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# Theory of random anisotropic magnetic alloys

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A mean-field–crystal-field theory is developed for random, multicomponent, anisotropic magnetic alloys. It is specially applicable to rare-earth alloys. A discussion is given of multicritical points and phase transitions between various states characterized by order parameters with different spatial directions or different ordering wave vectors. Theoretical predictions based on known parameters for the phase diagrams and magnetic moments for the binary rare-earth alloys of Tb, Dy, Ho, and Er, Tb-Tm, Nd-Pr, and pure double-hcp Nd agree qualitatively with the experimental observations. Quantitative agreement can be obtained by increasing the interaction between different alloy elements, in particular for alloys with very different axial anisotropy, e.g., Tb-Tm. A model system consisting of a singlet-singlet and singlet-doublet alloy is discussed in detail. A simple procedure to include fluctuation corrections in the mean-field results is also discussed.

## I. INTRODUCTION

The physics of anisotropic mixtures have several interesting aspects. Multicritical points (bi-, tri-, tetracritical points, etc.) may be realized for simple model systems. We shall discuss these within the context of mean-field theory. We show that the free energy near a phase transition reduces to the anisotropic Landau expansion, the critical behavior of which case has been discussed using scaling arguments or renormalization-group techniques by a number of workers (Fisher and Pfeuty[1] and Bruce and Aharony[2]). The theory is a generalization of the mean-field theory for an antiferromagnet in a magnetic field by Thomas,[3] and also of the theory by Wegner[4] for an antiferromagnetic mixture.

Another aspect of anisotropic magnetic alloys that is of interest is their significance for the understanding of the rare-earth metals. A number of experiments on rare-earth alloys have been made giving phase diagrams and magnetization curves, e.g., Er-Tb and Dy by Millhouse and Koehler,[5] Nd-Pr and Tm-Tb by Lebech *et al.*,[6] while a number of dilutions of rare-earth metals with the nonmagnetic Y or Yb have been described by Koehler.[7] To a large extent these data have not been analyzed and fully utilized to extract information about the crystal fields and exchange interactions in these materials. One of the reasons for initiating the mentioned experiments was to attempt to determine whether the origin of the anisotropy in the rare-earth metals was predominantly of single- or two-ion origin. The present theory may provide a basis for answering this question. Nagamiya[8] developed a complete theory for the pure heavy-rare-earth metals in which the crystal-field quenching of the magnetic moments to a good approximation can be neglected. This is not the case in general, and not in particular for the light-rare-earth metals. However, by formulating the theory in terms of susceptibilities the effect of the crystal field is easily taken into complete account.

The two-component theory is given in Sec. II, and the general case is briefly discussed. In Sec. III the case of competing order parameters is discussed, either with respect to moment directions or ordering wave vectors, or both. The various multicritical points are discussed in general terms. Appendix B gives a detailed calculation of the typical example of a singlet-singlet-singlet-doublet alloy. A similar treatment of the singlet-doublet system in an external magnetic field was discussed in detail by Wang and Khajehpour.[9] In Sec. IV the theory is applied to a number of rare-earth alloys. Section V gives concluding remarks. Appendix C presents a simple procedure to go beyond the mean-field approximation and include fluctuation corrections in the single-ion free energy used in the theory.

## II. MOLECULAR-FIELD THEORY FOR PHASE TRANSITIONS

Let us begin by considering the phase diagram for magnetic phases of an alloy of two elements with different susceptibilities; for example an alloy of ions of types 1 and 2. When the exchange interaction between the ions is of long range, as for the rare-earth metals, the fluctuation in local concentration is unimportant. The virtual-crystal approximation is then valid and the Hamiltonian can be written

$$\mathcal{H}=\sum_i\Big[c_1\Big(V^i_{c_1}-c_1\sum_j \mathcal{J}_{11}(ij)\vec{J}_{1i}\cdot\vec{J}_{1j}\Big)+\sum_i c_2\Big(V^i_{c_2}-c_2\sum_j \mathcal{J}_{22}(ij)\vec{J}_{2i}\cdot\vec{J}_{2j}\Big)-c_1c_2\sum_{ij}2\mathcal{J}_{12}(ij)\vec{J}_{1i}\cdot\vec{J}_{2j}\Big]\,, \qquad (1)$$

where $c_n$ are the concentrations, $V^i_{c_n}$ the crystal fields, and $\mathcal{J}_{nm}(ij)$ the isotropic exchange interaction between the angular momenta $\vec{J}_{ni}$ and $\vec{J}_{mj}$. At the same level of approximation we may treat (1) by the molecular-field theory whereby (1) reduces to a single-site Hamiltonian. For simplicity we shall in detail first consider the case where $\langle\vec{J}_1\rangle$ and $\langle\vec{J}_2\rangle$ are parallel in the ordered phase. The general case considering ordering in arbitrary directions for a multi component alloy with anisotropic exchange interaction is treated subsequently; it is more complicated, but analogous. The molecular fields are then

$$\begin{aligned}H_1&=c_1\mathcal{J}_{11}(\langle J_1\rangle+s_1)+c_2\mathcal{J}_{12}(\langle J_2\rangle+s_2)\,,\\ H_2&=c_1\mathcal{J}_{21}(\langle J_1\rangle+s_1)+c_2\mathcal{J}_{22}(\langle J_2\rangle+s_2)\,,\end{aligned}\qquad (2)$$

where $s_n$ are variational parameters set equal to zero in the final result; the Fourier-transformed interaction constants and angular momenta are

$$\begin{aligned}\mathcal{J}_{nm}&=\sum_R 2\mathcal{J}_{nm}(R)e^{i\vec{Q}\cdot\vec{R}}\,,\\ \vec{J}_m&=\sum_R e^{i\vec{Q}\cdot\vec{R}}\vec{J}_{mR}\,,\end{aligned}\qquad (3)$$

and $\vec{Q}$ is the wave vector characterizing the ordering. We have then obtained two single-ion Hamiltonians

$$\mathcal{H}_1=-H_1J_1+V_{c_1}\,,\quad \mathcal{H}_2=-H_2J_2+V_{c_2}\,. \qquad (4)$$

The total free energy is

$$\mathcal{F}(s_1,s_2)=c_1F_1(s_1,s_2)+c_2F_2(s_1,s_2)\,, \qquad (5)$$

where the elemental free energies are determined from

$$e^{-\beta F_n(s_1,s_2)}=\mathrm{Tr}_n e^{-\beta\mathcal{H}_n}\,,\quad \beta=1/k_BT\,. \qquad (6)$$

The phase diagram and the magnetic moments as a function of temperature can be obtained from the free energy (5).

The transition temperature for a second-order phase transition can, however, be obtained simpler by the following observation. Near the ordering temperature the molecular fields are small, and the magnetic moment induced at a site is proportional to the molecular field, with the proportionality constant being the paramagnetic susceptibility (see Appendix A):

$$\begin{aligned}\langle J_1\rangle&=H_1\chi_1^0=(\mathcal{J}_{11}c_1\langle J_1\rangle+\mathcal{J}_{12}c_2\langle J_2\rangle)\chi_1^0\,,\\ \langle J_2\rangle&=H_2\chi_2^0=(\mathcal{J}_{21}c_1\langle J_1\rangle+\mathcal{J}_{22}c_2\langle J_2\rangle)\chi_2^0\,.\end{aligned}\qquad (7)$$

Nontrivial solutions can only be found if the determinant for the equation system is zero. This gives the condition

$$\begin{aligned}(\mathcal{J}_{12})^2c_1c_2&=1/(\chi_1\chi_2)\\ &=(1/\chi_1^0-c_1\mathcal{J}_{11})(1/\chi_2^0-c_2\mathcal{J}_{22})\,,\end{aligned}\qquad (8)$$

where $\chi_n$ is the enhanced susceptibility. The condition for ordering of a pure system is, as is well known, that the inverse enhanced susceptibility goes to zero at the transition temperature. Equation (8) is clearly a generalization of this condition to the alloy case, expressing that the product of the inverse elemental susceptibilities must equal the squared interaction between the systems. If we express the concentrations in terms of $c=c_1$ and $1-c=c_2$, then the condition for the ordering temperature $T_N$ is an equation of second order in $c$:

$$Ac^2+Bc+C=0\,, \qquad (9)$$

with the coefficients

$$\begin{aligned}A&=\mathcal{J}_{11}\mathcal{J}_{22}-(\mathcal{J}_{12})^2\,,\\ B&=\mathcal{J}_{11}/\chi_2^0-\mathcal{J}_{22}/\chi_1^0-A\,,\\ C&=-(1/\chi_2^0-\mathcal{J}_{22})/\chi_1^0\,.\end{aligned}\qquad (10)$$

$B$ and $C$ depend on $T$ through the susceptibilities $\chi_n(T)$.

By considering the free energies (5) we find the ratio between the two elemental momenta in the ordered phase near $T_c$:

$$c_1\langle J_1\rangle/c_2\langle J_2\rangle=(\chi_1^0/\chi_2^0)c_1\mathcal{J}_{12}\chi_2\,. \qquad (11)$$

Both systems therefore "order" simultaneously, although the induced moments may be significantly different. In some cases it may be more illustrative to say that one system orders spontaneously, but polarizes the other by its molecular field. Equation (11) is valid near the transition temperature $T_c$ when the molecular fields are small enough to allow a linearization of the equations which determine the moments. We notice the ratio between the moments using the simple equation (7) is incorrect in the ordered phase, although $T_c$ is correctly given. Away from $T_c$ when the molecular fields become stronger a simple magnetic structure described by one $\vec{Q}$ vector (3) is no longer consistent with molecular-field theory. Then an expansion of the type

$$J_Q = \sum_n a_n \sum_R e^{in\vec{Q}\cdot\vec{R}} J_R$$

is required in order to satisfy the nonlinear self-consistency equation. The higher harmonics with wave vectors $n\vec{Q}$ lead to a "squaring up" of the moment distribution[7] and give rise to extra satellite peaks in a neutron diffraction pattern. The effect was discussed in detail by Nagamiya,[8] who derived the expression and temperature dependence for $a_n$ for a simple model system. The theory for the alloy can easily be generalized to take this effect into account. However, if no higher-order satellites are observed experimentally, the theory is greatly simplified by ignoring $a_n$ for $n \neq 1$. In the numerical calculation this is assumed and the phase boundaries are obtained by a self-consistent calculation of the free-energy and the magnetization components.

The concentration dependence of the paramagnetic transition temperature $T_N(c)$ is found from (9) with the coefficients (10). This result is quite general and holds when the ordered moments $\langle \vec{J}_1 \rangle$ and $\langle \vec{J}_2 \rangle$ are parallel. Special cases have been derived for the singlet-singlet model by Shiles *et al.*,[10] and we have used it for illustration purposes for the (singlet doublet)-(Kramers doublet) alloy of Pr-Nd (Lebech *et al.*[6]) (see Fig. 1). On Fig. 2 is shown a comparison between the calculated (full line) and measured $T_c(c)$ for Pr-Nd using the complete level scheme. Possible $T_c(c)$ curves for alloys of two singlet ground-state elements are also shown (broken lines).

The generalization of Eq. (7) to a multicomponent alloy with anisotropic exchange interaction $\mathcal{J}_{ln}^{\gamma\beta}$ and the ordered moments in arbitrary directions is simply the equation system

$$\langle J_n^\alpha \rangle = \sum_\beta H_n^\beta \chi_n^{0\beta\alpha} = \sum_{\substack{l \\ \beta,\gamma}} \langle J_l^\gamma \rangle c_l \mathcal{J}_{ln}^{\gamma\beta} \chi_n^{\sigma\beta\alpha} , \tag{12}$$

where $\chi_n^{0\beta\alpha}$ is the paramagnetic susceptibility tensor, with the components indicated by greek indices and the alloy elements by italic indices; the concentrations are of course subject to the constraint $\sum_l c_l = 1$. More details are given elsewhere.[11]

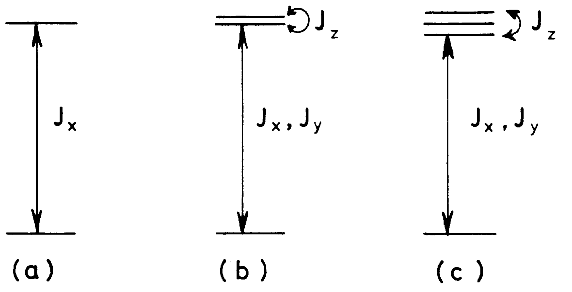

FIG. 1. Level schemes and transition probabilities for the model systems considered in Sec. III. (a) Singlet singlet; (b) singlet doublet; and (c) singlet triplet.

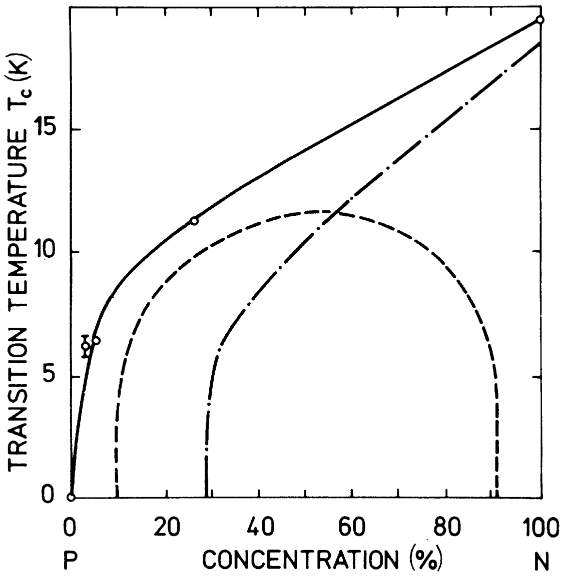

FIG. 2. Transition temperatures vs concentration for alloys of crystal-field-split systems. The full curve shows a (singlet doublet)–(Kramers doublet) system, for instance $P = \mathrm{Pr}$ and $N = \mathrm{Nd}$. The critical ratio for Pr was found (Ref. 6) to be $0.95 < 1$. The dot-dashed curve shows the typical behavior of an alloy of two (singlet doublet) systems, as for instance $P = \mathrm{Pr}$ and $N = \mathrm{Tb}$, for which $P$ is undercritical and $N$ is overcritical. The dashed curve is typical of a mixture of two strongly interacting, undercritical systems. The points show the Néel temperatures for Pr-Nd alloys obtained by neutron diffraction (Ref. 6).

## III. PHASE TRANSITIONS BETWEEN ORDERED PHASES AND MULTICRITICAL POINTS

So far we have considered the stability limits between an ordered and a disordered phase. Phase transition between phases with different order parameters is also possible.

A point in a phase diagram at which several phases consist we shall here denote a multicritical point (MCP). The investigation of critical phenomena is of particular interest near a MCP since it may provide a sensitive test of theories of critical phenomena.[1,2] Using the molecular-field theory we shall show that the anisotropic magnetic alloys exhibits a variety of MCP.

### A. Uniaxial antiferromagnet in a magnetic field

A well known example of a *bicritical* point[3] is the spin-flop transition in a uniaxial antiferromagnet in a magnetic field along this axis. The bicritical point at which the paramagnetic and the two antiferromagnetic phases coexist, with the antiferromagnetic moment parallel and perpendicular to the field direction, is determined by

$$1/\chi_{\parallel}(H,T)=1/\chi_{\perp}(H,T)=0\,, \tag{13}$$

where $\chi_n(H,T)$ is the enhanced paramagnetic staggered susceptibility in the presence of the field. The phase separation line between the ordered phases is of first order in the ordered phase. If the axial anisotropy is strong, and therefore $\chi_{\perp}$ is small, it may not be possible to fulfill (13) until at a critical field $H_0$ and temperature $T_0$ at which the transition to the paramagnetic phase becomes of first order at higher fields. This point $(H_0, T_0)$ is a so-called tricritical point (Griffiths[12]). This has been observed in $FeCl_2$ by Birgeneau *et al.*[13] The two situations are illustrated schematically in Fig. 3.

### B. Multicritical points in anisotropic magnetic alloys

An analogous situation arises in anisotropic alloys where the enhanced susceptibility varies with the concentration. The competing order parameters are the different spatial components of the angular momenta or corresponding mean fields. In a coordinate system, where the enhanced susceptibilities are diagonal, the condition for having a multicritical (bi- or tetra-) point is simply that (8) is fulfilled for two components $\alpha$ and $\beta$. That is when

$$\chi_1^{\alpha\alpha}(c,T)\chi_2^{\alpha\alpha}(c,T)=\chi_1^{\beta\beta}(c,T)\chi_2^{\beta\beta}(c,T)\,. \tag{14}$$

In the mean-field approximation the nature of the transition between the ordered phases is most conveniently discussed using the Landau expansion[14] of the free energy near the multicritical point. The most general expansion in the order parameter components $m_\alpha$ is

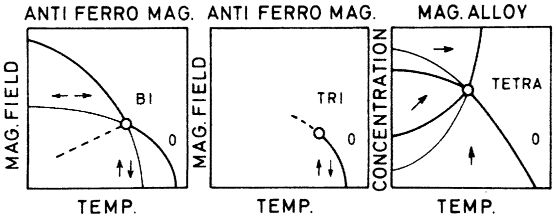

FIG. 3. Schematic phase diagrams showing multicritical points. An antiferromagnet in a uniform magnetic field shows a bi- and a tricritical point. The solid lines represent the locus of $\chi_{\parallel}^{-1}(H)$ and $\chi_{\parallel}^{-1}(H)$ equal to zero. A tetracritical point is exemplified by an anisotropic magnetic alloy.

$$\delta^2F(c,T)=\sum_{\alpha}A_\alpha(c,T)m_\alpha^2+\sum_{\alpha\beta}B_{\alpha\beta}(c,T)m_\alpha^2m_\beta^2+\sum_{\alpha\beta\gamma}C_{\alpha\beta\gamma}(c,T)m_\alpha^2m_\beta^2m_\gamma^2+\cdots\,. \tag{15}$$

The second-order phase boundaries between the ordered and disordered phase is given by $A_\alpha(c,T)=0$. The multicritical point occurs when $A_\alpha(c,T)=A_\beta(c,T)=0$. If the coefficient matrix $B_{\alpha\beta}$ to the fourth-order term is indefinite (i.e., not all eigenvalues are positive), the transition between the ordered phases is of first order and the transition point is called *bicritical*. If $B_{\alpha\beta}$ is positively definite (i.e., all eigenvalues are positive), there exists an intermediate mixed phase and all four phase boundaries are of second order—the transition point is then called a *tetracritical* point. If one or more of the eigenvalues of $B_{\alpha\beta}$ are zero, the minimum condition for $\delta^2F$, for finite $m_\alpha$, is determined by $C_{\alpha\beta\gamma}$, the coefficient to the sixth-order term. We shall denote such a point a *tricritical* point. This is a slight generalization of the conventional tricritical point which is the point along $A_\alpha(c,T)=0$ at which $B_{\alpha\alpha}(c,T)$ goes to zero and the second-order phase line becomes of first order. It is not possible to have a bicritical point with second-order transitions between the ordered phases and a first-order transition from the disordered to the mixed phase—although some of the matrix elements of $B_{\alpha\beta}$ are negative. The various cases are shown schematically in Fig. 3.

Let us illustrate the general discussion by a simple example that approximately describes many systems in practice. The details are given in Appendix B. A simple model system which shows two kinds of multicritical points is an alloy of (i) a singlet-singlet ion ($S_{\text{eff}}=\frac{1}{2}$) and (ii) a singlet-doublet ion ($S_{\text{eff}}=1$), with the crystal-field splitting $2D'$ and $2D$, respectively. We assume that the singlet-singlet spontaneously order in the $z$ direction and therefore has the susceptibility components $\chi_1^{0xx}=\chi_1^{0yy}=0$ and $\chi_1^{0zz}=(1/D')(1-n')/(1+n')$, where $n'=e^{-2D'/kT}$. The singlet-doublet is assumed also to order in the $z$ direction at high temperature, but with the $x$-$y$ plane being favorable at low temperatures. The susceptibility components are then $\chi_2^{0xx}=\chi_2^{0yy}=(1/D)(1-n)/(1+2n)$ and $\chi_2^{0zz}=(r/kT)n/(1+2n)$, where $n=e^{-2D/kT}$ and $r$ is a matrix element, the other matrix elements are put equal to 1 for simplicity.

The result is shown in Fig. 4. The second-order phase lines are obtained from Eqs. (8)–(10) and are shown as bold, full lines. The thin full lines in the ordered phase (the dilution lines) are the second-order lines as they would appear if the competing order did not give rise to any perturba-

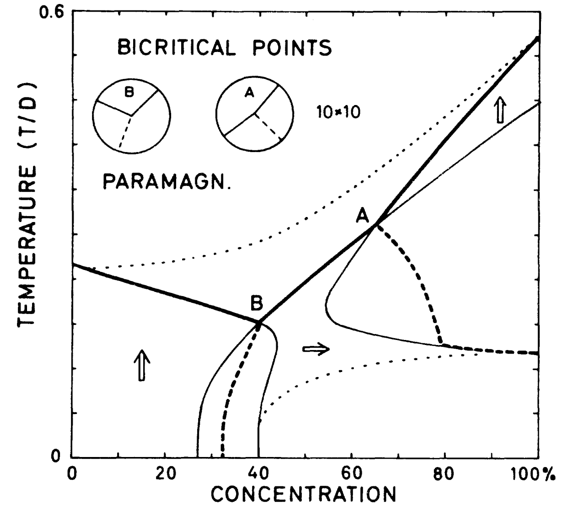

FIG. 4. Phase diagram for a singlet-singlet (left-hand side), singlet-doublet (right-hand side) alloy with the same crystal-field splitting $D$, and the exchange interactions $\mathcal{J}_Q^{11}/D=\frac{5}{3}$, $\mathcal{J}_Q^{12}/D=\frac{4}{3}$, $\mathcal{J}_Q^{22}/D=\frac{11}{3}$, and $r^2=\frac{5}{3}$. The full lines are the second-order phase separation lines, the broken curve the first-order lines. The two ordered phases are indicated by the arrow. Two types of bicritical points $A$ and $B$ are shown. The inserts show the MCP in 10×10 times magnification. The dotted lines show the calculated second-order phase lines with $\mathcal{J}_Q^{12}/D=2$. No MCP exist in this case. The details of the calculation are given in Appendix C.

tion. We distinguish two types of MCP. Point $B$ is genuinely due to the effect that the alloy elements have different order parameters, symbolized by the vertical and horizontal arrows. Point $A$ is simply due to a change of the relative magnitude of the enhanced susceptibility components for element 2—an effect which could also be obtained with a nonmagnetic dilution. This case is closely analogous to the antiferromagnet in a magnetic field. The first-order phase lines are denoted by a bold, broken curve. In general, both types of MCP will not occur simultaneously, but they may in principle also coincide and give rise to a special MCP. For a different choice of the interaction $\mathcal{J}_{12}$, shown as the dotted phase line, no MCP exists although system 2 may undergo a first order transition at low temperatures. The first-order lines were determined by an iterative numerical calculation of the locus of equal mean-field free energies in the ordered phase. At $A$ we notice that it breaks away from the second-order line with a kink and joins it again with a sharp bend.

This completes the example. The simplified level schemes suffices for determining the paramagnetic phase boundaries when the higher levels are at so high energies that the population there off is small at the transition temperature. The simplified level scheme is on the other hand not satisfactory to describe the ordered state since the developed molecular field may significantly mix all the states.

It is possible to physically predict whether one can expect to find a tetracritical or a bicritical point. The presence of order gives rise to a mean field $\vec{h}$, which we may in fact consider to be the order parameter. If (a) this perturbs the low-lying energy levels only very *weakly*, the alloy elements will order (second-order transition) close to the dilution lines and give rise to a net mean field $\vec{h}$ that is a mixture of the two competing fields. That is we have a tetracritical point. In the mean-field alloy theory we assume this field to act equally on any site in the crystal. However, different alloy atoms, of types $n$ and $m$, in the crystal will respond differently and produce the following local moment:

$$\vec{M}_n=\underline{\chi}_n(c,T)\cdot\vec{h}\,. \tag{16}$$

Since the elemental susceptibility is anisotropic the alloy moment, of type $n$, will attempt to order in the preferred direction for the pure element and not follow the direction of the mean field. If (b) the mean field $\vec{h}$ does perturb the low-lying energy levels *strongly*, the mixed phase region shrinks and results in a first-order transition between the pure phases. That is, we have a bi-critical point.

The multicritical points are interesting from a phase transition point of view for several reasons:

(i) A change in critical behavior (in the example, from a one- to two-component order parameter system or an Ising to an $X$-$Y$-model system) in general from a $p$- to $q$-component order parameter system. The critical behavior studied by the $\epsilon$-expansion technique is complicated by the presence of several fixed points and even lines of fixed points. In the latter case scaling does not hold. A careful investigation of MCP may therefore provide a test ground for the limitations of scaling ideas and the renormalization group technique. A recent theoretical investigation of the behavior of the bi- and tetracritical phase lines was done by Fisher and Nelson[15] using scaling arguments, and by Bruce and Aharony[2] using $\epsilon$-expansion technique—both yielded the result that the phase lines had a common tangent at the MCP. This is contrary to the simple mean-field prediction, which in fact seems to be in accordance with existing experiments. Aharony and Fishman[16] have recently argued that this is in fact the behavior to be expected for quenched random alloys with competing anisotropies. However, further experimental study of this is of importance.

(ii) Near a bicritical point it is possible to study first-order phase transitions that are very close to being second-order transitions.

(iii) Study of these phenomena in anisotropic magnetic alloys has the advantage of giving information about simple and nontrivial model systems which can be directly realized.

The rare-earth alloys (and also, for example, mixed rare-earth pnictides, chalcogenides or $Al_2$ compounds) are particularly favorable systems to study experimentally. They are highly anisotropic and the relative influence of the crystal field is well described by the Stevens[17] factors. The relative exchange interactions scale well with the de Gennes factor.[18] This considerably limits the number of parameters. The long-range nature of the exchange interaction makes the simple molecular-field theory valid for a large concentration range. Thus the phase separation line for the Pr-Nd alloy (Lebech *et al.*[6]) is perfectly described by the above model for all measured concentrations, 3–100 at. % (Fig. 2). Finally the rare-earth elements form ideal mixtures at all concentrations with no drastic changes in the lattice parameters. The order parameter may be studied by neutron scattering. The Tm-Tb alloy[19] is an example of the kind shown in Fig. 4, for which the two pure elements spontaneously order in perpendicular directions.

An investigation of the phase diagrams of the Er-based binary rare-earth alloys has been made by Millhouse and Koehler.[5] In this case the magnetic order parameter not only changes direction, but also character—i.e., it goes from ferromagnetic to spiral or cone structure. We shall treat this problem in Sec. III C.

### C. Transitions between different types of magnetic order

In mixed magnetic insulators transitions are often found between different types of magnetic order (antiferromagnetic). Wegner[4] discussed the case of a binar mixture of isotropic antiferromagnets such as $(Mn_{1-x}Fe_x)WO_4$. The Landau expansion of the free energy reduces to that discussed in Sec. III B and Appendix B. The multicritical-point behavior is therefore identical.

A slightly more complicated situation arises in rare-earth elements or mixtures with different incommensurate magnetic structures. Here we can distinguish two cases for a single element. (i) The incommensurate structure imposed by the exchange interaction is compatible with the crystal symmetry—e.g., a spiral structure in an axial crystal field, with the spiral vector $\vec{Q}$—and we may treat the case as discussed previously. (ii) The most complicated case is when the exchange structure is incompatible with the crystal field. This situation arises if we add a hexagonal crystal field to the previous example. For a general magnitude of $Q$ no sites will be equivalent. The result is that a bunching of the moments along the easy directions occurs together with a variation in the magnitude. If the exchange interaction is much stronger than the crystal field, the bunching effect dominates and we may neglect the variation in the magnitude. This case was considered by Nagamiya,[8] using a number of simplifying assumptions. When the crystal field is strong it may be reasonable to assume a commensurate structure and treat the finite number of inequivalent sites, which then occur, as different alloy elements and calculate the structure and magnitude of the moments as indicated in Sec. II.

In order to elucidate the principle for an alloy we shall restrict a detailed discussion to the simple case of an alloy of two elements with different incommensurate exchange structures, described by $Q_1 \neq Q_2$, which are compatible with the crystal field. The ordering and transition temperature for the pure elements are determined by the elemental enhanced susceptibilities $1/\chi_n = 1/\chi_n^0 - \mathcal{J}_{Q_n}^{nn} = 0$, from which it is clear that $Q_n$ is that wave vector $q$, for which $\mathcal{J}_q^{nn}$ is maximum. The ordering temperature of the alloy is from (8) determined by the vector which at the highest temperature gives $(1/\chi_1^0 - c\mathcal{J}_Q^{11})[1/\chi_2^0 - (1-c)\mathcal{J}_Q^{22}] = c(1-c)(\mathcal{J}_Q^{12})^2$. $Q(c)$ is in general different from $Q_1$ and $Q_2$ since it depends on the wave-vector dependence of the product of the enhanced inverse susceptibilities and the wave-vector dependence of the interaction $\mathcal{J}_q^{12}$, see Fig. 5. However, at the transition from the paramagnetic to the ordered phase $Q(c)$ is most likely to be close to the $Q_n$, $Q_1$ say, for the diluted element with the highest transition temperature or the largest $J_Q$. As the temperature is further lowered the condition for a second-order transition $(1/\chi_1)/\chi_2 = c(1-c)(J_Q^{12})^2$ may again be met at a wave vector $Q$ close to $Q_2$ corresponding to the other element. In this case elemental susceptibilities are to be calculated in the presence of the order characterized by $Q_1$. At lower temperatures the structure is therefore in this case characterized by the two ordering wave vectors $\sim Q_1$ and $\sim Q_2$. At a given concentration we may then have a tetracritical point at which the paramagnetic and three ordered phases exist with the wave vectors $\sim Q_1$, $\sim Q_2$ and a mixed phase with both wave vectors. The situation is clearly analogous to the case discussed in Sec. III B, where the competing order parameters were different components of the momentum vector. A bicritical point arises under the analogous conditions. The combined case is therefore a superposition of the possible

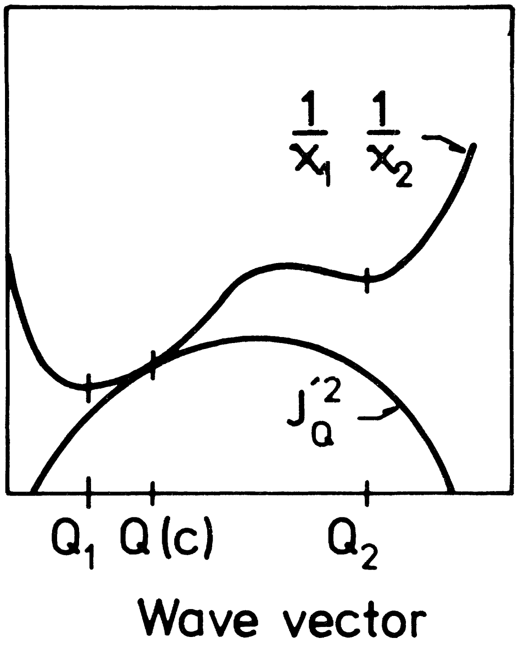

FIG. 5. Schematic presentation of the condition $(1/\chi_1)/\chi_2 = c(1-c)(\mathcal{J}_Q^{12})^2$ for a second-order phase transition in an alloy with different elemental ordering wave vectors $Q_1$ and $Q_2$ and with a wave-vector-dependent interaction $\mathcal{J}_Q^{12}$.

transitions involving both changes in directions and wave vectors.

## IV. APPLICATIONS

The theory will be applied to the following alloys of the rare-earth metals for which experimental data are available. The Tb-Er, Dy-Er, Tb-Ho, and Dy-Ho alloys were measured by Millhouse and Koehler[5] and the Tb-Tm alloys have recently been investigated by Hansen and Lebech.[19] Tb, Dy, and Ho order with spiral ordering with the moments in the basal hexagonal plane and Er and Tm order with a $c$-axis modulated (CAM) structure with the moments along the hexagonal $c$ axis. No detailed analysis has yet been made of these data, we shall therefore as a first calculation only include the dominant physical features in the basic model. Let us describe the determination of the parameters for the Tb based alloys—the procedure is analogous for the other alloys. The Hamiltonian is a Heisenberg exchange interaction plus a crystal field, which is assumed for simplicity to contain only the axial $B_2O_2^0$ term and the hexagonal $B_6(O_6^0 + \frac{77}{8}O_6^6)$. One exchange constant is obtained from the experimental $T_N$; this is the interaction between Tb-Tb. The remaining exchange interactions are obtained using the scaling by the de Gennes factors[7] which relates $J_{11} : J_{12} : J_{22}$ as $1 : [(g_2-1)/(g_1-1)] : [(g_2-1)/(g_1-1)]^2$, where $g_i$ are the Landé factors. $B_2$ is obtained from the measured difference between the paramagnetic Curie temperatures[7] $\theta_\parallel - \theta_\perp$. $B_6$ is for Tb obtained from the spin-wave energy gap and $B_2$(Tb). For Er and Tm it is obtained by scaling the $B_6$(Tb) by the appropriate Steven's factors.[17] The parameters are summarized in Table I. The calculation is done self-consistently in the magnetization components and using the complete level schemes. The resulting, calculated phase diagrams are shown in Figs. 6 and 7. A comparison between Fig. 6 and the experimental results in Fig. 8 for Tb-Er shows that the above simplified model describes the experiments quite well. A large region of helical ordering is found and a small pocket near the Er or Tm end with CAM structure, separated from the helical ordering by a mixed phase. The critical point is in agreement with experiment found to be a *tetracritical* point. The calculation does not consider the other observed structure changes such as for example to the ferromagnetic order. In a more detailed analysis of the phase diagrams it is clear that one has to include other crystal-field terms as well as magnetostriction, which is known[7] to play an important role at the ferromagnetic transition. The phase diagrams therefore contain valuable additional information about the interactions in the rare earth which has not previously been fully utilized. In addition they show examples of multicritical points. On the

TABLE I. Parameters, in units of K, used in the calculation of the phase diagrams for the alloys. The exchange interaction between the different elements is according to the de Gennes scaling $\mathcal{J}_{12} = (\mathcal{J}_{11}\mathcal{J}_{22})^{1/2}$. The Nd(hex)-Nd(cub) interaction is chosen to be 0.05 K. For dhcp Nd we do not make a distinction between the ordering wave vectors $\vec{Q}_h$ and $\vec{Q}_c$ for the hexagonal and cubic sites.

| | Tb | Dy | Er | Tm | Ho | Nd(hex) | Nd(cub) |
|---|---|---|---|---|---|---|---|
| $B_2$ | 0.89 | 0.63 | −0.39 | −1.37 | 0.18 | 0.602 | 0.602 |
| $B_4 \times 10^2$ | 0 | 0 | 0 | 0 | 0 | 0.364 | 0.364 |
| $B_6 \times 10^4$ | 0.2 | −0.2 | −0.4 | 1.0 | 0.2 | −2.4 | −2.4 |
| $2J^{nn}$ | 15.4 | 7.7 | 3.0 | 2.0 | 5.3 | 4.32 | 2.50 |

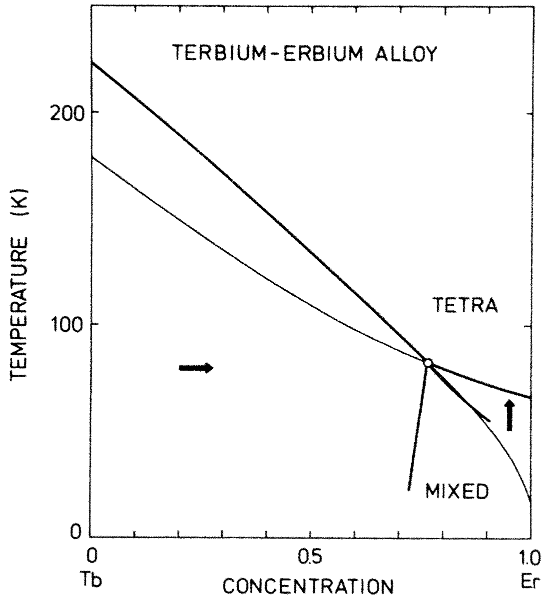

FIG. 6. Calculated phase diagram for the Tb-Er alloys using the parameters in Table I. The heavy full lines show the second-order phase transition lines. The thin full lines show where the ordering would occur if the system was not perturbed by the different order, already present.

Tb-Tm phase diagram we have indicated that a tricritical point is possible in the ordered phase in analogy with the antiferromagnetic in an external magnetic field (Fig. 3).

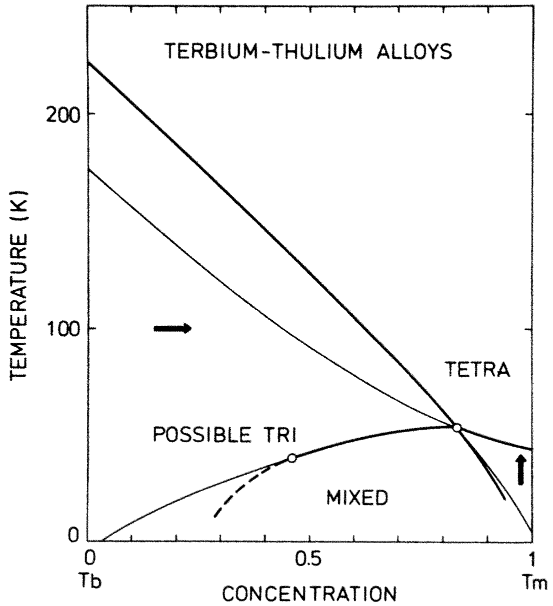

FIG. 7. Same as for Fig. 6. A possible *tricritical* point is indicated in the ordered phase at which the transition between the helical and mixed phase may become of first order.

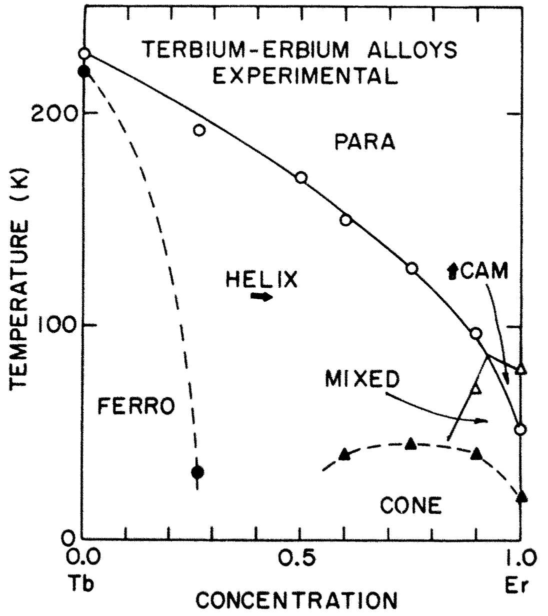

FIG. 8. Experimental data for the Tb-Er alloys from Ref. 7.

After having obtained a good qualitative agreement between the experiments and the simplified rare-earth model it is of course tempting to improve the fit by refining the model. Let us first consider the crystal-field effects. For all the experimentally investigated materials the paramagnetic transition takes place above 60 K. In the present theory all temperature effects enter via the elemental (noninteracting) susceptibilities $\chi_n^0(T)$. By comparing with the experimentally measured (noninteracting) susceptibilities for the diluted rare-earth–Y alloys,[20] shown on Fig. 9, it

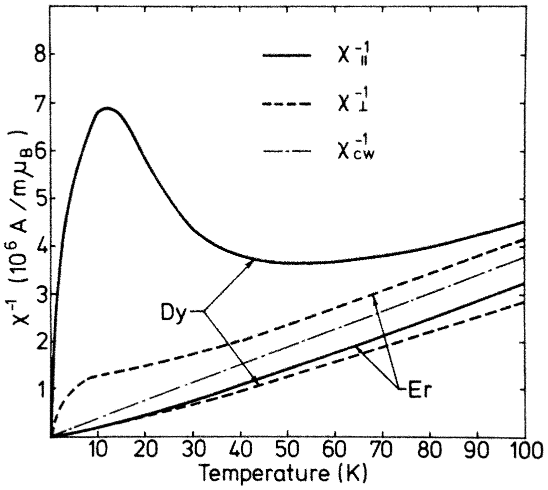

FIG. 9. Typical inverse noninteracting susceptibilities measured in diluted systems (Ref. 20).

is evident that above 60 K, $\chi^0_{\parallel}(T)$ and $\chi^0_{\perp}(T)$ to a good approximation approach straight lines with the constant difference $\chi^0_{\parallel}(T) - \chi^0_{\perp}(T) = \delta$ which is proportional to $B_2$ only. We have chosen not to use the susceptibilities, or crystal-field parameters, determined for the dilute alloys[20] because (perhaps due to difficulties with scaling) they do not give the same $B_2$ as measured for the pure elements. The paramagnetic phase separation lines are clearly not very sensitive to the higher-order terms in the crystal field which gives rise to the more dramatic Van Vleck deviations from the Curie-Weiss susceptibility at low temperatures. By diluting additionally with, for example, $Y$ transitions in a lower temperature range could be studied.

Next we consider the exchange interaction. It is well known that the de Gennes scaling[18] underestimate the exchange interaction (or paramagnetic transition temperature) in the weakly coupled systems[21] (e.g., Er) or dilute alloys (e.g., Tb-Y). We find that perfect agreement with the phase separation lines can be obtained, shown on Fig. 10, by increasing the interaction between different alloy elements significantly: $J_{AB} = \alpha(J_{AA}J_{BB})^{1/2}$ with $\alpha = 1$ to 2; $\alpha$ should be equal to one for pure de Gennes scaling. However, the predicted tetracritical point falls at too high concentration. Another (or additional) possible effect is an anisotropic exchange interaction such that $J^{\perp} > J^{\parallel}$, i.e., a stronger interaction between the spin components in the basal plane than between the components along the axial direction. This could certainly shift the tetracritical to lower concentrations. Against this possibility speaks the fact that the Tb-Tm[19] observed elemental moments tend to behave as in the pure elements in accordance with the isotropic model and single-ion anisotropy, Eq. (6). Finally the mean-field model may not be more reliable than to predict the general qualitative behavior. The best fit to the paramagnetic phase separation lines using $J_{12}$ as a fitting parameter is shown on Fig. 10 for the available alloys. The ratio $\alpha$ is given on the figures.

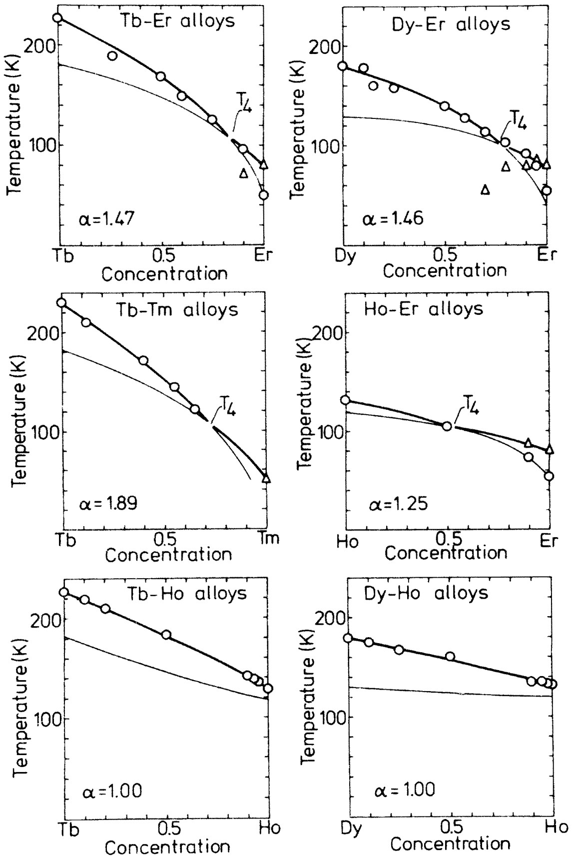

FIG. 10. Calculated paramagnetic phase separation lines compared with experiments. One fitting parameter $\alpha$ is used varying the strength of the inter-alloy element exchange interaction $\mathcal{J}_{12} = \alpha(\mathcal{J}_{11}\mathcal{J}_{22})^{1/2}$. The value of $\alpha$ is given on the figure.

The pure double hcp (dhcp) Nd crystal may be considered as a (50–50)% alloy of cubic- and hexagonal-site Nd. Information about the hexagonal site Nd was obtained by considering the Nd-Pr alloys.[6] We assume the crystal-field parameters to be the same for the cubic and hexagonal sites, which they would be in a point-charge model. The observed magnetic structure on the hexagonal sites is sinusoidally modulated with the moments in basal-plane $[10\bar{1}0]$ direction. In the dhcp structure this ordering gives rise to a very small molecular field on the cubic sites. The interaction between the hexagonal and cubic sites is therefore expected to be small due to cancellation effects. However, the interaction between the cubic sites is expected to be of similar magnitude as that between the hexagonal sites. Table I shows the parameters used in the calculation of the temperature dependence of the magnetic moments on the hexagonal and cubic sites shown in Fig. 11. The calculation shows that the hexagonal sites induce a weak magnetic order on the cubic sites in the same $[10\bar{1}0]$ direction and with the same ordering vector $Q_h$. At ~8 K a second-order phase transition makes the cubic sites order with the moments in essentially the same direction. At lower temperatures a perpendicular component develops, which turns the moments on the cubic sites to an angle of approximately 30° from the hexagonal sites (with an ordering vector $Q_c$, which may be different from $Q_h$). This is in agreement with a preliminary analysis of neutron scattering measurements on pure Nd single crystals.[20]

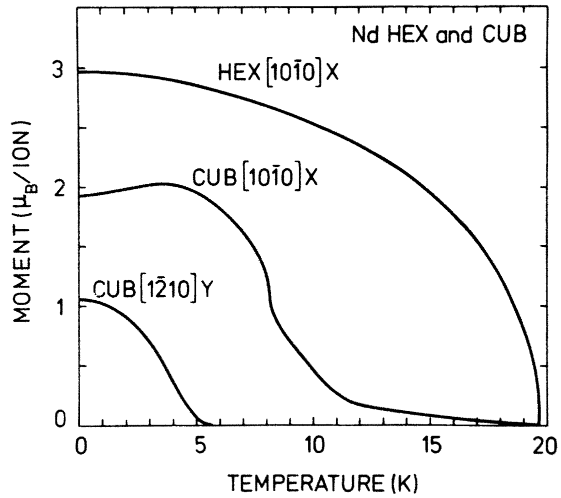

FIG. 11. Calculated temperature dependence of the magnetization for dhcp Nd, using the parameters in Table I. At 19.5 K the hexagonal sites order with the moment in the [10$\bar{1}$0] $x$ direction. This causes a weak polarization of the cubic sites along the same direction. Owing to the interaction between the cubic sites a second-order phase transition occurs at 9 K and at lower temperatures a component along the [1$\bar{2}$10] $y$ direction develops, which causes the cubic moments to turn to about 30° away from the hexagonal moment direction. This is in accordance with a preliminary analysis of Nd (Ref. 19).

## V. CONCLUSION

A mean-field theory for random anisotropic magnetic multicomponent alloys is presented and it is shown that several regions of magnetic order are possible as a function of concentration and temperature. The phase transition between these regions gives rise to multicritical points (bi-, tri-, or tetracritical points). These may be of interest to explore with great accuracy from the point of view of critical phenomena since the magnetic systems are simple and direct model systems. It was shown that the mean-field random alloy theory taking into account isotropic exchange interaction and a single-ion crystal field agrees qualitatively with observations for the rare-earth alloys for all measured concentrations. The reason for the success of the simple theory is presumably (i) that the two-ion interaction in the rare-earth metals is of long range, and (ii) that the real order parameters in the theory are the mean fields which to a much greater degree of accuracy are site independent than the individual moments. A quantitative fit can be obtained by increasing the interaction between different alloy elements. Finally the theory may also be applied to other anisotropic mixtures, the statistics of which can be simulated by a spin system. Using the expansion of the free energy in terms of the two-ion interaction discussed in Appendix C, it is simple to include the effects of fluctuations on the mean-field results.

## ACKNOWLEDGMENTS

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## APPENDIX A: MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility for noninteracting ions with Stark split energy levels of energy $E_n$ was first considered by Van Vleck[22] and later by Wang and Cooper.[23] Second-order perturbation theory gives

$$(g\mu_B)^2\chi^0|_{\alpha\beta}=\frac{(g\mu_B)^2}{kT}\Bigg(\sum_{\substack{n,m\\E_n=E_m}}\langle n|J_\alpha|m\rangle\langle m|J_\beta|n\rangle\frac{1}{Z}e^{-E_n/kT}-\sum_n\langle n|J_\alpha|n\rangle\frac{1}{Z}e^{-E_n/kT}\sum_m\langle m|J_\beta|m\rangle\frac{1}{Z}e^{-E_m/kT}\Bigg)$$
$$+2(g\mu_B)^2\sum_{\substack{n,m\\E_n\neq E_m}}\frac{\langle n|J_\alpha|m\rangle\langle m|J_\beta|n\rangle}{E_m-E_n}\frac{1}{Z}e^{-E_n/kT}, \tag{A1}$$

where the partition function is $Z=\sum_n e^{-E_n/kT}$. The first two terms are called the Curie-Weiss susceptibility and the last, off-diagonal term is called the Van Vleck term.

## APPENDIX B: SINGLET-SINGLET-SINGLET-DOUBLET ALLOY SYSTEMS

We shall here give the details of the theory for the simple model system discussed in Sec. III B. The energy levels and matrix elements are given in Figs. 1(a) and 1(b). The Hamiltonian describing this system is

$$\begin{aligned}\mathcal{H}=&-\sum_{\substack{np\\ij}}\alpha_n\alpha_n\mathcal{J}_{np}(R_{ij})c_nc_pS^z_{ni}S^z_{pj}\\&-\sum_{ij}\gamma^2\mathcal{J}_{22}(R_{ij})c_2^2(S^x_{2i}S^x_{2j}+S^y_{2i}S^y_{2j})\\&-\sum_{i,n}g_nc_n\mu_B\vec{\mathrm{h}}_i\cdot\vec{\mathrm{S}}_i+V_c,\\V_c=&-\sum_i c_i2D'S^x_{1i}-\sum_i c_22D(S^z_{2i})^2,\end{aligned}\tag{B1}$$

where $n$ and $p$ denote the type of atom, 1 or 2, $\alpha_m$ and $c_m$ denote the respective matrix elements and concentrations (occupation probabilities), and $g_n$ are the corresponding $g$ factors. In the mean-field–random-alloy approximation this Hamiltonian is replaced by (since $x$ and $y$ are equivalent we consider only the $x, z$ plane)

$$\mathcal{H} = H_{z'} S^z_{1Q} + H_z S^z_{2Q} + H_x S^x_{2Q} + V_c \,, \tag{B2}$$

where the mean fields $H_\alpha$ acting on the Fourier components of the effective spins are, denoting $c_1 = c$ and $c_2 = (1-c)$,

$$\begin{aligned} H_{z'} = z' &= -[\mathcal{J}_{11} c \langle S^z_{1Q}\rangle + \mathcal{J}_{12}(1-c)\langle S^z_{2Q}\rangle] \\ &\quad + [g_1 c + g_2(1-c)]\mu_B h_z \,, \\ H_z = z &= [\mathcal{J}_{12} c \langle S^z_{1Q}\rangle + \mathcal{J}_{22}(1-c)\langle S^z_{2Q}\rangle] \\ &\quad + [g_1 c + g_2(1-c)]\mu_B h_z \,, \\ H_x = x &= -\mathcal{J}^x_{22}(1-c)\langle S^x_{2Q}\rangle + g_2(1-c)\mu_B h_x \,, \end{aligned} \tag{B3}$$

in terms of the Fourier-transformed reduced exchange functions

$$\begin{aligned} \mathcal{J}_{np} &= \alpha_n \alpha_p \sum_R 2\mathcal{J}_{np}(R) e^{i\vec{Q}\cdot\vec{R}} \,, \\ \mathcal{J}^x_{22} &= \gamma^2 \sum_R 2\mathcal{J}^x_{22}(R) e^{i\vec{Q}\cdot\vec{R}} \,. \end{aligned} \tag{B4}$$

In order to simplify the notation we denote $H_\alpha$ by $\alpha$. Equations (B2) and (B3) hold, in zero field $\vec{h}$, for any magnetic structure described by the wave vector $\vec{Q}$ (ferromagnetic, spiral, or cone-structure, etc.), which is consistent with the axial symmetry of the crystal field $V_c$. For a finite field $\vec{h}$ and a nonferromagnetic structure, or for complicated magnetic structures, a number of unequivalent sites will exist. They may be regarded as different alloy elements. Here we restrict ourselves to equivalent sites and $\vec{h} = 0$. The singlet-doublet model in a magnetic field has been extensively discussed by Wang and Khajehpour.[9]

Let us regard the mean fields as the order parameters of the problem. The advantage of this choice, rather than choosing the elemental moments, is that the mean fields are to a good approximation equal for all sites. As discussed in Sec. III B this does not require the elemental moments to be equal in magnitude or in direction. On the other hand, the fields vanish when the ordered moments vanish at the ordering temperature. The energy levels of the two systems for the Hamiltonian (B2) can be found analytically. Near the ordering temperature we may expand in the mean fields, and obtain for the singlet-singlet system the energies including terms of forth order:

$$\begin{aligned} E_{11} &= -D'[1 + \tfrac{1}{2}(z'/D')^2 - \tfrac{1}{8}(z'/D')^4] \,, \\ E_{12} &= D'[1 + \tfrac{1}{2}(z'/D')^2 - \tfrac{1}{8}(z'/D')^4] \,, \end{aligned} \tag{B5}$$

and for the singlet-doublet system the energies

$$\begin{aligned} E_{20} &= -D(1+R) \,, \\ E_{21} &= D(1 + \tfrac{1}{2}R - P) \,, \\ E_{22} &= D(1 + \tfrac{1}{2}R + P) \,, \end{aligned} \tag{B6}$$

where

$$\begin{aligned} R &= \tfrac{1}{2}(x/D)^2 - \tfrac{1}{8}(x/D)^4 + \tfrac{1}{8}(x/D)^2(z/D)^2 \,, \\ P^2 &= (z/D)^2 + \tfrac{1}{16}(x/D)^4 - \tfrac{1}{4}(x/D)^2(z/D)^2 \,. \end{aligned} \tag{B7}$$

The free energy is then obtained in terms of the elemental internal energies and entropies as follows:

$$\mathcal{F} = c(\mathcal{E}^0_1 - kT\mathcal{S}_1) + (1-c)(\mathcal{E}^0_2 - kT\mathcal{S}_2) \,, \tag{B8}$$

where the total internal energy is

$$\begin{aligned} \mathcal{E}_0 &= c\mathcal{E}^0_1 + (1-c)\mathcal{E}^0_2 \\ &= \tfrac{1}{2}(\mathcal{J}_{22} z'^2 - 2\mathcal{J}_{12} z' z + \mathcal{J}_{11} z^2)/A + \tfrac{1}{2}x^2/\mathcal{J}^x_{22} \,, \\ A &= \mathcal{J}_{11}\mathcal{J}_{22} - \mathcal{J}^2_{12} \,, \end{aligned} \tag{B9}$$

and the entropies are obtained from

$$\mathcal{S}_n = \ln Z_n = \ln \sum_p e^{-E_{np}/kT} \,. \tag{B10}$$

Using (B5) and (B6) we find the free energy near the transition point to be

$$\begin{aligned} \mathcal{F} &= a_2 z'^2 + b_2 z^2 + c_2 x^2 + 2d_2 z' z + a_4 z'^4 \\ &\quad + b_4 z^4 + c_4 x^4 + 2d_4 x^2 z^2 \,. \end{aligned} \tag{B11}$$

The coefficients depend on the temperature and linearly on the concentration; they are given in Table II. From the minimum condition $\partial\mathcal{F}/\partial x = \partial\mathcal{F}/\partial z = \partial\mathcal{F}/\partial z' = 0$ we can eliminate $z$ by

$$z = -z'(a_2 + 2a_4 z'^2)/d_2 \,, \tag{B12}$$

and two coupled equations result

$$\begin{aligned} z'(a + bz'^2 + b'x^2) &= 0 \,, \\ x(a' + b'z'^2 + b''x^2) &= 0 \,, \end{aligned} \tag{B13}$$

where the coefficients are given in Table II. The equation system (B13) is identical to the one discussed by Wegner[4] for the problem of an alloy of two different antiferromagnetic substances. We have therefore used the same notation. By the Landau expansion we find the second-order phase lines to be given by

$$a \sim (1/\chi^{zz}_1)/\chi^{zz}_2 - \mathcal{J}^2_{12} c(1-c) = 0$$

and

$$a' \sim [1/\mathcal{J}^x_{22} - \chi^{xx}_{20}(1-c)] = 0 \,,$$

TABLE II. Coefficients for the Landau expansion for a singlet-singlet (with concentration $c$) and a singlet-doublet alloy. $A=\mathcal{J}_{11}\mathcal{J}_{22}-\mathcal{J}_{12}^2$, $\beta=1/kT, d'=\beta D'$, and $d=\beta D$. $\chi_{10}^{\alpha\alpha}$ and $Z_i$ are the elemental susceptibilities and partition functions and $n=e^{-d}$. The right-hand column gives the coefficients expanded for small crystal-field splittings $d'$ and $d$. The last five terms are the coefficient in the reduced Landau expansion (B13). The information in the table can also be used to discuss alloys of two singlet singlets or two singlet doublets.

| | Exact expressions | For small crystal fields |
|---|---|---|
| $a_2$ | $\frac{1}{2}\mathcal{J}_{22}/A-\chi_{10}^{zz}c$ | $\frac{1}{2}\mathcal{J}_{22}/A-\frac{1}{4}\beta(1-\frac{1}{2}d'^2)c$ |
| $b_2$ | $\frac{1}{2}\mathcal{J}_{11}/A-\chi_{20}^{zz}(1-c)$ | $\frac{1}{2}\mathcal{J}_{11}/A-\frac{1}{3}\beta(1-\frac{2}{3}d)(1-c)$ |
| $c_2$ | $1/(2\mathcal{J}_{22}^{x})-\chi_{20}^{xx}(1-c)$ | $1/(2\mathcal{J}_{22}^{x})-\frac{1}{3}\beta(1+\frac{1}{3}d)(1-c)$ |
| $d_2$ | $-\frac{1}{2}\mathcal{J}_{12}/A$ | $-\frac{1}{2}\mathcal{J}_{12}/A$ |
| $a_4$ | $c(\beta^2/d'^2)(\frac{1}{2}\chi_{10}^{zz}-\beta/Z_1^2)$ | $\frac{1}{48}\beta^3(1-\frac{4}{5}d'^2)c$ |
| $b_4$ | $(1-c)\frac{1}{12}\beta^3(4n-1)/Z_2^2$ | $\frac{1}{36}\beta^3(1-2d)(1-c)$ |
| $c_4$ | $(1-c)(\beta^2/d^2)[2\chi_{20}^{xx}-\beta(5+n)/Z_2^2]$ | $\frac{1}{36}\beta^3(1+d)(1-c)$ |
| $d_4$ | $(1-c)(\beta^2/d^2)(\chi_{20}^{zz}-\chi_{20}^{xx}+3\beta d/Z_2^2)$ | $\frac{1}{36}\beta^3(1-d)(1-c)$ |
| $a$ | $(a_2/d_2)\chi_{10}^{zz}\chi_{20}^{zz}[(1/\chi_1^{zz})\chi_2^{zz}-\mathcal{J}_{12}^2c(1-c)]/A$ | |
| $a'$ | $c_2$ | |
| $b$ | $2(a_2/d_2)[b_4(a_2/d_2)^3+a_4(b_2/d_2)]$ | |
| $b''$ | $2c_4$ | |
| $b'$ | $d_4(a_2/d_2)^2$ | |

in accordance with (8). In agreement with Wegner we find that a mixed phase exists for $bb''>b'^2$. The phase separation lines and the order parameters are given in Table III. Typical phase diagrams are shown in Figs. 3 and 4. It is clear from (B3) and (B11) that the effect of an external magnetic field, which leaves the sites equivalent, is simple to include since none of the coefficients in Table II are altered. We also remark that Tables II and III can be used to discuss a binary alloy of singlet singlet or one of the singlet doublets. Sufficient information is therefore available for additionally discussing an anisotropic antiferromagnet in a magnetic field which gives rise to two unequivalent sites.

## APPENDIX C: FLUCTUATION CORRECTION TO THE SINGLE-ION FREE ENERGY

We wish to derive a simple procedure to include the fluctuations in a system that is dominated by single-ion interactions. The corrections to the mean-field–crystal-field result are obtained by expanding the free energy regarding the two-ion interaction as a perturbation. Let the Hamiltonian be

$$\mathcal{H}(\lambda)=A+\lambda B\,, \tag{C1}$$

where the single-ion Hamiltonian is

$$A=\sum_i V_i^c+\vec{\mathrm{H}}_i^{\mathrm{MF}}\cdot\vec{\mathrm{S}}_i$$

TABLE III. Regions of stability for the ordered phase for an anisotropic magnetic alloy on the basis of the Landau expansion (B13). The result is identical to that found by Wegner (1974) for antiferromagnetic mixtures. Regions with no, pure, and mixed order are possible in the $c$, $T$ plane, depending on the coefficients given in Table II.

| Type | Magnetic order | | Region | |
|---|---|---|---|---|
| | $z^2$ | $x^2$ | | |
| No | 0 | 0 | $a>0$ | $a'>0$ |
| Pure | $-a/b$ | 0 | $a<0$ | $a'>(b'/b)a$ |
| Pure | 0 | $-a'/b''$ | $a>(b'/b'')a'$ | $a'<0$ |
| Mixed | $(a'b'-ab'')/(bb''-b'^2)$ | $(ab'-a'b)/(bb''-b'^2)$ | $a<(b'/b'')a'$<br>for $bb''>b'^2$ | $a'<(b'/b)a$ |

and the two-ion perturbation is

$$B=\sum_{i,j}\mathcal{J}_{ij}^{\alpha\alpha}(S_i^\alpha-\langle S_i^\alpha\rangle)(S_j^\alpha-\langle S_j^\alpha\rangle)\,;\quad \langle\cdot\circ\cdot\rangle$$

denotes the unperturbed average. We notice that $\langle B\rangle=0$. According to Tyablikov,[24] the standard expansion of the free energy then gives the following exact correction to second order:

$$F_2=F_0-\beta\lambda^2\int_0^\beta\!\!\int_0^x\langle B(x)B(x')\rangle\,dx\,dx'\,,\qquad\text{(C2)}$$

which shows that $F_2$ is a better approximation to the true free energy than the mean-field free energy since $F_{\text{true}}\leq F_2\leq F_0$. Equation (C2) is an exact expression that may be evaluated using the definition for $B$. We can, however, express (C2) approximately in terms of a well-known function by use of the following inequality which holds for $\beta>0$:

$$\int_0^\beta g^2(x)\,dx\geq\frac{1}{\beta}\left(\int_0^\beta g(x)\,dx\right)^2>0\,.\qquad\text{(C3)}$$

If we regard $B$ in (C1) as the perturbation due to an external field $H$, i.e., $B=\sum_i H^\alpha(S_i^\alpha-\langle S_i^\alpha\rangle)$, the correction term in (C2) is $-\frac{1}{2}\lambda^2(H^\alpha)^2(\chi_0^{\alpha\alpha})$. Using the unperturbed susceptibility function $\chi_0^{\alpha\alpha}$ we find the following simple fluctuation correction to the mean-field free energy $F_0$:

$$F_{\text{fluct}}=F_0-kT\sum_{R,\alpha}(\mathcal{J}_R^{\alpha\alpha})^2\frac{1}{(g\mu_B)^4}(\chi_0^{\alpha\alpha})^2\,,\qquad\text{(C4)}$$

which satisfies $F_{\text{true}}\leq F_2\leq F_{\text{fluct}}\leq F$. The advantage of using (C4) rather than the more correct (C2) is that it is easy to estimate when fluctuation corrections are of importance by considering the usually well-known susceptibility function $\chi_0^{\alpha\alpha}$.

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