First-Order Transitions, Symmetry, and the ϵ Expansion*

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The first-order nature of the antiferromagnetic transitions in Cr, Eu, UO_2, and MnO can be explained by noting that the corresponding Landau-Ginzburg-Wilson Hamiltonians possess *no* stable fixed points in $4-\epsilon$ dimensions. We predict that all fcc type-I ($\vec{m}\perp\vec{k}$), type-II, and type-III ($\vec{m}\perp[100], \vec{k}=[\frac{1}{2}01]$) antiferromagnetic transitions are first order.

According to universality, critical behavior should depend only upon a small number of a system's properties, such as the spatial dimensionality, the number of components of the order-parameter, and the symmetry of the Hamiltonian. In recent years much progress has been made in grouping together second-order transitions into universality classes. The relation between a system's symmetry properties and its phase transitions can be studied using Landau's[1] phenomenological theory. The Landau theory has been extended to include effects of fluctuations by using Wilson's[2] ϵ expansion. In fact, the renormalization-group approach introduced by Wilson and Kogut[2] provides a general formalism in which the ideas of universality and scaling are given a unified treatment. The ϵ expansion is a perturbation theory enabling one to compute universal quantities such as critical exponents directly from renormalization-group equations. In this note we wish to consider the intriguing question as to whether symmetry considerations are not only useful to classify second-order transitions, but are also sufficient to predict that certain phase transitions are first order. We have used the group-theoretical method of Landau and Lifshitz[1] to construct effective Hamiltonians describing certain antiferromagnetic order-disorder transitions which have order parameters with $n \geq 4$ components,[3] and we have then performed a renormalization-group analysis in $4-\epsilon$ dimensions.[4] We have found systems for which the renormalization-group equations in $4-\epsilon$ dimensions possess *no* stable fixed points.[4] The question naturally arises as to whether the lack of a stable fixed point within the ϵ expansion implies the transition is first order. In this paper we present support for this rule and we propose specific experiments to test it.

According to the theory of Landau and Lifshitz the symmetry-breaking order parameter associated with a second-order transition transforms according to an irreducible representation R of the symmetry group G_0 of the disordered phase. Using Landau symmetry arguments one can immediately predict three classes of order-disorder transitions expected to be first order (barring the simultaneous vanishing of two or more coefficients not related by symmetry):

(1) If the symmetric part of R^3, denoted $[R^3]$, contains the identity representation, i.e., $[R^3] \supset E$, then the Landau expansion includes third-order invariants and the transition is predicted to be first order.

(2) Transitions for which the order-parameter transforms according to a *reducible* representation of G_0 are expected to be first order.

(3) If the direct product of the antisymmetric part of R^2, denoted $\{R^2\}$, and the vector representation contains the identity representation, i.e., $\{R^2\}\otimes V \supset E$, and if the propagation vector $\vec{k}$ of the low-temperature phase is *temperature independent*, then the transition is predicted to be first order. Such transitions might be expected to result in a *commensurate* low-temperature phase.[5]

When none of these three criteria are satisfied, then the transition may be either first order or second order, depending on the values of the coefficients in the Landau expansion. We wish to propose a fourth phenomenological rule which will be predictive in certain cases when the above Landau symmetry criteria are not.

(4) If there is *no stable fixed point* within the ϵ expansion then the transition is first order.

Symmetry does not allow the existence of third-order invariants for the magnetic systems we consider, so rule (1) is not predictive. Rule (2) predicts first-order transitions in the type-II antiferromagnets[6] DySb and HoSb where the magnetic moment lies along the [001] direction, with components both parallel and perpendicular to the propagation vector $\vec{k}$. The order parameter for these systems has twelve independent components and belongs to two irreducible representations. The transition in DySb is known to be

first order,[7] while the nature of the transition in HoSb is not well established.

The antiferromagnetic transition[8] in $MnBr_2$ is associated with a temperature-independent propagation vector $\vec{k} = [\frac{1}{4}0\frac{1}{4}]$. Since the representation R satisfies $\{R^2\} \otimes V \supset E$, rule (3) predicts the transition to be first order in agreement with experiment.

Transitions not involving a change in the unit cell are described by $n \leq 3$ component order parameters, while certain phase transitions which involve a change of the unit cell are described by $n \geq 4$ component order parameters.[3] Brezin, Le-Guillou, and Zinn-Justin[9] have noted that the isotropic fixed point is always stable for $n \leq 3$ systems in $4 - \epsilon$ dimensions. We have found five different $n \geq 4$ component Hamiltonians for which there exist *no* stable fixed points in $4 - \epsilon$ dimensions, and rule (4) suggests the corresponding transitions are first order. We now describe the physical systems corresponding to these Hamiltonians:

Type-I antiferromagnets $\vec{m} \perp \vec{k}$ *(e.g., UO_2*[10]*).*—These are fcc crystals with space group $Fm3m$ exhibiting an antiferromagnetic structure with propagation vector $\vec{k}_1 = [100]$ and magnetization perpendicular to $\vec{k}_1$. The star of $\vec{k}_1$ consists of the three vectors: $\vec{k}_1 = [100]$, $\vec{k}_2 = [010]$, and $\vec{k}_3 = [001]$. Two components of the order parameter are associated with each $\vec{k}_i$ $(i = 1, 2, 3)$, corresponding to the two independent directions of the magnetization in the plane perpendicular to $\vec{k}_i$. The transition is described by a six-component Hamiltonian constructed from the five independent fourth-order invariants which can be formed from the order parameter. The transition in UO_2 is known to be first order.[10]

Type-II antiferromagnets $\vec{m} \perp \vec{k}$ *(e.g., MnO,*[11] *NiO,*[11] *MnSe,*[11] *ErSb,*[6] *EuTe*[12]*).*—These are fcc crystals with space group $Fm3m$ whose ordered state is composed of ferromagnetic (111) planes coupled antiferromagnetically. The magnetization is perpendicular to the propagation vector $\vec{k}_1 = [\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ and the star of $\vec{k}_1$ consists of the four vectors $\vec{k}_1 = [\frac{1}{2}\frac{1}{2}\frac{1}{2}]$, $\vec{k}_2 = [-\frac{1}{2}\frac{1}{2}\frac{1}{2}]$, $\vec{k}_3 = [\frac{1}{2}\frac{1}{2}-\frac{1}{2}]$, and $\vec{k}_4 = [\frac{1}{2}-\frac{1}{2}\frac{1}{2}]$. Two components of the order parameter are associated with each $\vec{k}_i$ $(i = 1, \ldots, 4)$, corresponding to the two independent directions of the magnetization in the plane perpendicular to $\vec{k}_i$. The eight-component Hamiltonian is constructed from the six fourth-order invariants which can be formed from the order parameter. It has recently been shown[13] that MnO indeed has a first-order transition. The nature of the transitions in NiO and MnSe are not yet well established. Measurements of the order parameter[14] of ErSb indicate the transition is second order, but specific-heat measurements[15] indicate there may exist a latent heat. We urge that further experimental work be done on ErSb.

Type-II antiferromagnets $\vec{m} \parallel \vec{k}$ *(e.g., TbAs, TbSb, TbP*[6]*).*—Since the magnetization is parallel to the propagation vector, the order parameter has four independent components corresponding to $\vec{k}_i$ $(i = 1, \ldots, 4)$, and the effective Hamiltonian is constructed from the three fourth-order invariants which can be formed from the order parameter. Previous measurements[6] on these systems have been performed far below the transition temperature with the objective of determining the ordered state. We suggest it is worthwhile to study these substances very close to the transition temperature to see if the transition is first order.

Type-III antiferromagnets $\vec{m} \perp [100]$, $\vec{k} = [\frac{1}{2}01]$. —These are fcc crystals with space group $Fm3m$, exhibiting an antiferromagnetic order in which the nonprimative unit cell is doubled in the x direction (corresponds to $\vec{k}_1 = [\frac{1}{2}01]$) and in this case the magnetization is perpendicular to the x axis. The star of $\vec{k}_1$ consists of the six vectors $\pm\vec{k}_1 = \pm[\frac{1}{2}01]$, $\pm\vec{k}_2 = \pm[1\frac{1}{2}0]$, and $\pm\vec{k}_3 = \pm[01\frac{1}{2}]$. There is only one compound, β-MnS,[16] which exhibits this type-III structure, but its paramagnetic space group is $F\bar{4}3m$, a subgroup of $Fm3m$. The corresponding $n = 12$ representation is reducible $(12 = 6 + 6)$, so the transition is predicted to be first order by Landau rule (2). The nature of the transition in β-MnS is not known and we feel it is of interest to test whether it is first order.

Cr.[17,18]—This is a bcc crystal with space group $Im3m$ exhibiting a transverse sinusoidal magnetic structure with propagation vector $\vec{k}_1 = [k00]$. The star of $\vec{k}_1$ consists of the six vectors $\pm\vec{k}_1 = \pm[k00]$, $\pm\vec{k}_2 = \pm[0k0]$, and $\pm\vec{k}_3 = \pm[00k]$. Two components of the order parameter are associated with each $\vec{k}$ vector, corresponding to the two independent directions of the magnetization. The twelve-component Hamiltonian is constructed from the seven fourth-order invariants which can be formed from the order parameter. The phase transition in Cr is known to be first order.

Eu.[19]—This is also a bcc crystal and it exhibits a spiral magnetic order corresponding to a propagation vector $\vec{k}_1 = [k00]$. The order-parameter and Hamiltonian are the same as for Cr. Mössbauer effect and specific-heat measurements[19]

show that the phase transition in Eu is first order.

The first-order transition in Cr has puzzled theorists for years. The discontinuous nature of the transition was discovered by Arrott, Werner, and Kindrick[18] over a decade ago, and despite numerous attempts to clarify the origin of the transition using various microscopic models together with mean-field-like theories, no satisfactory explanation has yet been reported. Similarly, the first-order transition in UO_2[13] has defied explanation. Blume[20] tentatively proposed that the transition could be explained by a model assuming a singlet ground state, but it was later found that the ground state was not a singlet. In mean-field theory one is trying to find a physically reasonable mechanism for making the fourth-order coefficient in the corresponding Landau-type expansion negative. This has proved difficult and may be impossible for these systems.

Our main point is that even if the Landau theory (or mean-field theory) predicts a second-order transition, the ϵ expansion may imply the transition is first order.[21] If this is the case it is not necessary to discover a microscopic mechanism to explain the first-order nature of these transitions. Despite a comprehensive search through the literature, we have found no well-established ferromagnetic first-order transitions. Let us note that if one were to observe a first-order transition in a ferromagnet, then rule (4) could never be invoked to explain it, because ferromagnets are described by $n \leq 3$ component models for which the isotropic fixed point is always stable.[9]

First-order *magnetic* transitions from a disordered state to an ordered state which are not explained by Landau's arguments (2) and (3) are quite rare. In fact, the physical systems we have found corresponding to Hamiltonians with no stable fixed points exhaust many, and possibly all, of such known first-order transitions. In Table I, we list the materials corresponding to Hamiltonians with no stable fixed points and we distinguish those systems for which the transitions are known to be first order from those in which the nature of the transitions has yet to be determined. We predict these systems will all have first-order transitions and urge that experiments be performed to test our results. It would be interesting to investigate whether the systems which are predicted to be first order because of the lack of a stable fixed point behave differently from systems predicted to be first-order by Landau arguments. The agreement of our results with existing experiments lends support to the idea that the symmetry criteria for the absence of a stable fixed point in $4-\epsilon$ dimensions may be the same as in three dimensions. It would be of great interest to find a group-theoretical criterion for the absence of a stable fixed point in $4-\epsilon$ dimensions.

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TABLE I. Physical systems corresponding to Hamiltonians with no stable fixed points.

Antiferromagnetic order	Number of components of order parameter	Systems known to be first order	Systems predicted to be first order
Type I ($\vec{m} \perp \vec{k}$)	$n=6$	UO_2[a]	
Type II ($\vec{m} \perp \vec{k}$)	$n=4$		TbAs, TbSb, TbP,[b] CeS, TbSe, NdSe, NdTe[c]
Type II ($\vec{m} \perp \vec{k}$)	$n=8$	MnO[d]	NiO,[e] MnSe,[e] α-MnS,[f] ErP, ErSb,[b] EuTe[g]
Type III ($\vec{m} \parallel [100], \vec{k}=[\frac{1}{2}01]$)	$n=12$		
Sinusoidal ($\vec{m} \perp \vec{k}=[k00]$)	$n=12$	Cr[h]	
Screw spiral ($\vec{m} \perp \vec{k}=[k00]$)	$n=12$	Eu[i]	

[a]Ref. 10.
[b]Ref. 6.
[c]Ref. 12.
[d]Refs. 11, 13.
[e]Ref. 11.
[f]Ref. 16.
[g]Ref. 22.
[h]Refs. 17, 18.
[i]Ref. 19.

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[5]An oversimplified model free energy illustrating a discontinuous transition to a state characterized by a commensurate propagation vector k with $4k=K$ (a reciprocal-lattice vector) is

$$F(T)=\sum_q F_q=\sum_q [r_q(T)\psi_q\psi_{-q}+u\psi_q\psi_{-q}\psi_q\psi_{-q} - w(\psi_k{}^4+\psi_{-k}{}^4)\delta(q-q_0)],$$

where $r_q(T)=r(T)+c(T)q+q^2$. The value of q, denoted $q_m(T)$, for which $r_q(T)$ is a minimum varies with temperature T. Let $Q=q_m(T_c)$. If a second-order transition occurs at $r_Q(T_c)=0$, then by continuity one would expect the propagation vector below T_c to be temperature dependent. If $u-w<0$, then possibly $F_k(T_c)<F_Q(T_c)$, in which case the transition would go discontinuously to an ordered state characterized by the temperature independent k. The physical idea behind this argument is that for $4k=K$ there exists an extra invariant which can stabilize the commensurate state. We believe a correct Landau argument can be constructed by taking into account terms of mixed representations such as

$$w(q_1,q_2,q_3,q_4)\psi_{k+q_1}\psi_{k+q_2}\psi_{k+q_3}\psi_{k+q_4}\delta(\Sigma q_i).$$

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$$\Delta/n\sum_{i=1}^{n}\varphi_i{}^4,$$

and showed that one obtains a first-order transition in the limit $n\to\infty$, not found in mean-field theory.

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