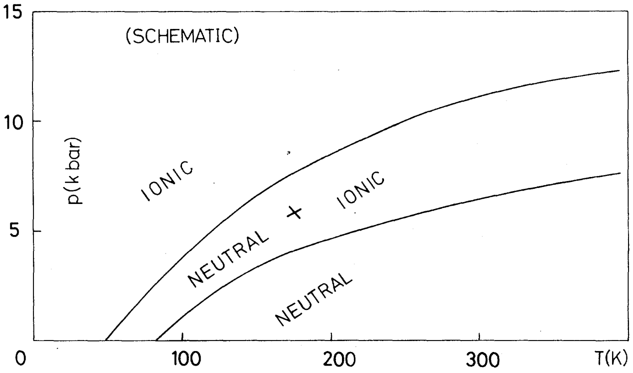

FIG. 5. Schematic phase diagram for TTF-chl.

appears to involve an intermediate region in which both neutral and ionic stacks coexist. A possible explanation for the existence of this anomalous intermediate region is offered in the following paper.[12]

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Model of the Neutral-Ionic Phase Transformation

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A model is presented describing how an organic solid transforms between a neutral and an ionic ground state. Whereas for a one-dimensional stack this transition is expected to be first order, the Coulomb interactions between stacks can cause the phase transition to occur over a broad temperature range by stabilizing an *intermediate* region in between the neutral and ionic phases, in which both neutral and ionized species coexist, as observed in tetrathiafulvalene-chloranil.

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The organic charge-transfer solid tetrathiafulvalene (TTF)-chloranil has mixed stacks, with the donor (TTF) and acceptor (chloranil) alternating along the *a* axis.[1] Between 50 and 84 K, this compound appears[2,3] to undergo some sort of phase transformation, above which the TTF and chloranil molecules are present as nominally neutral species,[1,2] but below which TTF^+ and $chloranil^-$ ions appear. At 300 K a similar transformation[4] appears under high pressure between ~6.5 and ~11 kbar and in other compounds at other pressures.[4] These transitions have been identified[2,4] as N-I[5] phase transitions. Here we will focus on the low-temperature transition in TTF-chloranil where more data are available, but the results will be readily applicable to the pressure-induced transitions as well. Surprisingly, this material does not change discontinuously from neutral to ionic. Rather, changes in the optical, Raman, infrared, and lattice constants occur over a broad temperature range from ~50 to 84 K, in which both neutral and ionized molecules coexist. It is our purpose to propose a simple model that accounts for these results.

The essential features of this transition can be described by considering the competition between the two largest interactions: (1) the net ionization energy (I-A) [required to ionize the donors (I), less the acceptor electron affinity (A)]; and (2) the electrostatic Madelung energy of the ionized solid. The differences in all other energies (band effects, polarization effects, etc.) are assumed to be less important. The energy difference may be written

$$E=\sum_i X_i q_i+\tfrac{1}{2}\sum_{ij}M_{ij}q_iq_j\,, \tag{1}$$

where if molecule i is an acceptor, the sign of the charge q_i is negative and $X_i=A$, but for a donor q_i is positive and $X_i=I$. M_{ij} represents the electrostatic Madelung interaction between molecules i and j. The $|q_i|$ must lie on the interval (0, 1), with $\sum_i q_i=0$ to preserve electrical neutrality. In a completely ionized configuration $|q_i|=1$ for all i and Eq. (1) for N DA pairs gives

$$E=N[(I\text{-}A)-M]\,, \tag{2}$$

where $M=-\tfrac{1}{2}\sum_{i,j}M_{ij}q_iq_j$. From Eq. (2), one sees that the completely ionized state will have a higher energy than the neutral state[6] if $M<I-A$. In an organic solid, the thermal contraction (or applied pressure) is expected to strongly increase M but weakly affect $I-A$. It is now postulated that in TTF-chloranil at 300 K, $M<I-A$, but that M and $I-A$ are sufficiently closely balanced that as the temperature is decreased, this inequality is reversed at some temperature $T=T_c$ and the ionized state appears as the new ground state.

While this simple description of the transition is probably correct in general terms, it does not correctly describe the experimental results[2] on TTF-chloranil. In particular, it suggests[6] that the transition should be first order and to a state in which all the molecules are ionized, contrary to the evidence provided[2] by the infrared and Raman data. In fact, these data indicate the coexistence of neutral and ionized molecules, which suggests one should return to the study of Eq. (1) and drop the *Ansatz* $|q_i|=1$ for all i. At any given temperature T, the M_{ij} in Eq. (1) will have some definite values. The problem of determining the configuration at that T then amounts to minimizing the energy (1) with respect to all the q_i subject to the conditions $0\leqslant|q_i|\leqslant 1$ and $\sum_i q_i=0$, a problem for which the general solution is not known. Here we shall explore the consequences of assuming that every $|q_i|$ takes on either the value 0 or 1 (but not some intermediate value). This problem closely resembles that of determining the ground state of an Ising model with long-range interactions and a magnetic field. Again, this is an unsolved problem and we are reduced to trying to guess reasonable solutions.

In order to motivate the solution we shall eventually present, let us examine some simpler cases. First, let us consider a single mixed stack of donors (D) and acceptors (A) shown schematically in Fig. 1(a). Each donor has as nearest neighbors two acceptors (and vice versa). It is fairly obvious that the only solutions[6] are those in which either $|q_i|=0$ or $|q_i|=1$ for all i. Which of these solutions gives the lower energy depends upon the relative values of $I-A$ and M_1, where M_1 is given by a sum of the M_{ij} restricted to the single stack. Thus, for the single stack, there will be some critical temperature T_1 where $M_1=I-A$ and at which the stack passes from a neutral to a completely ionized state, discontinuously.

Next, consider a plane of molecules in the TTF-chloranil lattice, for example, the *ac* plane, shown schematically in Fig. 1(b). Each donor has acceptors as intrastack *and* interstack nearest

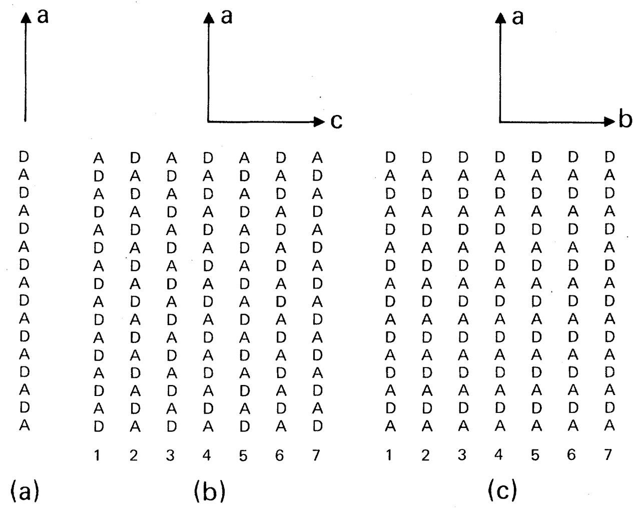

FIG. 1. (a) A single mixed stack along the *a* direction; (b) the arrangement of stacks in the *ac* plane of TTF-chloranil; and (c) the arrangement in the *ab* plane, showing the repulsion between stacks.

neighbors and vice versa, so that we would expect that the only solutions are the completely neutral or completely ionized. Thus, the plane should switch from neutral to ionic at temperature T_2^A determined by $M_2^A = I - A$, where M_2^A is the two-dimensional sum over the (attractive) interstack interactions in the *ac* plane. Viewed in another way: A single stack, say stack No. 4, will tend to ionize completely when T falls below T_1, which will encourage the neighboring stacks 3 and 5 to ionize, which in turn will make it easier for 2 and 6 to ionize, and so on. Thus, the stacks ionize cooperatively and we expect the attractive Coulomb interactions between stacks to make the transition of this plane of molecules easier, i.e., $T_2^A > T_1$, and still discontinuously.

The situation is quite different if we consider an *ab* plane, shown in Fig. 1(c). Again, each donor has two acceptor neighbors on the same stack, but its neighbors in adjacent stacks are now donors, giving rise to a repulsive Coulomb interaction between ionized stacks. Consequently, if one stack, say No. 4, were to ionize when T falls to T_1, it will inhibit ionization on the neighboring stacks 3 and 5. Indeed, it will inhibit the ionization on any of the other stacks. Thus, at $T = T_1$ at most one stack will ionize. If T is now lowered below T_1 more stacks will ionize because some net energy (roughly proportional to $T_1 - T$) may be gained by ionizing a stack and, provided not too many stacks are ionized, they may remain sufficiently far apart for this energy gain to exceed the energy loss due to their mutual repulsion. Thus, we would expect that when T falls below T_1 some ionized stacks (distantly spaced) will appear and that as T is lowered further, their number will increase until (possibly) a completely ionized state is reached. Thus, in this case, unlike the single-stack and *ac*-plane case, we do *not* expect to see a first-order transition but a gradual transition starting when T falls below T_1.

With these examples in mind, we can now consider the whole three-dimensional crystal. It is clear that a whole *ac* plane of molecules would like to ionize cooperatively when T reaches T_2^A. However, the kind of argument given in connection with the *ab* plane shows that when one of the *ac* planes ionizes, it inhibits ionization in all other *ac* planes. Following this line of argument, we conclude that as T falls below T_2^A the number of *ac* planes completely ionized increases until, when the temperature T_3 is reached, the three-dimensional lattice is completely ionized. Thus, the onset of the transition at T_c, which we now identify with T_2^A, is not required to be first order, and we have a simple explanation of the presence of both neutral and ionized species below T_c, which corresponds to neutral and ionic *ac* planes of molecules.

Let us examine this picture in more detail, and find the fraction, $F(T)$, of the *ac* planes that are ionized at any temperature T below the onset temperature T_c. For T close to T_c, only a few planes will be ionized and since the interaction energy $V(R)$ between planes is repulsive, the minimum-energy arrangement is that in which they are equally spaced. If this spacing is R, $F(T) = b/R(T)$, where b is the b-lattice parameter. For T near T_c, M_2 should vary linearly with $t \equiv T_c - T$ and the energy gained per DA pair by ionizing an *ac* plane of such pairs will have the form αt (α is some parameter). The total energy is just the sum of these two contributions:

$$E(R) = N(b/R)[-\alpha t + V(R)], \tag{3}$$

where we include only the repulsion between nearest-neighbor ionized planes. This is valid since we are interested in small t and, therefore, large R, in which case $V(R) = V_0 \exp(-kR)$. We may now determine R by minimizing $E(R)$, Eq. (3), which gives

$$\alpha t = V_0(1 + kR)\exp(-kR). \tag{4}$$

This problem is related to the separation between domain walls in the incommensurate-commensurate transition.[7,8] The solution to Eq. (4) gives $R(T)$ and hence $F(T)$ ($F = b/R$), which is sketched as the solid line in Fig. 2, curves *a* and *b*: As $t \to 0$, $R \to \infty$ and $F \to 0$, but with an infinite slope ($dF/dt \to \infty$).

What is the thermodynamic nature of the transition? Since the energy $E(t)$ is continuous through the transition, i.e., $E(0) = 0$ at $t = 0$, the transition is not first order. The specific heat is

$$c_p = dE/dT + p\, dV/dT. \tag{5}$$

Focusing on the first term of Eq. (5), we have from Eq. (3)

$$N^{-1} dE/dT = (\alpha b/R) + N^{-1}(dE/dR)(dR/dT) = \alpha F, \tag{6}$$

since R is chosen to make $dE/dR = 0$. Since $F(t) = 0$ at $t = 0$, Eq. (6) gives no divergent contribution to the specific heat at T_c, i.e., no contribution like a second-order transition. On the other hand, $N^{-1} d^2E/dT^2 = \alpha(dF/dT)$ does diverge at $t = 0$,

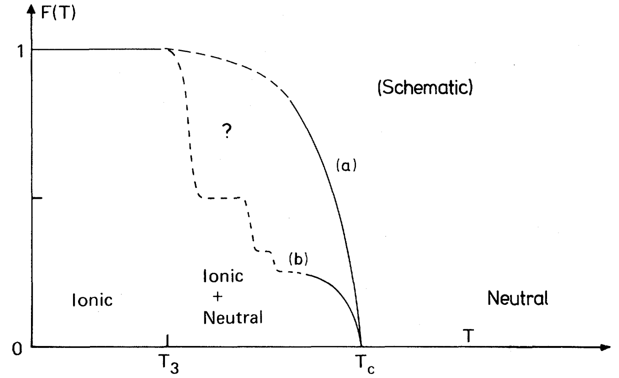

FIG. 2. The fraction, $F(T)$, of ionic molecules, showing the intermediate region predicted by the model between $T_3 \leq T \leq T_c = T_2{}^A$ (schematic), with the possibility of "staging" shown in curve b.

as in a third-order phase transition. Thus, at the onset temperature the first term of Eq. (5) is predicted to give rise to a weak effect on $c_p(T)$, a discontinuity in dc_p/dT, characteristic of a third-order phase transition. This feature may be an artifact of the calculation (which neglects fluctuations) and the measured c_p may be only second order. Also, there could be a large contribution to c_p from[3] the dV/dT at T_c [see Eq. (5)]. The remainder of the $F(T)$ curve in Fig. 2 is only schematic, since well below T_c of the onset, our approximations for $V(R)$ and $M(T)$ and our idealized model probably all break down. Clearly, the possibility of a devil's staircase and of "staging" phenomena could also arise, as when, for example, $P(T) = \frac{1}{2}$, every other ac plane would be ionized and there might be unusual difficulty in introducing further ionized planes.

The results of this paper may be summarized by discussing the fraction, $F(T)$, of ionized molecules shown in Fig. 2. At lowest temperatures, it is asserted that the Madelung energy is larger than the ionization energy ($M > I - A$) and the ground state is ionic. As the temperature is increased, the thermal expansion reduces the Madelung energy. Above a temperature T_3, $M < I - A$ and the fully ionic phase is energetically less favorable than the neutral phase. There could have been a discontinuous ionic-neutral transition at $T = T_3$, but in TTF-chloranil an intermediate, partially ionic region is stabilized by forming microscopically inhomogeneous structures containing both ionic and neutral regions. This intermediate region persists up to a temperature $T_c = T_2{}^A$, above which M is so low that the solid becomes fully neutral. Just below T_c we have considered an idealized model in which the intermediate phase consists of sheets of ionized molecules in the ac plane, separated by neutrals. These sheets (and hence this intermediate phase) are energetically stabilized by the anisotropy of the Coulomb interactions between charged molecules, i.e., attractive interactions within the sheets, but repulsive between sheets. The onset of the occurrence of these sheets just below T_c is predicted to give a contribution to the specific heat which is characteristic of a thermodynamically third-order phase transition, although in practice, the situation may be more complicated. Even though we have discussed a specific model of an ordered array of ionized ac planes, a number of other inhomogeneous (ordered and nonordered) structures are also possible. The essential physics of these structures would be basically the same as discussed here.

It is interesting to compare this partially ionic region between neutral and ionic in a mixed stacking solid discussed above with the case of a segregated stacking solid, where there are separate donor and acceptor stacks. The analog to Fig. 2 corresponds to considering[9] the degree of charge transfer ρ as a function of $I - A$, i.e., for a series of different compounds with various values of $I - A$. Compounds with low $I - A < M$ are fully ionic with $\rho = 1$ and are Mott insulators. As $I - A$ is increased to the point where $I - A > M$, the fully ionic phase is energetically less favorable than the neutral phase. There could have been a discontinuous ionic-neutral transition at this point, but instead an intermediate phase is found in which the compounds are partially ionic. In this case of segregated stacks, the stacks themselves have $\rho < 1$ and are partly ionic or mixed valence. This feature is responsible for the high conductivity of compounds from this intermediate region.[9] What stabilizes this region of mixed valence and $\rho < 1$? This is a fundamental and very controversial question, complicated by the large overlap along the stacks. Nevertheless, it has been argued[10] that this mixed-valence phase is stabilized in the same way we have suggested for the intermediate region in TTF-chloranil, but in the case of segregated stacks the direction of repulsive interactions is *along* the stack. Thus, the intermediate phase is imagined as a Wigner crystal where there are planes of ionized molecules perpendicular to the stacks, separated by a distance R. Whatever the explanation, the existence of these intermediate phases is one of the most important and interesting features of both types of stacked organic materials.

We wish to thank P. M. Horn for a number of enlightening discussions.

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Dynamics of Island Growth in a Simple Model of the Chemisorption System O on W(110)

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The dynamics of island growth have been studied with Monte Carlo techniques for a simple lattice-gas model of O on W(110) when the system is suddenly quenched at a constant coverage $\rho = 0.25$ to a temperature well below its transition temperature. The structure functions for the local coverage and $p(2\times1)$ order parameter exhibit a simple scaling with respect to certain characteristic time-dependent lengths. This scaling is qualitatively similar to that found in other systems such as binary alloys.

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An active branch of two-dimensional phase transitions involves the study of chemisorption systems such as O on W(110). Extensive experimental,[1,2] theoretical,[3,4] and Monte Carlo[4,5] investigations have been carried out on such systems in order to determine phase diagrams and estimate the adatom-adatom interactions. In addition, considerable attention[6] has been given to understanding the process of island formation which, for example, occurs in O on W(110), where one encounters ordered regions of $p(2\times1)$ and $p(1\times2)$ structures at low coverages ($\rho \leqslant 0.5$) and sufficiently low temperatures. The thermodynamics and some aspects of the kinetics of this ordering have been studied by low-energy electron diffraction (LEED) techniques.[1,6] Also, model calculations[7] have been carried out to determine the angular profile of Laue spots (obtained in LEED experiments) as a function, for example, of average island size.

In this Letter we wish to focus attention on an aspect of island growth and phase separation under conditions which have so far not been studied. Namely, we study by Monte Carlo techniques the dynamical evolution of a simple lattice gas of O on W(110) when the system is quenched from a high-temperature disordered "gas" state to a dynamically unstable state (i.e., inside the classical spinodal curve) below its "critical point" at a coverage of $\rho = \frac{1}{4}$ (Fig. 1). Since the low-temperature equilibrium consists of two-phase coexistence of $p(2\times1)$ [or $p(1\times2)$] islands with the "gas" phase, the quenched system immediately begins to phase separate. This proceeds by the formation of small islands of $p(2\times1)$ and $p(1\times2)$ order which then grow in a fashion somewhat similar to that observed in binary alloys[8] and other systems.[9] We investigate this island growth and phase separation by evaluating the nonequilibrium, time-dependent (circularly averaged) structu function $S_\alpha(k,t)$ ($\alpha = \rho$ or ψ), with $\rho(\vec{r})$ and $\psi(\vec{r}) \equiv (-1)^m \rho(\vec{r})$ denoting the local coverage and $p(2\times1)$ order-parameter density, respectively, where $\vec{r} = m\hat{a} + n\hat{b}$ represents a vector in the (110) plane with $\hat{a}$ and $\hat{b}$ being primitive vectors as shown in Fig. 1. Both structure functions describe