Order-disorder transitions in stage-2 graphite intercalation compounds

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Ordering phenomena in stage-2 graphite intercalation compounds are studied. Stacking faults in the graphite matrix provide a realization of McCoy-Wu one-dimensional randomness. We predict a smeared first-order transition to a phase characterized by long-range order parallel to, and glasslike structural disorder in the direction perpendicular to the graphite planes.

I. INTRODUCTION

The structure and physical properties of graphite intercalation compounds are the subject of numerous current experimental investigations.[1–10] These compounds consist of metallic layers sandwiched in between parallel carbon layers in graphite. Usually, two neighboring metal layers are separated by n graphite layers, forming a regular "stage-n" stacking sequence. At high enough temperature the metal ions are disordered (liquidlike) within layers. As the temperature is lowered the ions may undergo a transition to some ordered structure. In stage-1 compounds, such as C_8Cs, C_8Rb, C_6Li, C_6Yb, and C_6Eu (Refs. 1–5) a variety of ordered phases have been identified. The transitions to these structures have been recently analyzed on theoretical grounds.[11,12]

In the low-temperature phases of stage-one compounds the metal-ion system exhibits genuine three-dimensional long-range order. This seems not to be the case for stage-2 alkali intercalation compounds such as $C_{24}Cs$, $C_{24}Rb$, and $C_{24}K$.[5–10] Diffraction experiments performed on $C_{24}Cs$ (Refs. 5 and 6) show peaks characteristic of short-range order between *and* within planes. (At very low temperatures a commensurate 2×2 phase, which we are not going to discuss, coexists with this disordered phase.) In $C_{24}Rb$ and $C_{24}K$, structures with in-plane long-range order and disorder between planes have been reported.[7–10,13] The main purpose of this paper is to provide an explanation for the occurrence of such structures. We will argue that the difference between stage-one and stage-two compounds is due to stacking faults in the latter.

The graphite hexagonal layers can appear in one of of three different relative positions, A, B, or C. The stacking in pure graphite is $ABAB\cdots$. Stage-one compounds are stacked in a regular $AMAMA\cdots$ configuration where M denotes a metal-ion layer. An "ideal" stage-two compound may have the structure $AMABMBCMCAMA\cdots$.[13] However, in the physical intercalation process, stacking faults may easily be created, resulting for example, in the sequence $AMABMBAMACMC\cdots$ (Fig. 1). These faults give rise to a finite width of the graphite Bragg peaks[5–10] along the c axis. The experiments show that such faults appear on a microscopic scale at about one out of five layers.

In the absence of faults, the metal system may undergo a transition to a phase with three-dimensional long-range order. Transitions to such structures can be analyzed along the same lines as for the stage-one compounds. The occurrence of stacking faults imposes a very particular kind of randomness in the physical system. To our knowledge these compounds are the first physical realizations of one-dimensional randomness of the type introduced for the Ising model by McCoy and Wu,[14] and discussed in a general context by Lubensky.[15] The system is translationally invariant (nonrandom) in directions along the graphite planes, but translational invariance in the

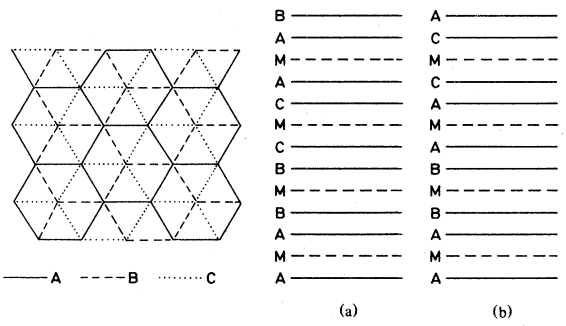

FIG. 1. Stacking sequences in stage-2 intercalation compounds (a) without and (b) with stacking faults.

c direction is lost.

We consider the effects such randomness can have on the structure of the ordered phases, and the nature of the phase transitions to them. We find that the ordered phase is characterized by a well-defined wave vector in the plane, but that there is no long-range order in the c direction. We also believe that the transition in $C_{24}K$ and $C_{24}Rb$ is a smeared first-order transition, of the type discussed by Imry and Wortis.[16] We do not believe that these transitions are realizations of two-dimensional melting. Rather, the structure can be viewed as regular ordered within planes and "glasslike" between planes.

II. ORDERING IN THE PRESENCE OF STACKING FAULTS

Although the presence of stacking faults has been demonstrated experimentally we shall consider first, for completeness, the order-disorder transition in hypothetical "pure" systems without stacking faults. As in most theoretical studies, the effect of defects will be analyzed as a perturbation around some pure system limit.

A. Systems without stacking faults

By analyzing diffraction patterns, Parry *et al.*[13] and Zabel *et al.*[9] have suggested an ordered structure of the form $A\alpha A\ B\gamma B\ C\gamma C$ for $C_{24}Rb$ and $C_{24}K$. This is consistent also with recent results by Hastings *et al.*[8] and by Suzuki *et al.*[10] In this notation α, β, and γ denote three symmetric positions of hexagonal metal layers incommensurate with, and rotated with respect to the graphite layers. This structure is characterized by a wave vector $\vec{k}$ which lies in the ab (graphite) plane. The order parameter describing a transition to this structure has twelve components corresponding to the twelve vectors in the star of $\vec{k}$. Since the appropriate Landau Hamiltonian (see Ref. 11) contains third-order invariants, mean-field theory will predict the transition to be first order. (Note, however, that in the closely related $n=6$ systems 2H-$TaSe_2$ and 2H-$NbSe_2$ there seems to be a second-order transition[17] despite the existence of third-order terms.[18])

In general, for any such structure where the unit cell is not doubled in the c direction a first-order transition is expected. On the other hand, if the transition *does* involve breaking a translational symmetry in the c direction, third-order terms will not occur and the transition may be continuous.[11,12] We now proceed to consider the effect of stacking faults on the nature of the ordered phase described above.

B. Ordered phase in a system with stacking faults

In this section we study how the structure and properties of an ordered metal-ion system will be affected by stacking faults. The graphite matrix gives rise to a spatially varying field acting on the metal ions. This field is periodic within graphite planes, but there is no translational symmetry in the c direction because of the randomness introduced by the stacking faults. Rather than treating the relatively complicated metal-ion system we consider a simpler, but closely related model. In this model the metal ions are subjected to a one-dimensionally modulated periodic field. We believe that the conclusions drawn for the simple model are valid for the real intercalant system. Generalization is possible to the realistic situation where the ions are moving to a realistic two-dimensionally modulated field imposed by the hexagonal graphite layers.[18]

To define our model, consider first a single metal-ion layer (Fig. 2). Such a system is conveniently described in terms of a phase $\phi(x,y)$ giving the position of the metal lattice in the x direction relative to the periodic field[19]

$$H=\left[\frac{d\phi}{dx}-\delta\right]^2-v\cos(\phi-\Delta)\ . \tag{2.1}$$

Here, the first term represents the elastic energy of the metal lattice which favors an incommensurate phase, $\phi=\delta x$. The second term represents the periodic potential which favors the commensurate phase $\phi=\Delta$. Turning now to the three-dimensional (3D) system we shall denote the phase in the ith layer by $\phi_i(x,y)$. The full Hamiltonian takes the form

$$H=\sum_i\left[\left[\frac{d\phi_i}{dx}-\delta\right]^2-v\cos[\phi_i(x)-\Delta_i]-\sum_j\tfrac{1}{2}u_{ij}[\phi_i(x)-\phi_j(x)]^2\right]\ , \tag{2.2}$$

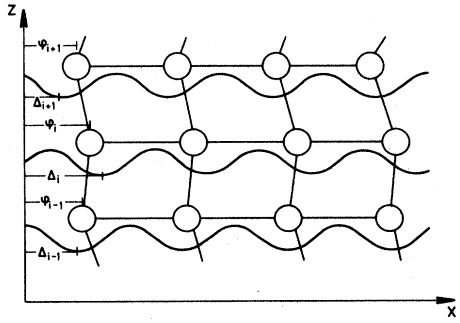

FIG. 2. Metal-ion lattice in periodic potentials. The potentials at different z coordinates, i, are shifted by the amount Δ_i to represent stacking faults.

where the last term is the coupling between layers, which favors a regular 3D metal crystal. Stacking faults will be represented by some random distribution such as $\Delta_i = \Delta\epsilon_i$ where, for example, $P(\epsilon_i) = p\delta(\epsilon_i) + (1-p)\delta(\epsilon_i - 1)$. Consider first the condition for mechanical equilibrium which yields the Euler-Lagrange equations

$$\frac{d^2\phi_i}{dx^2} + v\sin(\phi_i - \Delta_i) + \sum_j u_{ij}(\phi_i - \phi_j) = 0 \quad . \tag{2.3}$$

Consider first the effects of randomness on the commensurate structure. We look for commensurate solutions of the form $\phi_i(x) = c_i$:

$$v\sin(c_i - \Delta_i) + \sum_j u_{ij}(c_i - c_j) = 0 \quad . \tag{2.4}$$

These are N equations (for N layers) with N unknowns, and in general we expect a solution. To illustrate such a solution one can replace the cosine potential by a periodic parabolic one[18] (Fig. 3), $\frac{1}{2}v(\phi_i - \Delta_i)^2$, $-\pi < \phi_i - \Delta_i < \pi$. This leads to the equations

$$v(c_i - \Delta_i) + \sum_j u_{ij}(c_i - c_j) = 0 \quad . \tag{2.5}$$

The solution[20] to this system of linear equation is given by

$$c_k = v\int \frac{dq}{2\pi}\frac{\exp(iqk)}{\omega(q)}\Delta(q) \quad , \tag{2.6}$$

where

$$\Delta(q) = \frac{1}{N}\sum_l \exp(-iql)\Delta_l \tag{2.7}$$

and

$$\omega(q) = v + \sum_j u_{ij}\{1 - \exp[-iq(i-j)]\} \quad . \tag{2.8}$$

The diffraction pattern corresponding to this structure is given by

$$S(\vec{q} = \vec{G}_\perp, q_z) = \left| \sum_{G_\perp}\sum_l \exp(iG_x c_l + iq_z l) \right|^2 \quad , \tag{2.9}$$

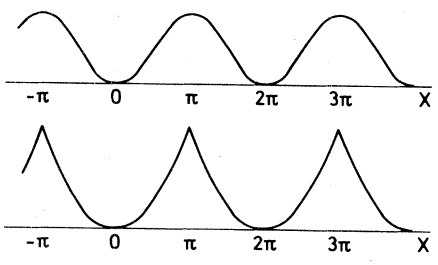

FIG. 3. Sinusoidal and truncated parabolic potential profiles.

where $\vec{G}_\perp$ are the reciprocal-lattice vectors parallel to the planes of the periodic potential. Since the c_l's are random, the diffraction pattern will have no sharp peaks in the q_z direction. Obviously one *does* get peaks which are sharp in the q_x, q_y directions. The physical picture that emerges is that the layers of the ordered metal crystal more or less follow the carbon stacking faults.

We now turn to the case where the metal system is incommensurate with the carbon system. We again consider the simplified situation with truncated parabolic potentials, and nearest-neighbor coupling between planes. In the absence of the locking term ($v = 0$) the incommensurate solution is given by

$$\phi_i = \delta x \quad . \tag{2.10}$$

Treating the locking term to first order in v and looking for solutions of the form

$$\phi_l = \delta x + v\psi_l \tag{2.11}$$

one finds

$$\psi_l(x) = \sum_m \int dx' G_{lm}(x,x') f_m(x') \quad , \tag{2.12}$$

where

$$G_{lm}(x,x') = \int \frac{dq_1 dq_2}{\omega^2(q_1,q_2)} \exp[iq_1(x-x') + iq_2(l-m)] \quad , \tag{2.13}$$

$$\omega^2(q_1,q_2) = q_1^2 + 2u(1-\cos q_2) \quad , \tag{2.14}$$

and

$$f_m(x) = \sin(\delta x - \Delta_m) \quad . \tag{2.15}$$

We have assumed nearest-neighbor coupling, u, only. Generally, the solutions have the form

$$\psi_l(x) = \delta x + v\sum_m a_{lm}\sin(\delta x - \Delta_m) + O(v^2) \quad . \tag{2.16}$$

Again, there will be sharp peaks in the q_x, q_y plane at positions

$$(q_x, q_y) = n\hat{x} + \vec{G}_\perp \quad , \tag{2.17}$$

i.e., at any position which can be written as a sum of a reciprocal-lattice vector of the incommensurate crystal plus a reciprocal vector of the periodic potential. Because of the randomness of the coefficients a_{lm} the peaks are *not* sharp in the z direction.[21] We expect that when the model is generalized to graphite these conclusions will still be correct.

C. Nature of the order-disorder transition

While until now we have studied the ordered phase far from the transition, we now turn to consider the nature of the transition itself. Starting with an ideal system without stacking faults the transition can be described by the appropriate Landau-Ginzburg-Wilson (LGW) Hamiltonian (see Ref. 11). Our first task is to identify the way in which the randomness induced by the stacking faults enters into the Hamiltonian.

The effects of randomness on phase transitions have been studied by Brooks-Harris[22] and Lubensky.[15] The situation we are studying corresponds to having a local transition temperature $T_c(z)$ which varies in a random way in the z direction, but is independent of the position within planes. Such randomness was found to be strongly *relevant*. Therefore, one would expect the critical behavior to be different from that of the pure (ideal) system. McCoy and Wu[14] did an exact calculation with such randomness for the 2D-Ising model and they found a *smeared* transition. Therefore there is reason to believe that in 3D one would also get a smeared transition. If the ideal system undergoes a first-order transition, one can repeat the arguments of Imry and Wortis[16] for the one-dimensional disorder and find that the first-order transition will indeed be smeared. The problem that we are considering falls into the category corresponding to their Fig. 3(b). Probably there will be inhomogeneities on a scale larger than the perpendicular correlation length in the system.

To demonstrate the connection of the ordering in the presence of stacking faults to the random systems mentioned above consider the following LGW Hamiltonian:

$$H=\sum_i r\psi_i\psi_{-i}+\left|\delta-i\frac{\partial\psi_i}{\partial x}\right|^2+w(\psi_i\psi_{-i})^2 - [v\exp(i\Delta_i\psi_i^n)+\text{c.c.}]+u\sum_{ij}(\psi_i\psi_{-j}+\text{c.c.}) \quad . \tag{2.18}$$

Here, ψ_i is a complex order parameter describing a commensurate mass density wave on layer i:

$$\rho(\vec{r})=\psi_{\pm i}\exp\pm i\vec{q}\cdot\vec{r},\quad \vec{q}=\frac{2\pi}{na}\hat{x} \quad . \tag{2.19}$$

Inserting $\psi_i(\vec{r})=A\exp[i\phi_i(\vec{r})]$ and expanding the interaction term in $(\phi_i-\phi_j)$, thus ignoring amplitude fluctuations, one immediately obtains a Hamiltonian like the one discussed in Sec. II B. Δ_i is the random variable which favors different phase shifts in different layers. Thus in this particular model randomness enters the Hamiltonian through a high-order term. However, in the vicinity of the phase transition fluctuations are important giving rise to effective renormalized coefficients. Through this procedure randomness will be transferred from the higher-order terms to the second-order term. At this point, our previous discussion based on Refs. 15 and 22 can be directly taken over.

III. CONCLUSION

In this paper we have considered possible ordering in stage-2 graphite intercalation compounds such as $C_{24}Rb$ and $C_{24}K$. We have argued that stacking faults in the graphite matrix have important effects both on the nature of the ordered state and on the phase transition. To be specific, a three-dimensional ordered state with long-range order parallel to graphite layers, but no translational symmetry perpendicular to them may exist. Such a state is consistent with available experimental observations of diffraction peaks that are sharp in the xy plane but have a finite width in the z direction. We predict the transition to be a smeared first-order transition.

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