[7]D. N. Paulson, M. Krusius, R. S. Safrata, and J. C. Wheatley, to be published.
[8]D. N. Paulson, M. Krusius, and J. C. Wheatley, Phys. Rev. Lett. 37, 599 (1976).
[9]D. N. Paulson, M. Krusius, and J. C. Wheatley, Phys. Rev. Lett. 36, 1322 (1976).
[10]N. D. Mermin, in *Quantum Fluids and Solids*, edited by S. B. Trickey, E. D. Adams, and J. W. Dufty (Plenum, New York, 1977), p. 3.
[11]M. Krusius, D. N. Paulson, and J. C. Wheatley, to be published.
[12]A. J. Leggett, Phys. Rev. Lett. 39, 587 (1977).

Phase Transitions in Two-Dimensional Systems

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Two recently studied experimental systems are shown to constitute realizations of two-dimensional anisotropic N-vector models. Along with a renormalization-group treatment of a general Hamiltonian encompassing these models, we discuss new kinds of multicritical points, nonuniversal critical behavior, and experiments for further study of these systems.

The study of phase transitions in adsorbed thin films is a rapidly developing field of high current experimental and theoretical activity. The experimental methods (such as thermal measurements and diffraction techniques) are approaching the point where reliable determinations of phase diagrams and critical exponents are becoming possible.[1] Theoretical models for overlayer systems can be derived by symmetry arguments[2] and analyzed by renormalization-group (RG) or other techniques. This comprehensive approach is applied here to the magnetic phase transition in molecular oxygen adsorbed on graphite[3,4] and to the order-disorder transition in atomic oxygen on tungsten.[5] These systems represent the first examples of two-dimensional (2D) anisotropic N-vector models (Heisenberg and XY with cubic anisotropy). Realizations of Ising and Potts models were discussed previously.[6] Anisotropic N-vector models in 2D[7] are of special interest since they exhibit features such as nonuniversal critical exponents,[8,9] new kinds of multicritical points, and new universality classes.[10] In 2D the anisotropic perturbations are relevant[7] and grow under RG iterations. This allows the mapping of the Landau-Ginzburg-Wilson (LGW) continuous-spin models, which are derived on grounds of symmetry,[2] onto discrete spin models, which can be conveniently analyzed by position-space RG methods. The two anisotropic N-vector models are shown to be related to special cases of a general, discrete N-state model termed the (N_α, N_β) model. The model is introduced and discussed. In this work, the hypothesis is made that if a discrete spin model and an experimental system are described by the same LGW Hamiltonian, all three belong to the same universality class. This hypothesis has not been extensively tested in 2D. Specifically, the phase diagram for the general six-state model is investigated using duality transformations[11] and Migdal's approximate RG recursion relations.[12] Experiments to test the applicability of the models and to investigate their properties are also discussed.

First, consider overlayers of molecular oxygen physisorbed on graphite. The system exhibits a phase transition into an antiferromagnetically ordered state [Fig. 1(a)] at $T_c = 11.3$ K, which is apparently continuous.[3,4] Neutron scattering experiments[3] indicate that the lattice structures of the disordered and ordered O_2 phases are incommensurate with the substrate and al-

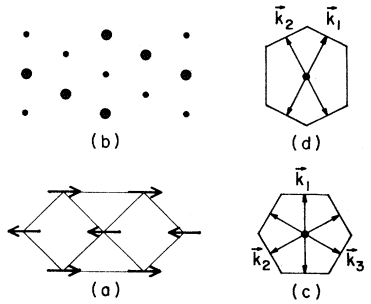

FIG. 1. Structures of the ordered phases of (a) O_2 adsorbed on graphite (the arrows denote the spin orientations on the distorted triangular lattice), and (c) oxygen adsorbed on tungsten (the heavy dots denote occupied sites). The Brillouin zones and wave vectors, $\vec{k}$, that define the different ordered states, are shown in (b) and (d), respectively.

most identical to the a-b planes of bulk β- and α-O_2. For this reason we will *assume* in the following that substrate effects can be neglected.[13] For $T > T_c$ the O_2 molecules form a closed-packed triangular lattice (symmetry $P6mm$). For $T < T_c$ the lattice is distorted [Fig. 1(a)]. The magnetic moments of the O_2 molecules are confined to the plane of the surface. Under these assumptions, symmetry arguments[2] yield the LGW Hamiltonian of Eqs. (1a)–(1c) below. The magnetic order parameter φ belongs to a three-dimensional irreducible representation, $\varphi_i = \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R})\vec{S}_{\vec{R}}\cdot\vec{v}_i$, where $\vec{v}_i \perp \vec{k}_i$ $(i = 1, 2, 3)$, defined in Fig. 1(b). The lattice distortion is described by components of the strain tensor ϵ_{ij} that belong to a two-dimensional representation, $\psi_1 = \epsilon_{xy}$ and $\psi_2 = \frac{1}{2}(\epsilon_{xx} - \epsilon_{yy})$. Hence the LGW Hamiltonian has the form $H = H_1(\varphi) + H_2(\psi) + wH_3(\varphi, \psi)$ with

$$H_1 = -\left[\tfrac{1}{2}\sum(\nabla\varphi_i)^2 + \tfrac{1}{2}r_1\sum\varphi_i^2 + u(\sum\varphi_i^2)^2 + v\sum\varphi_i^4\right], \tag{1a}$$

$$H_2 = -\left[\tfrac{1}{2}\sum(\nabla\psi_j)^2 + \tfrac{1}{2}r_2\sum\psi_j^2 + \overline{w}(\psi_2^3 - 3\psi_1^2\psi_2) + \overline{u}(\sum\psi_j^2)^2\right], \tag{1b}$$

$$H_3 = (\varphi_3^2 - \varphi_2^2)\psi_1 + (1/\sqrt{3})(3\varphi_1^2 - \sum\varphi_i^2)\psi_2. \tag{1c}$$

Suppose H_1 and H_2 exhibit transitions at $T_c^{(1)}$ and $T_c^{(2)}$ when $H_3 = 0$. What is the effect of the coupling term? When $T_c^{(1)} > T_c^{(2)}$, the φ fields order first, inducing via H_3 an effective ordering field on ψ. This mechanism yields a single transition of cubic Heisenberg character. When $T_c^{(1)} < T_c^{(2)}$, first the ψ fields undergo a continuous, three-state Potts transition, producing a distorted nonmagnetic intermediate phase. The coupling H_3 lowers the effictive quadratic coefficient of *one* φ component. Then at a lower temperature, this component will undergo an "elastically driven" Ising transition. This type of phase diagram is contained in Fig. 3, where it is exhibited by the "cubic" plane, $x_\alpha = z$.

Present experimental evidence is consistent with the assumption that O_2 on graphite has a *single*, continuous transition, which, therefore, could be of cubic Heisenberg character. The specific heat data exhibit one sharp peak.[4] In the neutron scattering experiment,[3] the question whether the magnetic order and the distortion appear at the same temperature was not investigated. Further measurements of the phase diagram and the critical exponents α and β are needed to confirm that the system belongs to this new universality class. The conclusion can also be tested by studying the phase transition in a magnetic field applied *perpendicular* to the substrate. If the system is in the cubic Heisenberg regime, the field is expected to lower the transition temperature and, when sufficiently strong, to cause a splitting of the transition. The point P is a special multicritical point as discussed below. In contrast, application of a field *parallel* to the substrate should result in two-dimensional bicritical behavior of the usual kind.

Second, consider atomic oxygen chemisorbed on the [110] face of tungsten.[5] The order-disorder transition exhibited by this overlayer is described by a 2D XY model with cubic anisotropy, Eq. (2). The W atoms form a 2D lattice of space-group symmetry $C2mm$. The oxygen overlayer orders into a superlattice consisting of diagonal rows of alternately occupied and unoccupied sites, Fig. 1(c). Thus the order parameter belongs to a two-dimensional irreducible representation, $\psi_{\vec{k}_1} \equiv \psi_1$ and $\psi_{\vec{k}_2} \equiv \psi_2$, with $\vec{k}_1, \vec{k}_2$ defined in Fig. 1(d). The appropriate LGW Hamiltonian is

$$H = -\left\{\tfrac{1}{2}\left[(\nabla\psi_1)^2 + (\nabla\psi_2)^2\right] + \tfrac{1}{2}r(\psi_1^2 + \psi_2^2) + u(\psi_1^2 + \psi_2^2)^2 + v(\psi_1^4 + \psi_2^4)\right\}, \tag{2}$$

which is identical to that of an XY model with cubic anisotropy. This model has been suggested to exhibit nonuniversal critical behavior, with exponents that vary continuously with the anisotropy, v.[9] Experiments testing this conjecture would be instructive. The anisotropy parameter v may be varied either by changing the coverage or by using different substrates and adsorbates that produce similar structures. All models known to exhibit continuously varying exponents[8] lead to LGW Hamiltonians of the form of Eq. (2). By a Hubbard transformation[14] we have mapped the Ashkin-Teller model onto (2) and found that v is a function of the parameter that governs the variation of the critical exponents.

The method of calculation is briefly described. The behavior of a Heisenberg system with cubic anisotropy[7] (such as O_2 on graphite) is investigated in three steps. *First,* we study the Hamiltoni-

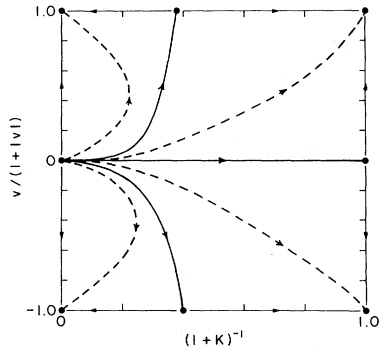

FIG. 2. Flow diagram for the two-dimensional Heisenberg model with cubic anisotropy, as obtained by the Migdal recursion scheme.

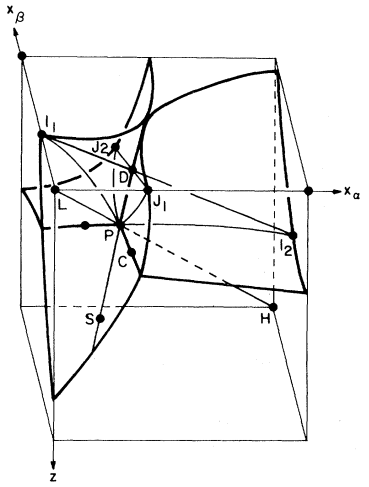

FIG. 3. Phase diagram of the $N_\alpha = 3$, $N_\beta = 2$ model, as obtained by Migdal recursion relations. The fixed points are L (H), low (high) temperatures; D, decoupled Ising and three-state Potts; P, six-state Potts; S, self-dual; C, cubic; I_1, I_2, Ising; J_1, J_2, three-state Potts. The plane $x_\alpha = z$ corresponds to the subspace of cubic symmetry; it contains cubic, Ising, and three-state Potts transition lines that meet at P.

an for fixed length spins on a square lattice,

$$H/k_B T = -K \sum_{<ij>} \vec{S}_i \cdot \vec{S}_j - v \sum_i \sum_{\alpha=1}^{3} (S_i^{(\alpha)})^4, \qquad (3)$$

by applying Migdal's approximate renormalization-group formalism.[12] Decimating every other spin, we evaluated the necessary integrals numerically, and determined K by projection onto $\vec{S}_i \cdot \vec{S}_j$ – const. The flow diagram of Fig. 2 is obtained. The result means that the critical behavior of model (3) is determined by a $|v| = \infty$ fixed point, i.e., that of a discrete-spin Hamiltonian. For $v > 0$ the spin can point in six directions and for $v < 0$ in eight directions. *Second*, to study the critical properties of such N-state systems we consider a generalization of the Potts model, termed the (N_α, N_β) model. In this model there are *two* discrete variables, $\alpha_i = 1, \ldots, N_\alpha$ and $\beta_i = 1, \ldots, N_\beta$, associated with each site of a square lattice,

$$H/k_B T = -\sum_{<ij>} [K_{0,0} \delta_{\alpha_i,\alpha_j} \delta_{\beta_i,\beta_j} + K_{0,1} \delta_{\alpha_i,\alpha_j} (1 - \delta_{\beta_i,\beta_j})$$
$$+ K_{1,0} (1 - \delta_{\alpha_i,\alpha_j}) \delta_{\beta_i,\beta_j} + K_{1,1} (1 - \delta_{\alpha_i,\alpha_j})(1 - \delta_{\beta_i,\beta_j})]. \qquad (4)$$

A convenient choice of variables is $x_\alpha = \exp(K_{1,0} - K_{0,0})$, $x_\beta = \exp(K_{0,1} - K_{0,0})$, and $z = \exp(K_{1,1} - K_{0,0})$. In the case of a ferromagnetic ground state the physical parameter space is in the cube $0 < x_\alpha, x_\beta, z < 1$. With $N_\alpha = 3$ and $N_\beta = 2$ the Hamiltonian defines a six-state model. The plane $x_\alpha = z$ corresponds to the Heisenberg system with cubic anisotropy. Migdal's approximate recursion relations[12] yield the phase diagram shown in Fig. 3. On the plane $x_\alpha = z$ the system exhibits either one phase transition (governed by the cubic fixed point C) or two phase transitions (governed by the three-state Potts and Ising fixed points J_2 and I_1), depending on whether x_α is greater or less than x_β. This is exactly the behavior that is expected for the Hamiltonian (1). *Third*, we performed a Hubbard transformation on (4) with $N_\alpha = 3$, $N_\beta = 2$, and $x_\alpha = z$, and obtained a LGW Hamiltonian identical to third order with (1a)–(1c). This completes our argument on the applicability of this model to the system O_2 on graphite.

The Migdal method involves crude approximations. Determining the phase diagram for the *general* $N_\alpha = 3$, $N_\beta = 2$ six-state model not only shows the cubic plane embedded in a larger parameter space but also allows us to check the method against special, exactly known results. The six-state model reduces to the following models: six-state Potts (on the line $x_\alpha = x_\beta = z$), decoupled Ising and three-state Potts (on the surface $x_\alpha x_\beta = z$), and planar six-state[9] (on the line $x_\alpha = z^3, x_\beta = z^4$). The Migdal recursion relations preserve all symmetries of the general model, including $x_\alpha = z$. We were not able to achieve that within the Niemeijer–van Leeuwen approach. The Migdal method has been also found to reproduce accurately the phase diagram[15] for the Ash-

kin-Teller model ($N_\alpha = N_\beta = 2$). The phase diagram in the cubic plane, $x_\alpha = z$, agrees with results by Aharony.[10] We note, however, that the vicinity of the Potts point P is not yet understood. The Migdal method, as well as the other approximate RG approaches, *fails* to reproduce the first-order character of the six-state Potts model.[16] Hence one might expect first-order phase transition lines to extend from P and new tricritical points separating them from the second-order lines governed by the fixed points C, I_1, and J_2. These questions are being investigated by Monte Carlo techniques. The application of exact expansion methods would also be useful.

An exact duality transformation,[11] $\vec{\tilde{x}} = \vec{D}(\vec{x})$, exists for the (N_α, N_β) model:

$$\tilde{x}_\alpha = [1 - x_\alpha + (N_\beta - 1)(x_\beta - z)]/\Delta,$$
$$\tilde{z} = [1 - x_\alpha - x_\beta + z]/\Delta, \tag{5}$$

where $\Delta = 1 + (N_\alpha - 1)x_\alpha + (N_\beta - 1)x_\beta + (N_\alpha - 1)(N_\beta - 1)z$. The equation for $\tilde{x}_\beta$ is obtained by interchanging α and β in (5). Having found the duality transformation, one can perform the decimation upon which Migdal's renormalization-group *Ansatz* is based. This leads to the recursion relations $\vec{x}' = \vec{D}^\lambda[\vec{D}^\lambda(\vec{x})]$ (λ denotes the scale parameter) that were used to derive the phase diagrams of Fig. 3 and of the Ashkin-Teller model.

In summary, we have pointed out that two recently studied experimental systems constitute physical realizations of theoretical models of current interest. We investigated the phase diagram and critical properties of the models, and suggested experiments for further study of these systems. Other systems that may provide realizations of 2D anisotropic N-vector models are layered magnetic compounds such as Rb_2FeF_4 and Rb_2CrCl_4.

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[1]M. Bretz, Phys. Rev. Lett. 38, 501 (1977).
[2]D. Mukamel and S. Krinsky, Phys. Rev. B 13, 5065 (1976), and 16, 2313 (1977).
[3]J. P. McTague and M. Nielsen, Phys. Rev. Lett. 37, 596 (1976).
[4]J. Stoltenberg and O. E. Vilches, unpublished.
[5]J. C. Buchholz and M. G. Lagally, Phys. Rev. Lett. 35, 442 (1975).
[6]S. Alexander, Phys. Lett. 54A, 353 (1975); E. Domany, M. Schick, and J. Walker, Phys. Rev. Lett. 38, 1148 (1977).
[7]R. A. Pelcovits and D. R. Nelson, Phys. Lett. 57A, 23 (1976).
[8]R. J. Baxter, Phys. Rev. Lett. 26, 832 (1971); L. P. Kadanoff and F. J. Wegner, Phys. Rev. B 4, 3989 (1971); J. M. J. van Leeuwen, Phys. Rev. Lett. 34, 1056 (1975); F. Y. Wu, J. Phys. C 8, 2262 (1975).
[9]J. V. José, L. P. Kadanoff, S. Kirkpatrick, and D. R. Nelson, Phys. Rev. B 16, 1217 (1977).
[10]A. Aharony, J. Phys. C 10, 389 (1977).
[11]F. Y. Wu and Y. K. Wang, J. Math. Phys. (N.Y.) 17, 439 (1976).
[12]A. A. Migdal, Zh. Eksp. Teor. Fiz. 69, 1457 (1975) [Sov. Phys. JETP 42, 743 (1975)]; L. P. Kadanoff, Ann. Phys. (N.Y.) 100, 359 (1976).
[13]The similarity of the observed structures in film and bulk O_2 implies that the distortion caused by the substrate potential is very small. Then, even if such a distortion should cause crossover to different behavior, the crossover region would be too narrow to be experimentally observable; it may be as narrow as the crossover to finite size (~ 100 Å) behavior, imposed by the Grafoil crystallites.
[14]J. Hubbard, Phys. Lett. 39A, 365 (1972).
[15]F. Y. Wu and K. Y. Lin, J. Phys. C 7, L131 (1974).
[16]R. J. Baxter, J. Phys. C 6, L445 (1973).