \simeq 0.3$ eV. I set $\gamma = 1$ eV, which corresponds approximately to the cleavage energy of graphite measured by Salzano and Aronson.[16] ϵ is more difficult to estimate but since $Z\epsilon$ is expected to be comparable to γ,[10] I set $Z\epsilon = 1$ eV. The results 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 relative number $f_i = \nu_i / \sum_j \nu_j$ of stage-i units present is plotted for each i against chemical potential μ. For large μ, $f_1 = 1$ (pure stage 1). With decreasing μ, f_1 decreases continuously to 0 in a very narrow range of μ, while f_2 increases from 0 to 1, whereupon the domain becomes pure stage 2. In the transition region the domain is a microscopically disordered mixture of stage-1 and stage-2 units. Similar continuous transitions occur from stage 2 to 3, 3 to 4, 4 to 5, 5 to 6, and 6 to 7 as μ decreases further, but with increasing stage the region of chemical potential in which the transition (and the stage disorder) occurs becomes broader relative to the region occupied by pure stages. For stages $i > 7$, pure stages no longer exist and the domain is always a disordered mixture of two or more different staging units. With increasing domain size the stage transitions become narrower (but remain continuous) and pure stages occur for higher values of i, as in Fig. 1(b) where for $N_0 = 2000$ pure staging
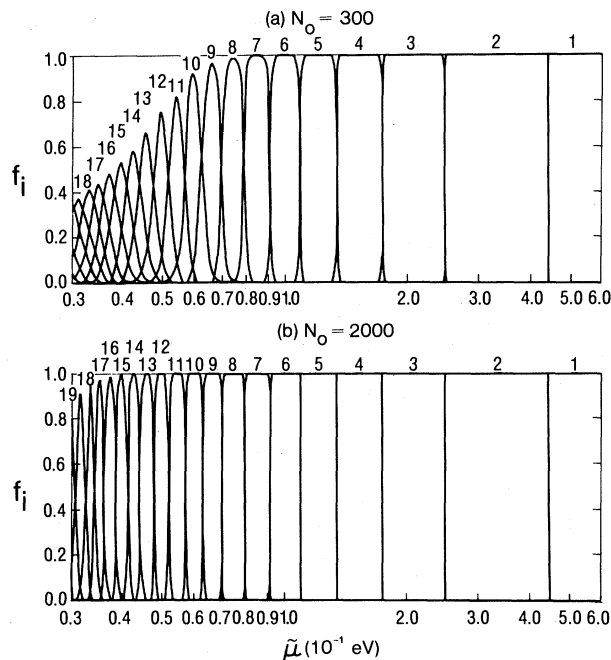

FIG. 1. Stage disorder in graphite-K. Fraction f_i of stage-i units vs $\tilde{\mu} = \mu - \mu_\infty$. μ_∞ is the lowest μ at which intercalation occurs for infinite domains. $kT = 0.03$ eV.

can be seen up to approximately stage 14. This dependence on domain size may explain why experimental results on stage disorder are very sample dependent. The present results clearly demonstrate that it is essential to measure the in-plane dimensions of the intercalant islands in any systematic experimental study of stage disorder.

This calculation assumes that the sample is homogeneously intercalated, but in graphite during a change of stage from stage n to $n - 1$, some regions of the sample usually have a higher concentration of intercalate and become stage $n - 1$ while other regions are still stage n. The present theory predicts that these pure-stage regions should be separated by a band of microscopically disordered stage-n and $-(n - 1)$ units. This band should migrate through the sample as more of it becomes stage $n - 1$. Since the width of the band of disorder is related to the range of μ in which the disordered state is stable, and this range is very narrow for low stages for even modest domain sizes, it is not surprising that Nishitani, Uno, and Suematsu[15] did not detect any such disorder during the staging transitions which they studied through stage 7. But the present prediction that *only* disordered staging should exist beyond a certain stage (stage 7 for 100-Å domains

at room temperature) agrees with the observation by Hastings et al.[5] of a disordered mixture of stage-7 and -8 units in graphite-K which shows greater order with decreasing T.

The effect of a smaller charge transfer (V_0 =0.60 eV) typical of graphite intercalated with acceptors is shown in Fig. 2 for N_0 =300. At kT =0.03 eV the results are similar to those in Fig. 1, but the transitions are relatively broader. This may explain why stage disorder is more often seen in acceptor than donor graphite intercalation compounds.[1,2] However, in any well founded experimental study comparing stage disorder in different compounds, the variation in domain size from compound to compound and from sample to sample must be taken into account.

The disorder increases with T. At kT =1 eV [in Fig. 2(c)] even a pure stage 2 is not found. In intercalated graphite this temperature is unrealistic, but in Li_xTiS_2 the scale of energies is lower,
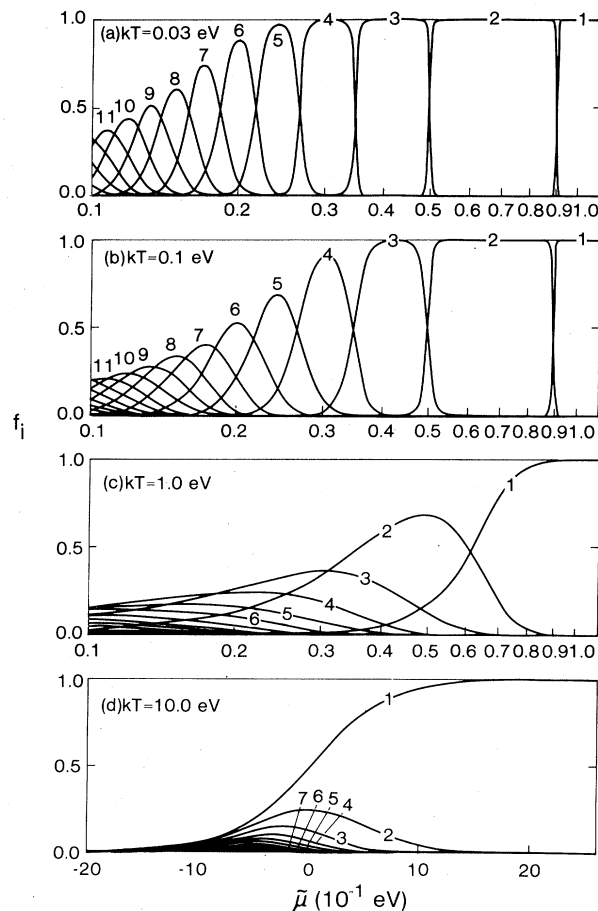

f_i

FIG. 2. Stage disorder for acceptorlike charge transfer. N_0 =300. Notation as in Fig. 1.

and behavior similar to that shown in Fig. 2(c) has been reported.[3,4] Li_xNbSe_2, where well ordered stages 1 and 2 but only a disordered stage 3 have been observed,[4] 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 since $f_1 \geq f_2$ for all μ.

These examples show that increasing the stage index or temperature or decreasing the domain size or charge transfer all have qualitatively similar effects on the degree of stage disorder. This is a result of the competition between the entropy of stage disorder and the energy of repulsion between intercalate layers. We may obtain a scaling rule which expresses this observation quantitatively by studying the high-stage limit where the stage index can be treated as a continuous variable. Then φ can be minimized analytically, yielding $f_i \simeq \bar{f} \exp\{-[(i - \tilde{i})/\sigma]^2/2\}$, where

$$\sigma^2 = kT/(N_0 x^2 d^2 u_i /di^2)_{i=\tilde{i}}$$

$$\simeq kT\tilde{i}^{\alpha+2}/[N_0 x^2 V_0 \alpha(\alpha+1)]$$

and $x = N/N_0$. $\tilde{i}$ is the dominant staging unit and σ is a measure of the stage disorder. This expression for σ provides an accurate scaling rule for the degree of stage disorder even in the low-stage case *if we reinterpret σ to be a measure of the relative prominence on a chemical potential scale* (as in Figs. 1 and 2) *of the disordered and pure-stage regions at stage $\tilde{i}$*. Comparison of this analytic expression for σ with the present numerical results reveals that the special case σ =0.29 is particularly important. Putting this value of σ into $\tilde{i} = [\alpha(\alpha+1)\sigma^2 N_0 x^2 V_0/kT]^{1/(\alpha+2)}$ yields $\tilde{i}$ =8, 15, 4.7, 3.1, 1.2, and 0.14 for the cases of Figs. 1(a), 1(b), 2(a), 2(b), 2(c), and 2(d), respectively, predicting very accurately the stage at which pure staging ceases to be possible. A value of $\tilde{i} < 1$ should be interpreted as 1 since a pure stage 1 can always be produced by choosing a high enough value of μ. Experimental verification of the predicted scaling behavior would be of considerable interest.

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[14]It should be noted that the present formalism does not allow one to calculate the value of N_0. One reason is that the free energy φ does not contain the energy required to create a domain wall so that it is only meaningful to minimize φ with respect to variations of x and $\{\nu_i\}$ at constant N_0, i.e., holding the number of domain walls fixed. Minimization of φ with respect to variations of N_0 is not permitted. A more fundamental reason is that the intercalation domain walls envisaged in the Daumas-Hérold model are nonequilibrium entities which are present because of the kinetics of intercalation and the topology of the host. Thus a calculation of the number and size of the domains based on equilibrium thermodynamics would yield unrealistic results even if the domain wall energy were included in φ.

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