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Classification of continuous order-disorder transitions in adsorbed monolayers

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We present a classification of continuous order-disorder transitions of an adsorbed monolayer on substrates with $P2mm$, $C2mm$, $P4mm$, and $P6mm$ symmetries, assuming the validity of the Landau-Lifshitz theory (apart from the rule against third-order invariants). The transitions belong to the universality class of the Ising, three- or four-state Potts model, and X-Y model with "cubic" anisotropy.

I. INTRODUCTION

The experimental study of physically and chemically adsorbed systems has the potential to contribute significantly to our understanding of critical phenomena in two dimensions. In order to help realize this potential, it seems important to undertake an inclusive study to determine what systems can be expected to display interesting critical behavior. On the other hand, the improvement of experimental resolution is essential to obtain reliable estimates for the various critical exponents. The experimental techniques used to investigate two-dimensional systems are rapidly improving, and we anticipate that critical exponents will be measured with increasing frequency within the next few years.[1] To encourage experiments on systems of particular interest in critical phenomena, we present here a catalogue of the different universality classes which can be observed in one kind of transition that commonly occurs in adsorbed systems, namely, structural order-disorder transitions.

Whenever adsorbed atoms or molecules are found with overwhelming probability at adsorption sites provided by the substrate, structural order-disorder transitions are to be expected. At high temperatures, the array of sites is randomly occupied while at low temperatures the sites may be occupied in an ordered manner such that the adsorbate is found in a superlattice structure. The existence of this ordered structure can be ascertained directly by low-energy-electron diffraction[2] (LEED), neutron[3] or x-ray diffraction,[4] or indirectly by measurements of vapor-pressure isotherms,[5] specific heat,[6] or nuclear magnetic resonance.[7]

We emphasize that the number of different adsorbate-substrate combinations that display such ordered structures is very large. A useful catalogue of the reported LEED observations is provided by Somorjai.[8] Most of these observations are limited to verifying the existence of the superlattice structure and ascertaining its periodicity. In this paper we point out that many of[9] the transitions that this large number of systems will undergo should fall into a small number of universality classes, several of which are of particular interest in critical phenomena. Thus, with the catalogue presented here, the choice of adsorbate-substrate combinations can be made so that a particular class of interest can be studied.

In a previous paper[10] we considered square and triangular arrays of adsorption sites, and superlattice structures which possessed the same rotational symmetry as the array. These arrays are denoted $(a \times a)\, R\theta$ if the dimension of the unit cell of the superlattice is larger by a factor a than that of the substrate cell and is rotated by θ.[11] In the present paper we generalize our analysis and study adsorption arrays with the symmetry of the four most common Bravais lattices.[12] Furthermore our analysis produces *all* possible superlattice structures on these arrays which can undergo a continuous transition [not only those denoted $(a \times a)\, R\theta$], *provided* certain symmetry arguments in the phenomenological theory of Landau and Lifshitz are valid. This theory is reviewed in Sec. II and applied in Sec. III. Our results are collected and discussed in Sec IV. We show that the classes of critical behavior that can be studied in such systems consist of the two-dimensional Ising, three- and four-state Potts models, and the X-Y model with cubic anisotropy. In two dimensions, the three- and four-state Potts systems undergo continuous transitions,[13] and the X-Y model with cubic anisotropy is predicted to be nonuniversal.[14,15] This rich variety of models leads us to believe that experiments on adsorbed systems can yield information on critical phenomena, which can hardly be provided by other systems.

II. METHOD OF ANALYSIS

In this section we present the model Hamiltonians for the adsorbed systems and review the phenomenological theory of Landau and Lifshitz which we shall apply to it.

The model Hamiltonian which we employ, that of a lattice gas, emerges naturally from the assumption that the adsorbate is found with overwhelming probability at adsorption sites. In the lattice gas model, the atom can *only* be found at the sites. Thus the occupation number $n(\vec{r})$ takes only the value zero or one. The vector $\vec{r}$ denotes the position of the site. By characterizing the adsorbate entirely by its position, that is by $n(\vec{r})$, we are assuming that there are no other variables associated with it, such as internal degrees of freedom. This assumption excludes, for example, consideration of a long molecule which, while occupying a single site, can align itself along one of a few symmetry directions of the substrate. With this exception the use of a lattice-gas description in no way restricts our analysis. This is because the Landau-Lifshitz theory depends on considerations of symmetry and the symmetry of both the disordered and the commensurate ordered states of the adsorbed system are the same as those of the lattice gas.

The particular lattice-gas Hamiltonian which contains only two-particle interactions,

$$H-\mu N=\frac{1}{2}{\sum_{r,r'}}' v(\vec{r}-\vec{r}')n(\vec{r})n(\vec{r}')-\mu\sum_{r}n(\vec{r}), \tag{2.1}$$

where the prime on the sum indicates $\vec{r}\neq\vec{r}'$ and μ is the chemical potential, is often employed for the calculation of phase diagrams. As this Hamiltonian does not contain the weak three-body forces which are expected to be present in any real system, it possesses, for a particular value of μ, a symmetry under the interchange of particles and holes [i.e., $n(\vec{r})\rightleftarrows 1-n(\vec{r})$] which the physical system does not. This additional symmetry permits such a model system to exhibit classes of critical behavior which the physical system is not expected to manifest. We do not restrict our analyses to the particular lattice-gas Hamiltonian of Eq. (2.1) and thus do not employ the additional particle-hole symmetry. We shall note in Sec. III, however, where the use of this Hamiltonian would produce unphysical classes of transitions.

The order-disorder transition can now be described in terms of the lattice-gas model. At high temperatures, in the disordered state, the density of the adsorbate $\rho(\vec{r})=\langle n(\vec{r})\rangle$ is the same at each site. Therefore, the density is invariant under the symmetry operations of the space group G_0 that leaves the Hamiltonian (2.1) invariant. In the ordered phase, this symmetry is spontaneously broken and a state of lower symmetry $G\subset G_0$ is observed. The density is no longer the same at each site but can be written[16]

$$\rho(\vec{r})=\rho_0(\vec{r})+\delta\rho(\vec{r}),$$

where $\rho_0(\vec{r})$ has the symmetry G_0 and $\rho(\vec{r})$ the symmetry G. Their difference can be expanded as a linear combination of real functions which transform according to the irreducible representations of G_0,

$$\delta\rho(\vec{r})=\sum_{l}{}'\sum_{i}c_{li}\phi_{li}(\vec{r}), \tag{2.2}$$

where l enumerates the representations and i specifies the functions within a representation. The prime on the l sum means that the unit representation is excluded as it already appears in the density through $\rho_0(r)$.

We wish to know whether this order-disorder transition can take place continuously. The theory of Landau and Lifshitz answers this question by stating that *a transition can be continuous if certain conditions are satisfied.* These conditions are the "Landau rules" which have been discussed in detail by Mukamel and Krinsky,[17] who also provide relevant references.

The symmetry group of the ordered phase G can be determined experimentally using LEED. Thus a classification of ordered structures based on the various possible groups G is of experimental relevance. Once G is known, the functions ϕ_{li} that can appear in (2.2) are limited. The first Landau rule states that a transition can be continuous only if the order parameter belongs to a single irreducible representation, which we will call the "leading" representation. This rule needs to be employed with care, since the occurence of a nonzero-order parameter in the leading representation may indirectly induce contributions to (2.2) from other representations, due to higher order invariants in the free energy.[18] In the instances where more than one representation is needed to construct $\delta\rho(r)$ with a given G, two possibilities can occur. In the first case one can identify a single "leading" representation, which causes other representations to participate in the order. In the second case, no such identification can be made, and then the first Landau rule can be used to predict first-order transitions to many experimentally observed structures.[10]

Rather than considering, for the various substrates (or G_0), all the possible subgroups G, we investigate all the irreducible representations that can appear in (2.2). Let us denote by k the value of l for the single representation that characteriz-

es $\delta\rho$ (or the leading representation, when more than one is needed), and denote its dimensionality by m. Then we can define the m-component order parameter

$$\psi_{ki} = \sum_{\vec{r}} \phi_{ki}(\vec{r}) n(\vec{r}), \quad i = 1, 2, \ldots, m. \tag{2.3}$$

In the disordered state $\langle \psi_{ki} \rangle = 0$.

There is an infinite number of irreducible representations that lead to superlattice structures of different symmetries. However, the second and third rules state that the representation cannot be an arbitrary one but must satisfy certain conditions. If we denote the representation by T, then the second rule states[16] that the symmetric part of T^3 must not contain the unit representation. This is equivalent to stating that it must not be possible to construct a third-order invariant from the ψ_{ki}. Although this rule appears to be valid in three dimensions, it is violated in two dimensions by the three- and four-state Potts models which undergo continuous[13] transitions, even though one can construct such third-order invariants.[19] Thus a classification scheme based upon this rule is incorrect in two dimensions[20] and we do not employ this rule to limit the possible representations.

The third rule, the so-called Lifshitz condition,[16,21] states that the antisymmetric part of T^2 cannot contain the vector representation. Goshen *et al.*[21] have shown that this is not a necessary condition for the transition to be continuous. However, if a continuous transition occurs for which this condition is not satisfied then the symmetry of the ordered state in general changes with temperature. In a LEED experiment this would result in the continuous change with temperature of the position of the extra LEED spots due to the superlattice. *All such cases are excluded* from our classification scheme and we use the Lifshitz condition to reduce the allowed representations to a very small number.

Having determined the allowed single or leading representations, we construct for each one the independent densities $\rho(\vec{r})$ from Eq. (2.2). For the lattice gas the form of the functions ϕ_{ki} is

$$\phi_{ki}(\vec{r}) = \cos \vec{k}_i \cdot \vec{r} \quad \text{or} \quad \phi_{ki}(\vec{r}) = \sin \vec{k}_i \cdot \vec{r}.$$

The vectors $\vec{k}_i$ are the n independent vectors of the star of $\vec{k}$ in the Brillouin zone. (By independent, we mean unrelated by a reciprocal lattice vector.) The star of $\vec{k}_i$ is generated by applying to any $\vec{k}_i$ the elements of the point group which is an invariant subgroup of G_0.

Next, in order to determine the universality class of the transition, we construct from the order-parameter components ψ_{ki} the Landau-Ginzburg-Wilson (LGW) Hamiltonian. In practice this reduces to constructing all products of three or four ψ_{ki} which are invariant under the operations of G_0. Although there is no systematic way of doing this, invariance under translations requires a third-order invariant to be of the form $\psi_{\vec{k}_1}\psi_{\vec{k}_2}\psi_{\vec{k}_3}$, where $\vec{k}_1 + \vec{k}_2 + \vec{k}_3$ equals a reciprocal lattice vector. A similar restriction holds for higher-order invariants too. This simplification permits such invariants to be obtained by inspection. We compare the resulting LGW Hamiltonian with those describing known models (e.g., Ising, q-state Potts, etc.) If the LGW Hamiltonian of the system of interest is identical to that of one of these models, we identify the universality class of the transition of interest with that of the known model.

Finally, to determine what ordered structures can be reached via the transition, we consider all invariants that can be constructed from the representation k and any other representation k', and that are *linear in* $\psi_{k'i}$. It is exactly this type of coupling that can induce contributions to (2.2) from other than the leading representation. Even when such coupling term is absent, the ordered structure depends on the signs of the various anisotropic invariants. We consider all cases up to fourth-order terms in the LGW Hamiltonians.

We proceed to apply this method to four space groups which are of particular interest in adsorption experiments: $P2mm$, $C2mm$, $P4mm$, and $P6mm$.

Note that apart from the second rule (excluding representations with third-order invariants), our analysis assumes the validity of the remainder of the Landau-Lifshitz theory. Whereas none of the other rules is at present known to be wrong in two dimensions, each is based upon the same sort of classical, phenomenological reasoning as the second rule. This, together with the fact that the Landau theory disagrees with renormalization-group analysis for some three-dimensional systems,[17] suggests that a classification scheme, such as ours, which makes considerable use of it must be regarded as tentative and in need of additional theoretical and experimental confirmation. If a model or experimental system exhibits a continuous transition in a case which we predict to be first order, this is evidence for an additional breakdown of Landau theory.

III. APPLICATION

A. *P2mm*

This is the space group of a general rectangular array of adsorption sites. The atoms in the (110) face of an fcc crystal, for example, are in such an array. This space group has three real one-dimensional representations and an infinite number

of two- and four-dimensional representations. The Lifshitz rule permits continuous transitions only to states whose density transforms like one of the three one-dimensional representations. We label these representations by the vectors which generate them, $\vec{p}$, $\vec{q}$, and $\vec{s}$, shown in the Brillouin zone in Fig. 1(a). Let us denote the position of any adsorption site by $\vec{r}=n\vec{a}+m\vec{b}$, where n and m are integers. Then the densities which transform according to each of three representations can be written

$$\rho_{\vec{p}}=\rho_0+A_{\vec{p}}\cos\vec{p}\cdot\vec{r}=\rho_0+A_{\vec{p}}\cos n\pi\,, \tag{3.1}$$

$$\rho_{\vec{q}}=\rho_0+A_{\vec{q}}\cos\vec{q}\cdot\vec{r}=\rho_0+A_{\vec{q}}\cos m\pi\,, \tag{3.2}$$

and

$$\rho_{\vec{s}}=\rho_0+A_{\vec{s}}\cos\vec{s}\cdot\vec{r}=\rho_0+A_{\vec{s}}\cos(n+m)\pi \tag{3.3}$$

In the above, $A_{\vec{p}}, A_{\vec{q}}, A_{\vec{s}}$ are constants. Equation (3.1) shows that the density is periodic with twice the lattice constant in the $\vec{a}$ direction but does not vary in the $\vec{b}$ direction (i.e., is periodic with the lattice period in the $\vec{b}$ direction). Such a state is denoted (1×2) and is shown in Fig. 1(b). The ordered state with the density $\rho_{\vec{q}}$ is similar, with the directions $\vec{a}$ and $\vec{b}$ interchanged. The corresponding pattern, shown in Fig. 1(c), is denoted (2×1). Lastly, the density $\rho_{\vec{s}}$ is shown in Fig. 1(d). This pattern is denoted $c(2\times2)$. All three states have a single-component order parameter and the LGW Hamiltonian of each is that of the Ising model. Therefore, transitions to any of these states can be continuous and in the Ising class. Transitions to all other states are predicted to be first order. As to construction of an invariant linear in functions that do not belong to the leading representation, the only such invariant is $\psi_{\vec{p}}\psi_{\vec{q}}\psi_{\vec{s}}$. Close to the transition, this invariant will not alter the ordered state.

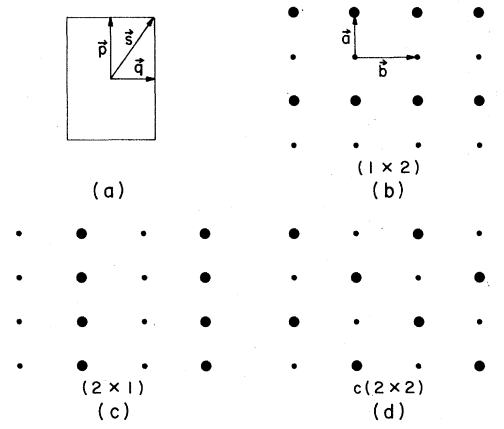

FIG. 1. Adsorption sites form a lattice with space group $P2mm$; (a) the Brillouin zone and the vectors $\vec{p}$, $\vec{q}$, $\vec{s}$, that correspond to the structures of (b), (c), and (d), respectively.

B. $C2mm$

This is the space group of the array of atoms in the (110) plane of a bcc crystal. The Brillouin zone is shown in Fig. 2(a). This group has a single one-dimensional representation and an infinite number of two- and four-dimensional representations. The Lifshitz rule permits continuous transitions only to states whose densities transform according to the one-dimensional representation generated by the vector $\vec{q}$ of Fig. 2(a) or to the two-dimensional representation generated by the vectors $\vec{k}_1$ and $\vec{k}_2$. The density associated with the vector $\vec{q}$ is

$$\rho_{\vec{q}}=\rho_0+A_{\vec{q}}\cos\vec{q}\cdot\vec{r}=\rho_0+A_{\vec{q}}\cos\pi(n+m)\,, \tag{3.4}$$

where $\vec{r}=n\vec{a}+m\vec{b}$ and $A_{\vec{q}}$ is constant. This state is shown in Fig. 2(b) and is denoted $c(2\times2)$. Constructing the LGW Hamiltonian, one finds that the transition is in the Ising class. No invariant linear in another representation can be constructed.

From the two vectors $\vec{k}_1$ and $\vec{k}_2$ we can construct the two independent densities

$$\rho_{\vec{k}_1}=\rho_0+A_{\vec{k}_1}\cos\vec{k}_1\cdot\vec{r}=\rho_0+A_{\vec{k}_1}\cos\pi n \tag{3.5}$$

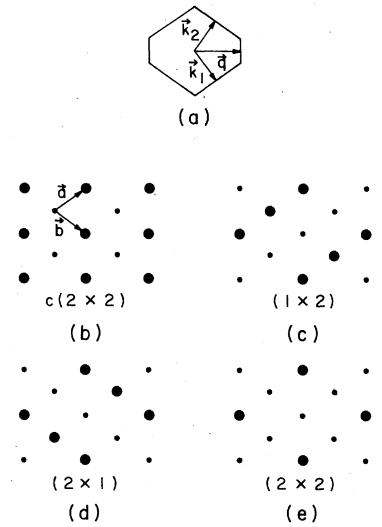

FIG. 2. (a) Brillouin zone of $C2mm$ lattice: $\vec{q}$ corresponds to the structure of (b); the structures of (c) and (d) are generated by the two-dimensional representation that belongs to $\vec{k}_1$ and $\vec{k}_2$. The structure of (e) belongs to two irreducible representations. In (e) the adsorbate density need not, in general, be identical at all sites denoted by the small dots. Rather the general pattern is one which repeats itself after translations of two lattice spacings along the principal symmetry directions. The pattern can be described by four sublattices.

and

$$\rho_{\vec{k}_2} = \rho_0 + A_{\vec{k}_2} \cos \vec{k}_2 \cdot \vec{r} = \rho_0 + A_{\vec{k}_2} \cos \pi m \,. \tag{3.6}$$

These states are denoted (2×1) and (1×2), respectively, and are shown in Fig. 2(c) and 2(d). The LGW Hamiltonians which can be constructed from the two components of the order parameter $\psi_{\vec{k}_i}$ is

$$H = \tfrac{1}{2} r_k \sum_i \psi_{\vec{k}_i}^2 + \frac{1}{2} \sum_i (\nabla \psi_{\vec{k}_i})^2 + u_k \Big(\sum_i \psi_{\vec{k}_i}^2 \Big)^2 + v_k \sum_i \psi_{\vec{k}_i}^4 , \tag{3.7}$$

which is that of the X-Y model with cubic anisotropy.[15] The ordered state will have the structure of Fig. 2(c) [or 2(d)] if the anisotropy term v is positive. For $v_k < 0$, however, a state with a different symmetry G, with both $\langle \psi_{\vec{k}_1} \rangle \neq 0$, and $\langle \psi_{\vec{k}_2} \rangle \neq 0$, will appear. In this case, however, we expect $\langle \psi_{\vec{q}} \rangle \neq 0$. To see this, consider the LGW Hamiltonian which can be constructed from the two components $\psi_{\vec{k}_1}$ and $\psi_{\vec{k}_2}$ of the leading representation as well as the one-dimensional representation $\psi_{\vec{q}}$. It has the form

$$H = \tfrac{1}{2} r_q \psi_{\vec{q}}^2 + \tfrac{1}{2} r_k \sum_i \psi_{\vec{k}_i}^2 + \tfrac{1}{2} (\nabla \psi_{\vec{q}})^2 + \frac{1}{2} \sum_i (\nabla \psi_{\vec{k}_i})^2 + w \psi_{\vec{q}} \psi_{\vec{k}_1} \psi_{\vec{k}_2} + u_q \psi_{\vec{q}}^4 + u_k \Big(\sum_i \psi_{\vec{k}_i}^2 \Big)^2 + v_k \sum_i \psi_{\vec{k}_i}^4 . \tag{3.8}$$

When $v_k < 0$, the nonvanishing value of $\langle \psi_{\vec{k}_1} \psi_{\vec{k}_2} \rangle$ acts as an ordering field which couples to $\psi_{\vec{q}}$, causing it to be nonvanishing. The resultant density

$$\rho_{\vec{k},\vec{q}} = \rho_0 + A \cos \pi (n+m) + B \cos \pi n \pm B \cos \pi m , \tag{3.9}$$

repeats itself after two lattice spacings in each direction and this gives rise to the same extra LEED spots as does the (2×2) structure of Fig. 2(e). Note that the structures of Fig. 2(e) and Eq. (3.9) differ in that the densities on three of the four sites in the unit cell are equal in the former, whereas they need not be in the latter. However, they have the same symmetry G. Thus, a state with the symmetry of the (2×2) structure *can* be reached via a continuous transition. Transitions to all structures with symmetries that differ from those of Figs. 2(b)–2(e) are predicted to be first order.

The transition of a system with the LGW Hamiltonian (3.7) has recently been predicted to be nonuniversal.[14,15] This prediction is based on the fact[15] that various models known to exhibit nonuniversal behavior have this LGW Hamiltonian. These models include[15] the eight-vertex (Baxter) model,[22] the $p = 4$ model treated by José *et al.*,[14] the antiferromagnetic model treated by van Leeuwen[22] and by Mukamel and Krinsky,[23] the Ashkin-Teller model, and the Union Jack model[22] solved by Wu.

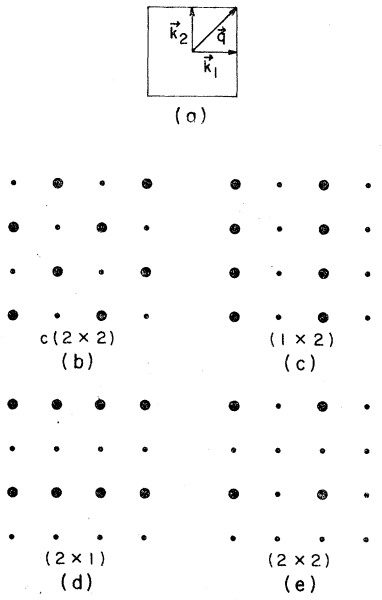

FIG. 3. Brillouin zone for $P4mm$ (a); the structure (b) corresponds to q; (c) and (d) to $\vec{k}_1$ and $\vec{k}_2$, respectively. (e) belongs to two representations. Remarks in the caption of Fig. 2 (e) apply to (e).

C. *P4mm*

This is the space group of a square array of sites. The (100) faces of bcc and fcc crystals provide such an array. The Brillouin zone is shown in Fig. 3(a). In addition to the unit representation, there is a one-dimensional representation generated by $\vec{q}$, a single two-dimensional representation generated by $\vec{k}_1$ and $\vec{k}_2$, and an infinite number of four- and eight-dimensional representations. The Lifshitz condition permits continuous transitions only to states whose densities transform according to the one-dimensional or two-dimensional representation. The analysis of the states which correspond to these representations is essentially identical to the $C2mm$ symmetry. In particular the density associated with the vector $\vec{q}$ is shown in Fig. 3(b) and is denoted $c(2 \times 2)$ or $(\sqrt{2} \times \sqrt{2})R45$. The transition to this state is in the Ising class. The states constructed from the $\vec{k}_1$ and $\vec{k}_2$ are shown in Figs. 3(c) and 3(d) and are denoted (2×1) and (1×2). Transitions to these states are in the class of the X-Y model with cubic anisotropy.[23]

Again, depending on the sign of the cubic anisotropy term, the ordered state may have the symmetry G of the (2×2) structure[10] of Fig. 3(e). Transitions to other structures are predicted to be first order.

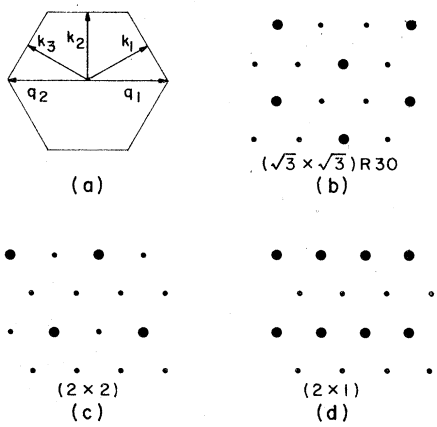

FIG. 4. (a) Brillouin zone for $P6mm$. (b) The structure that belongs to the two-dimensional representation with $\vec{q}_1, \vec{q}_2$. (c) and (d) belong to the three-dimensional representation (with $\vec{k}_1$, $\vec{k}_2$, $\vec{k}_3$). Remarks in the caption of Fig. 2 (e) apply to (c). The densities in (b) need not be the same on sites denoted by the small dots but only consistent with translations of $\sqrt{3}$ times the lattice constant along directions 30° from the principal symmetry directions.

D. *P6mm*

This is the space group of a triangular array of sites. The atoms in the (111) face of either a bcc or fcc crystal are in this array. The sites for physisorption provided by the basal planes of graphite are also in this array. The Brillouin zone is shown in Fig. 4(a). In addition to the unit representation there is a two-dimensional representation generated by $\vec{q}_1$ and $\vec{q}_2$, a three-dimensional representation generated by $\vec{k}_1$, $\vec{k}_2$, and $\vec{k}_3$, and an infinite number of six- and twelve-dimensional representations. The Lifshitz condition permits continuous structural transitions only to the states whose densities transform like the two- or three-dimensional representation. We consider the former first. The vectors $\vec{q}_1$ and $\vec{q}_2$ are related to one another by

$$\vec{q}_2 = -\vec{q}_1 , \tag{3.10}$$

and the set of basis functions for the representation can be taken to be $\cos\vec{q}_1\cdot\vec{r}$ and $\sin\vec{q}_1\cdot\vec{r}$, leading to a two-component order parameter

$$\psi_1 = \sum_r \cos(\vec{q}_1\cdot\vec{r})n(\vec{r}) ,$$
$$\psi_2 = \sum_r \sin(\vec{q}_1\cdot\vec{r})n(\vec{r}) . \tag{3.11}$$

To determine the universality class of the transition we construct the LGW Hamiltonian

$$H = \frac{1}{2}r_a\sum_i \psi_i^2 + \frac{1}{2}\sum_i (\nabla\psi_i)^2 + w(\psi_1^3 - 3\psi_1\psi_2^2) + u_4(\psi_1^2+\psi_2^2)^2 , \tag{3.12}$$

which, for a general value of w, is that of the three-state Potts model.

For $w<0$, the ordered state is characterized by the three independent densities

$$\rho_1 = \rho_0 + A\cos\vec{q}_1\cdot\vec{r} ,$$
$$\rho_2 = \rho_0 - \tfrac{1}{2}A(\cos\vec{q}_1\cdot\vec{r} + \sqrt{3}\sin\vec{q}_1\cdot\vec{r}) , \tag{3.13}$$
$$\rho_3 = \rho_0 - \tfrac{1}{2}A(\cos\vec{q}_1\cdot\vec{r} - \sqrt{3}\sin\vec{q}_1\cdot\vec{r}) .$$

These densities are of the form shown in Fig. 4(b), a pattern which is denoted $(\sqrt{3}\times\sqrt{3})R30$. For $w>0$ the ordered state is characterized by the densities obtained from (3.13) by interchanging $\cos\vec{q}\cdot\vec{r}$ and $\sin\vec{q}\cdot\vec{r}$; for example,

$$\rho_1 = \rho_0 + A\sin\vec{q}_1\cdot\vec{r} . \tag{3.14}$$

The ordered state that corresponds to this structure has a lower symmetry G than $P6mm$; the point group is C_{3v}. Thus the LEED diffraction pattern from a single domain of the structure (3.14) will exhibit different intensities at $\vec{q}_1$ and $\vec{q}_2$. Alexander[24] was the first to note that the critical behavior of this model should be the same as that of the $(\sqrt{3}\times\sqrt{3})R30$ transition. If the particular lattice-gas Hamiltonian of Eq. (2.1) is employed, then for a particular value of the chemical potential corresponding to $\rho_0 = \frac{1}{2}$, w will vanish due to the particle-hole symmetry of the lattice-gas Hamiltonian. In this case, the LGW Hamiltonian is that of the X-Y model with a sixth-order anisotropy. This model has also been discussed by José *et al.*[14] As a consequence of particle-hole symmetry, the phase diagram of a lattice gas undergoing the $(\sqrt{3}\times\sqrt{3})R30$ transition would show two surfaces of three-state Potts transitions symmetric about $\rho_0 = \frac{1}{2}$ and meeting there with a different critical behavior. This has been observed in Monte Carlo[25] and renormalization-group[26] calculations. However, as noted earlier, the particle-hole symmetry is broken in the physical system. Consequently, this behavior is not expected in experimental situations, and the transition remains in the three-state Potts class.

We turn now to the three-dimensional representations. There are three independent density differences,

$$\delta\rho_i = \cos\vec{k}_i\cdot\vec{r} . \tag{3.15}$$

The densities of the physical states corresponding to these $\delta\rho_i$ vary along only one of the three symmetry directions. One of these states is shown in Fig. 4(d); it is denoted (2×1). There is another

highly symmetric set of density differences which can be constructed from the three $\delta\rho_i$ above. They are

$$\delta\rho_4 = \cos\vec{k}_1\cdot\vec{r} + \cos\vec{k}_2\cdot\vec{r} + \cos\vec{k}_3\cdot\vec{r},$$
$$\delta\rho_5 = \cos\vec{k}_1\cdot\vec{r} + \cos\vec{k}_2\cdot\vec{r} - \cos\vec{k}_3\cdot\vec{r}, \qquad (3.16)$$
$$\delta\rho_6 = \cos\vec{k}_1\cdot\vec{r} - \cos\vec{k}_2\cdot\vec{r} - \cos\vec{k}_3\cdot\vec{r}.$$

The states corresponding to these densities are shown in Fig. 4(c) and are denoted (2×2). These states are distinguished from the three (2×1) states by the values of the expectation of the three order-parameter components

$$\psi_{k_i} = \sum_r \cos(\vec{k}_1\cdot\vec{r})n(\vec{r}). \qquad (3.17)$$

In the (2×1) state, two of these components vanish. In the (2×2) states all three components are nonzero. To determine which states are expected to be reached by the continuous transition, we construct the LGW Hamiltonian

$$H = \tfrac{1}{2}r_k\sum_i \psi_{\vec{k}_i}^2 + \frac{1}{2}\sum_i (\nabla\psi_{\vec{k}_i})^2 + w\psi_{\vec{k}_1}\psi_{\vec{k}_2}\psi_{\vec{k}_3}$$
$$+ u_k\left(\sum_i \psi_{\vec{k}_i}^2\right)^2 + v_k\sum_i \psi_{\vec{k}_i}^4. \qquad (3.18)$$

In general, w is nonvanishing. The (2×2) states for which the product $\psi_{\vec{k}_1}\psi_{\vec{k}_2}\psi_{\vec{k}_3}$ is negative clearly give a lower energy than the (2×1) states for which the product vanishes. Thus we predict that the (2×2) states will be reached by the continuous transition, not the (2×1) states. To identify the class of this transition we note that the above Hamiltonian is that of the four-state Potts model,[19] provided that w does not vanish. Particle-hole symmetry of the particular lattice-gas model of Eq. (2.1) does force w to vanish at $\rho_0 = \frac{1}{2}$, leaving the LGW Hamiltonian of the Heisenberg model with cubic anisotropy. This model, recently discussed by Domany and Reidel,[15,27] has different critical behavior from the four-state Potts model. As noted earlier, however, the physical system does not possess particle-hole symmetry, so that at $\rho_0 = \frac{1}{2}$ this different behavior is not predicted to be observed. Rather the critical behavior will remain that of the four-state Potts model.

Returning to the case $w \neq 0$, note that we assumed that the lowest-order anisotropy term [i.e., the third-order anisotropy term in (3.18)] determines the ordered structure. If the sign of the fourth-order term is such that it competes with the third-order term (i.e., if $v_k < 0$ and, say, $\langle\psi_{\vec{k}_1}\rangle \neq 0$, $\langle\psi_{\vec{k}_2}\rangle = \langle\psi_{\vec{k}_3}\rangle = 0$ is preferred), the system may exhibit a first-order transition from one ordered phase to another.

Finally, we remark that for neither the two-dimensional or the three-dimensional representation can an invariant linear in a different representation be constructed. Transitions to structures not listed above are expected to be first order.

In this section we have determined the critical behavior which can be observed in order-disorder transition on various substrate arrays. We have restricted our treatment to simple arrays, i.e., identical to the Bravais lattice. An important case in adsorption is that of a hexagonal or honeycomb array of sites which has a triangular ($P6mm$) Bravais lattice and a basis of two adsorption sites per unit cell. Extension of our method to classify the continuous transitions for a honeycomb and other arrays will be presented elsewhere.

IV. SUMMARY

We have presented a classification of possible continuous order-disorder transitions on all simple adsorbing substrates. Our study did not include experimental situations where the adsorbate has different possible orientations with respect to the substrate (i.e., adsorbed molecules). Also, we have limited the discussion to the case of a single adsorption site per substrate unit cell.

These restrictions are not essential, and their removal will result only in the need to consider more complicated representations than was necessary so far.

We have also assumed that the periodicity of the superlattice does not vary continuously with temperature. This seems to be satisfied by a great number of reportedly observed structures. We believe that the cases that *are* included in our study cover the majority of systems of current experimental interest. The various universality classes that can be realized are summarized in Table I. The entries in the first row are based on the exact solution for the Ising model, while for the X-Y model with cubic anisotropy on Refs. 14 and 15. For the three-state Potts model, we quote recent series estimates,[28] while for the four-state Potts model the exact results for the Baxter-Wu[29] model (which has the same LGW Hamiltonian as four-state Potts) are quoted.

One central assumption was used in making the identification of the universality classes. We assumed that a transition can be completely characterized by the Landau-Ginzburg-Wilson Hamiltonian of the system. This assumption has not been extensively tested in two dimensions. The only experimental confirmations we can invoke are for various Ising-like systems[30,31] and one single measurement of the specific heat of a three-state Potts-like system.[1] In addition, apparently continuous transitions were observed for one system[32] predicted to behave as four-state Potts, and one[33]

TABLE I. Substrates (first column) of various symmetries. Universality classes that can be realized and the expected critical behavior are listed in first row. The entries identify the corresponding ordered superlattice structures.

	Ising $\alpha=0$ (log) $\beta=0.125$	X-Y with cubic anisotropy nonuniversal	Three-state Potts $\alpha\sim 0.42\pm 0.05$ $\beta\sim 0.1$	Four-state Potts $\alpha=0.6667$ $\beta=0.0833$
$P2mm$	(2×1)			
Ex fcc(110)	(1×2)			
	$c(2\times2)$			
$C2mm$	$c(2\times2)$	(2×1)		
Ex bcc(110)		(2×2)		
$P4mm$	$c(2\times2)$	(2×1)		
Ex fcc(100)		(2×2)		
bcc(100)				
$P6mm$				
Ex bcc(111)			$(\sqrt{3}\times\sqrt{3})R30°$	(2×2)
fcc(111)				
Graphite				

of anisotropic X-Y character.

As to theoretical verification, renormalization-group studies[26] confirm our assumption—namely, that systems that on symmetry grounds are expected to exhibit Potts-like behavior do yield values of exponents in the approriate range.

In addition, we can compare our predictions with studies of hard square-lattice models.[34,35] In most cases our conclusions about the order of the transition agree with the results of the various matrix methods quoted by Runnels.[34]

In the case of a (2×2) structure on a triangular lattice, we predict that the transition can be continuous with a four-state Potts model behavior, while the matrix methods[36] yield a first-order transition in the corresponding lattice gas of hard hexagons. These two results are not inconsistent, in that the matrix method deals with a particular case, and it is quite possible that phase transitions with this particular symmetry change are continuous for certain choices of parameters in the Hamiltonian and first order for other choices—a situation which occurs (for example) on the vicinity of a tricritical point.[37]

Finally, we point out that some of the realizable universality classes are of great current theoretical interest, and express our hope that this investigation will stimulate experimental interest in the study of appropriate adsorbed systems in the critical region.

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