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Symmetry classification of continuous phase transitions in two dimensions

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Extending earlier work by Domany *et al.*, this paper provides a group-theoretical classification of continuous phase transitions of systems of arbitrary $d = 2$ space-group symmetry with a scalar ordering density. Based on the Lifshitz condition, the classification finds the symmetries for which continuous phase transitions are possible and identifies the corresponding universality classes according to the associated Landau-Ginzburg-Wilson Hamiltonians. Tentatively unidentified universality classes appear, associated with the space groups $p4gm$, $p3$, $p31m$, and $p6$. Applications to atomic and molecular adsorption and to surface reconstruction are given.

I. INTRODUCTION

Consider a statistical mechanical system, characterized by an ordering density $\langle\rho(\vec{r})\rangle$, whose Hamiltonian is invariant under a group G_0 of symmetry operations. Typically there is a high-temperature, symmetric phase in which $\langle\rho(\vec{r})\rangle$ is invariant under all of the operations in G_0. There may also be a low-temperature, broken-symmetry phase in which $\langle\rho(\vec{r})\rangle$ is invariant only under the operations of a subgroup $G \subset G_0$. The transition between these two phases may be either first order (discontinuous) or second order (continuous). Mukamel and Krinsky[1] have argued how, on the basis of symmetry considerations alone, to make nonrigorous but apparently reliable predictions of (a) which transitions may be second order[2] and (b) for those that are, to which universality classes they belong. A summary of the logic of the analysis[3] is given in the following paragraph. This theory was recently applied by Domany *et al.*[4,5] to study structural order-disorder transitions of adsorbed atomic monolayers. Substrate arrays consisting of Bravais, honeycomb, and kagomé lattices were studied in detail. This paper treats the general situation where $\langle\rho(\vec{r})\rangle$ is a real scalar density (usually a mass, charge, spin, or number density) and where G_0 is any one of the 17 two-dimensional space groups,[6] thus extending the work of Domany *et al.*[4,5] The analysis here applies to many situations besides atomic monolayer adsorption. Examples are given in Sec. VI.

Within the context of mean-field theory there is a set of rules due to Landau and Lifshitz[7] which determines on the basis of symmetry considerations alone whether a particular transition is allowed to be second order.[2] These Landau-Lifshitz rules are not rigorously valid beyond mean-field theory; however, with proper interpretation they remain a useful guide for predicting when second-order behavior may be expected.[1] In particular it is observed empirically[4,5] that the large fluctuations which occur in two dimensions render one of the Landau-Lifshitz rules (the second, see Sec. II) inoperative. For each symmetry-allowed transition it is possible to construct[1] (again, on the basis of symmetry considerations alone) the corresponding Landau-Ginzburg-Wilson (LGW) model. The "smoothness postulate"[8] leads one to expect that, when second-order behavior occurs, it belongs to the universality class of the corresponding LGW model.

The layout of this paper is as follows: In Sec. II the three Landau-Lifshitz rules are stated and briefly interpreted. Since a transition is labeled by a representation R as well as a group G_0, the theory of representations of space groups is discussed in Sec. III. The procedure of constructing LGW Hamiltonians is outlined in Sec. IV. In Sec. V the transitions (G_0,R) which may be continuous are presented and the previously identified universality classes which arise are briefly described. A simple explanation of how to determine G_0 and R for a given continuous transition is also included. Applications to atomic and molecular adsorption and surface reconstruction are given in Sec. VI. Section VII suggests directions for future extensions of this work. In the Appendix we give a microscopic model for one of the tentatively unidentified universality classes and also give examples of transitions in atomic adsorption which belong to this class.

II. RULES OF LANDAU AND LIFSHITZ

The first rule of the Landau-Lifshitz theory[1,7] results from assuming that the transition is an ordinary critical point, i.e., not a multicritical point. It states that the order parameter characterizing a continuous transition must transform as a single "real irreducible" representation R of the symmetry group G_0. For irreducible representations $\tilde{R}$ which are real, $R \equiv \tilde{R}$; for those which are complex, $R \equiv \tilde{R} + (\tilde{R})^*$. The unit representation is specifically excluded. Higher-order invariants in the free energy can induce contributions from other representations. This mixing of different representations[9] must be considered when one determines possible physical states of the ordered phase but is irrelevant sufficiently near T_c and will be ignored in our classification scheme.

The second Landau-Lifshitz rule asserts that there can be no cubic terms in the free energy, if a continuous transition is to occur. If such terms exist, then the minimization of the free energy with respect to an overall scale of the order-parameter components yields a first-order transition.[7] This rule is satisfied when no third-order invariants can be constructed from R.[10] In two dimensions it is known that this rule is violated by the three- and four-state Potts model.[11] Since mean-field theory neglects fluctuations, and since fluctuations are more dominant in two dimensions than in three dimensions, it is not surprising that this rule does not necessarily apply in two dimensions. We shall not require this rule to be satisfied in our classification (Sec. V).

The third Landau-Lifshitz rule results from the minimization of the free energy in $\vec{k}$ space.[12] It states that the coefficient of any term which antisymmetric and quadratic in the order-parameter components and linear in a spatial derivative must be zero at the critical point, if a continuous transition is to occur. This vanishing is guaranteed by symmetry[13] when the so-called "Lifshitz condition" is satisfied, i.e., when the antisymmetric square of R and the vector representation have no representation in common.

III. REPRESENTATION THEORY

In the representation theory of space groups[14,15] the irreducible representation of a given space group G_0 is labeled by a wave vector $\vec{k}$ and an additional label $\tilde{A}$ which depends on both $\vec{k}$ and G_0. Roughly speaking, one can say that $\vec{k}$ characterizes translations of the unit cells into each other while $\tilde{A}$ characterizes the "rotations" within a unit cell. The "small representation" $\tilde{R}_s$ is identified by $\tilde{A}$. To understand $\tilde{R}_s$, it is best to first introduce the concepts of the group of $\vec{k}$ and the star of $\vec{k}$.

The group of $\vec{k}$ is the point group consisting of all different nontranslational parts of the elements of the space group G_0, which leave the vector $\vec{k}$ unchanged or transform $\vec{k}$ into an equivalent vector $\vec{k}'$ (i.e., $\vec{k}'$ differs from $\vec{k}$ by a reciprocal-lattice vector). The star of $\vec{k}$ is the set of all different inequivalent $\vec{k}$ vectors which are formed by acting on $\vec{k}$ with all different nontranslational parts of the elements of G_0. For two-dimensional space groups which do not include glide lines, i.e., symmorphic space groups, the small representations $\tilde{R}_s$ are just the irreducible representations of the group of $\vec{k}$. For nonsymmorphic space groups $\tilde{R}_s$ is defined in a slighty more complicated way.[14]

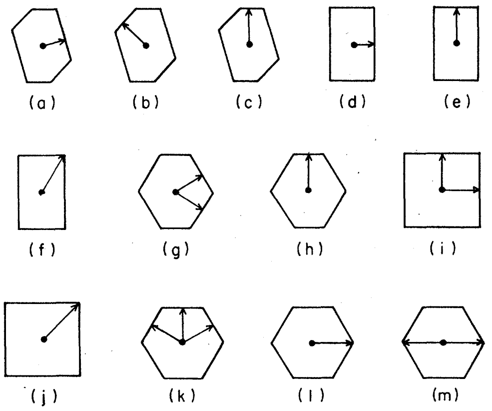

FIG. 1. Selected stars of two-dimensional space groups. The real irreducible representations which satisfy the Lifshitz condition are associated with one of these stars.

To actually find which real irreducible representations R satisfy the Lifshitz condition, we have made use of several of the results found in Lyubarskii.[14] We begin with a group G_0 and a wave vector $\vec{k}$ and proceed to find both the star of $\vec{k}$ and the group of $\vec{k}$. After we find the characters of one of the small representations $\tilde{R}_s$, we determine whether the corresponding irreducible representation $\tilde{R}$ is real, using these characters. Then, we calculate the characters of the vector representation of the group of $\vec{k}$. Using these characters and the properties of G_0, we can then determine if the Lifshitz condition is satisfied.[16]

For future convenience we introduce the "real small representation" R_s: if the small representation $\tilde{R}_s$ is not real, then $R_s \equiv \tilde{R}_s + (\tilde{R}_s)^*$; otherwise $R_s \equiv \tilde{R}_s$. In labeling a real irreducible representation R, we choose to use the star of $\vec{k}$ instead of $\vec{k}$ itself and R_s instead of $\tilde{R}_s$. We will write $R = \{(z) , A\}$, where (z) labels a star (such as in Fig. 1) and A labels the row of the character table which is associated with R_s.

IV. CONSTRUCTING THE LGW HAMILTONIANS

For each real irreducible representation R we can construct the Landau-Ginzburg-Wilson (LGW) Hamiltonian which is associated with R.[17] The number of order-parameter components[18] associated with R is given by $m = rsl$. Here s is the number of (inequivalent) vectors in the star of $\vec{k}$ and l is the dimension of the small representation $\tilde{R}_s$. $r = 2$ if (a) $\tilde{R}_s$ is not real or (b) $\vec{k}$ and $-\vec{k}$ are not equivalent and no operation in G_0 transforms $\vec{k}$ into $-\vec{k}$; otherwise, $r=1$. The easiest way to represent the space group G_0 is first to associate the "pattern" from Ref. 19 with G_0 and then to assign a number to each position of the pattern, thus forming basis functions for R. We must find m basis functions $\phi_1, \ldots, \phi_m$ for each R, which transform into each other under the elements of G_0. The determination of these basis functions has previously been discussed for a symmorphic G_0.[5] Once the transformation properties of these basis functions are known, the construction of the LGW Hamiltonian is straightforward.[1]

We consider here the example of a nonsymmorphic space group, $(G_0,R)=(p2gg,\{(f),(i)\})$, where (f) denotes a star from Fig. 1 and (i) denotes a line of the character table of Table I. From the construction of this character table,[20] we find that $\tilde{R}_s$ is real. Since the star of $\vec{k}$ is a single vector,[21] we see that the number of basis functions we need to construct is $m=rsl=2$. Figure 2 gives the appropriate pattern from Ref. 19 along with a convenient choice of axes. From G_0 we determine a set of basic "rotations,"

$$S_1=\{E,C_2,t_{\vec{a}_1/2+\vec{a}_2/2}\sigma_{\vec{a}_1},t_{\vec{a}_1/2+\vec{a}_2/2}\sigma_{\vec{a}_2}\} ,$$

and a set of basic translations, $S_2=\{t_{\vec{a}_1},t_{\vec{a}_2}\}$. Here $t_{\vec{b}}$ denotes a translation by $\vec{b}$ and $\sigma_{\vec{a}_1}$ is a reflection across the $\vec{a}_i$ axis. The basis function ϕ_1 and ϕ_2 are chosen so that, under the operations in S_1, the resulting character table is (i) from Table I, while under the operations in S_2, $t_{\vec{a}_i}\phi_j=\exp(i\vec{k}\cdot\vec{a}_i)\phi_j$. After a small amount of trial and error, we find that the basis functions of Fig. 3 satisfy the above requirements since they transform, under the sets S_1 and S_2, as

$$E \text{ or } C_2\text{:}\ \ \phi_1\rightarrow\phi_1,\ \phi_2\rightarrow\phi_2 ,$$

$$t_{\vec{a}_1/2+\vec{a}_2/2}\sigma_{\vec{a}_1} \text{ or } t_{\vec{a}_1/2+\vec{a}_2/2}\sigma_{\vec{a}_2}\text{:}\ \ \phi_1\rightarrow\phi_2,\ \phi_2\rightarrow-\phi_1 ,$$

$$t_{\vec{a}_1} \text{ or } t_{\vec{a}_2}\text{:}\ \ \phi_1\rightarrow-\phi_1,\ \phi_2\rightarrow-\phi_2 .$$

TABLE I. Those character tables not found in point-group character tables which label the real small representations of Table II.

	E	C_2	σ_v	σ_v'
(i)	2	2	0	0
(ii)	2	−2	0	0

	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_v'$
(iii)	2	2	0	0	0
(iv)	4	−4	0	0	0

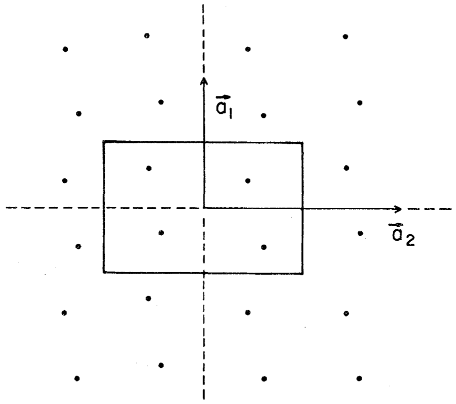

FIG. 2. Pattern from Ref. 19 for the space group $p2gg$. $\vec{a}_1$ and $\vec{a}_2$ are the primitive lattice vectors for the pattern. A convenient choice for the unit cell is shown.

Constructing the LGW Hamiltonian such that each term is invariant under the above six operations, we find[18]

$$H=\tfrac{1}{2}r(\psi_1^2+\psi_2^2)+[(\nabla\psi_1)^2+(\nabla\psi_2)^2]$$
$$+u(\psi_1^2+\psi_2^2)+v(\psi_1^4+\psi_2^4)+\cdots .$$

A similar analysis when R is $\{(f),(ii)\}$ yields the basis functions of Fig. 4 and the same LGW Hamiltonian.

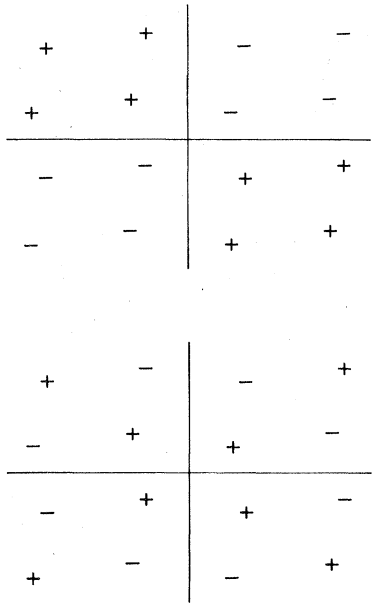

FIG. 3. Set of basis functions of the real irreducible representation $R=\{(f),(i)\}$, where $G_0=p2gg$, (f) is from Fig. 1, and (i) is from Table I.

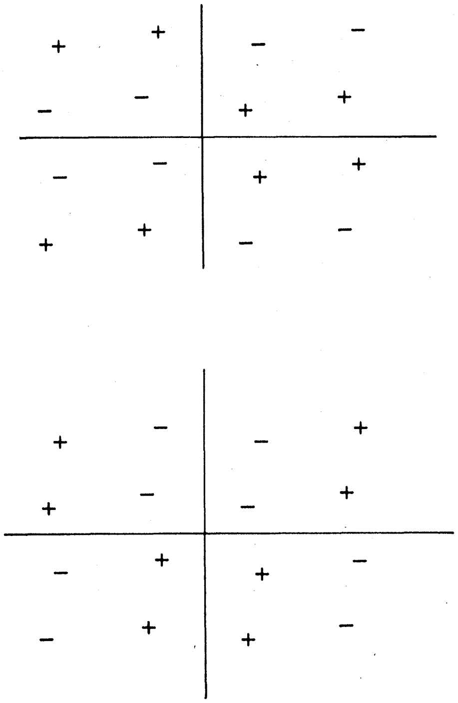

FIG. 4. Set of basis functions of the real irreducible representation $R = \{(f), (ii)\}$, where $G_0 = p2gg$, (f) is from Fig. 1, and (ii) is from Table I.

V. RESULTS

Table II lists those transitions (G_0, R) which may be continuous.[2] Continuous transitions are possible for all 17 of the two-dimensional space groups G_0. The row of the character table of a real small representation R_s is labeled as in the point-group character tables of Ref. 22 or the character tables of Table I.

Given an experimental transition, one can use Table II in the following manner. (1) Determine G_0 from the symmetric phase. (2) Construct the difference $\delta\langle\rho(\vec{r})\rangle$ of the ordering density $\langle\rho(\vec{r})\rangle$ in the symmetric phase from its value in the broken-symmetry phase. (3) From the $\vec{k}$ which characterizes the translational symmetry of $\langle\rho(\vec{r})\rangle$, find the appropriate star of $\vec{k}$ in Fig. 1. (4) The group of $\vec{k}$ is given in Table II. If G_0 is nonsymmorphic, replace the group of $\vec{k}$ by the set of basic "rotations" of G_0.[23] (5) Perform the operations of the set in (4) on $\delta\langle\rho(\vec{r})\rangle$ to form a set of functions S. Use the linearly independent functions of S as a basis of the real small representation R_s and calculate the corresponding characters of the elements of the set in (4). (6) If R_s is included in Table II, a continuous transition is symmetry allowed. If the transition is indeed continuous,[2] the table gives the universality class via the LGW Hamiltonian.

The LGW Hamiltonians referred to in Table II are

$$H = H_1 \ , \tag{1}$$

$$H = H_2 + v \sum_{i=1}^{2} \psi_1^4 + t \sum_{i=1}^{2} \psi_1^6 + \cdots \ , \tag{2a}$$

$$H = H_2 + t_1(\psi_1^3 - 3\psi_1\psi_2^2)^2 + \cdots \ , \tag{2b}$$

$$H = H_2 + t_1(\psi_1^3 - 3\psi_1\psi_2^2)^2 + t_2(\psi_1^3 - 3\psi_1\psi_2^2)(\psi_2^3 - 3\psi_2\psi_1^2) + \cdots \ , \tag{2c}$$

$$H = H_2 + w_1(\psi_1^3 - 3\psi_1\psi_2^2) + t_1(\psi_1^3 - 3\psi_1\psi_2^2)^2 + \cdots \ , \tag{2d}$$

$$H = H_2 + w_1(\psi_1^3 - 3\psi_1\psi_2^2) + w_2(\psi_2^3 - 3\psi_2\psi_1^2) + t_1(\psi_1^3 - 3\psi_1\psi_2^2)^2 + t_2(\psi_1^3 - 3\psi_1\psi_2^2)(\psi_2^3 - 3\psi_2\psi_1^2) + \cdots \ , \tag{2e}$$

$$H = H_3 + v \sum_{i=1}^{3} \psi_i^4 + \cdots \ , \tag{3a}$$

$$H = H_3 + w\psi_1\psi_2\psi_3 + v \sum_{i=1}^{3} \psi_i^4 + \cdots \ , \tag{3b}$$

$$\begin{aligned} H = H_4 = {} & v_1 \sum_{i=1}^{4} \psi_i^4 + v_2(\psi_1^3\psi_2 - \psi_2^3\psi_1 - \psi_3^3\psi_4 + \psi_4^3\psi_3) + v_3(\psi_1^3\psi_3 - \psi_2^3\psi_4 - \psi_3^3\psi_1 + \psi_4^3\psi_2) \\ & + v_4(\psi_1^3\psi_4 + \psi_2^3\psi_3 + \psi_3^3\psi_2 + \psi_4^3\psi_1) + v_5(\psi_1^2\psi_2\psi_3 + \psi_2^2\psi_1\psi_4 + \psi_3^2\psi_1\psi_4 + \psi_4^2\psi_2\psi_3) \\ & + v_6(\psi_1^2\psi_3\psi_4 - \psi_2^2\psi_3\psi_4 - \psi_3^2\psi_1\psi_2 + \psi_4^2\psi_1\psi_2) + v_7(\psi_1^2\psi_2\psi_4 - \psi_2^2\psi_1\psi_3 - \psi_3^2\psi_2\psi_4 + \psi_4^2\psi_1\psi_3) \\ & + v_8(\psi_1^2\psi_2^2 + \psi_3^2\psi_4^2) + v_9(\psi_1^2\psi_4^2 + \psi_2^2\psi_3^2) + v_{10}\psi_1\psi_2\psi_3\psi_4 + \cdots \ , \end{aligned} \tag{4}$$

TABLE II. The real irreducible representations of two-dimensional space groups which satisfy the Lifshitz condition, and the associated LGW Hamiltonians. The entries under "star of $\vec{k}$" correspond to Fig. 1. The real small representations R_s agree with the labeling in Ref. 22 and Table I. The LGW Hamiltonians are labeled as is Sec. V.

Space group	$p1$		
Star of $\vec{k}$	(a)	(b)	(c)
Group of $\vec{k}$	C_1	C_1	C_1
R_s	A	A	A
LGW Ham.	(1)	(1)	(1)

Space group	$p211$						
Star of $\vec{k}$	$\{\vec{0}\}$	(a)		(b)		(c)	
Group of $\vec{k}$	C_2	C_2		C_2		C_2	
R_s	B	A	B	A	B	A	B
LGW Ham.	(1)	(1)	(1)	(1)	(1)	(1)	(1)

Space group	$p1m1$						
Star of $\vec{k}$	$\{\vec{0}\}$	(d)		(e)		(f)	
Group of $\vec{k}$	C_s	C_s	C_s			C_s	
R_s	A''	A'	A''	A'	A''	A'	A''
LGW Ham.	(1)	(1)	(1)	(1)	(1)	(1)	(1)

Space group	$p1g1$		
Star of $\vec{k}$	$\{\vec{0}\}$	(e)	
Group of $\vec{k}$	A_s	C_s	
R_s	A''	A'	A''
LGW Ham.	(1)	(1)	(1)

Space group	$c1m1$			
Star of $\vec{k}$	$\{\vec{0}\}$	(h)		(g)
Group of $\vec{k}$	C_s	C_s		C_1
R_s	A''	A'	A''	A
LGW Ham.	(1)	(1)	(1)	$(2a)$

Space group	$p2mm$														
Star of $\vec{k}$	$\{\vec{0}\}$			(d)				(e)				(f)			
Group of $\vec{k}$	C_{2v}			C_{2v}				C_{2v}				C_{2v}			
R_s	A_2	B_1	B_2	A_1	A_2	B_1	B_2	A_1	B_2	B_1	B_2	A_1	A_2	B_1	B_2
LGW Ham.	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)

Space group	$p2mg$						
Star of $\vec{k}$	$\{\vec{0}\}$			(d)			
Group of $\vec{k}$	C_{2v}			C_{2v}			
R_s	A_2	B_1	B_2	A_1	A_2	B_1	B_2
LGW Ham.	(1)	(1)	(1)	(1)	(1)	(1)	(1)

Space group	$p2gg$				
Star of $\vec{k}$	$\{\vec{0}\}$			(f)	
Group of $\vec{k}$	C_{2v}			C_{2v}	
R_s	A_2	B_1	B_2	(i)	(ii)
LGW Ham.	(1)	(1)	(1)	$(2a)$	$(2a)$

Space group	$c2mm$								
Star of $\vec{k}$	$\{\vec{0}\}$			(h)				(g)	
Group of $\vec{k}$	C_{2v}			C_{2v}				C_{2v}	
R_s	A_2	B_1	B_2	A_1	A_2	B_1	B_2	A	B
LGW Ham.	(1)	(1)	(1)	(1)	(1)	(1)	(1)	$(2a)$	$(2a)$

Space group	$p4$						
Star of $\vec{k}$	$\{\vec{0}\}$		(i)		(j)		
Group of $\vec{k}$	C_4		C_2		C_4		
R_s	B	E	A	B	A	B	E
LGW Ham.	(1)	$(2a)$	$(2a)$	$(2a)$	(1)	(1)	$(2a)$

Space group	$p4mm$												
Star of $\vec{k}$	$\{\vec{0}\}$				(i)				(j)				
Group of $\vec{k}$	C_{4v}				C_{2v}				C_{4v}				
R_s	A_2	B_1	B_2	E	A_1	A_2	B_1	B_2	A_1	A_2	B_1	B_2	E
LGW Ham.	(1)	(1)	(1)	$(2a)$	$(2a)$	$(2a)$	$(2a)$	$(2a)$	(1)	(1)	(1)	(1)	$(2a)$

Space group	$p4gm$					
Star of $\vec{k}$	$\{0\}$				(j)	
Group of $\vec{k}$	C_{4v}				C_{4v}	
R_s	A_2	B_1	B_2	E	(iii)	(iv)
LGW Ham.	(1)	(1)	(1)	$(2a)$	$(2a)$	(4)

Space group	$p3$			
Star of $\vec{k}$	$\{\vec{0}\}$	(k)	(l)	
Group of $\vec{k}$	C_3	C_1	C_3	
R_s	E	A	A	E
LGW Ham.	$(2e)$	$(3b)$	$(2e)$	$(2e)$

Space group	$p3m1$					
Star of $\vec{k}$	$\{\vec{0}\}$		(k)		(m)	
Group of $\vec{k}$	C_{3v}		C_s		C_3	
R_s	A_2	E	A'	A''	A	E
LGW Ham.	(1)	$(2d)$	$(3b)$	$(3a)$	$(2d)$	$(2d)$

Space group	$p31m$					
Star of $\vec{k}$	$\{\vec{0}\}$		(k)		(l)	
Group of $\vec{k}$	C_{3v}		C_s		C_{3v}	
R_s	A_2	E	A'	A''	A_1	A_2
LGW Ham.	(1)	$(2d)$	$(3b)$	$(3a)$	$(2e)$	$(2c)$

Space group	$p6$					
Star of $\vec{k}$	$\{\vec{0}\}$			(k)		(m)
Group of $\vec{k}$	C_6			C_2		C_3
R_s	B	E_1	E_2	A	B	A
LGW Ham.	(1)	$(2e)$	$(2c)$	$(3b)$	$(3a)$	$(2d)$

Space group	$p6mm$										
Star of $\vec{k}$	$\{\vec{0}\}$					(k)				(m)	
Group of $\vec{k}$	C_{6v}					C_{2v}				C_{3v}	
R_s	A_2	B_1	B_2	E_1	E_2	A_1	A_2	B_1	B_2	A_1	A_2
LGW Ham.	(1)	(1)	(1)	$(2b)$	$(2d)$	$(3b)$	$(3a)$	$(3a)$	$(3a)$	$(2d)$	$(2b)$

where

$$H_n = \tfrac{1}{2} r \left(\sum_{i=1}^{n} \psi_i^2 \right) + \tfrac{1}{2} \sum_{i-1}^{n} (\nabla \psi_i)^2 + u \left(\sum_{i=1}^{n} \psi_i^2 \right)^2 + t \left(\sum_{i=1}^{n} \psi_i^2 \right)^3 + \cdots \ .$$

For each equation above, the "···" means higher-order terms than those given. Using $\psi_1 = \rho \cos\theta$ and $\psi_2 = \rho \sin\theta$, we can also write the $n = 2$ LGW Hamiltonians to sixth order as

$$H = H_2' + v' \rho^4 \cos 4\theta + t' \rho^6 \cos 4\theta + \cdots \ , \tag{2a$'$}$$

$$H = H_2' + t_1' \rho^6 \cos 6\theta + \cdots \ , \tag{2b$'$}$$

$$H = H_2' + t_1' \rho^6 \cos 6\theta + t_2' \rho^6 \sin 6\theta + \cdots = H_2' + \bar{t} \rho^6 \cos(6\theta + \alpha) + \cdots \ , \tag{2c$'$}$$

$$H = H_2' + w_1 \rho^3 \cos 3\theta + t_1' \rho^6 \cos 6\theta + \cdots \ , \tag{2d$'$}$$

$$\begin{aligned} H &= H_2' + w_1 \rho^3 \cos 3\theta + w_2 \rho^3 \sin 3\theta + t_1' \rho^6 \cos 6\theta + t_2' \rho^6 \sin 6\theta + \cdots \\ &= H_2' + \bar{w} \rho^3 \cos(3\theta + \alpha_1) + \bar{t} \rho^6 \cos(6\theta + \alpha_2) + \cdots \ , \end{aligned} \tag{2e$'$}$$

where

$$H_2' = \tfrac{1}{2} r \rho^2 + \tfrac{1}{2} \{ (\Delta\rho)^2 + \rho^2 (\Delta\theta)^2 \} + u' \rho^4 + t' \rho^6 + \cdots \ .$$

LGW Hamiltonian (1) is that of the Ising model. Equation (2a) corresponds to the *XY* model with "cubic" anisotropy (as well as several other models[24–26]), while Eq. (2b) is that of José *et al.*[25] Equations (2d) and (3b) correspond to the three- and four-state Potts model, respectively.[11] Equation (3a) corresponds to a model discussed by Domany and Riedel.[26,27] If the variations in ρ are frozen out and the appropriate higher-order terms are irrelevant, then Eq. (2c) has the same critical behavior as Eq. (2b), and Eq. (2e) has the same critical behavior as Eq. (2d). Under general circumstances Eqs. (2c) and (2e) may correspond to classes different from those identified in the past. Also Eq. (4) has not been identified in the past. Notice that the transitions with LGW Hamiltonians (2d), (2e), and (3b) do not satisfy the second Landau-Lifshitz rule, while the remaining ones do.

VI. APPLICATIONS

A. Monolayer adsorption of atoms

In the usual lattice-gas model,[28] we assume that the adsorbed atoms can be described only by the occupation numbers $n(\vec{r}) = 0, 1$ where $\vec{r}$ denotes the site positions. We assume a pattern of sites which repeats itself in two nonparallel directions, so the pattern can be associated with a space group. The model Hamiltonian is

$$H - \mu N = \tfrac{1}{2} \sum_{\vec{r}\,\vec{r}\,'} V(\vec{r} - \vec{r}\,') n(\vec{r}) n(\vec{r}\,') - \mu \sum_{\vec{r}} n(\vec{r}) \ .$$

The order-parameter components are

$$\psi_i = \sum_{\vec{r}} \phi_i(\vec{r}) n(\vec{r}) \ ,$$

where i labels the basis functions of the real irreducible representation in question.

We introduce here the "modified lattice-gas model," in which some sites are more likely to be occupied than others because of the potential which the substrate offers to the adatoms. One common example[5,29] of this is adsorption on laminar halides or (111) crystal faces of fcc or bcc crystals in which the substrate atoms are in a close-packed triangular array. In these cases a hexagonal lattice of sites is present at the surface, but layers of substrate atoms below the topmost make one half of the sites more likely for an adsorbed atom to occupy than the other half. Figure 5 displays the symmetry of the "disordered" phase. We will label the "dot" sublattice by A and the "circle" sublattice by B, so in this phase $\langle n(\vec{r}_A) \rangle \neq \langle (\vec{r}_B) \rangle$. The model Hamiltonian becomes

$$\begin{aligned} H - \mu_A N_A - \mu_B N_B = {} & \tfrac{1}{2} \sum_{\vec{r}_A \vec{r}\,'_A} V_{AA}(\vec{r}_A - \vec{r}\,'_A) n(\vec{r}_A) n(\vec{r}\,'_A) + \tfrac{1}{2} \sum_{\vec{r}_B \vec{r}\,'_B} V_{BB}(\vec{r}_B - \vec{r}\,'_B) n(\vec{r}_B) n(\vec{r}\,'_B) \\ & + \sum_{\vec{r}_A \vec{r}_B} V_{AB}(\vec{r}_A - \vec{r}_B) n(\vec{r}_A) n(\vec{r}_B) - \mu_A \sum_{\vec{r}_A} n(\vec{r}_A) - \mu_B \sum_{\vec{r}_B} n(\vec{r}_B) \ . \end{aligned}$$

The chemical potentials $\mu_A \neq \mu_B$ incorporate the difference between the two types of sites. The space group G_0 is $p3m1$. Only the real irreducible representations $\{(k), A'\}$ and $\{(m), A\}$ (see Table II) can be realized in this

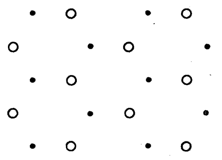

FIG. 5. Structure of the disordered phase described in Sec. VI A. In this disordered phase, the dot sites are more likely to be occupied than the circle sites because of the substrate potential. The space group associated with this structure is $p3m1$.

case. Allowed ordered structures in a continuous transition are illustrated in Fig. 6. The order-parameter components are

$$\psi_i = \sum_{\vec{r}_A} \phi_i(\vec{r}_A) n(\vec{r}_B) + \sum_{\vec{r}_B} (\vec{r}_B) n(\vec{r}_B) \ .$$

Similar results hold for an arbitrary number of different types of sites $A,B,C,\ldots$.

This modified lattice-gas model can easily be generalized into a continuum model. In this case the model Hamiltonian is

$$H - \int d\vec{r}\, \mu(\vec{r}) n(\vec{r}) = \frac{1}{2} \int d\vec{r}\, d\vec{r}\,' V(\vec{r}-\vec{r}\,') \rho(\vec{r}) \rho(\vec{r}\,') - \int d\vec{r}\, \mu(\vec{r}) \rho(\vec{r}) \ .$$

The order-parameter components become

$$\psi_i = \int d\vec{r}\, \phi_i(\vec{r}) \rho(\vec{r}) \ .$$

Notice that $\mu(\vec{r})$ must be invariant under the elements of G_0. The first two models are special cases of this continuum model. For example, when

$$\rho(\vec{r}) = \sum_i n(\vec{r}_i) \delta(\vec{r}-\vec{r}_i)$$

and

$$\mu(\vec{r}) = \mu \ ,$$

the continuum model reduces to the usual lattice-gas model. This continuum model has the following advantages: it can be used to describe molecular adsorption, and also it can be used to describe surface reconstruction. In the next two sections we will include examples of how the continuum model applies in these cases.[30]

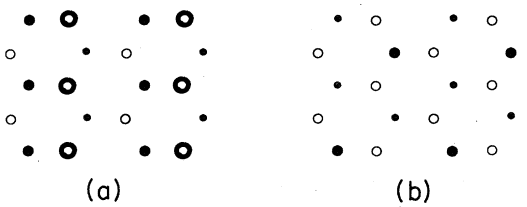

FIG. 6. Structures which can occur in a continuous transition from the structure of Fig. 5. The real irreducible representations are $\{(k),A'\}$ for (a) and $\{(m),A\}$ for (b).

B. Monolayer adsorption of molecules

The results of the Landau-Lifshitz theory in Sec. V can easily be applied to order-disorder phase transitions of molecular monolayer adsorption. First,[5] if in the high-temperature (disordered) phase only one orientation of the molecule occurs for a fixed center of mass, then the lattice-gas description can be used. One can simply describe a molecule by its center of mass, just as if it were an atom. For this case to be realized, the point group of the adsorption site must be a subset (or equal to) the point group of the molecule. The following example of this case has been treated earlier[5]: the adsorption of diatomic molecules on a hexagonal substrated, where the molecules occupy the "bridge sites" midway between pairs of substrate atoms, is equivalent to the adsorption of atoms on a kagomé lattice. Similarly, in the case of acetylene on Ni(111),[31] the molecules occupy the bridge sites of a $p6mm$ lattice, as shown in Fig. 7. The equivalent lattice for this example is a hexagonal lattice.

In other cases a molecule with a fixed center of mass can orient itself in one of several equivalent but different ways. The simple lattice-gas description cannot be used in this case, if we describe the molecules by their centers of mass only. It is easiest to resort to the continuum description. We will illustrate here the adsorption of benzene on (0001) gra-

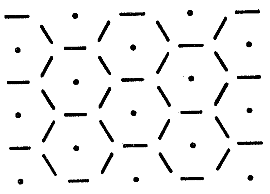

FIG. 7. Allowed locations of acetylene adsorbed on Ni(111). The dots represent the nickel atoms of the topmost substrate layer. The acetylene molecules occupy the positions shown: the center of masses are midway between the nickel atom (when projected on this plane) and the long axes of the molecules are oriented as shown.

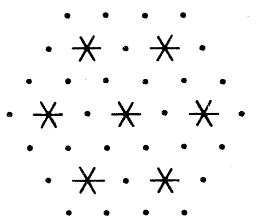

FIG. 8. Allowed projections of benzene on (1000) graphite. The dots represent the carbon atoms of the topmost substrate layer. The benzene molecules occupy the positions shown. Each position is equally probable in the disordered phase. The space group associated with this structure is $p6mm$.

phite.[32] The benzene molecules are known to stand up on the surface in a certain range of temperatures and coverages. Assuming a two-dimensional description is sufficient, we need only consider the projection of the molecule on the surface, so our analysis here could apply as well to a diatomic molecule lying flat on a surface of the proper symmetry. Figure 8 illustrates the equivalent orientations of the disordered phase, each of which would be occupied with the same probability. The structures which are allowed in a continuous transition are displayed in Fig. 9, labeled by the corresponding real irreducible representations. (For simplicity we illustrate not the structures which would actually occur near the critical point, but rather structures of the same symmetry as those which would be found.) Experiments have not yet been performed to test the predictions of this paragraph.

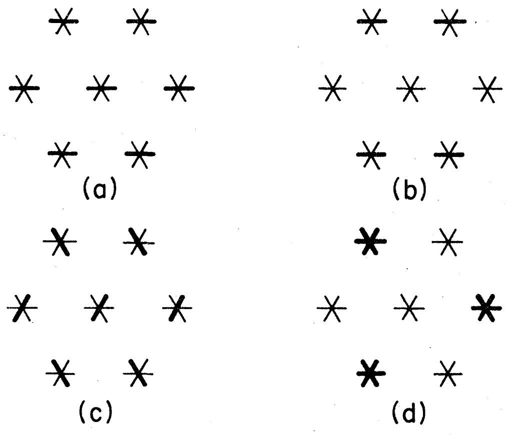

FIG. 9. Structures with the same symmetries as those which can occur in a continuous transition from the structure of Fig. 8. The real irreducible representations are (a) $\{\{\vec{0}\},E_2\}$, (b) $\{(k),A_1\}$, (c) $\{(k),A_2\}$, and (d) $\{(m),A_1\}$.

C. Surface reconstruction

The results of the Landau-Lifshitz theory can also be applied to surface reconstruction phase transitions. Bak[33,34] has discussed one method of applying the Landau-Lifshitz theory to surface reconstruction. He uses, as an order parameter, the vector

$$\vec{\psi}_i = \sum_{\vec{r}} \phi_i(\vec{r})\vec{u}(\vec{r}) \ ,$$

where $\vec{r}$ denotes the position of a nonreconstructed site and $\vec{u}$ is a displacement operator. If one treats the displaced atoms as point particles, then the corresponding ordering density is

$$\vec{\rho}(\vec{r}) = \sum_{\vec{r}'} \vec{u}(\vec{r}')\delta(\vec{r}-\vec{r}') \ .$$

In the following paragraph we illustrate how to describe surface reconstruction without resorting to vector order parameters.

As an example, we analyze the second example which Bak[33] considered, illustrated in Fig. 10. In general we can write

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

where $\langle \rho(\vec{r},T) \rangle$ is the mass density of the reconstructed phase, $\langle \rho_0(\vec{r},T) \rangle$ has the symmetry of G_0 ($p4mm$ in our example), and $\delta\langle \rho(\vec{r},T) \rangle$ is a linear combination of the basis functions of the real irreducible representation(s) of G_0. For our example only one basis function is necessary if the atomic displacement is sufficiently small; it is of the real irreducible representation $\{(j),E\}$ of $p4mm$ (see Table II). Since the basis function $\delta\langle \rho(\vec{r},T) \rangle$ belongs to a single real irreducible representation of G_0, and this representation is in Table II, the transition illustrated may be a continuous one of the universality class of the XY model with cubic anisotropy, as found by Bak.[33]

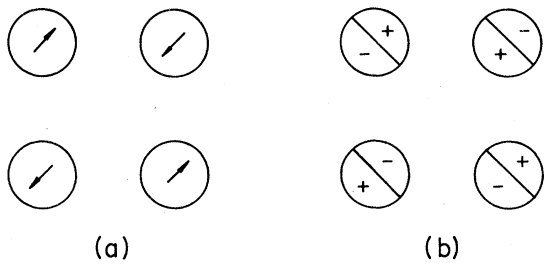

FIG. 10. Example of surface reconstruction considered in Sec. VI. In (a) the arrows indicate the direction in which the atoms, denoted by the circles, are displaced. To lowest order in the displacement, $\delta\langle \rho(\vec{r},T) \rangle$ has the symmetry of (b), which is a basis function of the real irreducible representation $\{(j),E\}$.

TABLE III. The energies associated with the possible nearest-neighbor interactions of the first model in the Appendix.

State of the site on sublattice 1	A	B	C	A	B	C	A	B	C
State of the site on sublattice 2	A	B	C	B	C	A	C	A	B
Energy	ϵ_1	ϵ_1	ϵ_1	ϵ_2	ϵ_2	ϵ_2	ϵ_3	ϵ_3	ϵ_3

Notice that the basis functions of $\delta\langle\rho(\vec{r},T)\rangle$, as well as $\langle\rho_0(\vec{r},T)\rangle$, change their functional form as the temperature T changes. The Landau-Lifshitz theory still applies when this happens since what is important is the symmetry of the functions immediately above and below the transition. If we had used the continuum model for atomic monolayer adsorption and included the random thermal vibrations of the adatoms, the functional form of the appropriate ordering densities in this case would change as T changes since the adatoms would spend more time away from the equilibrium positions as T increases.

VII. CONCLUDING REMARKS

We hope that the investigation here will stimulate continued experimental interest in systems which are expected to exhibit the transitions discussed. Of special interest are systems which we predict to be in the possibly new universality classes of the LGW Hamiltonians (2c), (2e), and (4) of Sec. V. In the future we expect to treat two-dimensional symmetry groups which contain space groups as subgroups. We hope to describe transitions in magnetic systems which have time-reversal symmetry. We also hope to treat coadsorption of two or more particles in which particle-exchange symmetries play an essential role.

ACKNOWLEDGMENTS

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APPENDIX

We have found a ferromagnetic discrete model which yields the LGW Hamiltonian (2e) of Sec. V.[35] The model is composed of two interpenetrating square sublattices, labeled 1 and 2. Each site interacts with its four nearest neighbors only. The states, A, B, and C, are associated with each site. The energies E associated with the nine possibilities for a given pair of nearest neighbors are given in Table III. When $\epsilon_2=\epsilon_3$, this model reduces to the three-state Potts model. The energy E can also be written in terms of the variables s_i, where $i=1,2$ labels the sublattices, and $s_i=1(0,-1)$ if the site of sublattice i is in the state $A(B,C)$. Then

$$\begin{aligned}E(s_1,s_2)&=a+b_1s_1+b_2s_2+c_1s_1^2+c_2s_2^2\\&\quad+c_3s_1s_2+d_1s_1^2s_2+d_2s_1s_2^2+es_1^2s_2^2\\&=A+B\sin\frac{2\pi}{3}(s_1-s_2)+C\cos\frac{2\pi}{3}(s_1-s_2)\ ,\end{aligned}$$

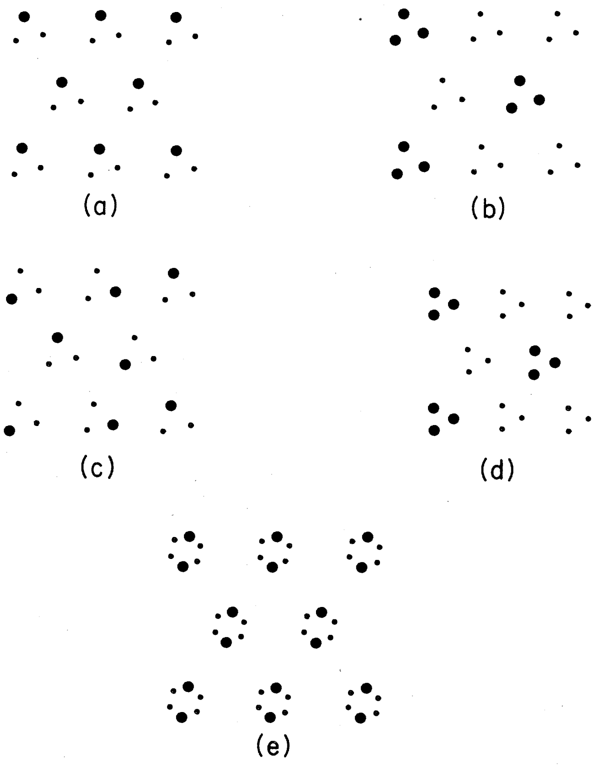

FIG. 11. Ordered structures for $\frac{1}{3}$ coverage in which the order-disorder transition is characterized by LGW Hamiltonian (2e).

TABLE IV. The real irreducible representations of the symmetries illustrated in Fig. 10 and properties of the coefficients of the discrete Hamiltonians which would yield such symmetries.

Pattern from Fig. 5	Space group	Star of $\vec{k}$	Real small representation	$\frac{V}{\lvert V\rvert}$	$\frac{W}{\lvert W\rvert}$	$\frac{X}{\lvert X\rvert}$	$\frac{Y}{\lvert Y\rvert}$
(*a*)	$p3$	$\{\vec{0}\}$	E	−1	−1	−1	0
(*b*)	$p3$	(1)	A	1	−1	−1	0
(*c*)	$p3$	(1)	E	−1	−1	1	0
(*d*)	$p31m$	(1)	A_1	1	−1	−1	0
(*e*)	$p6$	$\{\vec{0}\}$	E_1	−1	−1	1	−1

where

$$a=\epsilon_1\ ,$$

$$b_1=-b_2=\tfrac{1}{2}(\epsilon_2-\epsilon_3)\ ,$$

$$c_1=c_2=-\epsilon_1+\tfrac{1}{2}(\epsilon_2+\epsilon_3)\ ,$$

$$c_3=\tfrac{1}{2}\epsilon_1-\tfrac{1}{4}(\epsilon_2+\epsilon_3)\ ,$$

$$d_1=-d_2=\tfrac{3}{4}(\epsilon_2-\epsilon_3)\ ,$$

$$e=\tfrac{3}{2}\epsilon_1-\tfrac{3}{4}(\epsilon_2+\epsilon_3)\ ,$$

$$A=\tfrac{1}{3}(\epsilon_1+\epsilon_2+\epsilon_3)\ ,$$

$$B=\frac{1}{\sqrt{3}}(\epsilon_2-\epsilon_3)\ ,$$

$$C=\tfrac{1}{3}(2\epsilon_1-\epsilon_2-\epsilon_3)\ .$$

We have also found antiferromagnetic models which can prove useful in predicting adsorbed monolayer transitions which are characterized by the LGW Hamiltonian (2e). The patterns of the sites which a particle can occupy are given in Fig. 11, along with ordered structures for $\frac{1}{3}$ coverage at $T=0$. In terms of the variables $n_i=0,1$, the discrete Hamiltonians required are of the form

$$H-\mu N=V\sum_{\mathrm{NN}}n_in_j+W\sum_{\mathrm{NNN}}n_in_j+X\sum_{\mathrm{3NN}}n_in_j+Y\sum_{\mathrm{4NN}}n_in_j-\mu\sum_i n_i\ ,$$

where "3NN" denotes third nearest neighbor, etc. Table IV summarizes which terms above are nonzero, what the signs of the nonzero terms are, and the real irreducible representation which each model corresponds to. A similar analysis can be performed for each of the other transitions in Table II.

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[1] D. Mukamel and S. Krinsky, Phys. Rev. B 13, 5065 (1976).

[2] Note, that in situations where a second order transition is symmetry allowed, the actual transition may be first order, depending on interaction parameters.

[3] See, also, the review of M. N. Barber, Phys. Rep. 59, 380–385 (1980).

[4] E. Domany, M. Schick, J. Walker, and R. B. Griffiths, Phys. Rev. B 18, 2209 (1978).

[5] E. Domany and M. Schick, Phys. Rev. B 20, 3828 (1979).

[6] Systems with *additional* symmetry beyond pure space-group symmetry require separate analysis, e.g., the two-dimensional Ising system in zero magnetic field, which possesses time-reversal symmetry.

[7] E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics*, 3rd ed. (Pergamon, New York, 1980), Part 1, Chap. XIV; L. D. Landau, Zh. Eksp. Teor. Fiz. 7, 19 (1937); E. M. Lifshitz, J. Phys. 6, 61 (1942). English translations of Landau's papers may be found in D. TerHaar, *Collected Papers of L. D. Landau* (Gordan and Breach, New York, 1965).

[8] R. B. Griffiths, Phys. Rev. Lett. 24, 1479 (1970).

[9] References 4 and 5 give a more detailed explanation and also provide examples where this mixing does occur.

[10] Alternatively, the second rule may be satisfied when the coefficient of this term vanishes "accidentally" at the critical point. See Ref. 1 for further details.

[11] R. J. Baxter, J. Phys. C 6, L445 (1973); J. P. Straley and M. E. Fisher, J. Phys. A 6, 1310 (1973); R. K. P. Zia and D. J. Wallace, *ibid.* 8, 1495 (1975).

[12] Reference 1 gives a more detailed physical interpretation.

[13] If the coefficient described above vanishes "accidentally" (i.e., despite violation of the Lifshitz condition) *at* the transition, thus satisfying the third rule, but not elsewhere in the ordered phase, the symmetry of ordered state changes with temperature. See Ref. 1.

[14] G. Ya. Lyubarskii, *The Application of Group Theory in Physics* (Pergamon, New York, 1960), Chap. VII.

[15] Reference 14 gives a detailed discussion on pp. 91–102. Also a more physical treatment may be found in L. M. Falicov, *Group Theory and its Physical Applications* (Univer-

sity of Chicago, Chicago, 1966), Chap. VI.

[16] We follow the recipe set forth in the example of Ref. 14, pp. 134–46.

[17] The discussion here extends the work of Ref. 1 to include nonsymmorphic space groups and cases in which $\tilde{R}$ is not real.

[18] The order-parameter components ψ_i and the basis functions ϕ_i are associated in a one-to-one fashion. See Sec. VI.

[19] *International Tables for X-ray Crystallography* (Knoch, Birmingham, England, 1952).

[20] The table is constructed when we determine if the Lifshitz condition is satisfied. See Ref. 14 for the construction of such a table.

[21] Several of the subsequent prescriptions in this paragraph are only valid when the star of $\vec{k}$ is a single vector. However we see from Table II that for *nonsymmorphic* groups which satisfy the Lifshitz condition the star of $\vec{k}$ is *always* a single vector.

[22] L. D. Lifshitz and E. M. Lifshitz, *Quantum Mechanics,* 3rd ed. (Pergamon, New York, 1977), pp. 377-378.

[23] This amounts to taking the product of certain elements of the group of $\vec{k}$ with translational operators such that the resulting set is a subset of G_0. The observation of Ref. 21 has been used in Eq. (4).

[24] R. J. Baxter, Phys. Rev. Lett. 26, 832 (1971); J. M. J. van Leeuwen, *ibid.* 34, 1056 (1975); J. Ashkin and E. Teller, Phys. Rev. 64, 178 (1943); F. Y. Wu, J. Phys. C 8, 2262 (1975).

[25] J. José, L. P. Kadanoff, S. Kirkpatrick, and D. R. Nelson, Phys. Rev. B 16, 1217 (1977).

[26] E. Domany and E. Riedel, J. Appl. Phys. 49, 1315 (1978).

[27] E. Domany and E. Riedel, Phys. Rev. Lett. 40, 561 (1978).

[28] References 4 and 5 develop the theory of this paragraph in much more detail.

[29] Y. Larher, J. Colloid Interface Sci. 37, 836 (1971).

[30] The theory of this paper does not apply to commensurate-incommensurate transitions, since for these transitions there is no association of the order-parameter components and the basis functions in a one-to-one fashion as in this section. See, P. Bak and D. Mukamel, Phys. Rev. B 19, 1604 (1979); and P. Bak, D. Mukamel, J. Villain, and K. Wentowska, *ibid.* 1610 (1979).

[31] J. E. Demuth, Surf. Sci. 69, 365 (1977).

[32] R. Stockmeyer and H. Stortnik, Surf. Sci. 81, L315 (1979); B. Boddenberg and J. A. Moreno, J. Phys. (Paris) 38, C4-52 (1977). See also J. Tabony, J. W. White, J. C. Delachaume, and M. Coulon, Surf. Sci. 95, L282 (1980).

[33] P. Bak, Solid State Commun. 32, 581 (1979).

[34] For each transition which we have considered, the two methods yield the same universality class. We thank M. Schick for pointing out to us Bak's use of a vector order parameter.

[35] This model is related to Eq. (2e) in the same sense that the three-state Potts model is related to Eq. (2d).