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Phase Diagrams and Multicritical Points in Randomly Mixed Alloys

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The Landau-Ginzburg-Wilson model associated with the random alloy $Fe_{1-x}Co_xCl_2$ is analyzed. It is observed that the model includes a coupling term which has thus far been overlooked. Renormalization-group calculations in $d = 4 - \epsilon$ dimensions suggest that the multicritical behavior of this system is *not* associated with the "decoupled" fixed point found in previous theories. This prediction is consistent with recent experiments. A microscopic mechanism which generates this term is considered. It is suggested that similar terms may appear in other quenched alloys.

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Phase diagrams and critical behavior of alloy systems with competing order parameters have been of considerable theoretical[1-5] and experimental[6-10] interest in recent years. Such systems are obtained by mixing two compounds which exhibit two types of magnetic ordering. A simple example is the one in which the two compounds exhibit competing spin anisotropies.[5] Such a system may, in general, be described by an m-component order parameter $\vec{S} \equiv (S_1, \ldots, S_m)$. The first component of the mixture tends to align the first m_1 spin components, $\vec{S}_{\parallel}$, while the other tends to align the remaining (perpendicular) $m_2 (= m - m_1)$ components, $\vec{S}_{\perp}$. Mean-field analysis shows that the phase diagram in the concentration-temperature plane should exhibit two critical lines associated with the transitions from the paramagnetic phase to the two magnetically ordered phases. These lines meet at a multicritical point[11,12] whose nature (whether a bicritical or a tetracritical point) depends on the details of the magnetic interactions in the system. However, recent renormalization-group (RG) studies by Fishman and Aharony[5] (FA) suggest that the phase diagram of

the alloy with random anisotropies should be *tetracritical-like,* irrespective of the numerical values of the various parameters appearing in the Landau-Ginzburg-Wilson (LGW) Hamiltonian. According to this study the critical behavior associated with the tetracritical point is governed by a "decoupled" fixed point. At such a point each order parameter undergoes its own transition even when the two transitions occur simultaneously. In order to test these and other theoretical predictions, several experimental studies on various systems[6-10] have been carried out. It has been found that most alloys seem to exhibit a tetracritical (and not a bicritical) point, as predicted by the theory. In certain cases, however (such as in[9,10] the alloy $Fe_{1-x}Co_xCl_2$), it was observed that the two competing order parameters are not decoupled near the multicritical point, in disagreement with the FA theory.

In the present Letter I point out that one should be careful in applying the results of the FA theory to specific physical systems. This theory assumes that the two competing order parameters are coupled via an energy-energy-like term $|S_\parallel|^2 \times |S_\perp|^2$ in the LGW Hamiltonian. While this may be the case for certain alloys, it need not be correct in general. In some cases other coupling terms, which are allowed by the symmetry of the problem, should be included in the LGW Hamiltonian. This may in turn change the nature of the phase diagram. As an example I consider the random alloy $Fe_{1-x}Co_xCl_2$, which is a simple system with competing spin anisotropies. This alloy[9,10] has been studied with use of susceptibility measurements and neutron-diffraction techniques. These studies indicate that the two competing order parameters are *not* decoupled, in the vicinity of the multicritical point. By analyzing the LGW Hamiltonian associated with this system I find that the model should include a coupling term which is *not* included in the FA theory. The "decoupled" fixed point is found to be *unstable,* indicating that the phase diagram is not necessarily tetracritical-like. The phase diagram is discussed, and a microscopic mechanism which generates this new term is presented.

The pure compounds $FeCl_2$ and $CoCl_2$ are rhombohedral, exhibiting an antiferromagnetic ordering in which ferromagnetic (001) planes are ordered antiferromagnetically.[13] In the case of $FeCl_2$ the magnetic anisotropy favors an ordering along the z axis. The system is thus described by an $m_1 = 1$ component order parameter, $S_\parallel = S_z$. On the other hand, the magnetic anisotropy in $CoCl_2$ favors an ordering in the x-y plane. The order parameter in this case has $m_2 = 2$ components, $\vec{S}_\perp = (S_x, S_y)$. In order to analyze the phase diagram of the alloy, I first consider the LGW Hamiltonian associated with the three-component order parameter $\vec{S} = (S_x, S_y, S_z)$. The effect of randomness is then taken into account[14] by considering n replicas of this model and taking the limit $n \to 0$. The symmetry group of $FeCl_2$ and $CoCl_2$ is $R\bar{3}m$ (D_{3d}^5). The most general LGW model associated with the order parameter $\vec{S}$, which is invariant under this symmetry group, is

$$H = \int d^dR \{ -\tfrac{1}{2}r_1 S_z^2 - \tfrac{1}{2}r_2(S_x^2 + S_y^2) - \tfrac{1}{2}[(\nabla S_x)^2 + (\nabla S_y)^2 + (\nabla S_z)^2] v_{11} S_z^2 - v_{22}(S_x^2 + S_y^2)^2 - 2v_{12} S_z^2 (S_x^2 + S_y^2) - w S_z (S_x^3 - 3 S_x S_y^2) \}. \quad (1)$$

In this Hamiltonian the x axis is defined such that the x-z plane is a minor plane of the group $R\bar{3}m$ (see Fig. 1). The coupling term w has been overlooked in previous analyses of the phase diagram of this system.

I now consider the phase diagram associated with the model (1). Within the mean-field approximation, it is found that the model exhibits two ordered phases: one in which $\langle S_z \rangle \neq 0$ and $\langle \vec{S}_\perp \rangle = 0$, and a mixed phase in which both thermodynamic averages, $\langle \vec{S}_\perp \rangle$ and $\langle S_z \rangle$, are nonzero. The model does not exhibit a phase in which only $\langle \vec{S}_\perp \rangle$ is nonvanishing. The reason is that if $\langle S_x \rangle$ becomes nonzero it induces an *ordering field,* $\sim w \langle S_x \rangle^3$, which is coupled linearly to S_z. This field tilts the sublattice magnetization out of the x-y plane. The transition between the two ordered phases is expected to be first order. This transition may be studied by replacing S_z by $\langle S_z \rangle$ in the LGW model (1). The resulting $m_2 = 2$ component model, corresponding to the spin-flop (SF) transition, belongs to the universality class of the three-state Potts model and the transition is expected to be first order.[15] As a result, the phase diagram associated with the model (1) is *bicritical-like.* Note that this conclusion is independent of the numerical values of the other parameters, v_{ij}, appearing in the Hamiltonian.[16]

In order to take into account the effect of fluctuations, I study the renormalization-group equations associated with the model (1). This model with $w = 0$ has been studied by Nelson, Kosterlitz, and Fisher,[12] who found that the multicritical

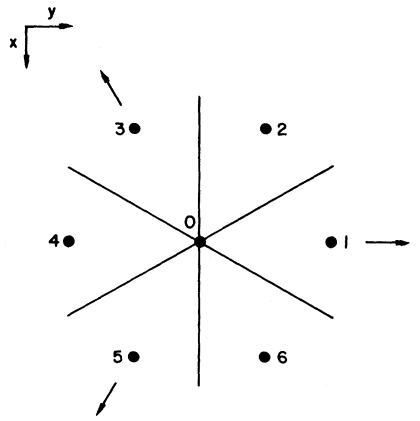

FIG. 1. The crystallographic structure of a (001) plane of $CoCl_2$ and $FeCl_2$, showing a magnetic site (0) and its six nearest-neighbor sites (1–6). Mirror planes are indicated by lines and two-fold axes by arrows. The origin of the coordinate system is at (0).

point is described by the isotropic $m=3$ fixed point, $v_{11}^*=v_{22}^*=v_{12}^*=\epsilon/4(m+8)K_4$, where K_4 is a constant. Near fixed points with $w^*=0$ the stability exponent λ_w associated with the parameter w is given by

$$\lambda_w=\epsilon[1-24(v_{12}^*+v_{22}^*)K_4]. \quad (2)$$

For the $m=3$ isotropic fixed point one has $\lambda_w<0$, and the point is stable. One therefore expects that the phase diagram associated with the (nonrandom) model (1) should be bicritical-like. The critical behavior of the bicritical point is governed by the isotropic fixed point, as in the case $w=0$.

I now analyze the phase diagram of the random alloy, and consider first the critical behavior of the multicritical point. This is done by taking n replicas of the model (1) and considering the limit $n\to 0$. This analysis has been carried out by Fishman and Aharony for $w=0$. They find that the "decoupled" fixed point is stable. At this fixed point one has

$$v_{12}^*=0, \quad v_{22}^*=\frac{\epsilon}{4(m_2+8)}\frac{1}{K_4}. \quad (3)$$

Inserting (3) into (2), one finds that the $m_2=2$ decoupled fixed point is unstable with respect to w, and hence, all fixed points with $w^*=0$ are unstable. In order to analyze the multicritical behavior, one has to study all fixed points with $w^*\neq 0$. This calculation has not been carried out. Experimentally, the multicritical point seems to be second order in nature. The critical behavior of this point should therefore be governed by one of the *coupled* $w^*\neq 0$ fixed points.[17] In considering the spin-flop transition, I note that most RG studies of systems with random impurities[5,14] are restricted to the paramagnetic region. A detailed study of the phase transitions occurring *inside* the ordered phases has not been carried out so far. However, one may make some qualitative statements concerning these phase transitions, based on general considerations. The longitudinal component S_z is expected to induce a random-ordering field coupled to $\vec{S}_\perp$, as a result of random off-diagonal exchange terms.[10] The SF transition is therefore described by the three-state Potts model in a random field. One would expect this transition to be similar to that of the Ising model in a random field. It has recently been shown[18] that this system does not exhibit long-range order for $d\leq 3$. The transition is therefore expected to be smeared in $d=3$ dimensions.

In order to estimate the magnitude of the new coupling term, I discuss a microscopic mechanism which leads to such a term in the LGW model. In both $CoCl_2$ and $FeCl_2$, the ferromagnetic intralayer exchange J is much larger than the antiferromagnetic interlayer coupling[13] J', $|J'/J|=0.1$. For simplicity, I neglect the intralayer coupling J', and consider a spin-$\frac{1}{2}$ model on a triangular lattice.[19] Taking the most general nearest-neighbor exchange allowed by the symmetry group of the lattice $\bar{3}m$, one finds the following Hamiltonian:

$$H=-J_1\sum_{\langle ij\rangle}\sigma_{zi}\sigma_{zj}-J_2\sum_{\langle ij\rangle}(\sigma_{xi}\sigma_{xj}+\sigma_{yi}\sigma_{yj})+\sum_{\langle ij\rangle}H_{ij}', \quad (4)$$

where the sums are over nearest-neighbor sites $\langle ij\rangle$. The last term H_{ij}' is an off-diagonal exchange, which for the pair $\langle ij\rangle=\langle 01\rangle$ (see Fig. 1) takes the form[20]

$$H_{01}'=-J_3(\sigma_{z0}\sigma_{x1}+\sigma_{x0}\sigma_{z1}). \quad (5)$$

The corresponding term H_{ij}' for other pairs of nearest-neighbor spins is obtained from H_{01}' by applying the appropriate translations and rotations which transform the pair $\langle 01\rangle$ onto $\langle ij\rangle$. Note that this term may account for the random-ordering field induced by S_z in the ordered phases. The LGW model associated with the Hamiltonian (4) and (5) may be obtained by the Hubbard transformation.[21] I find, after

some algebra,

$$H_{\mathrm{LGW}} = -\tfrac{1}{2}\sum_q \mathcal{H}_{0q} - \tfrac{1}{12}\sum_i (\varphi_{xi}^2 + \varphi_{yi}^2 + \varphi_{zi}^2)^2 + O(\varphi_i^6), \tag{6a}$$

$$\mathcal{H}_{0q} = \left(\frac{1}{\beta J_1(q)} - 1\right)\varphi_{zq}\varphi_{z-q} + \left(\frac{1}{\beta J_2(q)} - 1\right)(\varphi_{xq}\varphi_{x-q} + \varphi_{yq}\varphi_{y-q})$$

$$-\tfrac{3}{4}\frac{\beta J_3}{\beta J_1(q)\beta J_2(q)}[(q_x^2 - q_y^2)\varphi_{zq}\varphi_{x-q} - 2q_x q_y \varphi_{zq}\varphi_{y-q}], \tag{6b}$$

where $\varphi_{\alpha i}$, $\alpha = x, y, z$ are the fields conjugate to the spin components $\sigma_{\alpha i}$, respectively, and $\varphi_{\alpha q}$ and $J_l(q)$, $l = 1, 2$, are the Fourier components of $\varphi_{\alpha i}$ and $J_l(r_{ij})$, respectively. The sum $\sum_q$ is over the wave vectors $\vec{q}$ in the first Brillouin zone. The lattice constant, a, of the triangular lattice is taken to be 1. In deriving the expression (6) I have assumed $J_3 < J_1, J_2$, and considered only first-order terms in βJ_3.

By examining the LGW model (6) one can observe that J_3 introduces a $\vec{q}$-dependent off-diagonal quadratic term in the LGW Hamiltonian. This term vanishes at $\vec{q} = 0$, in agreement with general symmetry considerations. The model (6) does not include all the quartic terms appearing in (1). However, by integrating out the $\varphi_{\alpha q}$ variables corresponding to wave vectors $\vec{q}$ lying in the outer shell of the hexagonal Brillouin zone of the lattice, all four couplings v_{11}, v_{22}, v_{12}, and w are generated. Performing the integration, I find that the leading contribution to w is third order in J_3, and hence

$$w \sim (\beta J_3/\beta J_1 \beta J_2)^3. \tag{7}$$

The exchange J_3 couples nearest-neighbor spins in the x-y plane, and therefore it is expected to be of the same order of magnitude as J_1 and J_2. Thus w is not negligible at high temperatures, $\beta J_2 \approx 1$ or $\beta J_1 \approx 1$. The coupling constant w vanishes at $T = 0$. This is associated with the fact that w is induced by large-momentum *fluctuating* fields, which may contribute only at nonzero temperatures. At low temperatures I find $w \sim T^3$. It is clear that other microscopic mechanisms which may generate the w term in (1) are possible.

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