Correlation between Magnetic interactions and Magnetic structures in some Antiferromagnetic Rare Earth intermetallic compounds

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Chapter 3

Generalized molecular-field treatment of magnetic ordering in locally isotropic systems, applied to Gd-based compounds

3.1 Introduction

In the standard molecular-field treatment of the Heisenberg exchange interaction in systems consisting of two or more magnetic sublattices, the average spin moment at a certain lattice site is directly related to the magnetic moment of the sublattice to which that lattice site belongs (see e.g. the treatment of ferrimagnetism in ref. [1]). Consequently, in the derivation of the ordering temperature(s) the expected division in sublattices has to be assumed beforehand. However, in a more general approach, one considers the stability of e.g. the paramagnetic state with respect to any ordering mode. For periodic (crystalline) systems, in a natural way, the ordering modes correspond to the Fourier components of the magnetic moments. In general, only a single mode (i.e. Fourier component) will be involved in the magnetic ordering transition, and the derivation gives both the ordering temperature and the ordered structure itself (see e.g. refs. [2, 3]). Such a ‘generalized molecular-field treatment’ has been used to describe antiferromagnetic ordering of Gd moments in compounds of Gd with non-magnetic other atoms [4, 5]. In particular, it was argued that the behaviour described by the ‘classical’ antiferromagnetic two-sublattice model can be expected to occur for many other (helical) magnetic structures as well. Here, the model is worked out more explicitly, and some possible ways of extending the model are indicated. In particular, the interaction between localized (rare earth) moments and an itinerant electron band is taken into account, albeit in a phenomenological way.
First, the basic equations (equilibrium conditions and stability requirements) are derived, in a general way, valid for both amorphous and crystalline materials. Then, the approach is applied to systems with translational symmetry, and subsequently applied to Gd-moments interacting with an itinerant electron band.

### 3.2 The basic equations

For a set of $N_{\text{tot}}$ magnetic moments (spin operators $S_i$) the Heisenberg exchange hamiltonian is

$$\mathcal{H}_{\text{ex}} = - \sum_{ij} J_{ij} S_i S_j$$

(3.1a)

Here, the summation runs over all sites ($i, j = 1, 2, ..., N_{\text{tot}}$). In the molecular-field approximation this hamiltonian is reduced to a sum of ‘single-ion’ hamiltonians and correction terms

$$\mathcal{H}_{\text{ex}} = - \sum_{ij} 2J_{ij} <S_i> S_j + \sum_{ij} J_{ij} <S_i><S_j>$$

(3.1b)

For simplicity, we assume that the (thermal) average $<S_i>$ is related to the ‘local magnetic moment’ $\mu_i = -g_i <J_i> \mu_B$, where $g_i$ and $J_i$ are the Landé factor and the total angular momentum operator, respectively, of the atom at site $i$) by

$$<S_i> = -(g_i - 1) \mu_i / g_i \mu_B$$

(3.2)

The exchange energy can now be written as

$$E_{\text{ex}} = \langle \mathcal{H}_{\text{ex}} \rangle = - \sum_{ij} J_{ij} <S_i><S_j> = - \frac{1}{2} \sum_{ij} n_{ij} \mu_i \mu_j$$

(3.3)

with

$$n_{ij} = 2(g_i - 1)(g_j - 1)J_{ij} / (g_i g_j \mu_B^2)$$

(3.4)

From either eq. (3.1b) or eq. (3.3), we infer that a ‘molecular field’, $B_i^{\text{mol}} = \sum_j n_{ij} \mu_j$, acts on the moment $\mu_i$. In fact, we assume that $\mu_i$ is the (local) response to the local effective field $B_i^{\text{eff}} = B_i^{\text{mol}} + B_i^{\text{app}}$, where $B_i^{\text{app}}$ is the applied field at site $i$. Then, for the locally isotropic systems under consideration, $\mu_i$ and $B_i^{\text{eff}}$ should point in the same direction, so there must exist positive parameters $a_i$, such that $a_i \mu_i = B_i^{\text{eff}}$. Alternatively, one may state that, in equilibrium, the local field $B_i^{\text{eff}}$ should equal $V_c F_i (T, \mu_i)$, the gradient of the (temperature dependent) ‘local free energy’. Evidently, the parameters $a_i$ are not constant, but in general
depend on the value of $\mathbf{\mu}_i$ (and thus on $\mathbf{B}_i^{\text{eff}}$) and on the temperature $T$. Anyway, we find as our ‘basic equations’ the equilibrium conditions:

$$a_i \mathbf{\mu}_i - \sum_j n_{ij} \mathbf{\mu}_j = B_i^{\text{app}}$$

(3.5)

In fact, eq. 3.5 represents three sets of $N_{\text{tot}}$ equations, one set for each of the components in the $x$-, $y$-, or $z$-direction. The three sets have the same coefficient matrix, $a_i \delta_{ij} - n_{ij}$, and are (indirectly) coupled because of the relation $a_i \mathbf{\mu}_i = \nabla_{\mathbf{\mu}} F_i(T, \mathbf{\mu}_i)$. The matrix is real and symmetric, and consequently has real eigenvalues. The eigenvectors can be chosen to be real. Stability requires that the eigenvalues are non-negative, in general positive. Following the reasoning of Landau’s theory of second-order phase transitions, we may expect that (in zero applied field) at a certain temperature one of the eigenvalues changes sign. The resulting instability leads to a (change of) order. The ordering mode is determined by the eigenvector corresponding to the vanishing eigenvalue. Although the transitions described in this way are of second order, in practice, of course, first-order transitions may occur, in particular in case other interactions (e.g., magnetostriction) must be taken into account.

The presentation given above is valid for any set of coupled ‘local moments’, so actually for both amorphous and crystalline materials. Moreover, disregarding the rotational degeneracy (which in the usual way can be circumvented by application of infinitesimal bias fields) in first instance a collinear ordering structure is expected to be formed, with in general an amplitude modulated spin structure. In second instance, this ordered structure may appear not to be stable, and more intricate, non-collinear structures may result. In fact, we shall show in the next sections that in simple systems with translational symmetry so-called ‘helical’ equal moment, structures are preferred.

In order to be more specific, we consider now a set of R-atoms ($R =$ lanthanide, say, Gd) in the paramagnetic regime, at low fields. The ‘local free energy’ of a lanthanide moment $\mathbf{\mu}$ can simply be approximated by $F(T, \mathbf{\mu}) = \frac{1}{2}(T/C_R)\mu^2$, where $C_R$ is the appropriate Curie constant. Hence, we have $a_i = T/C_R$ for any atom $i$. The exchange energy (eq. 3.3) can be written in diagonalized form as $E_{\text{ex}} = -\frac{1}{2} \sum_q \mu_q \lambda_q$, where $\mu_q$ is the amplitude of the mode (eigenvector) $q$. The eigenvalues of the coefficient matrix are $\lambda_q = (T/C_R - n_q)$. The critical temperature is $T_{\text{cm}} = C_R n_Q$, where $Q$ designates the lowest eigenvalue $\lambda_Q$, i.e. the highest eigenvalue $n_Q$ of the exchange energy. The response to an applied homogeneous field $B$ is collinear, each mode responding with an amplitude $B c_q (T/C_R - n_q)$, where $c_q$ is the appropriate projection coefficient. In case, like in systems with translational symmetry, the
overall interaction does not depend on the site \( i \), i.e. \( \sum_i n_{ij} = n_{ij} \), the homogeneous mode is an eigenvector, with eigenvalue \( \lambda_0 = (T/C_R - n_{ij}) \), and the response to the applied homogeneous field is now simply \( C_R B/(T - \theta_p) \), where \( \theta_p \) \( = C_R n_0 \) is the (paramagnetic or asymptotic) Curie temperature.

### 3.3 RT-models (translational symmetry)

In this section we apply the `generalized` approach to systems with translational symmetry. For simplicity, we consider a Bravais lattice containing \( N \) primitive unit cells, with a basis consisting of one R atom (say, Gd) and one T unit (transition metal, representing the total moment of the itinerant electrons inside the cell).

The magnetic Fourier components are defined by

\[
m_X(q) = (1/N) \sum_R \mu_X(R) e^{-i q R}
\]  

(3.6a)

\[
\mu_X(R) = \sum_q m_X(q) e^{i q R} \quad [X = R, T]
\]  

(3.6b)

Since the magnetic moments are only defined at the Bravais lattice sites \( R \), the wave vector \( q \) is confined to the first Brillouin zone. The reality of the magnetic moments \( \mu_X(R) \) in eq. 3.6b requires \( m_X(q)^* = m_X(-q) \), which is obviously the case (see eq. 3.6a). Notice that \( m_X(q) \) is real for the special points \( q = 0 \) (chosen as zone center) and \( q = K/2 \neq 0 \), where \( K \) is a reciprocal-lattice vector (and thus \( K/2 \) is on the Brillouin zone boundary).

The exchange energy (eq. 3.3) can now be expressed in the Fourier components:

\[
E_{ex} = -\frac{1}{2} N \sum_q \sum_{X,Y} n_{X,Y} m_X(q) m_Y(-q) \quad [X,Y = R,T]
\]  

(3.7a)

\[
n_{X,Y} = \sum_R n_{X0,YR} e^{-i q R}
\]  

(3.7b)

here, \( n_{X0,YR} = n_{ij} \) (see eq. 3.4) for \( i = X0 \), the X atom in cell \( 0 \), and \( j = YR \), the Y-atom in cell \( R \). Since we consider only Bravais lattices with inversion symmetry, \( n_{X,Y}(q) \) may be assumed to be real. As expected, the energy expression is `almost` diagonalized by the Fourier transform. Furthermore, in case we restrict ourselves to the cases where \( a_i = a_R \) for any R-atom \( i \), and \( a_i = a_T \) for any T-atom \( i \), the basic equations (isotropic case) can be transformed to

\[
[a_R-n_{RR}(q)] m_R(q) - n_{RT}(q) m_T(q) = B^{app}(q)
\]  

(3.8a)
The Fourier components of the applied field are given by $B_{\text{app}}(q) = (1/N) \sum_R B_R^{\text{app}} e^{-i q R}$, where $B_R^{\text{app}}$ is the value of the applied field in cell $R$.

For each direction $(x, y, z)$, the $2N$ coupled equations (see eq. 3.5, for the $N_{\text{tot}} = 2N$ atoms) are reduced to $N$ separate pairs of equations (eqs. 3.8a and 3.8b, for each of the $N$ vectors $q$ in the first Brillouin zone). Again following the reasoning in the preceding section, we find the following stability criteria:

$$[a_T - n_{TT}(q)] > 0 \quad (3.9a)$$

$$[a_R - n_{RR}(q)] > 0 \quad (3.9b)$$

$$\det(q) = [a_R - n_{RR}(q)][a_T - n_{TT}(q)] - n_{RT}(q)^2 > 0 \quad (3.9c)$$

$\det(q)$ is the determinant of the coefficient matrix of the pair of equations 3.8.

In the preceding section it was stated that the eigenvectors could be chosen to be real. In the present case, we introduce the real modes by combining the (complex: $q \neq 0, K/2, K$: reciprocal lattice vector) modes $m_X(q)$ and $m_X(-q)$ as follows:

$$\mu_{X,q}(q) = m_X(q) + m_X(-q); \quad \mu_{X,q}(q) = -i(m_X(q) - m_X(-q)) \quad (3.10a)$$

$$m_X(q) = \frac{1}{2}(\mu_{X,q}(q) - i \mu_{X,q}(q)); \quad m_X(-q) = \frac{1}{2}(\mu_{X,q}(q) + i \mu_{X,q}(q)) \quad (3.10b)$$

For the special points $q = 0$ and $q = K/2$ we have simply $\mu_{X,q}(q) = m_X(q), \mu_{X,q}(q) = 0$ (or rather not defined). In this notation, we have

$$\mu_{X,q}(q) = (1/N) \sum_R \mu_X(R_j) \cos(q R_j) \quad (3.11a)$$

$$\mu_{X.q}(q) = (1/N) \sum_R \mu_X(R_j) \sin(q R_j) \quad (3.11b)$$

$$\mu_X(R_j) = \sum_q \{\mu_{X,q}(q) \cos(q R_j) + \mu_{X,q}(q) \sin(q R_j)\} \quad (3.11c)$$

The basic equations are now (recall: all $n_{RT}(q)$ are real)

$$[a_R - n_{RR}(q')] \mu_{R,q}(q') - n_{RT}(q') \mu_{T,q}(q') = B_{\text{app}}(q') \quad (3.12a)$$

$$-n_{RT}(q') \mu_{R,c} + [a_T - n_{TT}(q')] \mu_{T,c}(q') = B_{c,\text{app}}(q') \quad (3.12b)$$

$$[a_R - n_{RR}(q')] \mu_{R,c}(q') - n_{RT}(q') \mu_{T,c}(q') = B_{c,\text{app}}(q') \quad [q' \neq 0, K/2] \quad (3.12c)$$
Here, \( q' \) may have the values 0, \( K/2 \) and, of the other \( q \)-values, only one of each combination \( q, -q \). \( B_c^{\text{app}}(q') \) and \( B_T^{\text{app}}(q') \) are the appropriate Fourier components of the applied field, in this notation. In most cases, the right hand sides do vanish, and the vectors \( \mu_{R,c}(q') \) and \( \mu_{T,c}(q') \) are collinear, as well as the vectors \( \mu_{R,i}(q') \) and \( \mu_{T,i}(q') \). Notice that the total number of equations is still the same (2N for each direction). Moreover, without loss of generality, we may restrict the considerations to ‘modes’ with orthogonal vectors \( \mu_{X,c} \) and \( \mu_{X,s} \). Other modes are identical, apart from phase shifts and/or rotations.

An important special class of ‘modes’ is formed by the cases where the amplitudes \( \mu_{X,c} \) and \( \mu_{X,s} \) are equal: these are the (single) ‘equal moment’ (EM) modes. In a limited number of cases (see Tung’s thesis [4] for more details), a few single EM-modes can be combined to form a more general EM-structure.

In the present approach, EM-structures are of particular interest. Indeed, the fact that all atoms of the same kind (X) have equal moments does imply that they must have equal parameters \( a_i (= a_X) \). Above, we have stipulated that this is a necessary condition for the simplification by Fourier transformation. Notice also, that this condition is always fulfilled in the paramagnetic regime, where \( a_X = T/C_X \).

At the ordering temperature, an ordering mode with \( q = Q \) will be formed (see above). In the absence of other interactions (no crystal field, no magnetostriction and so on), the preferred ordering structure will be determined by the higher order terms in the local free energies, e.g. terms like \( \frac{1}{4} b_X |\mu_X(R)|^4 \) and so on. In fact, for small ordering parameters (i.e. just below the transition temperature), minimization of the free energy (restricted to the indicated lower order terms) leads directly to the conclusion that \( |\mu_{X,c}(Q)| \) equals \( |\mu_{X,s}(Q)| \). In other words, ‘equal moment’ modes are preferred in these ‘locally isotropic’ systems.

We now consider the combination of the homogeneous mode \( q = 0 \), induced by an applied homogeneous field \( B \), and the ‘ordering mode’ \( q = Q \). A single EM-mode is completely determined by its wave vector \( q \) and the vectors \( \mu_{R,i}(q) \) and \( \mu_{T,i}(q) \). To simplify the notation we may drop the index “c” and refer to these vectors as \( \mu_R(q) \) and \( \mu_T(q) \), respectively. The 0-mode vectors \( \mu_R(0) \) and \( \mu_T(0) \) are collinear with the applied field \( B \), which we choose to point in the \( z \)-direction. Then, the magnetic vectors of the ordering mode should remain (rotate) in the \( xy \)-plane in order to have an EM-structure still. So,
actually helical waves are formed. Moreover, for a determination of the properties of this system, we need only the equilibrium conditions for the two relevant modes, \textit{i.e.}

\begin{equation}
[a_R - n_{RR}(Q)] \mu_R(Q) - n_{RT}(Q) \mu_T(Q) = 0
\end{equation}

\begin{equation}
-n_{RT}(Q) \mu_R(Q) + [a_T - n_{TT}(Q)] \mu_T(Q) = 0
\end{equation}

\begin{equation}
[a_R - n_{RR}(\theta)] \mu_R(\theta) - n_{RT}(\theta) \mu_T(\theta) = B
\end{equation}

\begin{equation}
-n_{RT}(\theta) \mu_R(\theta) + [a_T - n_{TT}(\theta)] \mu_T(\theta) = B
\end{equation}

In eqs. 3.13a and 3.13b, $\mu_R(Q)$ and $\mu_T(Q)$ represent the amplitudes of the R- and T-components of the ordering wave (non-zero in case $\det(Q) = 0$). In the present, simplified, situation, we identify $\mu_R(Q)$ and $\mu_T(Q)$ with the corresponding $x$-components of the moments in the cell $R = 0$.

In eqs. 3.14a and 3.14b, we consider first the case $\det(\theta) > 0$. Then, in an analogous way, $\mu_R(\theta)$ and $\mu_T(\theta)$ are identified with the corresponding $z$-components of the moments in cell $R = 0$ ($B$ is taken to point in the $z$-direction; the components are non-zero in case $B > 0$). In case $\det(\theta) = 0$ for non-zero $B$, the two equations 3.14a and 3.14b must be identical, so we have $[a_R - n_{RR}(\theta)] = -n_{RT}(\theta) = [a_T - n_{TT}(\theta)] > 0$. With these fixed values of $a_R$ and $a_T$, we may exclude the co-existence with a $Q$-mode ($\det(Q) > 0$, apart from, say, incidental degeneracy). Notice also, that for both components, R and T, the condition $a_X \mu_X = \nabla_\mu F_X(T, \mu_X)$ should have a stable solution, like in the case of local moments of fixed magnitude. Then, we find the well-known linear relationship for the familiar two-sublattice RT-model (with antiferromagnetic RT-coupling, $n_{RT}(\theta) < 0$):

\[ M = \mu_R(\theta) + \mu_T(\theta) = B |n_{RT}(\theta)|. \]

This ‘zero-mode’ bending process must not be confused with the similar ‘bending’ process in the ordered region, where the $Q$-mode is gradually suppressed by the increasing applied fields, although eventually the same (paramagnetic) situation results, where the moments are forced to be parallel.

In this chapter we focus attention on the co-existence of a helical (ordering) mode $Q$ and the induced $\theta$ mode. So, we shall ignore this non-collinear $\theta$-mode behavior in the following, although in the actual computing program the occurrence of this possibility is duly checked. In short, we are left with two pairs of equations, one pair describing the (ratio of the) $x$-components, the other pair yielding the $z$-components. The pairs of equations are implicitly coupled, because $a_R$ depends on $\mu_R^2 \left[ = \mu_{R,x}^2 + \mu_{R,z}^2 \right]$, and $a_T$
depends on $\mu_T^2 \equiv \mu_{T,\perp}^2 + \mu_{T,\parallel}^2$. In the next section, this situation is worked out in more detail by giving explicit expressions for $a_R$ and $a_T$. In fig. 3.1 we show a possible way in which the R and T moments are forced to become parallel eventually by increasing the applied field, for different temperatures.

![Diagram showing magnetic moments in a weakly interacting R-T system](image)

**Figure 3.1.** Display of magnetic moments in a weakly interacting R-T system in different applied magnetic fields for different temperatures. For the chosen parameters, we have $T_N = 13$ K.

The antiferromagnetic RT-interaction is arbitrarily chosen to be rather weak in order to demonstrate (exaggerate) the non-collinear orientation of the moments. Recall that this pattern must be imagined to rotate with the wave vector $\mathbf{Q}$ through the lattice, and that there is no relation between the direction of the moments (as determined by the applied-field direction) and the direction of the wave vector.

Before proceeding, however, we want to show the relationship between the formalism presented above and some other, well-known, formalisms to describe ordered systems consisting of one kind of spins. As mentioned in the introduction, in the standard formalism the division in sublattices has to be indicated at the start. Here, we restrict the discussion to the standard two-sublattice model for antiferromagnetic order in a system of R-atoms with translational symmetry. In our formalism, we start by ignoring the coupling to the itinerant band (e.g., by assuming $a_T$ to be infinitely large), thus reducing our
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basic equations to \([a_R - n_{RR}(Q)] \mu_{R,R}(Q) = 0\) and \([a_R - n_{RR}(0)] \mu_{R}(0) = B\). Moreover, the standard antiferromagnetic order corresponds to \(Q = K/2\), leading to the formation of the two sublattices, with magnetic moments given by (dropping the subscript R):

\[
\begin{align*}
\mu_1 &= [\mu(Q) + \mu(0)]; \\
\mu_2 &= [-\mu(Q) + \mu(0)];
\end{align*}
\]

In the ordered region, we have \(a_R = n(Q)\), and thus \(\mu(0) = B/n(Q) - n(0)\). In the paramagnetic (or 'forced parallel') structure \(\mu(Q)\) vanishes and \(\mu(0)\) can be calculated self-consistently using the Weiss field approach (Brillouin function) [6]. In the standard two-sublattice model, the molecular field (at subl. 1) can be written as \(n_{11}(\frac{1}{2}\mu_1) + n_{12}(\frac{1}{2}\mu_2)\), the factor \(\frac{1}{2}\) reducing the actual local moment to the 'magnetization', i.e. the moment per Gd. Comparison with \(n(Q)\mu(Q) + n(0)\mu(0) = [n(Q) + n(0)]\mu_1/2 + [-n(Q) + n(0)]\mu_2/2\), leads to

\[
\begin{align*}
n_{11} &= [n(Q) + n(0)]; \\
n_{12} &= -[n(Q) - n(0)] < 0.
\end{align*}
\]

The 'equilibrium conditions' in the standard two-sublattice model are

\[
\begin{align*}
[a - \frac{1}{2} n_{11}] \, \mu_1 - \frac{1}{2} n_{12} \, \mu_2 &= B \quad (3.15a) \\
- \frac{1}{2} n_{12} \, \mu_1 + [a - \frac{1}{2} n_{11}] \, \mu_2 &= B \quad (3.15b)
\end{align*}
\]

A non-collinear solution (order) is only possible (again) in case these equations are identical, i.e. \(a - \frac{1}{2} n_{11} = \frac{1}{2} n_{12} (> 0)\), yielding the familiar expression

\[\mu = \frac{1}{2} (\mu_1 + \mu_2) = B/\{n_{11} - n_{12}\} \quad \text{per Gd}\]

in the ordered state \((T < T_N)\), evidently coinciding with the expression given above, \(\mu(0) = B/n(Q) - n(0))\).

The critical temperature, \(T_N\), can be found by putting \(a = T/C\) (for vanishing field \(B\)), and then solving \(\text{det(eq. 3.15)} = 0\), leading to \(T_N = \frac{1}{2} C \{ n_{11} - n_{12} \} = C n(Q)\), in accordance with our earlier result. In an analogous way, the asymptotic Curie temperature can be expressed as \(\theta = \frac{1}{2} C \{ n_{11} + n_{12} \} = C n(0)\).

It is illustrative to view this two-sublattice model in still another, equivalent, way, i.e. by assuming, in our approach with two atoms per cell, that the T-atom behaves as or actually is an R atom. In the literature, such models have been applied extensively. In our formalism, these two-sublattice models must be described as an ordering zero mode \((q = 0)\). Only eqs. 3.14a and 3.14b survive. In case the two species of atoms are identical these equations are simplified to the eqs. 3.15a and 3.15b.
The present description shows straightforwardly a way to determine the moments precisely, namely from the self-consistent calculation of the $a_R$ and $a_T$ values (as worked out in the next section).

### 3.4 Calculation of magnetization for Gd moments interacting with (T-)band electrons

In this section we consider again the simplified description of a RT Bravais lattice given in the preceding section. The R-atoms taken to be Gd atoms in order to justify the absence of crystal-field effects. Now, the local response of the R-atom at site $j$ is assumed to be described by the hamiltonian

$$\mathcal{H}_j = \mathcal{H}_{j,\text{ex}} - B^{\text{eff}} = \mathcal{H}_j^{\text{eff}} = B^{\text{eff}}_j = \mathcal{H}_j^{\text{eff}} = B^{\text{eff}}_j \mathcal{H}_j$$

(3.16)

In fact, for the EM-modes under consideration, it suffices to treat the cell $R = 0$, only.

The local response of the band (represented by the T-atom in the preceding section), we assume the 'Arrot plot' relation (for the 'local' band) [7]:

$$a_T(m, T) = a_{0T} + (\frac{1}{2} a_{2T} + ...) T^2 + (b_{0T} + ...) m^2 + c_T m^4 + d_T m^6 \ldots = B^{\text{eff}}_T m$$

(3.17)

$m$ is the local (T-)moment: $m^2 = \mu_T(\theta)^2 + \mu_T(Q)^2$, $\mu_T(\theta)$ being the (induced) $z$-component and $\mu_T(Q)$ the $x$-component (see preceding section). The $T^2$ dependence, for an itinerant band ascribed to Stoner excitations as mentioned in section 1.2, is adopted for the lowest order co-efficient only (in the present version of the calculating program).

The calculation is performed self-consistently, roughly in the following way. First, the existence of an ordering $Q$-mode is ignored, and, for a given initial set $\{a_R, a_T\}$ eqs. 3.14a and 3.14b are solved. Then, the effective field in eq. 3.16 is determined as well as $m$ in eq. 3.17. Application of quantummechanics (i.e. resulting in the Brillouin function, of course) yields then a new value of $a_R$, whereas eq. 3.17 yields a new value for $a_T$, and so on. For the eventually resulting set $\{a_R, a_T\}$ det$(Q)$ is calculated. In case det$(Q) < 0$, a new $a_R$ value is taken, such that det$(Q) = 0$. Application of eqs. 3.14a and 3.14b now yields the $z$-components. Subsequently, eqs. 3.13a and 3.13b yield the $x$-components, and, again, new values for $\{a_R, a_T\}$ can be determined, and so on.

Obviously, as presented here, the model may have an impressively large number of fitting parameters. Some of these parameters, however, are intended for future applications or to
anticipate generalizations. For instance, the higher order terms (the 4\textsuperscript{th} and the 6\textsuperscript{th}, etc.) in eq. 3.17 are necessary to cover cases where the itinerant band would show metamagnetic and weakly ferromagnetic behavior. In the present application, we take $a_{0T} > 0$, and $c_{T} = d_{T} = 0$. Moreover, the molecular-field parameter $n_{TT}(\theta)$ can be absorbed into $a_{0T}$, in case no explicit band calculations are performed.

Although also $g_{\text{Gd}}$ is considered to be a fitting parameter (in order to account for intra-atomic 4f-5d polarization), in the present application we take $g_{\text{Gd}} = 2$.

In order to reduce the number of ‘free’ parameters further, we use starting parameters derived from experiments:

- Since $T_{N}$ can be determined accurately from specific-heat data, $n_{RR}(Q)$ is calculated (for given $n_{RT}(Q)$, $a_{0T}$, $a_{2T}$ and $n_{TT}(Q)$) from: $\det(Q) = 0$ at $T = T_{N}$ (paramagnetic, $B^{\text{app}} = 0$).
- At low temperatures, the R-moments can be saturated in high fields. Then, the variation of the (experimentally determined) total magnetic moment with applied field determines $a_{0T} - n_{TT}(\theta)$ accurately enough, and also may indicate a value for the coefficient $b_{T}$.
- Moreover, from this approximation to the high-field magnetization data, one can derive the field (say $B^{\text{app}} = B^{\text{sat}}$) at which the molecular field acting on the itinerant band is compensated by the applied field, \textit{i.e.} $M_{T} = 0$, $M = M_{R}^{\text{sat}}$, so $n_{RT}(\theta) = B^{\text{sat}}/M_{R}^{\text{sat}}$.
- In the present application, the parameter $a_{2T}$ is only relevant at high temperatures, and is determined by ‘fine tuning’ of the reciprocal susceptibility in the paramagnetic region.
- In practice, the parameter $n_{RR}(\theta)$ can be determined rather well by fitting to the initial part of the low-temperature magnetization curve (say, the ‘bending’ part in the ordered region).

Remaining ‘free parameters’ are $n_{RT}(Q)$ and $n_{TT}(Q)$. In practice, reasonable agreement between calculated curves and experimental data can be obtained in a wide range of values for these parameters (\textit{i.e.} for ‘sets’ $\{n_{RR}(\theta), n_{RR}(Q), n_{RT}(Q), n_{TT}(Q)\}$). This feature should be taken into account when comparing the fitting results for a series of compounds, for instance. So one may choose vanishing values for $n_{RT}(Q)$ in a comparison of $n_{RR}(Q)$ values, or the other way round.

Instead of demonstrating here the calculations of the magnetic moment contributions in the RT coupled systems as functions of the applied magnetic field and temperature, the reader is referred to the fitting results obtained for the magnetic data of various Gd compounds, which are presented in chapters 4 and 5.
3.5 Free-energy considerations: calculation of the specific heat

Our model can be regarded as a member of the big family of models, which describe the system under consideration as an assembly of coupled ‘local units’. In principle, the properties of the local units are calculated exactly, either by performing a quantum-mechanical calculation or by assuming a phenomenological analytic expression. The coupling between the units is treated in some approximation, in our case in the molecular-field approach. In these models, the total free energy and, in particular, the specific heat should be calculated with some care, in order to avoid double counting, and so on. In this section, we address this problem in its simplest form, by assuming the presence of only two, magnetic, ‘units’, characterized by their magnetic moments $M_1$ and $M_2$, placed in an external field $B$. In order to analyze the problem, we assume that the free energy of each local entity can be defined as a function of its magnetic moment (e.g. by using restricted ensembles). Incorporating explicitly the volume $V$ (representing any strain) and the temperature $T$, the local free energy of unit 1 is written as $F_1(T; V, M_1)$, and so on. The total Gibbs free energy $G(T, P, B)$ is now written as a function $f(T, P, B; V, M_1, M_2)$, where it is understood that the variables after the semicolon, i.e. $V, M_1$ and $M_2$, have to be replaced by the corresponding functions of the variables $T, P$, and $B$:

$$G(T, P, B) = f(T, P, B; V, M_1, M_2)$$

$$= F_0(T; V) + F_1(T; V, M_1) + B M_1 + F_2(T; V, M_2) + B M_2 - n_{12} M_1 M_2 + PV$$  \tag{3.18}$$

with $\partial f / \partial V = \partial f / \partial M_1 = \partial f / \partial M_2 = 0$, so, e.g. $V = V(T, P, M_1, M_2)$ and, eventually $V = V(T, P, B)$, and so on. A possible volume or temperature dependence of the molecular-field parameter $n_{12}$ is ignored. The non-magnetic background is given by $F_0(T; V)$. The entropy, is given by

$$S(T, P, B) = - \partial G(T, P, B) / \partial T = - \partial f / \partial T - \partial f / \partial V \partial V / \partial T - \partial f / \partial M_1 \partial d M_1 / \partial T - \partial f / \partial M_2 \partial V / \partial T$$

$$= - \partial f / \partial T + 0.$$  

Hence

$$S(T, P, B) = S_0(T; V) + S_1(T; V, M_1) + S_2(T; V, M_2)$$  \tag{3.19a}$$

$$S_s(T; V, M_s) = - \partial F_s(T; V, M_s) / \partial T \quad \{s = 0, 1, 2\}$$  \tag{3.19b}$$
The main point here is that we have (also) distinct contributions to the specific heat

\[ C_s = T \frac{dS_c(T;V,M_s)}{dT} |_{PB} \quad \{s = 0, 1, 2\} \quad (3.20a) \]

\[ C_c(T) |_{PB} = -T \frac{\partial^2 F}{\partial T^2} - (T \frac{\partial^2 F}{\partial T \partial M_s}) dM_s / dT - (T \frac{\partial^2 F}{\partial T \partial V}) dV / dT \quad (3.20b) \]

We ignore the \( V \) dependence in the following.

Notice that the derivatives are taken with respect to the ‘local free energy’ only: the applied field and the molecular fields do not enter explicitly.

Let us now apply this reasoning to the RT-model above, specifying ‘rare earth units’ containing an atom \( R \), and ‘transition metal units’ containing an atom \( T \). Then the ‘local free energy’ \( F_R(T,M_R) \) contains only the entropy term \(-TS\):

\[ F_R(T,M_R) = T \left[ \frac{1}{2} M_R^2 / C_R + \frac{1}{4} M_R^4 / D_R + \ldots \right] - R \ln W, \]

where \( W \) is the multiplicity, \( W = 2J_R + 1 \). The expansion in terms of \( M_R^2 \) should not be regarded as an approximation, since, for this unit, the quantum-mechanical calculation is carried out straightforwardly. In the total (free) energy, the other terms involving the parameter \( M_R \) are

\[ -\frac{1}{2} n_{RR} M_R^2 - B M_R - n_{RT} M_T M_R = -B_R^{\text{eff}} M_R + \frac{1}{2} n_{RR} M_R^2, \]

where

\[ B_R^{\text{eff}} = B + n_{RR} M_R + n_{RT} M_T \quad (3.21) \]

The exchange interaction with the other \( R \)-units is taken into account here. Notice the ‘correction term’ \( +\frac{1}{2} n_{RR} M_R^2 \), inherent to the molecular-field approximation (see eq. 3.1b).

Indeed, the energy \( \langle \hat{H}_{\text{loc}} \rangle \) equals \(-B_R^{\text{eff}} M_R \) and thus overestimates the RR-exchange terms.

According to eq. (3.20), the specific heat of the \( R \)-part is given by

\[ C_R(T) |_{PB} = -B_R^{\text{eff}} dM_R(T) / dT \quad (3.22) \]

For the \( T \)-part we use again eq. 3.17. Then, in the local free energy, only the term \( \frac{1}{2} a_{2T} T^2 M_T^2 \) does explicitly depend on the temperature. With \( \frac{\partial^2 F}{\partial T^2} = \frac{1}{2} a_{2T} M_T^2 \); and \( \frac{\partial^2 F}{\partial T \partial M_T} = a_{2T} T M_T \), we find

\[ C_T(T) = -T \left( \frac{1}{2} a_{2T} M_T^2 \right) - a_{2T} T^2 M_T dM_T(T) / dT \quad (3.23) \]
The first term on the right hand side is the so-called Wohlfarth correction to the (linear) specific-heat coefficient, \( \gamma \), obtained from the ‘background’ \( F_0(T,P,V) = -\frac{1}{2} \gamma T^2 + \ldots \).

The second term \((-T^3\)) is often ignored, but should be taken into account for a consistent treatment, for instance to get \([dT(C_V/T) = 0 \text{ for } B=0 \text{ [8]} \). In our application, however, the T-part contribution to the specific heat is quite negligible in most cases.

3.6 Specific-heat curves for equal moment modes

It is well known that in the case that only one kind of magnetic atom is present, for equal-moment modes (in the ordered region) the specific-heat curves are completely determined by one parameter, e.g. the Néel temperature. Indeed, above we have shown that in our formalism for such a system the basic equations are reduced to \([\alpha_T - n_{RR}(Q)]\mu_{RR}(Q) = 0\) and \([\alpha_T - n_{RR}(0)]\mu_T(0) = B\). The Néel temperature fixes the molecular-field parameter \(n_{RR}(Q)\) via \(T_N = Cn_{RR}(Q)\). In the ordered region, we have \(\alpha_T(T, M_{R}) = n_{RR}(Q)\), independent of the temperature, and independent of any ‘bending’ caused by the applied field \(B\). This means that the effective field \(B_{R}^{\text{eff}}\), \(M_{R}(T)\) and the specific heat are unique functions of temperature, depending only on one parameter \(n_{RR}(Q)\) or \(T_N\), independent of the \(Q\) vector and the applied field \(B\).

**Figure 3.2.** Temperature dependence of the magnetic specific heat of a hypothetical system with a total angular momentum of the rare earth \(J = 1\).

**Figure 3.3.** Temperature dependence of the magnetic specific heat of a hypothetical system with a total angular momentum of the rare earth \(J = 8\).
Generalized molecular-field treatment...

For the interacting RT-system, we have $a_R(T,M_R) = n_{RR}(Q) + n_{RT}(Q)/a_T(T,M_T)$. Again, the intrinsic magnetization $M_R(T)$, and thus the specific-heat curve, is not expected to be appreciably affected, unless the RT-coupling is relatively strong and the temperature or magnetization dependence of the band part is strong too.

In the next two chapters, the calculations for the specific heat of the antiferromagnetic Gd compounds are shown. These $C/T$ curves exhibit a clear maximum (like a ‘Schottky anomaly’) below the magnetic ordering temperature. In order to elucidate the origin of this peak, we calculated the specific heat for two hypothetical systems with the quantum number $J$ of the rare earth being 1 and 8, respectively. Apart from $n_{RR}$, the band and exchange parameters are chosen as those derived for GdCu$_2$Ge$_2$ (see chapter 4). The exchange parameter $n_{RR}$ is fixed by taking the Néel temperature to be the same for both cases ($T_N = 13$ K). The occurrence of this maximum appears to depend on the multiplicity $(2J_R + 1)$ of the rare earth R. In figs. 3.2 and 3.3, it is shown that the hump is scarcely visible for a low multiplicity value and very distinct for a high value such as that for Ho.

References
