PHYSICAL REVIEW B VOLUME 25, NUMBER 3 1 FEBRUARY 1982

First-order phase transitions in Tb, Dy, and Ho

Zvi Barak and M. B. Walker
Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7
(Received 14 January 1981)

A renormalization-group analysis suggests that the paramagnetic-to-helical phase transitions in Tb, Dy, and Ho are of first order; this result is in disagreement with the conclusions and assumptions of previous experimental and theoretical papers. Results for the order of the phase transitions in $TbAu_2$, DyC_2, and stressed Cr and Eu are also given.

It is now believed that certain phase transitions which are continuous within mean-field theory are driven first order by critical fluctuations. For example, for MnO, UO_2, Cr, and Eu the lack of stable fixed points of the appropriate renormalization-group transformations suggests that the phase transitions should be first order,[1] in agreement with experimental observations.

In the present article, a number of systems having the same Landau-Ginzburg-Wilson Hamiltonian are considered. Although the renormalization-group transformation has a stable fixed point, critical behavior and a second-order phase transition associated with this fixed point is expected only if the initial Hamiltonian lies in the domain of the stable fixed point.[2] For the systems considered below, we are able to decide whether or not this is the case from an analysis of the symmetry of the ordered phase.

Experimentally, the phase transition from the paramagnetic to the helical spin structure in Tb, Dy, and Ho appears to be second order.[3–5] The measured critical exponents β are, however, all different [$\beta=0.25\pm0.01$ for Tb[3], $\beta=0.335\pm0.010$ for Dy,[4] and $\beta=0.39$ $(+0.04,-0.03)$ for Ho (Ref. 5)] indicating a nonuniversal behavior of β for these systems. The experimental value of β for Ho is in agreement with the theoretical[1,6] exponent β (calculated to second order in ϵ) associated with the stable fixed point of the appropriate renormalization-group transformation.

Below, we extend previous theoretical work[1,6] in such a way as to determine the domains associated with the fixed points of the renormalization-group transformation of the effective Hamiltonian describing Tb, Dy, Ho, and a number of other systems. We also deduce, from the fact that Tb, Dy, and Ho have helical as opposed to linearly polarized magnetic structures, that the appropriate initial Hamiltonian for Tb, Dy, and Ho lies outside the domain of the stable fixed point. On the basis of these theoretical arguments, the phase transitions in Tb, Dy, and Ho are expected to be first order, in disagreement with the assumption of a second-order transition made in previous experimental[3–5] and theoretical[1,6] work. The absence of universality in the critical behavior of Tb, Dy, and Ho is consistent with the above ideas, and is not consistent with the proposal that there are second-order transitions, associated with a particular fixed point, in all three metals. Further experimental work designed to look for direct evidence of a first-order transition in these metals, and to confirm the measured values of the critical exponents β, is clearly desirable.

DyC_2 and $TbAu_2$ are tetragonal crystals which exhibit incommensurate, transverse, linearly polarized, magnetic structures.[7] The characteristic wave vectors $\vec{Q}$ of these spin structures lie in either of two mutually perpendicular directions in the plane normal to the c axis, and the spins lie along the c axis. Although the neutron scattering results can be explained by the assumption that the ordered state is single $\vec{Q}$ (i.e., that the rare-earth magnetic moments are modulated along only one of the two equivalent $\vec{Q}$ directions), we were unable to find evidence which would rule out the possibility that the ordered state was a double-$\vec{Q}$ state (in which the moments would be modulated along both $\vec{Q}$ directions). In spite of the differences in symmetry and magnetic structure which exist between these tetragonal crystals and the hexagonal crystals of Tb, Dy, and Ho, the Landau-Ginzburg-Wilson Hamiltonians describing their magnetic phase transitions are formally identical[1] and thus have the same fixed points and domains. We shall show that if the single-$\vec{Q}$ state (as opposed to the double-$\vec{Q}$ state) is the ground state in $TbAu_2$ or DyC_2, then the initial Hamiltonian lies outside the domain of the stable fixed point and a first-order transition is to be expected. On the other hand, a transition to the double-Q state could display critical behavior characteristic of the stable fixed point. Thus, further experimental investigations of $TbAu_2$ and DyC_2 are desirable to determine if the ordered states are single-$\vec{Q}$ or double-$\vec{Q}$, to determine the order of the transition and the critical exponents, and hence to test our theoretical predictions.

The discussion of the critical behavior of Cr and Eu subjected to a [001] uniaxial stress of the appropriate sign to stabilize a single-$\vec{Q}$ state will also be

discussed briefly below.

The effective Hamiltonian density for Tb, Dy, and Ho can be written

$$-\mathcal{H} = r\vec{S}\cdot\vec{S}^* + \frac{\partial\vec{S}}{\partial x_\alpha}\cdot\frac{\partial\vec{S}^*}{\partial x_\alpha} + U_1(\vec{S}\cdot\vec{S}^*)^2 + U_2|\vec{S}\cdot\vec{S}|^2 \ , \quad (1)$$

where $\alpha = x,y,z$ is summed over, and $\vec{S}$ is a complex vector in the xy plane ($\vec{Q}$ is in the z direction); the spin density is $\vec{S}(\vec{r}) = \vec{S}\exp(i\vec{Q}\cdot\vec{r}) + \vec{S}^* \times \exp(-i\vec{Q}\cdot\vec{r})$. This Hamiltonian is equivalent to those used previously.[1,6] A mean-field analysis of (1) shows that the helical structure is stable (gives a minimum of $-\mathcal{H}$) if $U_2 > 0$, and the linearly polarized structure is stable if $U_2 < 0$. The renormalization-group recursion relations for (1) have been given previously[8] to order ϵ^2, as have the fixed points,[6,8] and the flow diagram which we have determined from these results is shown in Fig. 1. It is clear that the initial Hamiltonians describing Tb, Dy, and Ho (which must have $U_2 > 0$ by virtue of their helical ordered phases) do not lie in the domain of the stable fixed point, and the first-order transitions are therefore to be expected.

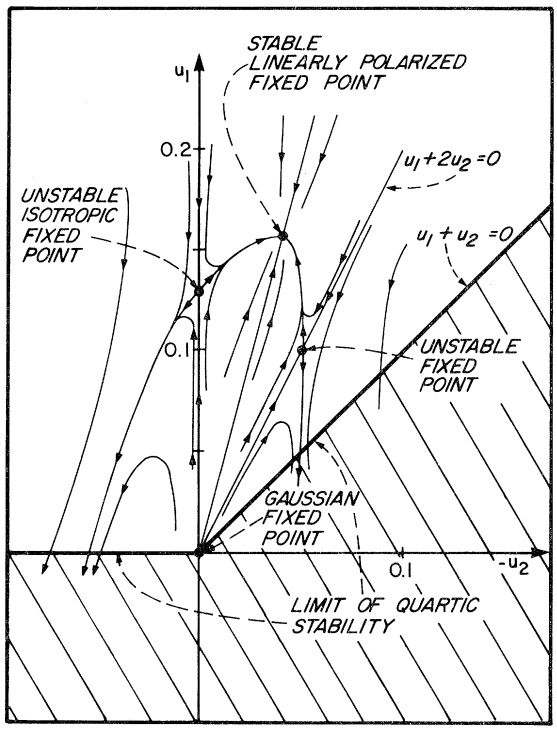

FIG. 1. Schematic flow diagram for the Hamiltonian of Eq. (1); U_1 and U_2 are given in units of $\epsilon/4K_4 = 2\pi^2\epsilon$ and the correct location of the fixed points for $\epsilon = 1$ is shown.

Notice that an initial Hamiltonian density of the form (1) with $U_2 > 0$, but with $U_2 << U_1$, will flow along a trajectory which passes close to unstable isotropic fixed point of Fig. 1. Such a system could, over some temperature interval, show critical behavior characterized by the exponents associated with the unstable isotropic fixed point. These exponents happen to be the same as those of the stable, linearly polarized fixed point[6] [i.e., $\beta = 0.39$ (Ref. 8) to second order in ϵ]. This provides a possible explanation of the exponent $\beta \sim 0.39$ observed[5] for Ho. Of course, as the Néel temperature is approached, a crossover to a first-order transition is expected, and there is indeed an indication of deviations from $\beta = 0.39$ in the experimental results[5] for Ho at temperatures close to the Néel temperature.

Defining $\vec{S} = \vec{S}_1 + i\vec{S}_2$, where $\vec{S}_1$ and $\vec{S}_2$ are real, and introducing new variables[1] by

$$S_{1x} = (\eta_1 + \eta_2)/\sqrt{2}, \quad S_{2y} = (\eta_1 - \eta_2)/\sqrt{2} \ ,$$
$$S_{2x} = (\bar{\eta}_1 + \bar{\eta}_2)/\sqrt{2}, \quad S_{1y} = (\bar{\eta}_2 - \bar{\eta}_1)/\sqrt{2} \ ,$$

Eq. (1) becomes

$$-\mathcal{H} = \tfrac{1}{2}\sum_i [r(\eta_i^2 + \bar{\eta}_i^2) + (\vec{\nabla}\eta_i)^2 + (\vec{\nabla}\bar{\eta}_i)^2] + U_1\left(\sum_i(\eta_i^2 + \bar{\eta}_i^2)\right)^2 + 4U_2(\eta_1^2 + \bar{\eta}_1^2)(\eta_2^2 + \bar{\eta}_2^2) \ , \quad (2)$$

where $i = 1, 2$. This effective Hamiltonian describes the magnetic phase transitions in $TbAu_2$ and DyC_2.[1] In the single-$\vec{Q}$ ordered phase either $\eta_1^2 + \bar{\eta}_1^2$ or $\eta_2^2 + \bar{\eta}_2^2$ is zero, whereas in the double-$\vec{Q}$ ordered phase both $\eta_1^2 + \bar{\eta}_1^2$ and $\eta_2^2 + \bar{\eta}_2^2$ are nonzero. A mean-field analysis of (2) shows that if $U_2 > 0$, the ordered phase is single-$\vec{Q}$, whereas if $U_2 < 0$ the ordered phase is double $\vec{Q}$. Thus, if the ordered phase of $TbAu_2$ or DyC_2 is found experimentally to be single $\vec{Q}$, we would predict (from Fig. 1 and $U_2 > 0$) a first-order transition. If the ordered phase is found to be double $\vec{Q}$, critical behavior characterized by exponents associated with the stable fixed point is possible [for the model of Eq. (2), the stable fixed point should be named the double-$\vec{Q}$ fixed point, rather than the linearly polarized fixed point].

The order parameter describing the magnetic phase transitions in unstressed Cr and Eu has twelve components,[1] and a renormalization-group analysis (which is the same for both Cr and Eu) yields no stable fixed points thus leading to the expectation that the transitions are first order,[1] in agreement with experiment.[9,10] It is known that the application of a [111] stress to MnO reduces the number of components of the order parameter and changes the first-order phase transition to a second-order one,[11,12] and it was suggested that the effect of a [100] stress of the right sign to stabilize the single-$\vec{Q}$ states in Cr and Eu be studied.[11] If the relatively small spin-orbit

coupling contributions of fourth order in $\vec{S}$ are neglected, the appropriate Hamiltonian density for sufficiently strong stress is given by Eq. (1). Thus, the transition in Eu (which has a helical ordered phase) will remain first order, while the transition in Cr (which has a linearly polarized phase) can become second order. In a more exact treatment, the small spin-orbit coupling contribution $U_3|S_x|^2|S_y|^2$ must be added to Eq. (1). Our calculations show (by a renormalization-group analysis to order ϵ^2) that although there is a fixed point which is stable on the surface $U_3=0$, U_3 is a relevant variable near this fixed point, thus causing the fixed point to become unstable. Thus, although we must expect a first-order transition in the case of Cr subjected to [001] tension, the discontinuities should be especially small because U_3 is small. It should also be noted that a sufficiently strong [110] compressive stress applied to chromium should stabilize a single $\vec{Q}$ and single polarization direction[13] producing a situation describable by the isotropic model with a two-component order parameter; in this case, a second-order transition is expected. Further details of these calculations will be published elsewhere.

In the systems studied above, the observed symmetry of the ground state has been used to determine whether or not the initial Hamiltonian belongs to the domain of the stable fixed point, and thus to make predictions of the order of the phase transition. Perhaps the most significant of the above predictions is that the phase transitions to the helical state in Tb, Dy, and Ho should be first order. Although the transitions in these metals appear continuous experimentally (e.g., see Refs. 3–5), the lack of a universal value of β suggests either that the measurements have not been made sufficiently close to the Néel temperature, or that the phase transition is first order. Clearly, further experimental work on the order of the transition and critical exponents is desirable. It should be noted that the phase transition in Cr was thought to be second order until the work of Arrott *et al.*,[9] which was carried out on a crystal of exceptional purity and crystallographic perfection, showed the transition to be first order. This suggests that future experiments on Tb, Dy, and Ho should be done on samples of the highest possible degree of purity and crystallographic perfection. Should it turn out that further experimental work on Tb, Dy, and Ho strengthens the case that transition is second order, it would cast serious doubts as to the validity of the use of second-order ϵ-expansion methods to predict the order of phase transitions, in spite of previous successes. One other example where the method may fail has been previously reported.[14]

After the completion of this work, we found that we had overlooked the high-resolution thermal-expansion measurements of Tyndall *et al.*[15] on holmium. These measurements show a discontinuity in length measured parallel to the *a* axis and thus provide clear evidence that the Néel transition in the Ho is first order. The length discontinuity is very small (~ 3 parts in 10^5) and the Néel transition is thus only weakly first order, which accounts for the fact that the first-order nature of the transition was not detected in the neutron scattering[5] results. A weak first-order transition is to be expected on the basis of the above theoretical arguments if one assumes that the phase transition is second order within mean-field theory since the fluctuations which drive the transition first order become significant only close to the Néel temperature. These experimental results[15] thus provide strong support for our theory. Unfortunately, thermal expansion experiments on Tb and Dy of comparable precision are not available.

After this work was completed, Dr. David Mukamel pointed out to us an article by Bak[16] on $Hg_{3-\delta}AsF_6$ which gave an analysis equivalent to our analysis of our Eq. (2) above describing $TbAu_2$ and DyC_2. Although Bak recognized that Tb, Dy, and Ho were described by an equivalent Hamiltonian, he did not attempt to ascertain whether or not the initial Hamiltonian for these rare-earth metals lay in the domain of the stable fixed point, and thus did not make predictions concerning the order of Néel transitions.

ACKNOWLEDGMENTS

Z. B. wishes to thank Dr. S. Fishman for stimulating discussions and for his hospitality during a visit to Cornell University where part of this work was done. Also, M.W. has had stimulating discussions on the problem of stressed chromium with E. Fawcett. This research was supported by NSERC of Canada.

[1]D. Mukamel and S. Krinsky, Phys. Rev. B 13, 5065 (1976); 5078 (1976); P. Bak and D. Mukamel, *ibid.* 13, 5086 (1976).

[2]K. G. Wilson and J. Kogut, Phys. Rep. 12C, 75 (1974).

[3]O. W. Dietrich and J. Als-Nielsen, Phys. Rev. 162, 315 (1967).

[4]E. Loh, C. L. Chien, and J. C. Walker, Phys. Lett. A49, 357 (1974).

[5]J. Eckert and G. Shirane, Solid State Commun. 19, 911 (1976).

[6]T. Garel and P. Pfeuty, J. Phys. C 9, L245 (1976).

[7]M. Atoji, J. Chem. Phys. 48, 560, 3384 (1968).

[8]D. Mukamel, Phys. Rev. Lett. 34, 481 (1975).

[9]A. Arrott, S. A. Werner, and H. Kenrick, Phys. Rev. Lett. 14, 1022 (1965). [The conclusion that the phase transition is first order has been challenged in E. W. Fenton and C.

R. Leavens, J. Phys. F 7, 1705 (1977).]
[10]A. H. Millhouse and K. A. McEwan, Solid State Commun. 13, 339 (1973).
[11]P. Bak, S. Krinsky, and D. Mukamel, Phys. Rev. Lett. 36, 829 (1976).
[12]D. Bloch, D. Hermann-Rouzaud, C. Vettier, W. B. Yelon, and R. Alben, Phys. Rev. Lett. 35, 963 (1975).
[13]M. B. Walker, Phys. Rev. B 22, 1338 (1980).
[14]H. R. Ott, J. K. Kjems, and F. Hulliger, Phys. Rev. Lett. 42, 1378 (1979).
[15]D. A. Tindall, M. O. Steinitz, and M. L. Plumer, J. Phys. F 7, L263 (1977).
[16]Per Bak, Phys. Rev. B 20, 2209 (1979).