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Thermodynamic model of staging transformation in intercalated graphite

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A simple, thermodynamic model of intercalated graphite which allows for variation of in-plane intercalant density, and takes explicit account of volume variation, is presented. Assuming random occupation of intercalant atoms pressure-temperature-concentration phase diagrams are calculated. The model is capable of explaining pressure-induced staging transformation, the appearance of fractional stage at high pressure, and other experimentally observed effects in alkali-metal–graphite compounds.

I. INTRODUCTION

The appearance of an ordered sequence of intercalant layers separated by carbon planes, the so-called staging phenomenon, is one of the many fascinating properties of graphite intercalation compounds.[1] Stage *n* refers to there being *n* carbon planes between successive intercalant layers. In alkali-metal–graphite compounds at ambient pressure and temperatures below $\sim 800\,^{\circ}\mathrm{C}$ stages higher than 1 occur with in-plane concentration corresponding to MC_{12} ($M=$K, Rb, Cs), while stage 1 appears to have a range of concentration MC_x, with x in the range of ~ 8–11.[2] Stage-1 MC_8 is considered to have "close-packing" density.

Clarke, Wada, and Solin[3] have observed pressure-induced, mass-conserving, transformation from stage-2 KC_{12} to stage-3 KC_8. Similar staging transformation with in-plane densification was also observed by Feurst *et al.*[4] in stage-1 KC_8. They also reported the appearance of a "fractional" stage $\frac{2}{3}$ (two layers filled, and one empty) as a result of applied pressure. It is not known whether these phenomena are controlled by kinetics or by equilibrium properties of the system.

The earliest attempt to model the occurrence of staged compounds with different in-plane concentrations was by Salzano and Aronson.[5] More recent work on staging[6] has taken into account the long-range, electrostatic interactions[7] responsible for the stabilization of high stages. Safran[6] showed that a simple, lattice gas model including in-plane attractive and interplane repulsive interactions was capable of describing the staging phenomenon. Later, Millman and Kirczenow[8] showed that inclusion of the elastic energy associated with intercalation, and a strongly screened interlayer potential, leads to the existence of pure stages only. These and other models[9,10] based on a lattice gas description also naturally lead to the same close-packing densities for all stages at low temperatures. Lower in-plane filling can occur only at high temperatures in these models. Further, since these models have been concerned only with ambient pressures, the variation of the volume of the sample upon intercalation was not included in them.

In this paper we present a simple thermodynamic model, similar in spirit to the earlier models but modified so as to give pure stages with variable concentrations and explain the observed pressure experiments based on equilibrium properties. In Sec. II the model is described in detail. Section III contains our results and discussion. Our conclusions are presented in Sec. IV.

II. MODEL

The lattice gas models mentioned earlier[6,8,9] all include interplane repulsive interaction and an in-plane, attractive interaction which favors the "close-packed" filling of the plane at $T=0$. We modify the form of the in-plane cohesive energy so that the optimum filling may have less than close-packed density. DiVincenzo and Mele[11] recently considered the electrostatic contribution to the cohesive energy of a graphite-intercalant-graphite sandwich. Their calculation was based on viewing the sandwich by means of a two-step process in which a two-dimensional metal is formed, followed by the separation of the negatively charged sheets, leaving behind the positively charged sheet in the middle. Following this picture we write for the in-plane energy per carbon atom in a layer

$$E_1^{(i)} = -\alpha(N_i/N_c)^{3/2} + \beta c_i (N_i/N_c)^2 \ , \tag{2.1}$$

where (N_i/N_c) is the ratio of the number of intercalant atoms to the number of carbon atoms in the plane, c_i is the sandwich thickness, and α and β are adjustable parameters. The first term is the cohesive energy of the two-dimensional metal, and the second term represents the energy to separate the charges. This form of energy yields that the optimum in-plane density scales as $1/c_i^2$. An inverse relationship between in-plane concentration and sandwich thickness has, in fact, been observed experimentally.[12]

We model the elastic energy (per carbon atom in a layer) in a manner similar to that proposed by Dahn, Dahn, and Haering[13]:

$$E_2^{(i)} = \tfrac{1}{2}k(c_i - c_0)^2 + \tfrac{1}{2}\kappa (N_i/N_c)(c_L - c_i)^2 \ . \tag{2.2}$$

Here k, c_0 and κ, c_L represent the force constant and equilibrium distance of carbon and intercalant atoms, respectively. In our calculations we will have occasion to consider $c_i > c_0$ as well as $c_i < c_0$, and we take $k=\lambda$ for $c_i > c_0$ and $k=\lambda\theta$ ($\theta \gg 1$) for $c_i < c_0$. In other words, we take the force constant for the compression of carbon-carbon layer separation to be significantly larger than that required for the separation of carbon layers in accordance with a Morse-curve fit to experimental data obtained by DiVincenzo, Mele, and Holzwarth.[14] We estimate $\lambda c_0^2 \sim 0.1$ eV, and $\theta \approx 23$ for $c_i < c_0$.

As in the work of Safran[6] we take the interaction energy between the intercalant sandwiches, per carbon atom in a layer, to be given by

$$V_{ij}=V_0(N_i/N_c)(N_j/N_c)/x_{ij}^P\ , \tag{2.3}$$

where N_i and N_j are the numbers of intercalant atoms in the ith and jth layers, respectively, and x_{ij} is the distance between the two. The power P is taken equal to 4 as in earlier work. Note that in our model $x_{ij}=\sum_{l=i}^{j} c_l$ depends on the occupancies of all the intermediate layers. This behavior mimics the effect of a density-dependent screening length. By contrast, previous models have taken the distance to be merely $c_0|j-i|$.

Now, consider a system of N graphite planes with N_c carbon atoms each. The space between the ith and $(i+1)$th planes is occupied by N_i intercalant atoms. The total number of intercalant atoms in the system, $\sum_i N_i=N_I$, is determined by the chemical potential μ. The total thickness of the sample is given by $L=\sum_i c_i$. We neglect any temperature variation of lattice constant (thermal expansion). We also assume that the system is subject to a homogeneous, uniaxial stress in the c direction only due to external pressure.

The entropy of the ith layer is taken to be (per carbon atom)

$$\begin{aligned}S^{(i)}=-k(N_0/N_c)[&(N_i/N_0)\ln(N_i/N_0)\\&+(1-N_i/N_0)\ln(1-N_i/N_0)]\ ,\end{aligned} \tag{2.4}$$

where it has been assumed that the intercalant atoms within a layer occupy the available sites randomly. Thus any in-plane order is ignored. This is justified by the observed insensitivity of the staging phenomenon to details of the in-plane order. In Eq. (2.4) N_0/N_c corresponds to close-packed occupancy ($\frac{1}{8}$ in the case of alkali compounds). Finally, the thermodynamic potential per carbon atom per layer is written as

$$\phi=\frac{1}{N}\sum_{i=1}^{N}\left(E_1^{(i)}+E_2^{(i)}+\sum_{j\,(>i)}V_{ij}-TS^{(i)}-\mu(N_i/N_c)+fc_i\right)\ . \tag{2.5}$$

The first four terms have already been explained. μ is the chemical potential, $f=P\sigma$, where P is the pressure, and σ is the area per carbon atom; c_i is the separation between the ith and $(i+1)$th carbon planes, i.e., the thickness of the ith sandwich.

The variation of the sandwich thickness c_i with the in-plane concentration of intercalant is determined by minimizing $E_1^{(i)}+E_2^{(i)}$, the sandwich energy, with respect to c_i. Then, for a given point (μ,T,f), the equilibrium configuration is one that minimizes the thermodynamic potential. This leads to a set of coupled, nonlinear algebraic equations, as is well known.

We have only considered four possible configurations and their mixtures; stages 1, 2, and 3, and the fractional stage $\frac{2}{3}$ (two filled, one empty). These already give us all the qualitative features of the phase diagrams. Extension to higher stages is quite straightforward.

III. RESULTS AND DISCUSSION

Before we turn to the results we comment on the choice of parameter values. We find it convenient to scale all lengths to units of c_0 ($=3.35$ Å) and all energies to λc_0^2, whose value is of the order of ~ 0.1 eV (by comparison with the Morse-curve fit to experimental data on cohesive energy[14]). Then, the parameters needed are α, β, κ, c_L, and V_0 [see Eqs. (2.1)–(2.4)]. We choose α and β such that the minimum value of the sandwich energy at MC_8 equals $-1.2\lambda c_0^2$. For greater flexibility, α and β may be stage dependent, although we have not done so for the results reported here. κ and c_L are chosen such that at $N_i/N_c=\frac{1}{8}$, $c=1.597c_0$, and at $N_i/N_c=\frac{1}{12}$, $c=1.612c_0$. All these values are of the correct order of magnitude for the alkali-metal–graphite compounds. V_0 is taken to be $100\lambda c_0^6$, but we have tried other values in this range and found no qualitative differences in our phase diagrams.

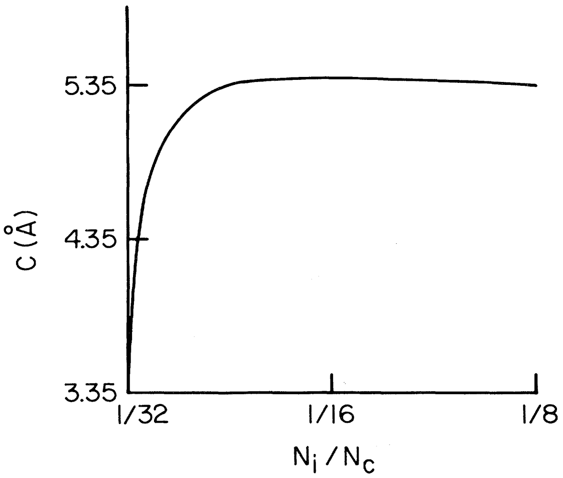

FIG. 1. Variation of carbon layer/intercalant layer/carbon layer sandwich thickness with in-plane concentration of intercalant atoms. Parameter values used are $\kappa/\lambda=230$, $\beta/\lambda c_0=144$, and $c_L/c_0=1.6964$. These parameters are described in the text.

Figure 1 shows the dependence of the sandwich thickness c on the in-plane concentration of intercalant in our model for $f=0$. There is an immediate opening of graphite planes as intercalant atoms are introduced, followed by a leveling off. There is also a small contraction (decrease in c) as the concentration increases to its close-packing value. Such a contraction has been observed in stage-2 Li compounds with varying in-plane density[12] as well as in overcharged acceptor compounds,[15] and interpreted as arising from the competition between electrostatic and elastic energies.[12]

In Fig. 2 the projection of the phase diagram on the temperature-concentration plane for $f=0$ is shown. The temperature is in units of $kT/(\lambda c_0^2)$. In-plane concentration for filled layers ($T=0$) is $N_i/N_c\approx\frac{1}{12}$ to $\frac{1}{13}$ for stages 2 and 3, and stage 1 occurs in the concentration range $\frac{1}{13}-\frac{1}{8}$. This range can be made narrower (almost equal to $\frac{1}{8}$) by taking different values for α and β for stage 1 than for the higher stages. Since our interest lies mainly with pressure-induced transitions in the higher stage compounds, we have not done so in our calculations here. The fractional stage $\frac{2}{3}$ does not occur for $f=0$ in our model. Previous models[8] have had to invoke strong screening to eliminate fractional stages under ambient conditions. As temperature increases stage 1 occupies more and more of the phase diagram and is the only stable stage at very high temperatures[6] (not shown).

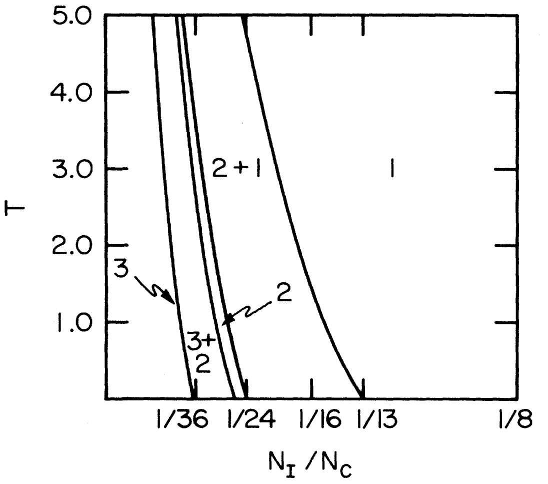

FIG. 2. Temperature-concentration plane projection of the phase diagram for zero pressure ($f=0$). Temperature is measured in units of $\lambda c_0^2/k_B$. Parameter values are $\alpha/\lambda c_0^2=109$, $V_0/\lambda c_0^6=100$; the other parameters are the same as for Fig. 1. The labels (1 +2), etc., designate regions of coexistence of stages. N_I/N_c is the average number of intercalants per carbon atoms in the whole sample.

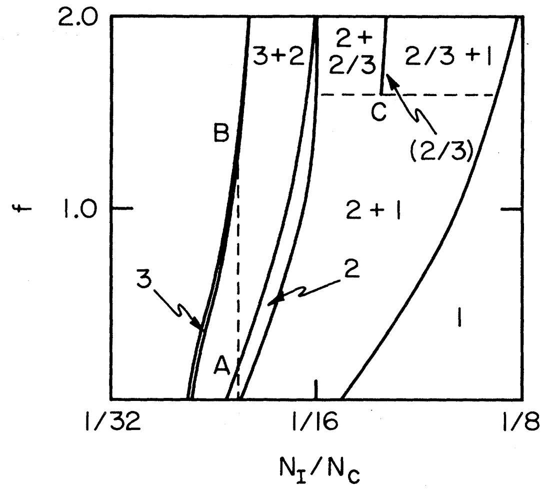

FIG. 4. Pressure-concentration plane projection of the phase diagram for $k_BT/\lambda c_0^2=0.5$. f is in units of λc_0. Parameters used are the same as for Figs. 1 and 2. The stage-2 to stage-3 transformation at constant concentration is indicated by the dashed line.

The effect of external pressure is seen by comparing Fig. 2 ($f=0$) with the corresponding diagram for $f=1$ (in units of λc_0) in Fig. 3. The primary difference is an increase in the in-plane density of all stages. This inverse relationship between sandwich thickness c and in-plane concentration was already mentioned in Sec. II. In Fig. 4 the projection of the phase diagram on the pressure-concentration plane for $T=0.5\lambda c_0^2$ is shown. From this projection one can obtain isothermal transformations as pressure is increased. Observe, in particular, the constant-concentration path *AB* shown as a dashed line at an overall concentration $N_I/N_c \approx \frac{1}{24}$. In going from *A* to *B* one observes a transition from a pure stage 2 to a mixture of stages 2 and 3, and finally a pure stage 3 at point *B*. The model provides a first-order staging transformation from stage 2 to a dense stage 3, in accord with the experiment of Clark *et al.*[3] For the choice $\lambda c_0^2=0.05$ eV, the temperature corresponding to Fig. 4 is ~350 K, and the pressure at point *B* corresponds to ~12 kbar.

The existence of the above transition may be inferred merely by noting that under external stress the system prefers the lowest volume. Assuming a sandwich thickness for KC_{12} and KC_8 of 5.4 Å, one finds that the volume of stage-3 KC_8 is lower than that of stage-2 KC_{12}. In our model the transition occurs when this gain in free energy by lowering the volume exceeds the cost in total cohesive energy.

From Fig. 4 we observe at slightly higher pressures the appearance of the fractional stage $\frac{2}{3}$. Indeed, such a structure has been observed recently in the work of Feurst *et al.*[4] We have found that invoking strong screening as in the work of Millman and Kirczenow[8] eliminates the fractional stage even under pressure.

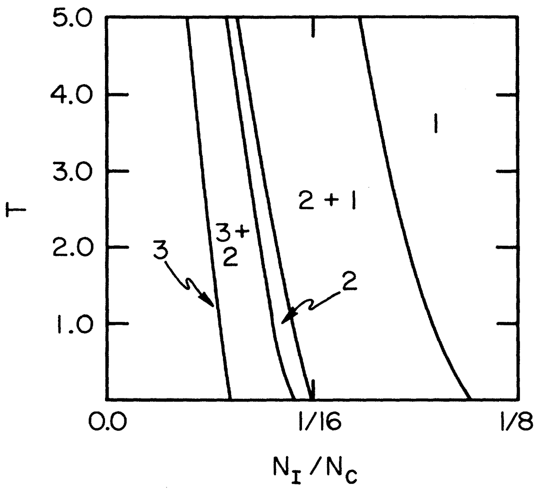

FIG. 3. Effect of finite pressure ($f/\lambda c_0=1$) on the phase diagram of Fig. 2.

IV. CONCLUSION

We have presented a simple thermodynamic model of alkali-metal–intercalated graphite which (i) includes a form of in-plane energy that gives rise to a preferred in-plane concentration of intercalants, (ii) allows the carbon layer/intercalant layer/cabon layer sandwich thickness to depend on the in-plane concentration, and (iii) includes the effects of pressure. The model is shown to be capable of describing several new experimental observations not addressed by previous models: (a) the contraction of sandwich thickness with increased in-plane concentration[12]; (b) the staging transformation under pressure at fixed concentration[3]; and (c) the absence at ambient pressures and the occurrence at higher pressures of fractional stage $\frac{2}{3}$.[4] Also, by the absence of fractional stage under pressure upon inclusion of strong screening[8] we conclude the latter to be inappropriate for describing staging in alkali-metal graphite. In conclusion, we believe the phenomenological model presented here, which retains the same simplicity of earlier models while having a broader scope, adequately describes the equilibrium staging properties of alkali-metal–graphite compounds. It may thus be used as the starting point for the study of domain growth kinetics and other studies.

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[1] For a review, see M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. 30, 140 (1981).

[2] F. J. Salzano and S. Aronson, J. Inorg. Nucl. Chem. 26, 1456 (1964).

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

[4] C. D. Fuerst, J. E. Fischer, J. D. Axe, J. B. Hastings, and D. B. Mc Whan, Phys. Rev. Lett. 50, 357 (1983).

[5] F. J. Salzano and S. Aronson, J. Chem. Phys. 45, 2221 (1966).

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

[7] S. A. Safran and D. R. Hamann, Phys. Rev. B 22, 606 (1980).

[8] S. E. Millman and George Kirczenow, Phys. Rev. B 26, 2310 (1982).

[9] S. E. Millman, G. Kirczenow, and D. Solenberger, J. Phys. C 15, L1269 (1982).

[10] Z. B. Djordjević and S.-H. Chen, Synth. Met. 2, 17 (1980).

[11] D. P. DiVincenzo and E. J. Mele, Phys. Rev. B 25, 7822 (1982).

[12] K. C. Woo, W. A. Kamitakahara, D. P. DiVincenzo, D. S. Robinson, H. Mertwoy, J. W. Milliken, and J. E. Fischer, Phys. Rev. Lett. 50, 182 (1983).

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

[14] D. P. DiVincenzo, E. J. Mele, and N. A. W. Holzwarth, Phys. Rev. B 27, 2458 (1983).

[15] A. Metrot and J. E. Fischer, Synth. Met. 3, 201 (1981).