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Theory of Random Anisotropic Magnetic Alloys

by

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Abstract

A mean field - crystal field theory is developed for random, multi-component, 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 for the phase diagrams and magnetic moments, based on known parameters for the rare earth alloys Nd-Pr, pure dhcp Nd, TbEr and TbTm alloys, agree with experimental observations. A simple procedure to include fluctuation corrections in the mean field results is also discussed.

1. 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 taking the crystal field, i.e. the anisotropy, exactly into account. 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 Pfeuty1), Bruce and Aharony2)). The theory is a generalization of the mean-field theory for an antiferromagnet in a magnetic field by Thomas3), and also of the theory by Wegner4) for an antiferromagnetic alloy.

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 Koehler5), Nd-Pr by Lebech *et al.*11), while a number of dilutions of rare earth metals with Y or Yb have been described by Koehler6). 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. The present theory may provide a basis for doing so. Nagamiya7) 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 exact account.

The two components theory is given in section 2, and the general case is discussed in appendix A. Section 3 gives a number of examples of transitions between disordered and ordered states in simple systems. In section 4 is discussed the case of competing order parameters, either with respect to moment directions or ordering wave vectors, or both. The various multicritical points are discussed in general terms. Appendix C gives a detailed calculation of the typical example of a singlet-singlet - singlet-doublet alloy. A similar discussion of the singlet-doublet system in an external magnetic field was discussed in detail by Wang and Khajehpour8). Section 5 gives concluding remarks. Appendix D 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.

2. Molecular Field Theory for Phase Transitions

Let us consider the phase diagram for magnetic phases of an alloy of two elements with different susceptibilities; for example an alloy of two rare earth metals. We shall assume a perfect random alloy of ions of types 1 and 2 for which the Hamiltonian can be written

$$\tilde{\mathcal{H}} = \sum_i \{c_1(V^i_{c_1} - c_1\sum_j \tilde{J}_{11}(ij)\, \vec{J}_{1i}\cdot\vec{J}_{1j}) + c_2(V^i_{c_2} - c_2\sum_j \tilde{J}_{22}(ij)\vec{J}_{2i}\cdot\vec{J}_{2j})$$

$$- c_1c_2\sum_{ij} 2\tilde{J}_{12}(ij)\vec{J}_{1i}\cdot\vec{J}_{2j}\}, \qquad (1)$$

where c_n are the concentrations, V^i_{cn} the crystal fields, and $\tilde{J}_{nm}(ij)$ the exchange interaction between the angular momenta $\vec{J}_{ni}$ and $\vec{J}_{mj}$. In the molecular field approximation (1) reduces to a single site Hamiltonian. For simplicity we shall in detail consider the case where $<\vec{J}_1>$ and $<\vec{J}_2>$ are parallel in the ordered phase. The general case, treated in appendix A, is more complicated, but analogous. The molecular fields are then

$$H_1 = c_1\tilde{J}_{11}(<J_1>+s_1) + c_2\tilde{J}_{12}(<J_2>+s_2)$$
$$H_2 = c_1\tilde{J}_{21}(<J_1>+s_1) + c_2\tilde{J}_{22}(<J_2>+s_2) \qquad (2)$$

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

$$\tilde{J}_{nm} = \sum_R 2\tilde{J}_{nm}(R)\, e^{i\vec{Q}\cdot\vec{R}}, \quad J_m = \sum_R e^{i\vec{Q}\cdot\vec{R}}\, J_{mR} \qquad (3)$$

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

$$\begin{aligned} \tilde{H}_1 &= - H_1 J_1 + V_{c1} \\ \tilde{H}_2 &= - H_2 J_2 + V_{c2} \end{aligned} \qquad (4)$$

The total free energy is

$$\tilde{F}(s_1,s_2) = c_1 F_1(s_1,s_2) + c_2 F_2(s_1,s_2) \qquad (5)$$

where the elemental free energies are determined from

$$e^{-\beta F_n(s_1,s_2)} = Tr_n \, e^{-\beta \tilde{H}_n} \qquad (6)$$

The phase diagram can be obtained from the free energy (5). We shall return to this point in the next section.

2.1. Physical Argument for Ordering

In order to gain some insight let us consider the problem physically. Near the ordering temperature the molecular fields are small, and we could expect that the magnetic moment induced at a site is proportional to the molecular field, with the proportionality constant being the paramagnetic susceptibility.

$$\begin{aligned} \langle J_1 \rangle &= H_1 \chi^0_1 = (\tilde{J}_{11} c_1 \langle J_1 \rangle + \tilde{J}_{12} c_2 \langle J_2 \rangle) \, \chi^0_1 \\ \langle J_2 \rangle &= H_2 \chi^0_2 = (\tilde{J}_{21} c_1 \langle J_1 \rangle + \tilde{J}_{22} c_2 \langle J_2 \rangle \;\; \chi^0_2 \end{aligned} \qquad (7)$$

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

$$(\tilde{J}_{12})^2 c_1 c_2 = \frac{1}{\chi_1}\,\frac{1}{\chi_2} = \left(\frac{1}{\chi_1^0} - c_1\tilde{J}_{11}\right)\left(\frac{1}{\chi_2^0} - c_2\tilde{J}_{22}\right) \qquad (8)$$

where χ_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 enhanced 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

$$A = \tilde{J}_{11}\tilde{J}_{22} - (\tilde{J}_{12})^2$$

$$B = \tilde{J}_{11}/\chi_2^0 - \tilde{J}_{22}/\chi_1^0 - A \qquad (10)$$

$$C = -(1/\chi_2^0 - \tilde{J}_{22})/\chi_1^0$$

B and C depend on T through the susceptibilities $\chi_n^0(T)$.

2.2. Exact Condition for Equilibrium and Ordering

Let us now proceed to derive the condition for ordering on the basis of the molecular field free energies (5) with no additional assumptions. The theory is a generalization of the molecular field treatment by Thomas[3)] of an antiferromagnet with weak anisotropy. The condition for a stable (or metastable) solution for $\langle J_1 \rangle$ and $\langle J_2 \rangle$ is that the free energy $\tilde{F}(s_1, s_2)$ has a minimum with respect to small variations of the parameters s_1 and s_2, i.e. with respect to variations in $\langle J_1 \rangle$ and $\langle J_2 \rangle$.

At equilibrium we demand

$$\frac{\partial \tilde{F}(s_1,s_2)}{\partial s_1} = \frac{\partial \tilde{F}(s_1,s_2)}{\partial s_2} = 0 \qquad (11)$$

and furthermore that

$$\delta^2 \tilde{F} = \sum_{nm} s_n \tilde{F}^{nm} s_m \quad \text{with} \quad \tilde{F}^{nm} = \frac{\partial^2 \tilde{F}}{\partial s_n \partial s_m} \qquad (12)$$

must be positively definite. This means that all eigenvalues of the hermitian matrix $\tilde{F}^{nm}$ are positive or zero. A second order phase transition occurs according to Landau[9)] when the coefficient to the term in the free energy of second order in the order parameter is zero. That is when an eigenvalue of $\delta^2 \tilde{F}$ is zero. The eigenvalues are

$$\lambda = \frac{1}{2}(\tilde{F}^{11}+\tilde{F}^{22}) \pm \sqrt{\frac{1}{4}(\tilde{F}^{11}+\tilde{F}^{22})^2 - (\tilde{F}^{11}\tilde{F}^{22} - \tilde{F}^{12}\tilde{F}^{21})} \qquad (13)$$

The conditions for a second order phase transition are therefore

$$(a)\ \frac{\partial\tilde{F}}{\partial s_1} = \frac{\partial\tilde{F}}{\partial s_2} = 0 \qquad \text{and (b)}\ \tilde{F}^{11}\tilde{F}^{22} = \tilde{F}^{12}\tilde{F}^{21}\,. \qquad (14)$$

The order parameter is the eigen vector corresponding to the eigenvalue zero.

By differentiating the free energy (5) we find condition (14a):

$$\frac{\partial\tilde{F}}{\partial s_1} = -\frac{1}{kT}\left\{c_1\langle J_1\rangle \frac{1}{\chi^0_1}\frac{\partial\langle J_1\rangle}{\partial s_1} + c_2\langle J_2\rangle \frac{1}{\chi^0_2}\frac{\partial\langle J_2\rangle}{\partial s_1}\right\} \overset{eq}{=} 0$$

$$\frac{\partial\tilde{F}}{\partial s_2} = -\frac{1}{kT}\left\{c_1\langle J_1\rangle \frac{1}{\chi^0_1}\frac{\partial\langle J_1\rangle}{\partial s_2} + c_2\langle J_2\rangle \frac{1}{\chi^0_2}\frac{\partial\langle J_2\rangle}{\partial s_2}\right\} \overset{eq}{=} 0 \qquad (15)$$

where χ^0_n is the elemental single ion susceptibility with the given values of $\langle J_1\rangle$ and $\langle J_2\rangle$. The homogeneous equations (15) have only non-trivial solutions if

$$\frac{\partial\langle J_1\rangle}{\partial s_1}\frac{\partial\langle J_2\rangle}{\partial s_2} = \frac{\partial\langle J_1\rangle}{\partial s_2}\frac{\partial\langle J_2\rangle}{\partial s_1} \qquad (16)$$

By differentiating (5) we can find each term in (16); for example

$$\frac{\partial\langle J_1\rangle}{\partial s_1} = \frac{\partial}{\partial s_1}\left\{\mathrm{Tr}_1 J_1 e^{-\beta\tilde{H}_1}/Z_1\right\} = \chi^0_1\frac{\partial H_1}{\partial s_1} \qquad (17)$$

$$= \chi^0_1\left\{c_1\tilde{J}_{11}\left(\frac{\partial\langle J_1\rangle}{\partial s_1}+1\right)+c_2\tilde{J}_{12}\frac{\partial\langle J_2\rangle}{\partial s_1}\right\}\,.$$

By solving the coupled equations of type (17) for $\frac{\partial\langle J_i\rangle}{\partial s_j}$, we can write equation (16)

$$(\tilde{J}_{11}/\chi_2 + (\tilde{J}_{12})^2 c_2)(\tilde{J}_{22}/\chi_1 + (\tilde{J}_{12})^2 c_1) = (\tilde{J}_{12})^2 \frac{1}{\chi_1^0} \frac{1}{\chi_2^0} \ . \quad (18)$$

This can be reduced to $c_1 c_2 (\tilde{J}_{12})^2 = 1/\chi_1 \ 1/\chi_2$, which is exactly the same condition as that obtained by the physical arguments (8). Since (15) and (18) are general conditions for the existence ordering, we find the ratio between the two elemental momenta in the ordered phase:

$$\frac{c_1 \langle J_1 \rangle}{c_2 \langle J_2 \rangle} = \frac{\chi^0}{\chi_2^0} c_1 \bar{J}_{12} \chi_2 \ . \quad (19)$$

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. Eq. (19) is valid near the transition temperature, T_c, when the molecular fields are small enough to allow a linearization of the equations which determines 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 is no longer consistent with molecular field theory. This is because only an expansion of the type

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

can satisfy the non-linear selfconsistency equation. The higher harmonics with wave vectors $n\vec{Q}$ lead to a "squaring up" of the moment distribution$^{6)}$ and give rise to extra satellite peaks in a neutron diffraction pattern. The effect was discussed in detail by Nagamiya$^{7)}$, 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 order to find the transition temperature we must also fulfil condition (14b) which makes one eigenvalue zero. By differentiating (15) with respect to s_1 and s_2 we find after a rather lengthy calculation that (14b) and (16 or 14a) are fulfilled simultaneously when $\langle J_1 \rangle = \langle J_2 \rangle = 0$. A general proof is given in appendix A. The temperature at which (18) or (8) is fulfilled is therefore the transition temperature T_N.

The concentration dependence of the 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.$^{11)}$).

3. Simple Examples

Let us illustrate the theory given in section 2 and appendix A by a number of examples. We shall use the general formula for the single-ion susceptibility given in appendix B.

a) Heisenberg Magnets with Magnetic Ground State Multiplets

The simplest case concerns an alloy of S-state ions with isotropic Heisenberg exchange interaction between the moments J_n. Because of the isotropic ground state the influence of the crystal field is negligible and the paramagnetic unenhanced susceptibility is the Curie-Weiss susceptibility

$$X_n^0\Big|_{\alpha\alpha} = \frac{1}{3kT} X_n \quad \text{where } X_n = J_n(J_n+1), \quad \alpha = x,y,z \ . \tag{20}$$

Equation (9),which determines the ordering temperature T_N, can then be reformulated to a second order equation in T_N with the solution

$$3kT_N = \frac{1}{2}\left(\tilde{J}_{11}X_1c + \tilde{J}_{22}X_2(1-c)\right) \pm \sqrt{\frac{1}{4}\left(\tilde{J}_{11}X_1c - \tilde{J}_{22}X_2(1-c)\right)^2 + \tilde{J}_{12}^2X_1X_2} \ . \tag{21}$$

It has a solution for any concentration c. This is a virtue of the molecular field theory because it is equivalent to the assumption of infinite range interactions. If the interactions are of short range the theory will break down at small concentrations. The paramagnetic phase separation curve versus concentration is convex if $\tilde{J}_{12}^2 X_1 > \tilde{J}_{22}^2 X_2$ (i.e. T_N of the alloy is larger than that corresponding to a non-magnetic dilution).It is concave if $\tilde{J}_{12}^2 X_1 < \tilde{J}_{22}^2 X_2$.

The phase diagram is very similar if the ionic levels are crystal field split, but with a magnetic multiplet as the ground state. The susceptibilities then have a Van Vleck[20)] term in addition. However, in most cases the influence of the crystal field can be represented by an effective spin characterizing the multiplicity of the ground state.

b) Singlet Ground State Magnets

Interesting phase diagrams occur in alloys involving singlet ground state magnets. Let us consider the level schemes in Fig. 1 with the first excited states being a singlet, doublet and triplet respectively, and with non-vanishing matrix elements for the operators indicated. The susceptibility tensor then has the components

$$\underline{\underline{\chi}}^0_{\text{singlet}} = \begin{pmatrix} VV_x & & \\ & 0 & \\ & & 0 \end{pmatrix}, \quad \underline{\underline{\chi}}^0_{\text{doublet}} = \begin{pmatrix} VV_x & & \\ & VV_y & \\ & & CW_z \end{pmatrix},$$

$$\underline{\underline{\chi}}^0_{\text{triplet}}\Big|_{\alpha\alpha} = (VV_\alpha + CW_\alpha) \ , \tag{22}$$

where the Van Vleck term is denoted $VV_\alpha = \frac{2}{D}(n_0 - n_1)|\langle 0|J_\alpha|1\rangle|^2$ and the Curie Weiss term (for the excited state) is denoted $CW_\alpha = \frac{n_1}{kT}|\langle 1|J_\alpha|1\rangle|^2$. The population factor for the ground state is $n_0 = 1/Z_p$ and that for the excited state is $n_1 = \exp(-D/kT)/Z_p$, where the partition function, when the excited state has multiplicity p, is $Z_p = 1 + p\exp(-D/kT)$.

Some typical phase diagrams obtained by using (9), (20), and (22) for alloys of these systems are shown in Fig. 2. The (singlet-doublet) - (Kramers' doublet) case is relevant for a Pr-Nd alloy and the experimental values for T_N are also shown (Lebech _et_ _al_.$^{11)}$). For singlet ground state magnets a critical magnitude of the exchange interaction is necessary for inducing spontaneous magnetism. Therefore, no ordering is possible for certain concentrations even in molecular field theory.

c) Alloys of Magnetic and Non-magnetic Ions

For alloys with non-magnetic elements or elements with zero susceptibility components (element 2) the molecular field condition for ordering, (8), reduces to $1/\chi^0_1\Big|_{\alpha\alpha} = c\tilde{J}_{11}$. The exchange interaction is simply reduced proportionally to the concentration. This equation was used by Cooper (1972) for $Tb_cY_{1-c}Sb$.

4. Phase Transitions between Ordered Phases and Multi Critical 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. It is of second order if two non-degenerate eigenvalues of δ^2F become zero at a particular concentration or magnetic field. It is of first order if the free energy of two phases becomes equal although δ^2F is finite. By a multi critical point (MCP) we here understand a point in a phase diagram at which several phases coexist.

4.1. Uniaxial Antiferromagnet in a Magnetic Field

A well known example of a bicritical point (Thomas 1969) 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

$$1/\chi_{\parallel}(H) = 1/\chi_{\perp}(H) = 0, \qquad (23)$$

where $\chi_n(H)$ 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 fulfil (23) until at a critical field H_o and temperature T_o, $\partial^4F/\partial M^4$ becomes negative. This point (T_o,H_o) is a so-called tricritical point (Griffiths$^{13)}$) at which the transition to the paramagnetic phase becomes of first order at higher fields. This has been observed in $FeCl_2$ by Birgeneau et al.$^{14)}$. The two situations are illustrated schematically in Fig. 3. Critical phenomena at tri- or multicritical points are of particular interest since the order parameter can fluctuate in several different ways. This influences the critical indices.

4.2. 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 α and β. That is when

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

In the mean field approximation the nature of the transition between the ordered phases is most conveniently discussed using the Landau expansion of the free energy near the multicritical point. The most general expansion in the order parameter components m_α is

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

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 $\delta^{2}F$, for finite m_{α}, 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 C. A simple model system which shows two kinds of multicritical point is an alloy of (1) a singlet-singlet ion ($S_{eff} = \frac{1}{2}$) and (2) a singlet-doublet ion ($S_{eff} = 1$), 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 $\chi^{xx}_{10} = \chi^{yy}_{10} = 0$ and $\chi^{zz}_{10} = \frac{1}{D'}(1-n')/(1+n')$, 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 $\chi^{xx}_{20} = \chi^{yy}_{20} = \frac{1}{D}(1-n)/(1+2n)$ and $\chi^{zz}_{20} = \frac{r^2}{kT}\, n/(1+2n)$, 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) to (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 perturbation. 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 non-magnetic 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 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.

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 h_α, which we may in fact consider to be the order parameter. If (a) this perturbs the low-lying energy levels only very <u>weakly</u>, 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:

$$\vec{M}_n = \chi_n(c,T)\cdot\vec{h} \ .$$

Since the elemental susceptibility is anisotropic the alloy atom, 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 h_a 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.

(1) 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 ϵ-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 tetra-critical phase lines was done by Fisher and Nelson15) using scaling arguments, and by Bruce and Aharony2) using ϵ-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. However, further experimental study of this is of importance. Aharony16) has recently conjectured that the transition may be described by a Gaussian-fixed point which produces results identical to the mean-field

theory.

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

(3) Study of these phenomena in anisotropic magnetic alloys has the advantage of giving information about simple and non-trivial 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.(11)) is perfectly described by the above model for all measured concentrations, 3% to 100%. 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(22) 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 the next section.

4.3. Transitions Between Different Types of Magnetic Order

In mixed magnetic insulators transitions are often found between different types of magnetic order (antiferromagnetic). Wegner4) 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 the previous section and appendix C. 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. (1) 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 $\vec{Q}$ along the axis. In this case all sites are equivalent irrespective of the value of Q - and we may treat the case as discussed previously. (2) 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$^{7)}$, 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 using appendix A.

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 $\frac{1}{\chi_n} = \frac{1}{\chi^{\upsilon}} - \tilde{J}^{nn}_{Q_n} = 0$, from which it is clear that Q_n is that wave vector q, for which $\tilde{J}^{nn}_{q}$ is maximum. The ordering temperature of the alloy is from (8) determined by the vector which at the highest temperature gives $(\frac{1}{\chi^{\upsilon}_1} - c\tilde{J}^{11}_{Q})(\frac{1}{\chi^{\upsilon}_2} - (1-c)\tilde{J}^{22}_{Q}) = c(1-c)(\tilde{J}^{12}_{Q})^2$. 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 $\tilde{J}^{12}_{q}$, 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 $\frac{1}{\chi_1}\frac{1}{\chi_2} = c(1-c)(J_Q^{12})^2$ may again be met at a wave vector Q close to Q_2 corresponding to the other element. In this case the 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 the previous section, 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 transitions involving both changes in directions and wave vectors.

4.4. Applications

The theory will be applied to the following alloys of the rare earth metals for which experimental data are available. The Tb-Er alloys were measured by Millhouse and Koehler$^{5)}$ and the Tb-Tm alloys are presently being investigated by Hansen and Lebech$^{22)}$. In both cases Tb orders 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. 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 factors6) which relates $J_{11}:J_{12}:J_{22}$ as $1:(\frac{g_2-1}{g_1-1}) : (\frac{g_2-1}{g_1-1})^2$, where g_i are the Landé factors. B_2 is obtained from the measured difference between the paramagnetic Curie temperatures6) $\theta_{\parallel}-\theta_{\perp}$. B_6 is for Tb obtained from the spinwave energy gap and B_2(Tb). For Er and Tm it is obtained by scaling the B_6(Tb) by the appropriate Steven's factors17). The parameters are summarized in table 1.

The calculation is done selfconsistently 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 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 <u>tetracritical</u> 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 known6) 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 Tb-Tm phase diagram we have indicated that a <u>tri-critical</u> point is possible in the ordered phase in analogy with the antiferromagnet in an external magnetic field, Fig. 3. Fig. 10 shows a fit to the phase diagrams using $\alpha = \tilde{J}_{12}/\sqrt{\tilde{J}_{11}\tilde{J}_{22}}$ as a parameter. A good fit can clearly be obtained. A more detailed discussion of this was recently published$^{24)}$ and further work shows that it is likely that the apparent strong interaction between different alloy elements is due to changes in the band structure in the alloys$^{25)}$.

The pure 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$^{11)}$. 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 cancalation effects. However, the interaction between the cubic sites is expected to be of similar magnitude as that between the hexagonal sites. Table 1 shows the parameters used in the calculation of the temperature dependence of the magnetic moments on the hexagonal and cubic sites shown in Fig. 9. The calculation shows that the hexagonal sites induce a weak magnetic order on the cubic sites in the same direction $(10\bar{1}0)$ 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^o 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 crystals23).

5. Conclusion

A mean-field theory for random anisotropic magnetic multi-component 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 tetra-critical 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 agrees with observations for the rare earth alloys for all measured concentrations. The reason for the success of the simple theory is presumably 1) that the two-ion interaction in the rare earth metals is of long range, and 2) 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. 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 D, it is simple to include the effects of fluctuations on the mean-field results.

Acknowledgment. It is a pleasure to thank B. Lebech and P.Å. Hansen for discussing experimental results.

Appendix A

General Molecular Field Theory for a Multi-Component Alloy

In this section we shall generalize the molecular field theory given in section 2 so as to take into account a general anisotropic biquadratic exchange interaction between the ions n and m:

$$- \sum_{ij} J^{\alpha}_{ni} \tilde{J}^{\alpha\beta}_{nm}(ij) J^{\beta}_{mj} . \qquad \text{A1}$$

The fourier transformed of the exchange interaction with the ordering wave vector $\vec{Q}_{nm}$ is denoted

$$\tilde{J}^{\alpha\beta}_{nm} = \sum_{\vec{R}} 2\tilde{J}^{\alpha\beta}_{nm}(\vec{R}) \, e^{i \vec{Q}_{nm}\cdot\vec{R}} . \qquad \text{A2}$$

We shall also take into account that in general the ordered moments $\langle\vec{J}_1\rangle$ and $\langle\vec{J}_2\rangle$ may point in different and arbitrary directions. We must therefore minimize the free energy $\tilde{F}(\vec{s}_n,\vec{s}_m)$ corresponding to (5) with respect to every component. We shall use Greek letters for the components and italic for the alloy type and adopt the usual convention of summation over repeated Greek indices. The molecular field components are

$$H^{\alpha}_{\ell} = \sum_{m} c_m \tilde{J}^{\alpha\beta}_{\ell m} (\langle J^{\beta}_{m}\rangle + s^{\beta}_{m}) . \qquad \text{A3}$$

The extremum condition (15) becomes

$$\frac{\partial \tilde{F}}{\partial s_\ell^\alpha} = - \frac{1}{kT} \sum_m c_m \langle J_m^\beta \rangle \frac{\partial H_m^\beta}{\partial s_\ell^\alpha} = 0 . \qquad \text{A4}$$

The phase boundary between the ordered phase and the paramagnetic phase in which $\langle J_r^\nu \rangle = 0$ is determined when the determinant of $\frac{\partial^2 \tilde{F}}{\partial s_n^\gamma \partial s_\ell^\alpha}$ is equal to zero (assuming that no eigenvalue is negative)

$$\left. \frac{\partial^2 \tilde{F}}{\partial s_n^\gamma \, \partial s_\ell^\alpha} \right|_{\langle J_r^\nu \rangle = 0} = \frac{1}{(kT)^2} \sum_m c_m \frac{\partial H_m^\varepsilon}{\partial s_n^\gamma} (\chi_m^0)_{\varepsilon\beta} \frac{\partial H_m^\beta}{\partial s_\ell^\alpha} . \qquad \text{A5}$$

However, from (A4) we see that non-trivial solutions only exist when the determinant of the matrix $\frac{\partial H_m^\beta}{\partial s_\ell^\alpha}$ is equal to zero. Since the determinant of the matrix product (A5) is equal to the product of the separate determinants we find that $\frac{\partial \tilde{F}}{\partial s_\ell^\alpha} = 0$, and the condition that at least one eigenvalue is zero is simultaneously fulfilled when the determinant of $\frac{\partial H_m^\beta}{\partial s_\ell^\alpha}$ is equal to zero. For finding the paramagnetic phase boundary, we can therefore obtain both the order parameter and ordering temperature from A4. This is much simpler than diagonalizing A5 as suggested by Thomas$^{3)}$. However, it seems to be necessary to diagonalize for finding second order phase boundaries in the ordered phase. The matrix $\frac{\partial H_m^\beta}{\partial s_\ell^\alpha}$ is found from

$$\frac{\partial H_m^\beta}{\partial s_\ell^\alpha} = \sum_n c_n \tilde{J}_{mn}^{\beta\gamma} \left(\frac{\partial\langle J_n^\gamma\rangle}{\partial s_\ell^\alpha} + \delta_{\alpha\gamma}\,\delta_{\ell n}\right) = (\chi_m^0)^{-1}_{\beta\phi}\,\frac{\partial\langle J_m^\phi\rangle}{\partial s_\ell^\alpha} \qquad \text{A6}$$

The partial derivatives of the angular momentum components are determined by the inhomogeneous equation system

$$\sum_n \left\{(\chi_m^0)^{-1}_{\beta\phi}\,\delta_{nm}\delta_{\gamma\phi} - c_n\tilde{J}_{mn}^{\beta\gamma}\right\}\frac{\partial\langle J_n^\gamma\rangle}{\partial s_\ell^\alpha} = -\,c_e\tilde{J}_{m\ell}^{\beta\alpha}, \qquad \text{A7}$$

which is a generalization of eq. (17). The solution can be inserted in A6 and the determinant of $\frac{\partial H_m^\beta}{\partial s_\ell^\alpha}$ found. The determinant clearly depends on the concentrations c_n, the fourier transformed exchange interaction tensor $\tilde{J}_{n\ell}^{\alpha\beta}$, and on the elemental susceptibility matrixes $(\chi_n^0)_{\alpha\beta}$, and thereby on the temperature T. The derivation is not restricted to two alloying elements. The summation over the elements (the italic index in eqs.A1 to A7) can therefore be extended to any value with the constraint $\sum_n c_n = 1$.

In order to gain some insight into the general formulae let us consider a simple case with two alloy elements and all susceptibility and exchange matrixes diagonal (but with arbitrary diagonal elements). Then the different angular momentum components are decoupled and the condition A6 reduces to the question: for which component α does the determinant $\frac{\partial H_m^\alpha}{\partial s_\ell^\alpha}$ first become zero as the temperature is lowered?

Since the ordered moments must be parallel the problem is reduced to that discussed in section 2. In the ordered phase it is possible for the system to undergo a spin flip transition where the moments choose a different direction. This transition can be of second order, namely if the corresponding eigenvalue is zero, or of first order if the free energies of the competing types of phases become equal.

Appendix B

Magnetic Susceptibility

The magnetic susceptibility for non-interacting ions with Stark split energy levels of energy E_n was first considered by Van Vleck[20)] and later by Wang and Cooper[19)]. Second order perturbation theory gives

$$(g\mu_B)^2 \chi^0\Big|_{\alpha\beta} = \frac{(g\mu_B)^2}{kT} \Big\{ \sum_n <n|J_\alpha|n><n|J_\beta|n> \frac{1}{Z} e^{-E_n/kT}$$

$$- \sum_n <n|J_\alpha|n> \frac{1}{Z} e^{-E_n/kT} \sum_m <m|J_\beta|m> \frac{1}{Z} e^{-E_m/kT} \Big\} \qquad (B1)$$

$$+ \; 2(g\mu_B)^2 \sum_{\substack{n,m \\ E_n \neq E_m}} \frac{<n|J_\alpha|m><m|J_\beta|n>}{E_m - E_n} \frac{1}{Z} e^{-E_n/kT} ,$$

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 C

Singlet-Singlet - Singlet-Doublet Alloy Systems

We shall here give the details of the theory for the simple model system discussed in section 4.2. The energy levels and matrix elements are given in Figs. 1a and b. The Hamiltonian describing this system is

$$\begin{aligned} \mathcal{H} = &- \sum_{\substack{np \\ ij}} \alpha_n \alpha_p \tilde{J}_{np}(R_{ij}) c_n c_p S^z_{ni} S^z_{pj} \\ &- \sum_{ij} \gamma^2 \tilde{J}_{22}(R_{ij}) c_2^2 \{S^x_{2i} S^x_{2j} + S^y_{2i} S^y_{2j}\} \\ &- \sum_{i,n} g_n c_n \mu_B \vec{h}_i \cdot \vec{S}_i + V_c \end{aligned} \qquad \text{(C1)}$$

$$V_c = - \sum_i c_1 2D' S^x_{1i} - \sum_i c_2 2D (S^z_{2i})^2 ,$$

where n and p denote the type of atom, 1 or 2, α_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)

$$\mathcal{H} = z' S^z_{1Q} + z S^z_{2Q} + x S^x_{2Q} + V_c , \qquad \text{(C2)}$$

where the mean fields acting on the fourier components of the effective spins are

$$z' = -<(\tilde{J}_{11}cS^z_{1Q} + \tilde{J}_{12}(1-c)S^z_{2Q})> + (g_1c + g_2(1-c))\mu_B h_z,$$

$$z = -<(\tilde{J}_{12}cS^z_{1Q} + \tilde{J}_{22}(1-c)S^z_{2Q})> + (g_1c + g_2(1-c))\mu_B h_z \qquad (C3)$$

$$x = -< \qquad \tilde{J}^x_{22}(1-c)S^x_{2Q})> + g_2(1-c)\mu_B h_x$$

in terms of the fourier transformed reduced exchange functions

$$\begin{aligned} \tilde{J}_{np} &= \alpha_n\alpha_p\sum_R 2\tilde{J}_{np}(R)e^{i\,\vec{Q}\cdot\vec{R}} \\ \tilde{J}^x_{22} &= \gamma^2 \sum_R 2\tilde{J}^x_{22}(R)e^{i\,\vec{Q}\cdot\vec{R}} \end{aligned} \qquad (C4)$$

This holds, 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 non-ferromagnetic structure,or for complicated magnetic structures, a number of unequivalent sites will exist. They may be regarded as different alloy elements and treated as discussed in appendix A. 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$^{8)}$.

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 section 4.2. 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 (C2) can be found analytically. Near the ordering temperature we may expand in the mean fields, and obtain for the singlet-singlet system the energies

$$\begin{aligned} E_{11} &= -D'\{1 + \tfrac{1}{2}(\tfrac{z'}{D'})^2 - \tfrac{1}{8}(\tfrac{z'}{D'})^4\} \\ E_{12} &= D'\{1 + \tfrac{1}{2}(\tfrac{z'}{D'})^2 - \tfrac{1}{8}(\tfrac{z'}{D'})^4\} \end{aligned} \tag{C5}$$

and for the singlet-doublet system the energies

$$\begin{aligned} E_{20} &= -D\{1+R\} \\ E_{21} &= D\{1+\tfrac{1}{2}R-P\} \\ E_{22} &= D\{1+\tfrac{1}{2}R+P\}, \end{aligned} \tag{C6}$$

where

$$\begin{aligned} R &= \tfrac{1}{2}(\tfrac{x}{D})^2 - \tfrac{1}{8}(\tfrac{x}{D})^4 + \tfrac{1}{8}(\tfrac{x}{D})^2(\tfrac{z}{D})^2 \\ P^2 &= (\tfrac{z}{D})^2 + \tfrac{1}{16}(\tfrac{x}{D})^4 - \tfrac{1}{4}(\tfrac{x}{D})^2(\tfrac{z}{D})^2 . \end{aligned} \tag{C7}$$

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

$$\tilde{F} = c(\tilde{E}_1^0 - kT\tilde{S}_1) + (1-c)(\tilde{E}_2^0 - kT\tilde{S}_2) \tag{C8}$$

where the total internal energy is

$$\tilde{E}_0 = c\tilde{E}_1^0 + (1-c)\tilde{E}_2^0 = \tfrac{1}{2}\{\tilde{J}_{22}z'^2 - 2\tilde{J}_{12}z'z + \tilde{J}_{11}z^2\}/A + \tfrac{1}{2}x^2/\tilde{J}^x_{22},$$
$$A = \tilde{J}_{11}\tilde{J}_{22} - \tilde{J}_{12}^2 \tag{C9}$$

and the entropies are obtained from

$$\tilde{S}_n = \ln Z_n = \ln \sum_p \exp(-E_{np}/kT) . \tag{C10}$$

Using C5 and C6 we find the free energy near the transition point to be

$$\begin{aligned}\tilde{F} &= a_2z'^2 + b_2z^2 + c_2x^2 + 2d_2z'z \\ &\quad + a_4z'^4 + b_4z^4 + c_4x^4 + 2d_4x^2z^2\end{aligned} \tag{C11}$$

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

$$z = -z'(a_2 + 2a_4z'^2)/d_2 \tag{C12}$$

and two coupled equations result

$$\begin{aligned}z'(a + bz'^2 + b'x^2) &= 0 \\ x(a' + b'z'^2 + b''x^2) &= 0\end{aligned} \tag{C13}$$

where the coefficients are given in table CI. The equation system (C13) 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

$$a \sim \left(\frac{1}{\chi_1^{zz}}\,\frac{1}{\chi_2^{zz}} - \tilde{J}_{12}^{\,2}c(1-c)\right) = 0 \text{ and } a' \sim \left(\frac{1}{\tilde{J}_{22}^{x}} - \chi_{20}^{xx}(1-c)\right) = 0$$

in accordance with (8). In accordance 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 CII. Typical phase diagrams are shown in Figs. 3 and 4. It is clear from (C3) and (C11) that the effect of an external magnetic field, which leaves the sites equivalent, is simple to include since none of the coefficients in table CI are altered. We also remark that tables CI and (C11) can be used to discuss a binary alloy of singlet-singlet or one of 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 D

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

$$\mathcal{H}(\lambda) = A + \lambda B \qquad \text{(D1)}$$

where the single ion Hamiltonian is $A = \sum_{i} (V_i^c + \vec{H}_i^{MF} \vec{S}_i)$ and the two-ion-perturbation is $B = \sum_{i,j,\alpha} \tilde{J}_{ij}^{\alpha\alpha}(S_i^\alpha - \langle S_i^\alpha \rangle)(S_j^\alpha - \langle S_j^\alpha \rangle)$; $\langle \ldots \rangle$ denotes the unperturbed average. We notice that $\langle B \rangle = 0$. According to Tyablikov$^{21)}$, the standard expansion of the free energy then gives the following exact correction to second order:

$$F_2 = F_0 - \beta\lambda^2 \int_0^\beta \int_0^x \langle B(x)\ B(x') \rangle\, dx dx' \qquad \text{(D2)}$$

which shows that F_2 is a better approximation to the true free energy than the mean field free energy since $F_{true} \leq F_2 \leq F_0$. (D2) is an exact expression that may be evaluated using the definition for B. We can, however, express (D2) approximately in terms of a well known function by use of the following inequality which holds for $\beta>0$

$$\int_0^\beta g^2(x)\,dx \geq \frac{1}{\beta}\left(\int_0^\beta g(x)\,dx\right)^2 > 0 \;. \qquad \text{(D3)}$$

If we regard B in (D1) 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 (D2) 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:

$$F_{\text{fluct.}} = F_0 - kT \sum_{R,\alpha} (\tilde{J}_R^{\alpha\alpha})^2 \frac{1}{(g\mu_B)^4} (\chi_0^{\alpha\alpha})^2 , \qquad \text{(D4)}$$

which satisfies $F_{\text{true}} \leq F_2 \leq F_{\text{fluct.}} \leq F_0$. The advantage of using (D4) rather than the more correct (D2) is that it is easy to estimate when fluctuation corrections are of importance by considering the usually well known susceptibility function $\chi_0^{\alpha\alpha}$.

Figure Captions

Fig. 1. Level schemes and transition probabilities for the model systems considered in section 3; (a) singlet-singlet (b) singlet-doublet,and (c) singlet-triplet.

Fig. 2. The transition temperatures versus concentration for alloys of crystal field split systems. The full curve shows a (singlet-doublet)-(Kramers' doublet) system, for instance P = Pr and N = Nd. The critical ratio for Pr was found[11)] 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 = Pr and N = Tb, for which P is under-critical and N is over-critical. The dashed curve is typical of a mixture of two strongly interacting, under-critical systems. The points show the Néel temperatures for Pr-Nd alloys obtained by neutron diffraction[11)].

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 tetra-critical point is exemplified by an anisotropic magnetic alloy.

Fig. 4. The phase diagram for a singlet-singlet (left), singlet-doublet (right) alloy with the same crystal field splitting D, and the exchange interactions $\tilde{J}_Q^{11}/D = 5/3$, $\tilde{J}_Q^{12}/D = 4/3$, $\tilde{J}_Q^{22}/D = 11/3$, and $r^2 = 5/3$. 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 $\tilde{J}_Q^{12}/D = 2$. MCP exist in this case. The details of the calculation are given in appendix C.

Fig. 5. Schematic presentation of the condition, $1/\chi_1 \; 1/\chi_2 = c(1-c)(\tilde{J}_Q^{12})^2$, 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 $\tilde{J}_Q^{12}$.

Fig. 6. The calculated phase diagram for the TbEr alloy using the parameters in table 1. 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.

Fig. 7. As for Fig. 6. A possible tri-critical point is indicated in the ordered phase at which the transition between the helical and mixed phase may become of first order.

Fig. 8. The experimental data for the TbEr alloy from$^{6)}$.

Fig. 9. The calculated temperature dependence of the magnetization for dhcp Nd, using the parameters in table 1. 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. Due 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$^{23)}$.

Fig. 10. .The calculated paramagnetic phase separation lines compared with experiments. One fitting parameter, α, is used varying the strength of the inter alloy element exchange interaction $\tilde{J}_{12} = \alpha \cdot \sqrt{\tilde{J}_{11} \cdot \tilde{J}_{22}}$. The value of α is given on the figure.

Table Captions

Table 1. The parameters, in units of K, used in the calculation of the phase diagrams for the alloys. The exchange interaction between the different elements Tb-Er, Tb-Tm and Nd(hex)-Nd(cub) is written under the last element. For dhcp Nd we do not make a distinction between the ordering wave vectors Q_h and Q_c for the hexagonal and cubic sites.

Table CI. The coefficients for the Landau expansion for a singlet-singlet (with concentration c) and a singlet-doublet alloy. $A = \tilde{J}_{11}\tilde{J}_{22}-\tilde{J}_{12}^2$, $\beta = 1/kT$, $d' = \beta D'$, and $d = \beta D$. $\chi_{io}^{\alpha\alpha}$ and Z_i are the elemental susceptibilities and partition functions and $n = \exp(-d)$. The right 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 (C13). The information in the table can also be used to discuss alloys of two singlet-singlets or two singlet-doublets.

Table CII. Regions of stability for the ordered phase for an anisotropic magnetic alloy on the basis of the Landau expansion (C13). 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 CI.

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Table I

	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

Table CI

	Exact expressions	for small crystal fields
a_2	$\frac{1}{2}\tilde{J}_{22}/A - \chi^{zz}_{10}c$	$\frac{1}{2}\tilde{J}_{22}/A - \frac{\beta}{4}(1-\frac{1}{2}d'^2)c$
b_2	$\frac{1}{2}\tilde{J}_{11}/A - \chi^{zz}_{20}(1-c)$	$\frac{1}{2}\tilde{J}_{11}/A - \frac{\beta}{3}(1-\frac{2}{3}d)(1-c)$
c_2	$1/2\tilde{J}^{x}_{22} - \chi^{xx}_{20}(1-c)$	$1/2\tilde{J}^{x}_{22} - \frac{\beta}{3}(1+\frac{1}{3}d)(1-c)$
d_2	$-\frac{1}{2}\tilde{J}_{12}/A$	$-\frac{1}{2}\tilde{J}_{12}/A$
a_4	$c\frac{\beta^2}{d'^2}\left(\frac{1}{2}\chi^{zz}_{10} - \beta/Z^2_1\right)$	$\frac{\beta^3}{48}(1-\frac{4}{5}d'^2)c$
b_4	$(1-c)\frac{\beta^3}{12}\left(4n-1\right)/Z^2_2$	$\frac{\beta^3}{36}(1-2d)(1-c)$
c_4	$(1-c)\frac{\beta^2}{d^2}\left(2\chi^{xx}_{20} - \beta(5+n)/Z^2_2\right)$	$\frac{\beta^3}{36}(1+d)(1-c)$
d_4	$(1-c)\frac{\beta^2}{d^2}\left(\chi^{zz}_{20} - \chi^{xx}_{20} + 3\beta d/Z^2_2\right)$	$\frac{\beta^3}{36}(1-d)(1-c)$
a	$\frac{a_2}{d_2}\chi^{zz}_{10}\chi^{zz}_{20}\left(\frac{1}{\chi^{zz}_1}\frac{1}{\chi^{zz}_2} - \tilde{J}^2_{12}c(1-c)\right)/A$	
a'	c_2	
b	$2(\frac{a_2}{d_2})\left(b_4(\frac{a_2}{d_2})^3 + a_4(\frac{b_2}{d_2})\right)$	
b''	$2c_4$	
b'	$d_4(\frac{a_2}{d_2})^2$	

Table CII

Type	Magnetic order		Region	
	z^2	x^2		
no	0	0	$a>0$	$a'>0$
pure	$-a/b$	0	$a<0$	$a'>\frac{b'}{b}a$
pure	0	$-a'/b''$	$a>\frac{b'}{b''}a'$	$a'<0$
mixed	$\frac{a'b'-ab''}{bb''-b'^2}$	$\frac{ab'-a'b}{bb''-b'^2}$	$a<\frac{b'}{b''}a'$ for $bb''>b'^2$	$a'<\frac{b'}{b}a$

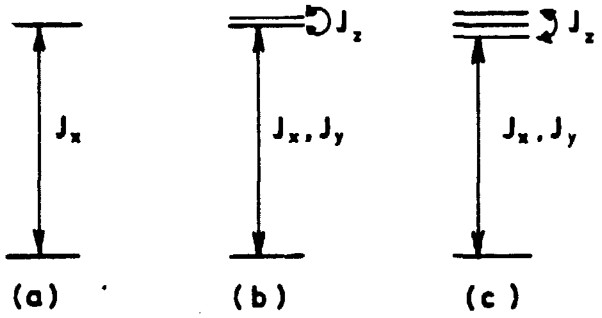


Fig. 1.

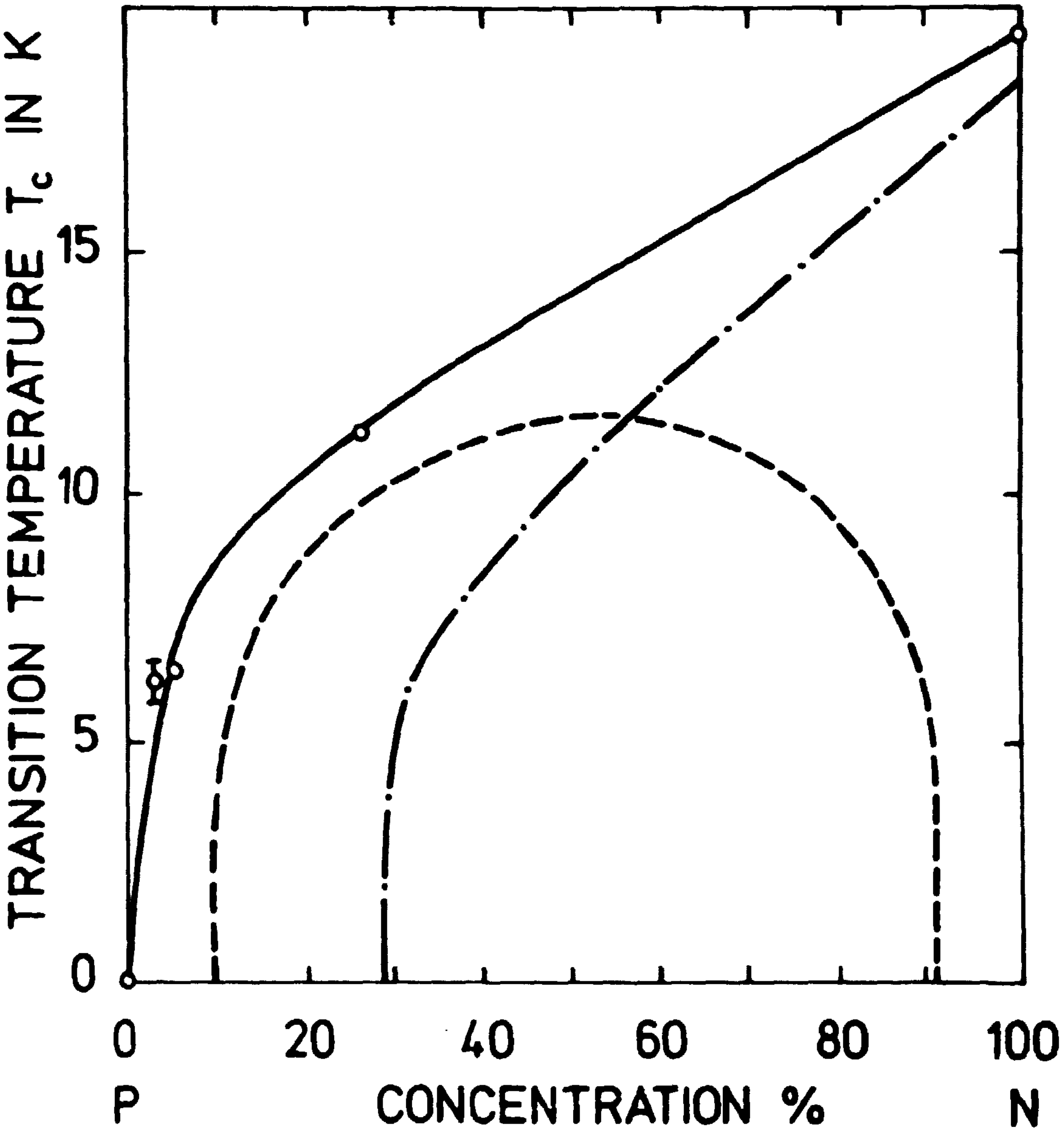

TRANSITION TEMPERATURE T_c IN K
0
5
10
15
0
20
40
60
80
100
P
CONCENTRATION %
N

Fig. 2.

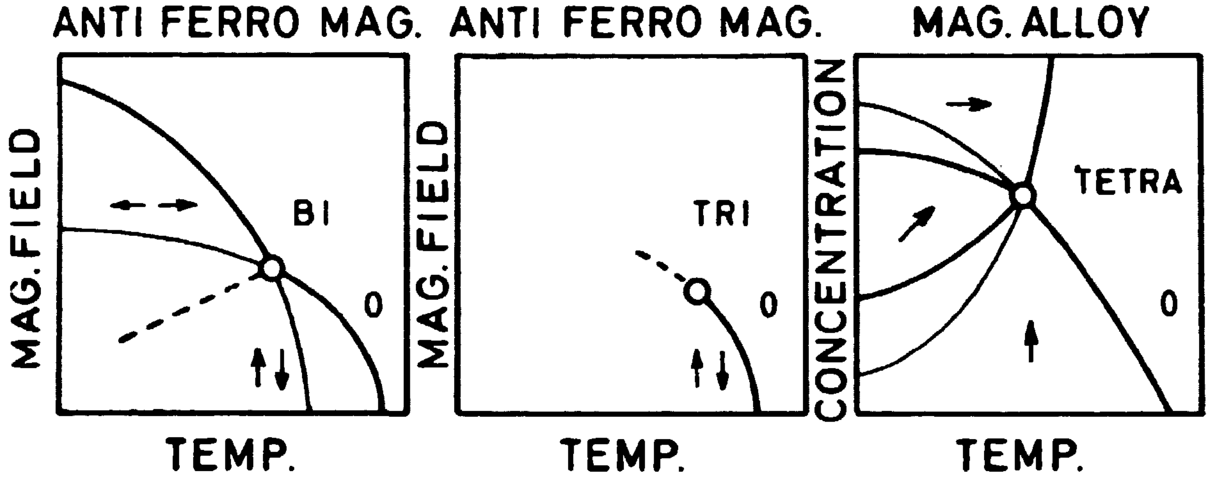
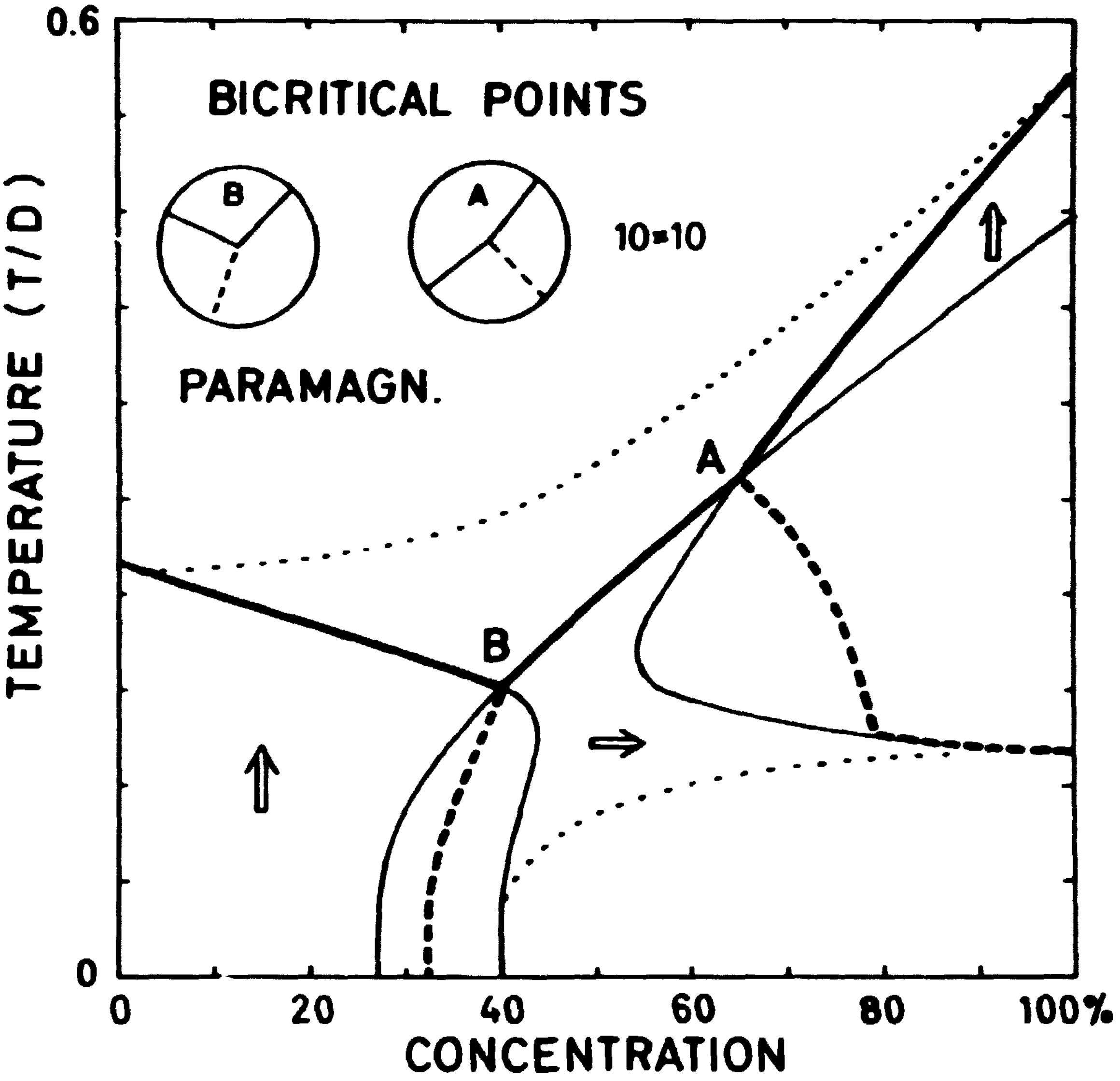

ANTI FERRO MAG.
ANTI FERRO MAG.
MAG. ALLOY
MAG. FIELD
BI
0
↑↓
TEMP.
MAG. FIELD
TRI
0
↑↓
TEMP.
CONCENTRATION
TETRA
0
TEMP.

Fig. 3.



BICRITICAL POINTS
B
A
10×10
PARAMAGN.
A
B
⇑
⇒
⇑
0.6
0
TEMPERATURE (T/D)
0
20
40
60
80
100%
CONCENTRATION

Fig. 4.

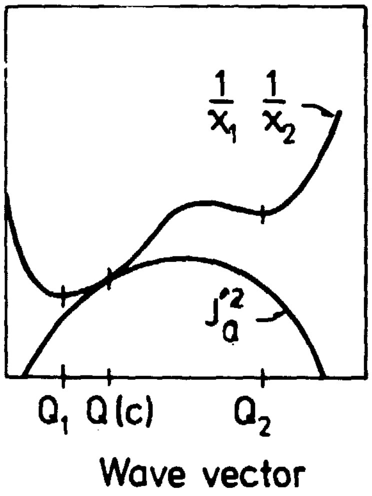


Fig. 5.

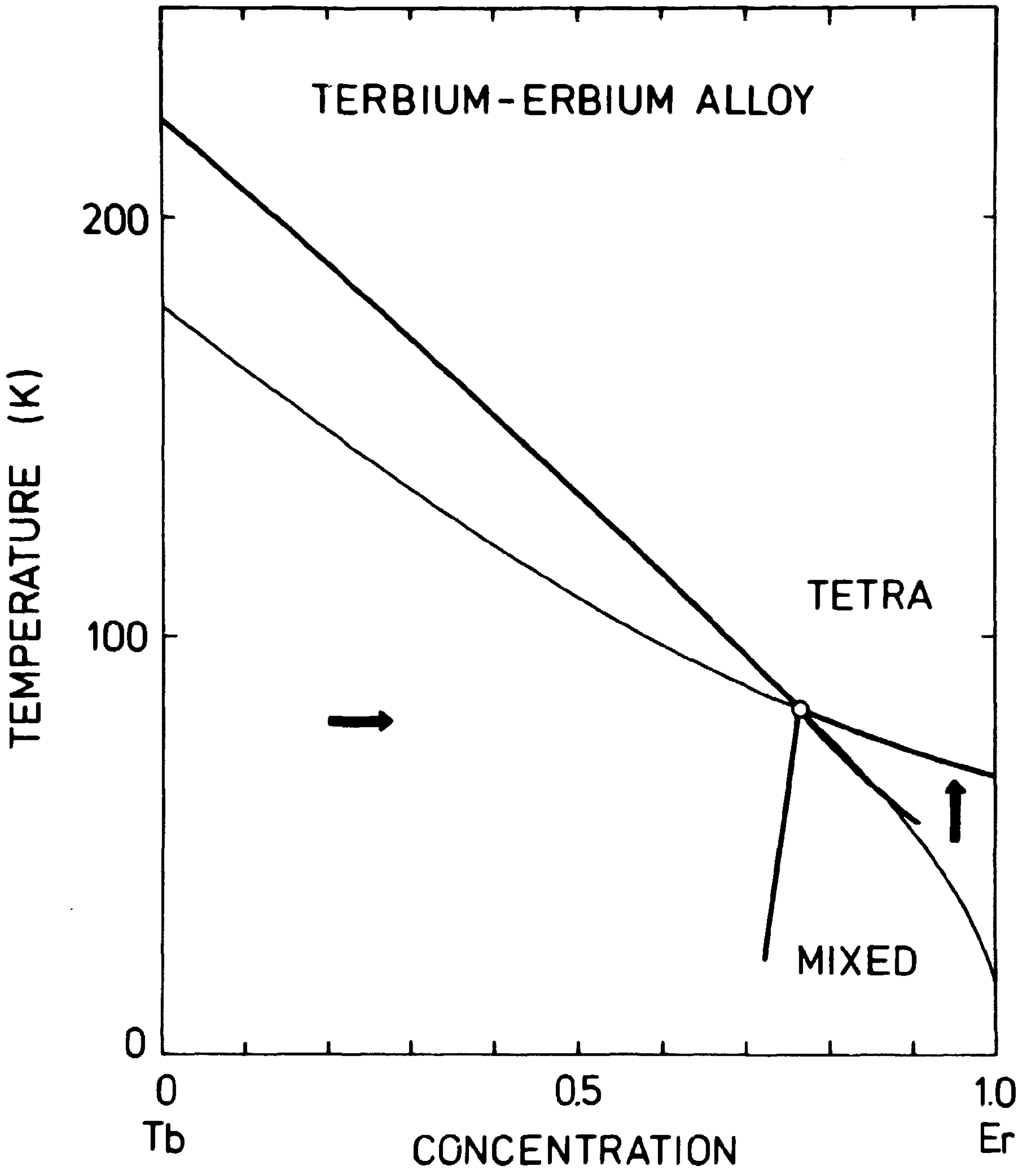
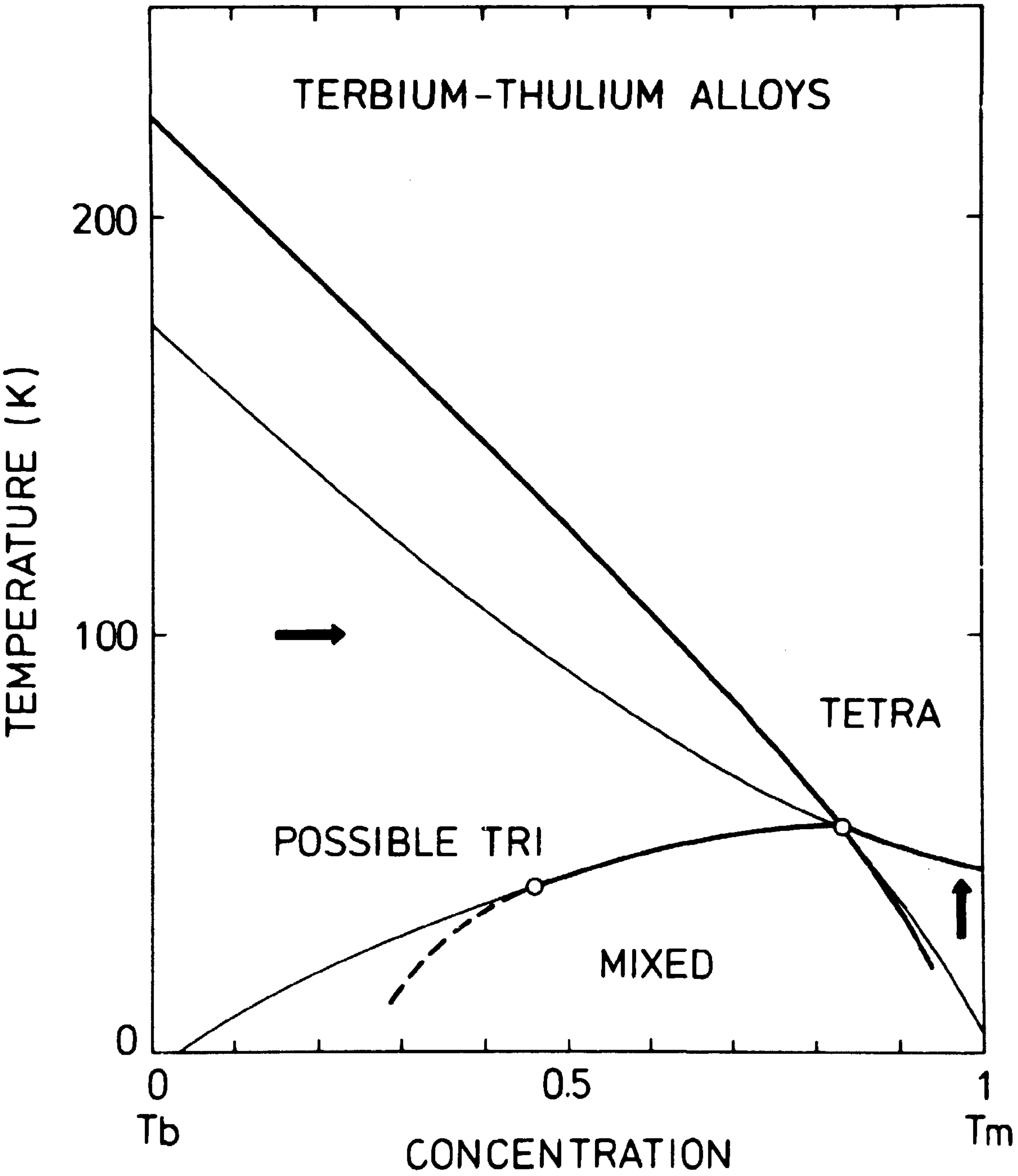

TERBIUM-ERBIUM ALLOY
TEMPERATURE (K)
200
100
0
TETRA
MIXED
0
Tb
0.5
1.0
Er
CONCENTRATION

Fig. 6.



TERBIUM-THULIUM ALLOYS
TEMPERATURE (K)
200
100
0
TETRA
POSSIBLE TRI
MIXED
0
Tb
0.5
1
Tm
CONCENTRATION

Fig. 7.

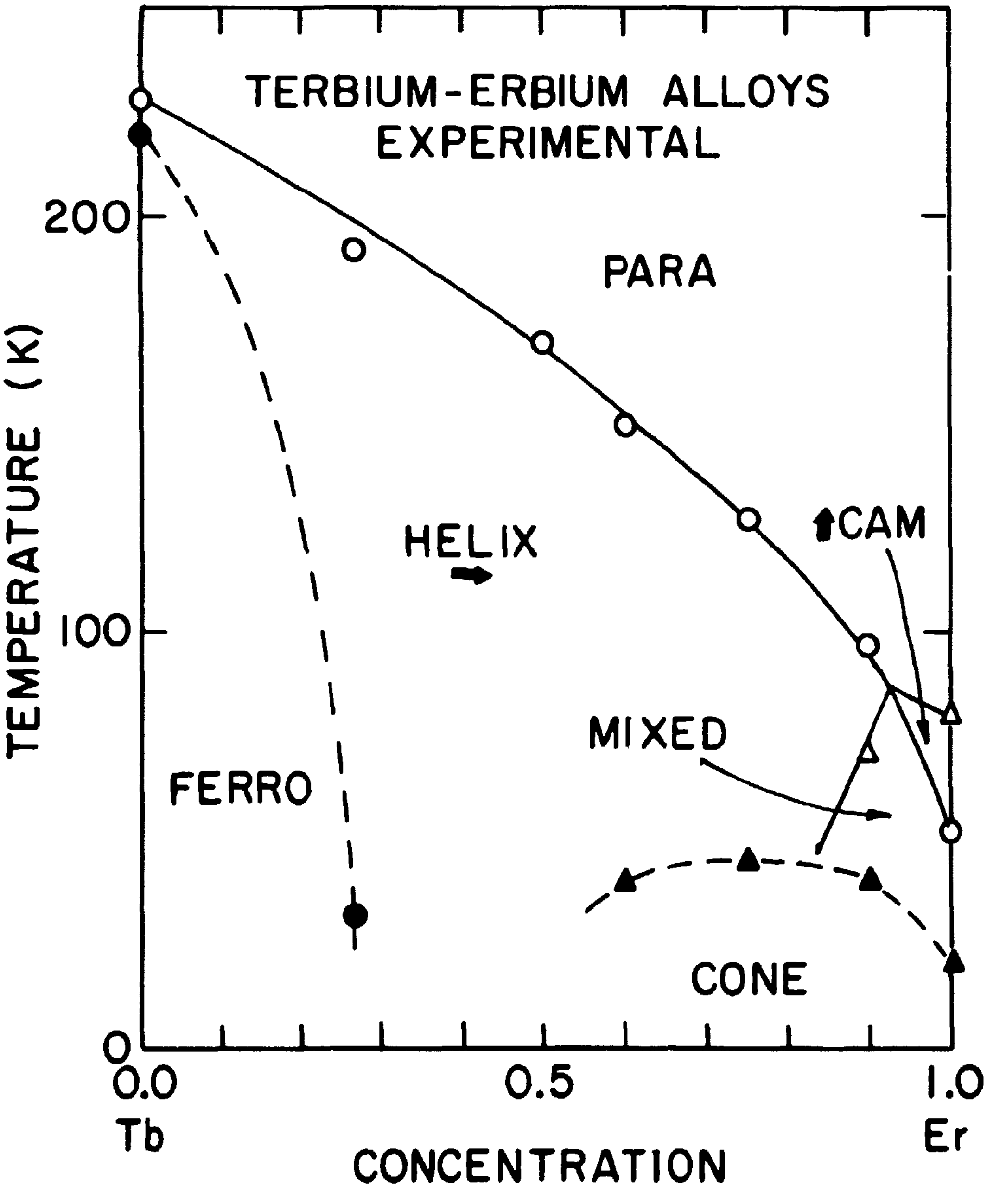
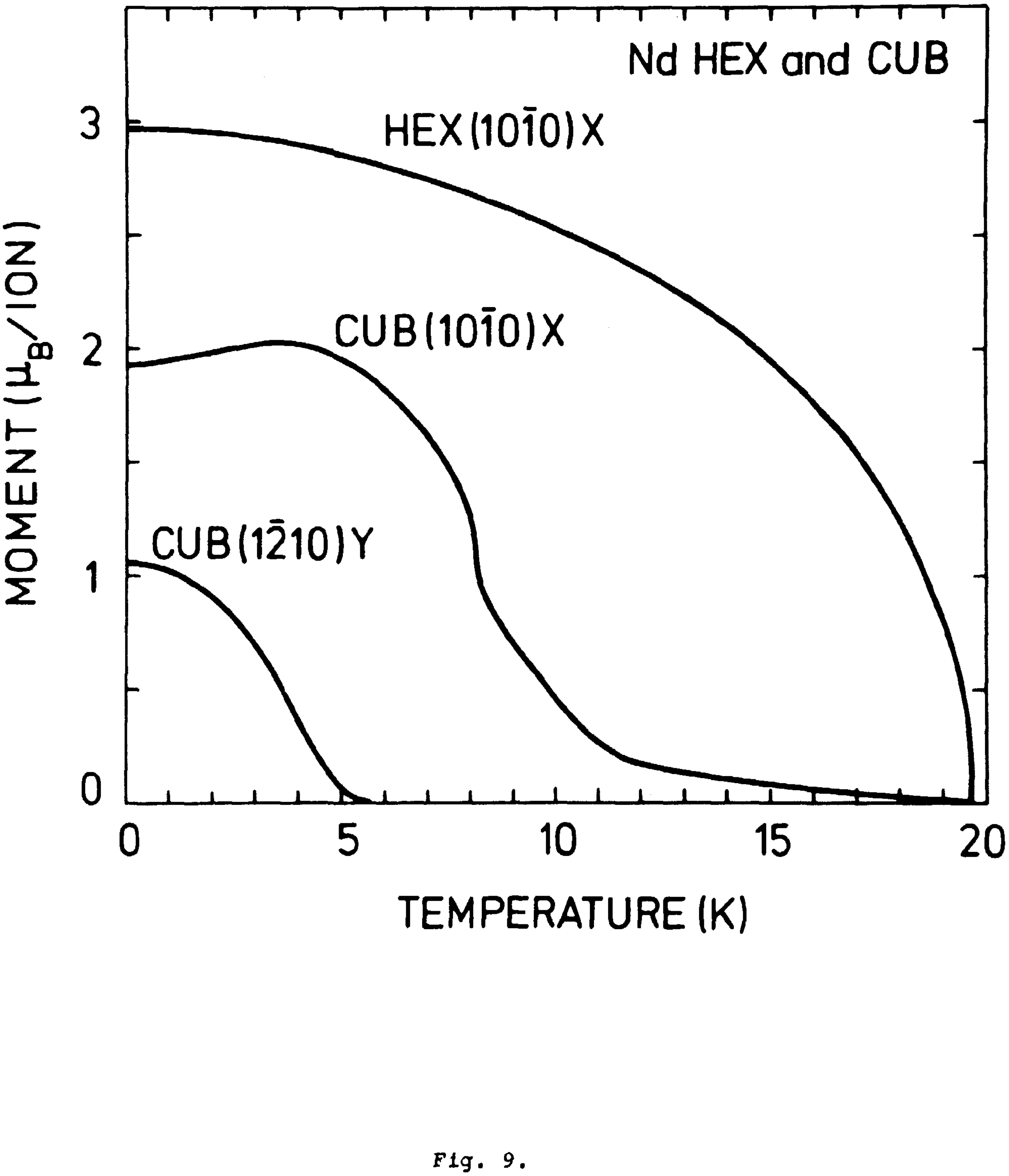

TERBIUM-ERBIUM ALLOYS
EXPERIMENTAL
PARA
HELIX
CAM
MIXED
FERRO
CONE
TEMPERATURE (K)
200
100
0
0.0
0.5
1.0
Tb
Er
CONCENTRATION

Fig. 3.



Nd HEX and CUB
HEX(10$\bar{1}$0)X
CUB(10$\bar{1}$0)X
CUB(1$\bar{2}$10)Y
MOMENT (μ_B/ION)
TEMPERATURE (K)
0
1
2
3
0
5
10
15
20

Fig. 9.

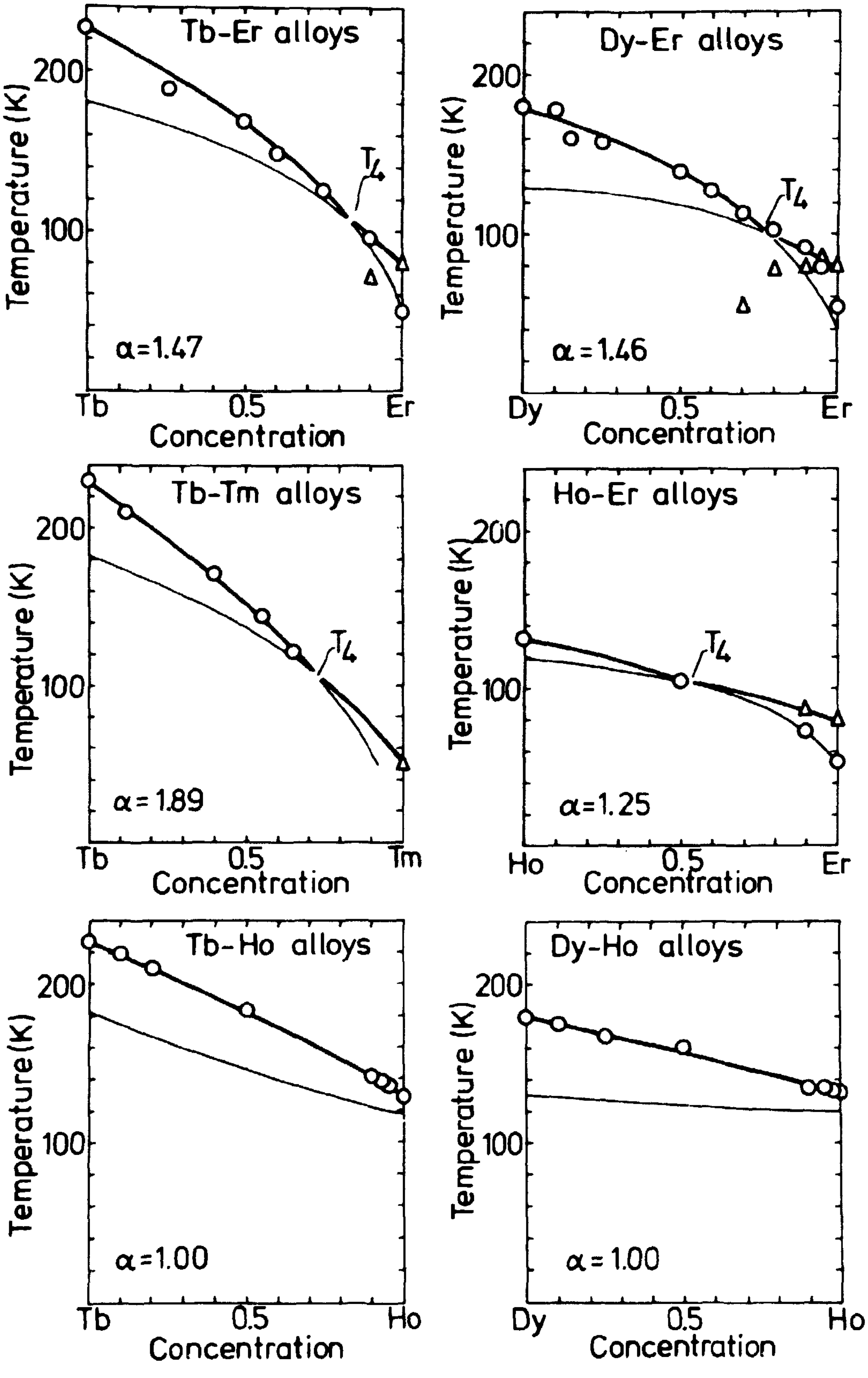

Tb-Er alloys
Temperature (K)
200
100
T4
α=1.47
Tb
0.5
Er
Concentration
Dy-Er alloys
Temperature (K)
200
100
T4
α=1.46
Dy
0.5
Er
Concentration
Tb-Tm alloys
Temperature (K)
200
100
T4
α=1.89
Tb
0.5
Tm
Concentration
Ho-Er alloys
Temperature (K)
200
100
T4
α=1.25
Ho
0.5
Er
Concentration
Tb-Ho alloys
Temperature (K)
200
100
α=1.00
Tb
0.5
Ho
Concentration
Dy-Ho alloys
Temperature (K)
200
100
α=1.00
Dy
0.5
Ho
Concentration

Fig. 10.