

and He^{++} at 3.5 MeV/amu. In any case, the magnitude of the effect is unassailable since even the undeconvoluted edge of the B^{5+} spectrum at 3.5 MeV/amu lies well to the high energy-loss side of the undeconvoluted peak of the H^+ spectrum.

No theories of higher-order Z_1 effects have been specifically compounded for the case of channeled ions. Theories developed are for random collisions and the analysis for valence electrons has not yet been completed, but it is difficult to see how polarization and Bloch corrections for valence electrons alone can be responsible for the observed effects. Increasing the ion velocity will increase the contribution of inner shells to the total stopping power.^{17,18} To first order this contribution is expected to scale as Z_1^2 , but polarization terms for large-impact-parameter collisions of channeled ions with $5p$, $5s$, and $4f$ electrons could be large and may be responsible for the increasing Z_1^3 effect at high velocities. The effects of dynamical screening,¹⁹ which have not been considered in detail thus far, also appear to scale only with Z_1^2 ; however, since the magnitude of this effect which tend to nullify charge differences is larger at lower velocities, deviations from Z_1^2 scaling may tend to suppress the Z_1^3 term for higher Z_1 at lower velocities.

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Classification of Order-Disorder Transitions in Common Adsorbed Systems: Realization of the Four-State Potts Model*

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Order-disorder transitions on square, triangular, and honeycomb arrays are classified according to whether they can be continuous or must be first order by applying a criterion of Landau. In particular, the transitions to 2×2 arrays on triangular and honeycomb lattices are predicted to be in the universality class of the four-state Potts model. A physical realization of this model, N_2 on Kr-plated graphite, is proposed.

In the literature of physical and chemical adsorption, numerous observations of ordered adsorbate structures are reported. Many of these structures are identified as superlattices in reg-

istry with the array of adsorption sites provided by the substrate.¹ In only a few cases, however, has the *transition* from the ordered to disordered state been studied.²⁻⁷ With the recent advances

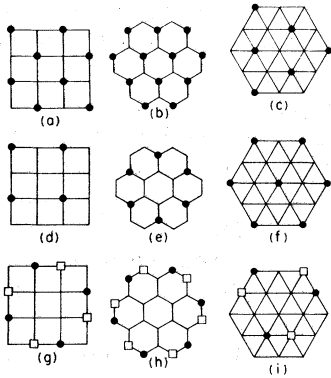


FIG. 1. Nine of the superlattice structures considered. The respective notations and transitions are (a) $(\sqrt{2} \times \sqrt{2})R45^\circ$, Ising; (b) $(1 \times 1)[\frac{1}{2}]$, Ising; (c) $(\sqrt{3} \times \sqrt{3})R30^\circ$, three-state Potts; (d) 2×2 , first order; (e) $(2 \times 2)[\frac{1}{4}]$, four-state Potts; (f) 2×2 , four-state Potts; (g) $(\sqrt{5} \times \sqrt{5})R26^\circ$, first order; (h) $(\sqrt{7} \times \sqrt{7})R19^\circ[\frac{1}{4}]$, first order; (i) $(\sqrt{7} \times \sqrt{7})R19^\circ$, first order. Two possible orientations are shown in (g), (h), and (i).

in experimental techniques, the number of such investigations has increased. Therefore, a systematic study of the possible ordered states and the nature of the transition to them seems to be an important undertaking. This is strengthened by the fact that some of the systems provide physical realizations⁸ of various theoretical models of current interest.

In this Letter we propose a classification scheme for commonly observed adsorbate structures. We predict the transition to most of these to be first order. The transitions that are predicted to be continuous belong to the universality class of either the Ising, three-state Potts, or four-state Potts models.⁹

We consider those substrates, which present adsorption sites forming either a square, triangular, or honeycomb array. Our procedure is readily applicable to other arrays. We also limit consideration to the most commonly observed kind of superlattices, those which possess the same rotational symmetry as the substrate. Such arrays are denoted¹ $(a \times a)R\theta$ if the dimensions of the unit cell of the superlattice is a factor "a" times the substrate cell and is rotated by θ . Several of the superlattices which we have investigated are shown in Fig. 1. On the honeycomb array, both honeycomb and triangular structures can be formed so that we append the coverage to the above notation in order to distinguish between them. Superlattices other than those treated here are easily handled.¹⁰ Finally, we consider only transitions from the disordered to the ordered

phase. Transitions between ordered phases can be treated in the same manner. The Hamiltonian of the systems under consideration is that of a lattice gas,

$$H - \mu N = \frac{1}{2} \sum_{i,j} V(\vec{r}_i - \vec{r}_j) \rho(\vec{r}_i) \rho(\vec{r}_j) - \mu \sum_i \rho(\vec{r}_i), \quad (1)$$

where $\rho(\vec{r}_i)$ takes the value 0 or 1 and is the occupation number of the adsorption site at \vec{r}_i . The disordered state is characterized by $\langle \rho(\vec{r}_i) \rangle = \rho_0$ for all i , where ρ_0 is the average density and the brackets denote an ensemble average.

In order to classify the transitions to the superlattice structures, we employ the theory of Landau and Lifshitz.^{11,12} According to this, a transition can be continuous if three phenomenological rules are satisfied: (1) The order parameter belongs to a single irreducible representation of the symmetry group G_0 of the system (in the disordered phase), (2) no third-order invariants can be constructed from this irreducible representation, and (3) no invariants can be constructed which contain first powers of spatial derivatives (the Lifshitz Rule). The predictions of these three rules have proved to be correct in three dimensions. In two dimensions, however, it is known that the second rule is violated¹³ by the three- and four-state Potts models.¹⁴ Since there are no known violations of the first rule, we make use of it as a simple yet powerful predictive tool to classify whether transitions from disordered states to the ordered structures of interest can be continuous or whether they must be first order.

In order to apply this rule to the transitions of interest, we must identify G_0 and define the order parameter. To identify G_0 note that the symmetry operations under which the disordered phase is invariant define the space group $P4mm$ for the square array and $P6mm$ for the triangular and honeycomb arrays. An additional particle-hole symmetry exists when $\rho_0 = \frac{1}{2}$ (corresponding to time-reversal invariance in the well-known magnetic analog of the lattice gas). The order parameter is defined as $\langle \rho(\vec{r}_i) \rangle - \rho_0$ which vanishes in the disordered state.

The transition to any superlattice structure characterized by a density $\langle \rho(\vec{r}_i) \rangle$ can now be examined in light of the first rule by simply determining whether $\langle \rho(\vec{r}_i) \rangle - \rho_0$ belongs to a single irreducible representation of G_0 —if it does, it can be continuous; if it does not, the transition must be first order. Mukamel¹⁵ and Mukamel and Krinsky^{10,12} have pointed out that, in the former case,

the order parameter will have n components, where n is the dimensionality of the representation. Furthermore, the density can be written in the form

$$\langle \rho(\vec{r}_i) \rangle = \rho_0 + \sum_{j=1}^n c_j \varphi_j(\vec{r}_i), \quad (2)$$

where the n functions φ_j transform like the basis of one irreducible representation of G_0 . Since $n+1$ linearly independent functions can be constructed from ρ_0 and the n functions φ_j , the ordered state will be $(n+1)$ -fold degenerate [for example, the structure of Fig. 1 (f) is fourfold degenerate].

Our investigation is considerably simplified by noting that the maximum dimensionality \mathcal{N} of the irreducible representation of G_0 is finite, being, for the lattice-gas models, 8 and 12 for the symmetries $P4mm$ and $P6mm$, respectively. It follows from Eq. (2) and the above discussion that any superlattice configuration which can be reached by a continuous transition from the disordered state must be characterized by not more than $\mathcal{N} + 1$ linearly independent function $\langle \rho(\vec{r}_i) \rangle$. Only a few superlattices have sufficiently small degeneracy to satisfy this criterion. *Transitions to all other superlattices must be first order.* These include $(a \times a)R\theta$ ordered states where $a > 3$ for square substrates, and $a > \sqrt{13}$ for triangular substrates. For honeycomb and triangular superlattices on honeycomb arrays, the limits are $\sqrt{13}$ and $\sqrt{7}$, respectively. Given an ordered state which is $(n+1)$ -fold degenerate with $n \leq \mathcal{N}$, it is a standard exercise in group theory to determine whether $\langle \rho(\vec{r}_i) \rangle - \rho_0$ belongs to one irreducible representation.¹⁶ We have done this for the superlattice structures noted above with the following results.

The transition to the structures shown in Figs. 1(a) and 1(b) are characterized by $n=1$ and described by the Ising model.³ In order to determine whether the other transitions are describable by known theoretical models, we have identified the corresponding Landau-Ginsburg-Wilson Hamiltonian by constructing from the φ_j of Eq. (2) the third- and fourth-order invariants. For the case with $n=2$ shown in Fig. 1(c), the corresponding Hamiltonian is that of the three-state Potts model,¹⁷ as first noted by Alexander.⁸ Recent specific-heat measurements of Bretz⁷ on He adsorbed on single-crystal exfoliated graphite, a system which exhibits this structure, yield $\alpha = 0.36$ for this transition. This clearly indicates

that the transition does not belong to the universality class of the Ising model as had been previously assumed.⁵

The order parameter of the 2×2 structure of Fig. 1(d) belongs to two irreducible representations. Thus a first-order transition is predicted.¹⁸ In contrast, the 2×2 structures on the honeycomb and triangular lattices Figs. 1(e) and 1(f) can be continuous and the order parameter has three components. Denoting the real basis of the irreducible representation by $\{\varphi_1, \varphi_2, \varphi_3\}$, we find the Landau-Ginsburg-Wilson Hamiltonian

$$H = \frac{1}{2} r \sum_i \varphi_i^2 + \frac{1}{2} \sum_i (\nabla \varphi_i)^2 + w \varphi_1 \varphi_2 \varphi_3 + u (\sum_i \varphi_i^2)^2 + v \sum_i \varphi_i^4, \quad (3)$$

which is that of the four-state Potts model.¹⁹ That this model should arise in adsorption studies is probably one of our most striking results. There is a single experimental finding which is germane to this case, the low-energy electron diffraction (LEED) observation² of a continuous transition to the 2×2 structure in the system Ni(111)-O.

It would be extremely interesting if one could prepare a physical realization which could be studied *both* by heat-capacity and scattering techniques. A likely candidate is obtained if we attempt to prepare the four-state Potts system on a honeycomb array of sites. Such an array can be obtained by preplating graphite with a close-packed layer of some atom of species A . If one now adsorbs on this layer an atom of species B which is larger than A , then the second-nearest-neighbor interaction will be repulsive as needed for the $(2 \times 2) \left[\frac{1}{4} \right]$ structure to form. In order that the system be thermodynamically stable, B must be less strongly bound to the graphite than A . A system which meets both these criteria is N_2 adsorbed on Kr-plated graphite. This system has several attractive features. The presence of the ordered phase, if it does exist, can be verified directly by either LEED or neutron scattering measurements. The specific heat is expected to be very strongly singular since the critical exponent α of the four-state Potts model is thought to be²⁰ about 0.5. A beautiful comparison—and an interesting experiment in its own right—would be afforded by replacing the N_2 by He, because He on Kr-plated graphite should order into the $(1 \times 1) \left[\frac{1}{2} \right]$ structure and display the logarithmic specific heat of the Ising model.

As to the structures of Figs. 1(g)–1(i), the first Landau rule is satisfied with $n=8$, 12, and 12,

respectively. However, in contrast to the preceding cases, the Lifshitz condition is not satisfied and thus one would expect first-order transitions. A LEED study of systems that display these structures would be interesting because observation of a continuous transition would prove the Lifshitz rule violated. Finally, transitions to all $(a \times a)R\theta$ structures not shown in Fig. 1 are predicted to be first order.

In summary, we have systematically surveyed the transitions to common superlattices on square, triangular, and honeycomb substrates. New results include the prediction of many first-order transitions and continuous transitions in the class of the four-state Potts model. These results have yet to be tested experimentally.

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Measurement of the Difference between the Dynamic NMR and Static Susceptibilities of Superfluid ³He-B Using an rf-Biased Superconducting Quantum-Interference Device*

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The temperature-dependent susceptibility of superfluid ³He-B has been measured both statically and via a pulse technique in a field of 309 G using an rf-biased superconducting quantum-interference device (SQUID). In the pressure range 26.5 to 18 bar, the dynamic NMR susceptibility agrees qualitatively with the theoretical weak-coupling predictions for the Balian-Werthamer state. However, the static susceptibility, measured using the same rf-biased SQUID and detection system, is significantly smaller than the dynamic susceptibility.

The difference between the susceptibility of superfluid ³He-B as measured statically by superconducting quantum-interference device

(SQUID) techniques and dynamically using NMR techniques is one of the most puzzling experimental discrepancies still existing in superfluid