Magnetic and Thermodynamic properties of RNi5 compounds
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2 Theoretical description of the RNi$_5$ intermetallics

2.1 Introduction

The intrinsic magnetic behaviour of the rare-earth (R) transition metal (T; here Ni), compounds can be described theoretically within different models. It is reasonable and helpful to decompose the system into two magnetically coupled sublattices: one associated with the R-ions and the other with the Ni-ions. The magnetic moment of the $4f$ electrons in the rare-earth ion is considered to be localized and is described in terms of concepts used in atomic theory. The $3d$ electrons of the transition metal are itinerant and the resulting magnetic moment is described in a band structure model. The Ni sublattice will be described, in paragraph 2.2, in a more phenomenological way after having indicated the origin of the magnetic moment in transition metals.

The rare-earth ions will be described with a hamiltonian for an atom in a solid

$$\mathcal{H} = \mathcal{H}_C + \mathcal{H}_{so} + \mathcal{H}_{cf} + \mathcal{H}_{ex} + \mathcal{H}_z \quad (2.1)$$

The first term is the Coulomb hamiltonian, which represents the intra-atomic Coulomb and exchange interactions. The second term, $\mathcal{H}_{so}$, is called the spin-orbit hamiltonian and represents the interaction of the spin of the electrons with their own orbital moment. These phenomena can also be found in the free atom. $\mathcal{H}_{cf}$, is the hamiltonian of the crystal field interaction with the (surrounding) charge distribution. $\mathcal{H}_{ex}$ represents the exchange interaction with surrounding atoms (these are the T-ions as well as other R-ions). In this single-ion hamiltonian it is described in a molecular field approximation. $\mathcal{H}_z$ is the Zeeman term representing the response of the system to an external magnetic field.

2.2 The 3d electrons of the transition metal

The $3d$ electrons are in the outer part of the transition-metal atom. There is almost no screening, although the $4s$ and $4p$ electrons partially screen the $3d$ electrons from the surroundings. The $3d$ electrons interact directly with their environment and the $\mathcal{H}_C$ in eq. 2.1, now considered for Ni, is dominant. In a rough comparison of the energies of the crystal field interactions, $\mathcal{H}_{cf}$ ($10^3$- $10^4$ K), and of the $d$ electrons spin-spin exchange interaction $\mathcal{H}_{ex}$ ($10^5$ K) this is clearly shown. As a good approximation, only the spins of the $3d$ electrons are considered, because the orbital moments are quenched.

Metallic or itinerant-electron ferromagnetism has a nonlocal distribution of the electrons. This is also a consequence of the large spatial extent of the $3d$ wavefunctions. These wavefunctions show a strong overlap with neighbouring atoms. This leads to itinerant $3d$-electron energy bands rather than $3d$ energy levels. Magnetism of the $3d$ transition-metal can be described with band models, among which the Stoner-Wohlfarth model is well known [Stoner 1938, Wohlfarth 1968]. The occurrence of a magnetic moment can be described by a picture where the $3d$ sub-band with spin-up and the spin-down sub-band are unequally filled. The effective exchange interaction between the $3d$ electrons can lead to spontaneous splitting as is the case for Ni metal.

In compounds of nickel with a rare-earth metal, the outer electrons of the rare-earth are only
partly transferred to the 3$d$-band [Buschow 1980]. The filling of the 3$d$-band is not complete, as can be seen in a calculated density of states (DOS) of YNi$_5$ (selfconsistent ASW calculation by R. Coehoorn, unpublished), see figure 2.1. These calculations show also hardly any charge transfer from the Y to the Ni. The Ni atoms in LaNi$_5$ and YNi$_5$ have no moment. The nickel sublattice is non-magnetic and has a Pauli paramagnetic susceptibility [Gignoux et al. 1976]. Band calculations [Kitagawa et al. 1997] show that YNi$_5$ may become magnetic at extremely high fields or by substituting a magnetic rare-earth atom for Y.

![Figure 2.1](image)

**Figure 2.1** Selfconsistent Augumented Spherical Wave method (ASW) calculations of the density of states (DOS) of YNi$_5$ (Coehoorn unpublished). Remark, that a high DOS at the $E_F$ indicates a not filled Ni(3$d$) band.

Expanding the free energy of the transition metal system in powers of the total magnetic Ni-moment we write

$$F_{Ni} = \frac{1}{2} AM_{Ni}^2 + \ldots - \mu_0 H_{eff} M_{Ni}$$  \hspace{1cm} (2.2)

with $M_{Ni}$ the magnetic moment per unit cell of the Ni-sublattice. $\mu_0 H_{eff}$ is the effective magnetic field acting on the nickel moments. In the molecular field approximation the effective field is the sum of the externally applied field and the molecular field exerted by the R-moments (see section 2.3.3), i.e., $\mu_0 H_{eff} = \mu_0 H + n_{RT} M_R$. The intra-sublattice Ni-Ni exchange is incorporated in the coefficient $A$, i.e. in the susceptibility. We find, in the linear approximation, the magnetization of the Ni-sublattice:

$$M_{Ni} = \chi_{Ni} \mu_0 H_{eff}$$  \hspace{1cm} (2.3)

RNi$_5$ Compounds
Here, $\chi_\text{Ni}$ ($= A^{-1}$) is the nickel susceptibility.

For example, ascribing the susceptibility of typical non-magnetic $R\text{Ni}_5$ compounds fully to the Ni ions, then for $Y\text{Ni}_5$, $\chi_\text{Ni}$ amounts to $4.1 \times 10^3 \mu_\text{B} \text{T}^{-1}(\text{f.u.})^{-1}$ at 4.2 K and for $\text{LaNi}_5$, $\chi_\text{Ni}$ amounts to $3.7 \times 10^3 \mu_\text{B} \text{T}^{-1}(\text{f.u.})^{-1}$. Both these values are slightly temperature dependent [Gignoux et al. 1976, Ohlendorf and Flotow 1980]. The high-field susceptibility of the $R\text{Ni}_5$ compounds throughout the whole rare-earth series is roughly the same.

2.3 The hamiltonian for the $4f$-ion

2.3.1 The $4f$ electrons

The $4f$ electrons of most rare-earths in the solid state are firmly localized. They play no role in the chemical bonding, due to their position well within the interior of the rare-earth ion. In most cases there is little or no direct interaction between $4f$ electrons. In the solid state, most rare-earths are trivalent, in rare-earth or elemental metals due to the large cohesive energy gained by promoting a $4f$ electron with the two $6s$ electrons into the conduction and $3d$ band. In these $R^{3+}$ ions the $4f$ electron shell is filled progressively as a function of the atomic number $Z$ and exhibits therefore a wide range of interesting magnetic properties. As an example, we mention that the values of the saturation magnetic moments vary from $0.71 \mu_\text{B}$ for $\text{Sm}^{3+}$ up to $10 \mu_\text{B}$ in the case of $\text{Dy}^{3+}$ and $\text{Ho}^{3+}$ (and vanishes for $\text{Eu}^{3+}$).

The total (single-ion) hamiltonian, $\mathcal{H}$, for the rare-earth is given in equation 2.1. The relative importance of $\mathcal{H}_\alpha$, $\mathcal{H}_\text{so}$ and $\mathcal{H}_\text{fi}$ is in this case reversed compared to the description of $3d$ electrons.

The strongest interactions for the $4f$ electrons are the intra-ionic Coulomb correlations which couple together the individual electron spins $s_i$ and orbital momenta $l_i$ to give the total spin angular momentum $S = \sum s_i$ and the orbital angular momentum $L = \sum l_i$. The effect of the spin-orbit interaction is then to couple $L$ and $S$ according to the Russel-Saunders scheme, $L + S = J$. The spin-orbit interaction, $\mathcal{H}_\text{so}$, can be written as

$$\mathcal{H}_\text{so} = \lambda S \cdot L$$

(2.4)

In this expression $\lambda$ denotes the spin-orbit coupling constant which is often treated as an empirical parameter. Positive and negative values for $\lambda$ refer to a less then half-full subshell and a more then half-full subshell, respectively. For a given $L$ and $S$, the Landé interval rule for the separation of multiplets $J$ and $J-1$ gives $E_J - E_{J+1} = \lambda J$. Hence, the ground state values of $L$, $S$ and $J$ can be given by Hund's rules. The $J$ value of the ground state multiplet is $|L-S|$ for the light rare-earth (La to Eu) and $L+S$ for the heavy rare-earth (Gd to Lu).

The energy separation between the ground state and the first excited multiplet can be calculated within the Hartree-Fock approximation or experimentally determined. For Eu the energy separation equals the spin-orbit coupling constant $\lambda$ amounting to $\sim 418$ K, and for Er the first excited multiplet lies about 9354 K [Williams et al. 1987] above the ground state ($\Delta = -\lambda 15/2$) (see Table 2.1.). With these large energy separations it is reasonable to restrict ourselves to the ground-state multiplet in calculations of the low-temperature electronic and magnetic properties.

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Theoretical description of the $R\text{Ni}_3$ intermetallics

Table 2.1. The $J$-values of the ground state $J$ and the first excited multiplets $J'$ of $R^{3+}$, and the energy separation ($\pm \Delta J$) between these multiplets as observed by inelastic neutron scattering (Williams et al. 1987).

<table>
<thead>
<tr>
<th>$R^{3+}$</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J,J'$</td>
<td>5/2,7/2</td>
<td>4,5</td>
<td>9/2,11/2</td>
<td>4,5</td>
<td>5/2,7/2</td>
<td>0,1</td>
<td>6,5</td>
<td>15/2,13/2</td>
<td>8,7</td>
<td>15/2,13/2</td>
<td>6,5</td>
<td>7/2,5/2</td>
</tr>
<tr>
<td>$\Delta$(K)</td>
<td>3168</td>
<td>3099</td>
<td>2739</td>
<td>2298</td>
<td>1439</td>
<td>418</td>
<td>2878</td>
<td>4746</td>
<td>7485</td>
<td>9354</td>
<td>11942</td>
<td>14820</td>
</tr>
</tbody>
</table>

Under influence of an external magnetic field $\mu_0H$ the $(2J+1)$ degeneracy of the multiplet is lifted. The Zeeman term (see eq. 2.1) can then be written as

$$\mathcal{H}_z = -\{g_\mu_B J \cdot \mu_0H\}$$

(2.5)

The Zeeman splittings are much smaller than the multiplet energy separations. Observe that $-g_\mu_B J$ is the magnetic moment operator.

For a rare-earth ion in the solid the crystal field interaction ($\mathcal{H}_{\text{cf}}$) and the exchange interaction ($\mathcal{H}_{\text{ex}}$) have to be taken into account (see eq. 2.1). These interactions are discussed in the following sections.

As a reminder, in Table 2.2 characteristic constants of the trivalent rare-earth ions are given.

2.3.2 Crystal field

In the $R\text{Ni}_3$ compounds crystal field interactions in particular at the $R$-site play a very significant role in modifying many properties, such as magnetic susceptibility, magnetization, magnetocrystalline anisotropy, thermodynamic properties, transport properties and so on.

The electric charge density distribution in a crystal leads to the presence of electrostatic fields at the atomic sites. This is called the crystal field ($=\text{CF}$) or crystalline electric field ($=\text{CEF}$). We will use the term crystal field (CF) throughout this thesis.

In the crystal field model, in a first approach, the non-spherical $4f$ orbitals are thought to be surrounded by a classical non-spherical charge distribution. The electrostatic potential at position $r_i$ due to the surrounding charge density $\rho(r)$ takes the form

$$V(r_i) = \frac{1}{4\pi\varepsilon_0} \int \frac{\rho(r)}{|r_i - r|} dr$$

(2.6)

For an $R$-ion the hamiltonian of the crystal field interaction can be written as a sum over the $4f$-electrons

$$\mathcal{H}_{\text{cf}} = -e \sum_i V(r_i)$$

(2.7)

If the charge density $\rho(r)$ exists mainly outside the ion, the potential energy above is a solution of Laplace’s equation and may be expanded in spherical harmonics ($Y_n^m(\theta, \phi)$) or in the more convenient renormalised spherical harmonics ($C_n^m(\theta, \phi)$). For an ion the crystal field hamiltonian is given by

$$\mathcal{H}_{\text{cf}} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} A_n^{m\text{m}} \sum_{i=1}^{m} r_i^n C_n^m(\theta_i, \phi_i)$$

(2.8)

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Table 2.2 Characteristic constants of magnetic trivalent rare-earth ions at zero temperature; $\gamma = 2(g_R - 1)/g_R$ and $g_R$ is the Landé factor for the rare-earth.

<table>
<thead>
<tr>
<th>$R^{3+}$</th>
<th>$4f^n$</th>
<th>$2s+1L_J$</th>
<th>$S$</th>
<th>$L$</th>
<th>$J$</th>
<th>$g_J$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0</td>
<td>$^1S$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>1</td>
<td>$^2F_{5/2}$</td>
<td>$1/2$</td>
<td>3</td>
<td>$5/2$</td>
<td>6/7</td>
<td>-1/3</td>
</tr>
<tr>
<td>Pr</td>
<td>2</td>
<td>$^3H_4$</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>4/5</td>
<td>-1/2</td>
</tr>
<tr>
<td>Nd</td>
<td>3</td>
<td>$^4I_{9/2}$</td>
<td>3/2</td>
<td>6</td>
<td>$9/2$</td>
<td>8/11</td>
<td>-3/4</td>
</tr>
<tr>
<td>Pm</td>
<td>4</td>
<td>$^5I_4$</td>
<td>2</td>
<td>6</td>
<td>4</td>
<td>3/5</td>
<td>-4/3</td>
</tr>
<tr>
<td>Sm</td>
<td>5</td>
<td>$^6H_{5/2}$</td>
<td>5/2</td>
<td>5</td>
<td>$5/2$</td>
<td>2/7</td>
<td>-5</td>
</tr>
<tr>
<td>Eu</td>
<td>6</td>
<td>$^7F_0$</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>3/2</td>
<td>2/3</td>
</tr>
<tr>
<td>Gd</td>
<td>7</td>
<td>$^8S_{7/2}$</td>
<td>7/2</td>
<td>0</td>
<td>7/2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Tb</td>
<td>8</td>
<td>$^7F_6$</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>3/2</td>
<td>2/3</td>
</tr>
<tr>
<td>Dy</td>
<td>9</td>
<td>$^6H_{15/2}$</td>
<td>5/2</td>
<td>5</td>
<td>15/2</td>
<td>4/3</td>
<td>$1/2$</td>
</tr>
<tr>
<td>Ho</td>
<td>10</td>
<td>$^5I_8$</td>
<td>2</td>
<td>6</td>
<td>8</td>
<td>5/4</td>
<td>2/5</td>
</tr>
<tr>
<td>Er</td>
<td>11</td>
<td>$^4I_{15/2}$</td>
<td>3/2</td>
<td>6</td>
<td>15/2</td>
<td>6/5</td>
<td>1/3</td>
</tr>
<tr>
<td>Tm</td>
<td>12</td>
<td>$^3H_6$</td>
<td>1</td>
<td>5</td>
<td>6</td>
<td>7/6</td>
<td>2/7</td>
</tr>
<tr>
<td>Yb</td>
<td>13</td>
<td>$^2F_{7/2}$</td>
<td>$1/2$</td>
<td>3</td>
<td>7/2</td>
<td>8/7</td>
<td>$1/4$</td>
</tr>
<tr>
<td>Lu</td>
<td>14</td>
<td>$^1S$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where the normalized spherical harmonics are given in terms of the position of the $i$th electron $(\theta, \phi)$. The $A_n^m$ are called the crystal field coefficients. They are given by

$$
A_n^m = -\frac{e}{4\pi\epsilon_0} \int \frac{\partial \rho(r)}{r^{n+1}} C_n^m(\theta, \phi) d^3r
$$

where $(r, \theta, \phi)$ are the spherical polar coordinates of $r$.

For $f$ electrons, only the matrix elements with $n = 0, 2, 4$ and $6$ are non-zero (see e.g. Heine [1960]). This upper-limit of 6 implies that the higher order crystal field terms do not affect the orbital states of the $4f$ electrons, no matter what the symmetry of the surrounding charges is. Electrons with angular momentum $l=3$ cannot have a multipole distribution with $n > 6$. The $n = 0$ ($m = 0$) term is omitted in calculations since it is a constant and therefore only responsible for an energy shift in all terms. The expressions $C_n^m(\theta, \phi)$ transform under rotation according to an irreducible representation of the rotation group. The Wigner-Eckhart theorem states that the matrix elements of any operator which transforms according to an irreducible representation are
proportional to those of any operator which transforms in the same way. The proportionality factor depends on the physical nature of the operator. Stevens [1952] was the first to point out, that, on the condition that we stay within a multiplet of constant J, the matrix elements of $\mathcal{H}_{cf}$ are proportional to those of operator equivalents, $O_n^m$, written in terms of the J operator. In this way, we have for the expansion of $\mathcal{H}_{cf}$ in these operator equivalents [see Hutchings 1964]:

$$\mathcal{H}_{cf} = \sum_{n=2,4,6} \sum_{m=0} B_n^m O_n^m = \sum_{n=2,4,6} \sum_{m=0} \theta_n A_n^m \langle r^n \rangle O_n^m$$  \hspace{1cm} (2.10)

with

$$B_n^m = \theta_n A_n^m \langle r^n \rangle.$$  \hspace{1cm} (2.11)

The $B_n^m$ are called the crystal field parameters. $\theta_n$ are the Stevens factors (which are usually denoted as $\theta_2 = \alpha$, $\theta_4 = \beta$, $\theta_6 = \gamma$), $\langle r^n \rangle$ represents the radial average over the 4f shell. Up to 1979 it was standard to use for $\langle r^n \rangle$ ($n=2, 4, 6$) values which were based on nonrelativistic Hartree-Fock calculations [Freeman and Watson 1962]. Since 1979 more accurate values based on relativistic calculations are available [Freeman and Desclaux 1979]. Notice, that only $\theta_n$ and $\langle r^n \rangle$ depend directly on the kind of 4f ion, whereas the $A_n^m$ describe the (external) charge distribution only. Determination of the parameters is subject of the analysis of experimental data.

In appendix A the relevant crystal field parameters for the rare earth in RNi$_5$ of the hexagonal CaCu$_5$ structure with P6/mmm symmetry are deduced. The $(B_2^0, B_4^0, B_6^0, B_2^6, B_4^6, B_6^6)$ are the only parameters which remain after these symmetry considerations. This leaves us with the crystal field hamiltonian

$$\mathcal{H}_{cf} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_2^6 O_2^6 + B_4^6 O_4^6 + B_6^6 O_6^6$$  \hspace{1cm} (2.12)

The crystal field parameters can in principle be calculated ab initio from the charge distribution in the metal. In the point charge approximation the surrounding charges located over the lattice sites are assumed to have point charges. The charge density is given then as a sum of $\delta$-functions. Substituting this into eq. (2.1) gives the $A_n^m$ as function of the location and value of the point charges. Depending on the given problem, one can take the summation over the nearest neighbours to more than 20 atomic shells. The values of the (atomic) point charges can be chosen semi-empirical. The values calculated for $A_2^0$ in this way can be used to give a satisfactory description of the crystal field effects. In recent treatments of these problems an on-site contribution $A_2^0$ val., which is the ratio of the interaction energy of the valence electron charge density contribution and the axial quadrupole moment of the 4f shell, is introduced and gives an improvement of the calculations [Coehoorn 1990]. There remain many problems in calculating the $A_n^m$ in the point charge approximation, only the first term $A_2^0$ calculated in this way gives reasonable correspondence with the experimentally derived values.

Values for $\theta_n(r^p)$, that represent the multipole charge moments of the 4f shell, are collected in Appendix B.

### 2.3.3 Molecular field modelling of the exchange interaction

Thus far, only an isolated free $R$-ion is regarded. Now, we look at the system with exchange interaction of rare-earth atoms and transition atoms. Before continuing we discuss the origin of the exchange interaction. There are two models proposed to describe the exchange interactions,

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$\mathcal{H}_{\text{ex}}$ between the 4f-4f electrons in the $R$-$T$ system. These interactions are thought to be indirect, because, due to their spatial localization, the 4f electrons have insufficient overlap. First, there is the RKKY model developed for pure rare-earth magnetism by De Gennes [1962]. Here the interaction is long-range oscillatory, mediated through the conduction electrons. In another model, suggested by Campbell [1972], the role of the 5d electrons is emphasized. The 5d spin is polarized through 4f-5d exchange by the localized 4f spins. The 4f-3d coupling then arises indirectly via the 3d-5d interaction (or hybridization), and the 4f-4f interaction via the 5d-5d interaction.

In this section we treat the exchange interactions within the mean-field theory as systems which can be split in separate magnetic sublattices. For simplicity, the $RT$-compounds are described as consisting of two sublattices, the $R$-sublattice and the $T$-sublattice. Consider $N$ unit cells, each cell containing $N_R$ rare-earth ions and $N_T$ transition metal ions. A magnetic moment per unit cell ($M_R$, $M_T$) is ascribed to each sublattice. These two sublattices have exchange within their sublattice (intra-sublattice) and exchange between the two different sublattices (inter-sublattice).

Summing over the lattice sites $(i, j)$ we assume that the indirect exchange interaction can be written in the isotropic Heisenberg form, and hence is given by

$$\frac{1}{2} \sum_i \sum_j \{-2J(i, j)\} S(i) \cdot S(j)$$

(2.13)

$J(i, j)$ is the exchange parameter and $S(i)$ the spin operator at site $i$ (summation over both lattices, i.e. over both $T$- and $R$-sublattice). This hamiltonian can only be solved exactly in special cases, in all other cases approximations have to be used. In our situation, the mean-field approximation is applied. This method neglects fluctuations of moments around their equilibrium values. Introducing $\langle S(i) \rangle$ as the averaged expectation value of the spin operator at site $I$, we use the identity

$$S(i) \cdot S(j) = S(i) \cdot \langle S(j) \rangle + S(j) \cdot \langle S(i) \rangle - \langle S(i) \rangle \cdot \langle S(j) \rangle$$

(2.14)

The mean field approximation then neglects the last term on the right-hand side as we expect $\langle S(i) - \langle S(i) \rangle \rangle$ to be small and the evaluation of the product of two small terms will be negligible. Inserting eq. 2.1 in the exchange hamiltonian 2.1 and collecting terms related to the spin operator $S(i)$ and using $J(i, j) = J(j, i)$, we find

$$\frac{1}{2} \sum_i \sum_j \{-2J(i, j)\} S(i) \cdot S(j) =$$

$$= \sum_i S(i) \sum_j \{-2J(i, j)\} \langle S(j) \rangle - \frac{1}{2} \sum_i \sum_j \{-2J(i, j)\} \langle S(i) \rangle \cdot \langle S(j) \rangle$$

$$= \sum_i \mathcal{H}_{\text{ex}}(i) - \frac{1}{2} \sum_i \sum_j \{-2J(i, j)\} \langle S(i) \rangle \cdot \langle S(j) \rangle$$

(2.15)

Here, we defined the (local) exchange hamiltonian:

$$\mathcal{H}_{\text{ex}}(i) = S(i) \sum_j \{-2J(i, j)\} \langle S(j) \rangle$$

(2.16)

The interaction $J(i, j)$ is supposed to decrease fast with increasing distance between sites $i$ and $j$. In most circumstances only the nearest neighbours are counted. Moreover, for each sublattice, the value $\langle S(j) \rangle$ is expected not to deviate much from the site averaged value ($S_R$ for the $R$ lattice, $S_T$ for the $T$ lattice). If we now consider a site $i$ on the $R$ sublattice, we split the summation in two
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parts, one contribution from the R sublattice and the other from the T sublattice. Inserting the averaged spin values $S_R$ and $S_T$ in eq. (2.1), we find

$$\mathcal{H}_{\text{ex}}(i) = S(i) \left\{ \sum_j R \{-2J_{RR}(i,j)\} S_R + \sum_j T \{-2J_{RT}(i,j)\} S_T \right\} \quad [i \text{ on } R]$$

$$= S(i) \left\{ \{-2J_{RR}z_{RR}\} S_R + \{-2J_{RT}z_{RT}\} S_T \right\} \quad [i \text{ on } R]$$

(2.17)

Notice that $z_{RT}$ is the number of nearest T-neighbours of a R site, $z_{RR}$ is the number of nearest neighbours on the R sublattice itself.

If we consider only the lowest $J$-multiplet, the Wigner-Eckart theorem implies that the matrix elements of $S$ are proportional to those of $J$. We write then

$$S(i) = (g_R - 1)J(i)$$

(2.18)

Here $g_R$ is the (rare-earth) Landé factor defined by the proportionality $(L+2S) = g_R J$, again under application of the Wigner-Eckhart theorem. The average spin of a R atom, $S_R$, is related to the moment of the R-sublattice by

$$M_R = N_R \{-g_R \mu_B \langle J(i) \rangle \} = N_R \{-\frac{S_R}{g_R - 1} \mu_B S_R \}.$$

Analogously, $S_T$ is related to the magnetic moment $M_T$ by

$$M_T = N_T \{-2 \mu_B S_T \}$$

with $g_T = 2$ and $J(i) = S(i)$ for a T-site $i$ in eq 2.1 (due to the quenched orbital moment of the transition metal atom). Taking into account the external field $\mu_B H$, and the (local) CF hamiltonian $\mathcal{H}_F$, we arrive at

$$\mathcal{H} = \mathcal{H}_F - \{-g_R \mu_B J(i) \} \left\{ \mu_0 H + n_{RR} M_R + n_{RT} M_T \right\} \quad [i \text{ on } R]$$

(2.19)

introducing the molecular field constants

$$n_{RR} = \left[ \frac{2(g_R - 1)}{g_R \mu_B} \right]^2 \frac{J_{RR} z_{RR}}{2N_R}, \quad n_{RT} = \frac{2(g_R - 1) J_{RT} z_{RT}}{g_R \mu_B^2 2N_T}$$

(2.20a,b)

Analogous arguments can be used to derive that the molecular field exerted by the R-moments on a T-moment is given by $n_{RT} M_R$.

If we now concentrate on the nickel sublattice in the $R\text{Ni}_5$ compounds, the sublattice is Pauli paramagnetic. The magnetic moment of the T-sublattice is given by eq. 2.1 (recall that there the intra-sublattice Ni-Ni exchange is incorporated in $\chi_{Ni}$). Hence,

$$M_T = \chi_T (\mu_0 H + n_{RT} M_R)$$

(2.21)

$H$ is the applied magnetic field (in fact the internal field, that is the external field corrected for demagnetization effects), and $\chi_T = \chi_{Ni}$ in the case under consideration.

Now rewriting the part between square brackets of equation (2.1) with all the above given remarks about the nickel, we deduce a more explicit single ion rare-earth hamiltonian:

$$\mathcal{H} = \mathcal{H}_F - \{-g_R \mu_B J(i) \} \left\{ (1 + n_{RT} \chi_T) \mu_0 H + (n_{RR} + n_{RT}^2 \chi_T) M_R \right\} \quad [i \text{ on } R]$$

(2.22)

In going from eq. 2.1 to 2.1 , the effective magnetic field acting on each R-ion, $\mu_0 H_{\text{eff}}^R$ is written as

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\[ \mu_0 H_{\text{eff}}^R = \mu_0 H + n_{RR} M_R + n_{RT} M_T \]
\[ = (1 + n_{RT} \chi_T)\mu_0 H + (n_{RR} + n_{RT}^2 \chi_T) M_R \]

(2.23)

In Barthem et al. [1988] the nickel contribution is interpreted as two separate contributions: (i) an enhancement of the applied magnetic field by the factor $(1 + n_{RR} \chi_{Ni})$, and (ii) a change of the exchange interaction between the $R$ ions by a factor $n_{RR} + n_{RR}^2 \chi_{Ni}$. In the literature [e.g. Barthem et al. 1988, Nait Saada 1980] $n_{RR} \chi_{Ni}$ is often referred to as $\alpha$ and the term $n_{RR} + n_{RR}^2 \chi_{Ni}$ is called the isotropic bilinear exchange parameter and named $n$.

In a sense, reducing the spontaneous moment of the nickel to zero makes this a 'one-sublattice' system. There is only the ferromagnetic coupling of the rare-earths and an induced moment on the nickel sublattice. In fact, the system is equivalent to a “one-sublattice” system with an “enhanced” (or “reduced”) moment $(1 + n_{RT} \chi_T) M_R$ depending on a parallel (or antiparallel) configuration of the $R$ and $T$ moments, and an effective molecular field parameter $n_{RR} + n_{RT} \chi_T / (1 + n_{RT} \chi_T)$.

2.4 The total magnetic moment; the free energy

2.4.1 The total magnetic moment

Equation (2.1) has now to be solved. For a chosen parameter set, the hamiltonian is taken with the desired external field and with an arbitrary start value for $M_R$. After diagonalization, the calculation of the expectation value $\langle J_R \rangle$ results in a magnetic moment of the rare earth, $M_R$. With this we determine a new molecular field which will serve as a starting point for a new calculation of the expectation value $\langle J_R \rangle$, iteratively until the change in the molecular field is lower than a certain criterion.

In this approach, based on eq. 2.1 we did not talk explicitly about the nickel moment. But if we add the moment of the $R$ sublattice and that of the $T$ sublattice to get the total moment, we deduce the following expression (see eq. 2.1)

\[ M_{\text{tot}} = M_R + M_T = \chi_T \mu_0 H + (1 + \chi_T n_{RT}) M_R \]

(2.24)

Again, we see that the system is effectively reduced to a one-sublattice system. Compare the final remark in section 2.3.3.

2.4.2 Free energy of the complete system

To determine different macroscopic properties we start by discussing the free energy expression. As stated before we consider $N$ unit cells, each one containing now $N_R (=1) R$-sites occupied by one kind of $R$-atoms and $N_T (=5) T$-sites occupied by Ni-atoms. Recapitulating a few basic thermodynamic results, we write the free energy as

\[ NF = -kT \ln Z = -kT \ln \left( \sum_{\phi} e^{-\frac{\langle \phi | H_{\text{tot}} | \phi \rangle}{kT}} \right) \]

(2.25)

The summation runs over a complete set of states describing the total system. $F$ is the free energy.
per cell.

The total hamiltonian for the total system of $N$ cells contains a contribution in which only Ni-ion operators do occur, another contribution in which only $R$-ion operators do occur and the $RT$-exchange interaction term. In the molecular field approximation, these latter two-ion terms are reduced to single-ion operators (see eq. 2.1), at the expense of the ‘correction terms’, i.e. such as the second term at the right hand side of eq. 2.1. Apart from these correction terms, the hamiltonian now consists of two parts, each part containing operators connected to one of the sublattices only. Accordingly, the free energy can be written as a sum of sublattice contributions, in addition to the ‘correction terms’. Notice that these correction terms give a c-number contribution that is transferred directly into a contribution to the free energy. In section 2.2 (eq. 2.1) we introduced a phenomenological expression for the sublattice free energy in terms of the average Ni-moment per cell, $M_{Ni}$. Applying a well known method in statistical mechanics, now for the subsystems separately, we restrict the summation in eq. 2.1 to the states with an expectation value for the total sublattice moment of $NM_{Ni}$ and $NM_{R}$, respectively. The approximation is valid in case $M_{Ni}$ and $M_{R}$ are chosen to be the equilibrium values: $M_{Ni}$ in the presence of an effective field $\mu_{0}H_{Ni}^{eff} = \mu_{0}H + n_{RT}M_{R}$ (see below eq. 2.1), and $M_{R}$ being the equilibrium value in the $R$-subsystem under the influence of an effective (external) field $\mu_{0}H + n_{RT}M_{T}$. Notice that a molecular field approximation for the intra-sublattice exchange interaction (Ni-Ni and R-R) is not necessary so far. In section 2.2, the equilibrium value $M_{Ni}$ is obtained by minimizing $F_{Ni}$ as given by eq. 2.1, obviously eventually leading to an expression for the free energy of the Ni-subsystem per cell

$$F_{Ni}(H_{eff}...) = -\frac{1}{2}\chi_{Ni}(\mu_{0}H_{eff}^{Ni})^2$$

(2.26)

We remark again that, in this free energy contribution, the intra-sublattice Ni-Ni exchange interactions are incorporated.

Now focussing attention to the $R$-sublattice, we see that here, for the intra-sublattice R-R interaction, the molecular field approximation is necessary to accomplish the reduction to single-ion terms. In much the same way as described above for the R-T interaction, it is essential to keep track of the occurring ‘correction terms’ carefully. These terms now can be written as $\frac{1}{2}Nn_{RR}M_{R}^2$ to be compared with the terms (compare eq 2.1)

$$\sum_{i} n_{RR}M_{R} \{ g_{R} \mu_{B} I(i) \} \approx -NN_{R}n_{RR}M_{R} M_{R} = -Nn_{RR}M_{R}^2$$

(2.27)

Together, these contributions would yield the familiar exchange interaction free energy $-\frac{1}{2}Nn_{RR}M_{R}^2$ (notice the sign). Here, however, the reduction to single ion operators allows the calculation of the free energy of the $R$-subsystem in a proper quantum statistical way (as $NN_{R}$ times the single ion contribution in the effective field $\mu_{0}H_{eff}^{R} = \mu_{0}H + n_{RT}M_{T} + n_{RR}M_{R}$, in addition to the correction term $\frac{1}{2}Nn_{RR}M_{R}^2$). In principle, one can calculate now the magnetic moment of the $R$-sublattice for given input values $M_{T}$ and $M_{R}$, and use this as the first step in an iterative procedure. The simple form of the response of the Ni-subsystem, however, allows to simplify the procedure by inserting directly $M_{Ni} = \chi_{Ni}(\mu_{0}H + n_{RT}M_{R})$ (see eq. 2.1) in the expression for $\mu_{0}H_{eff}^{2} + H_{eff}^{2}$, in fact already given in eq. 2.1. It is even possible to incorporate the free energy of the Ni-subsystem $NF_{Ni}$ given by eq. 2.1, as a c-number in the total hamiltonian, together with the correction terms. In this way we arrive at

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$$\mathcal{H}^{4\text{tot}} = N \sum_{i \text{cell}} \left[ \mathcal{H}_{\text{el}}(i) - \{ -g_R \mu_B J(i) \} \right] \left\{ (1 + n_{R\text{Ni}_5} \mathcal{X}_{R\text{Ni}_5}) \mu_0 H + \left( n_{R\text{Ni}_5} + n_{R\text{Ni}_5}^2 \mathcal{X}_{R\text{Ni}_5} \right) M_R \right\}$$

$$+ \frac{1}{2} \left( n_{R\text{Ni}_5} + n_{R\text{Ni}_5}^2 \mathcal{X}_{R\text{Ni}_5} \right) \mathcal{M}_R^2 - \frac{1}{2} \mathcal{X}_{R\text{Ni}_5} \left( \mu_0 H \right)^2$$

(2.28)

In the present case the cell ($R\text{Ni}_5$) contains only one $R$-atom, so the expression between [...] is just a single ion hamiltonian, essentially given by eq. 2.1. As described in the preceding subsection, this hamiltonian is diagonalized, and the iteration procedure mentioned in paragraph 2.4.1 is applied. Then, the eigenvalues are known, and the different thermodynamic quantities can be calculated.

Using the iteration procedure, the magnetization of the system under consideration is obtained directly, as a function of the applied field. In a linear approximation the susceptibility can be calculated by $\chi = \mathcal{M} / \mathcal{H}$. If correctly done a tensor should be calculated but in our simple calculation we only calculated the susceptibility along the principal crystallographic axes.

The free energy $F$ is calculated with eq. 2.25. Also the energy $\langle E \rangle = U$ is calculated in the standard way. Subsequently, the entropy is obtained by using

$$S = \frac{\langle E \rangle - F}{T}$$

(2.29)

The magnetic contribution to the specific heat is found by calculating the appropriate derivative. Two equivalent ways are used to calculate the specific heat:

$$C_v = \frac{d \langle E \rangle}{dT} \quad \text{or} \quad C_v = T \frac{dS}{dT}$$

(2.30)

In practice, i.e. in the computer programme (authors J.H.P. Colpa and A. Szewczyk), the derivative is calculated by taking two values of $\langle E \rangle$ or $S$, with small temperature difference, and dividing them by that temperature difference.

2.5 Analysis of measurements

2.5.1 Specific heat

The total specific heat, as measured, is analysed by splitting the heat capacity into four parts:

$$C = C_N + C_{\text{el}} + C_{\text{ph}} + C_{\text{m}}$$

(2.31)

a nuclear ($C_N$), an electronic ($C_{\text{el}}$), a lattice (or phonon) ($C_{\text{ph}}$) and a magnetic ($C_{\text{m}}$) contribution. In most cases the nuclear contribution, which is related to the hyperfine interaction of the 4f shell with the nuclear moment of the 4f ion, is not observed in $R\text{Ni}_5$ in the temperature range we measured. The nuclear specific heat only contributes significantly below 1 K. Information about the electronic and lattice contributions to the heat capacity is provided by the specific heat of an analogous material with a nonmagnetic rare earth ion. In our case we have measured LaNi$_5$ and

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YNi$_5$; neither lanthanum nor yttrium bears a moment.

Analysing the experimental data we have used three methods for subtracting the non-magnetic rare-earth contribution to the specific heat. The first method simply subtracts the measured data sets of the magnetic and non-magnetic compounds.

The second method implies that a correction is made for the difference in molar mass of the compounds. The measured specific heat of LaNi$_5$ is approximated by a combination of two Debye functions with different partial Debye temperatures for Ni and R atoms [Hofmann et al. 1956]. In that model, $c_v(T)$ of a non-magnetic binary compound of the type $R_X$ consists of the electronic and lattice contributions only and is given by the expression:

$$c_v(T) = \gamma T + \left( a f_D \left( \frac{\Theta_R}{T} \right) + b f_D \left( \frac{\Theta_X}{T} \right) \right)$$

Here, $c_v$ is the specific heat measured at constant volume, $f_D(\cdot)$ is the Debye function, $\Theta_R$ and $\Theta_X$ refer to the partial Debye temperatures associated with $R$ and $X$ respectively. The electronic contribution is written as $\gamma T$. Making the simplifying assumption that all the atoms in the crystal have the same mean-square displacement, it follows that

$$(\Theta_R)^2 m_R = (\Theta_X)^2 m_X$$

where $m_R$ and $m_X$ are the molar mass of the $X$ and $R$ elements respectively. At low temperatures an effective Debye temperature can be defined by considering a single Debye function

$$c_v(R_{a}X_{b}) = (a + b) f_D \left( \frac{\Theta_D(R_{a}X_{b})}{T} \right)$$

Identifying the coefficients of the $T^3$ terms in the low temperature expansion of eq. 2.31 and 2.33 leads to the following relations between the Debye temperatures

$$\frac{a + b}{\Theta(R_{a}X_{b})^3} = \frac{a}{(\Theta_R)^3} + \frac{b}{(\Theta_X)^3}$$

Assuming that the partial Debye temperatures of $X$ atoms are not modified when $R$ is replaced by $R'$, the following relation between the corresponding effective Debye temperatures can be deduced

$$\Theta_D(R_{a}X_{b}) = \left[ \frac{(m_R)^{3/2} + (m_X)^{3/2}}{(m_R)^{3/2} + (m_X)^{3/2}} \right]^{1/3} \Theta_D(R'_{a}X'_{b})$$

This relation can be used to evaluate the lattice contribution of the magnetic compound $R_{a}X_{b}$ by multiplying the temperature values by this scaling factor in the $C$ versus $T$ curve obtained for the non-magnetic compound $R'_{a}X'_{b}$. Subtracting the corrected data from the measured heat capacity of the magnetic compound, we arrive at the magnetic contribution to the specific heat. In the third method the two partial Debye functions of the non-magnetic compound are approximated by fitting the calculated values to the measurements. In this way we can calculate with eq. 2.33 the lattice contribution of another compound with an equivalent lattice. The theoretical curve obtained, the lattice contribution to the specific heat and the electronic contribution, can be used as non-magnetic reference system. This last method is only used to investigate the validity of the two-Debye temperatures model. In chapter 6.1 (YNi$_5$) and in
2.6 Data analysis

2.6.1 Magnetization

In figure 2.2 we show schematically some examples of the magnetization curves. In the RNi$_5$ compounds magnetization is measured with the magnetic field along each of the three main crystallographic directions, in the orthohexagonal notation (and between brackets the hexagonal notation), $a_0$ ([100] direction), $b_0$ ([120]) and $c_0$ ([001]). The terminology of the different axes will be discussed in chapter 3. The magnetization parallel to these applied fields is measured. This magnetization is mainly due to the $R$-moment and depends mainly on the crystalline field and the exchange interaction. RNi$_5$ is ferromagnetic with a hexagonal magnetic lattice below the ordering temperature. We consider the simple case that the sign of the crystal field coefficient $B^2_{\perp}$ determines the easy direction of the magnetic moment.

In figure 2.2a the $B^2_{\perp}$ term is negative and the easy direction lies along the [001] axis. Extrapolation of the magnetization along the easy axis, from higher fields to zero field, gives the spontaneous magnetization as the intercept with the y-axis. The full moment of the free rare-earth ion is equal to $-g_J \mu_B J$. A smaller magnetization value indicates the possibility of an opposite moment lowering the spontaneous magnetization. In our materials this is always the case, as there

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**FIGURE 2.2.** Schematic example of magnetization curves in the ordered state as seen in the ferromagnetic system RNi$_5$ with the field applied along the three main symmetry axes of the hexagonal structure. In (a), the easy direction of the magnetization lies along the [001] direction. The magnetization with the field in the hexagonal plane is induced. In figure (b) the spontaneous magnetization is in the basal plane, in this case along the [100] axis, and the magnetization along the hexagonal axis is induced.
is always a (small induced) Ni moment. In fig. 2.2a along the [100] and [120] directions, perpendicular to [001], no spontaneous magnetization is observed. The difference between [100] and [120] axis depends on the anisotropy in the basal plane, which is usually very weak.

In the second case with a positive $B^0_5$, the spontaneous magnetization lies in the basal plane, see figure 2.2b. Just as in the first case, the higher order terms determine which axis in the basal plane is the easiest direction. If $B^0_5$ is positive then the maximum magnetization lies along the [120] axis and with a negative $B^0_5$ the [100] axis is the easy one.

### 2.6.2 The effect of the crystalline field on the susceptibility

For sufficiently high temperatures Bouton [1973] derived a formula for the temperature dependence of the susceptibility. The calculations are general and start from a hamiltonian including arbitrary high-order exchange and arbitrary crystal field terms. It is found that the second order term of the susceptibility (or constant term of the inverse susceptibility) depends only on bilinear exchange (see next section) and the second-order crystal field term. In a hexagonal symmetry the susceptibility can be split in two parts: parallel and perpendicular.

\[
\chi_{\perp(001)} = \frac{C_R}{T} \left[ 1 + \frac{(2J - 1)(2J + 3)B^0_2}{10kT} \right] + O\left(\frac{1}{T^3}\right) \tag{2.37}
\]

\[
\chi_{\parallel(001)} = \frac{C_R}{T} \left[ 1 - \frac{(2J - 1)(2J + 3)B^0_2}{5kT} \right] + O\left(\frac{1}{T^3}\right) \tag{2.38}
\]

with $C_R$ the Curie constant

\[
C_R = \frac{N(g\mu_B)^2}{3k} J(J + 1) \tag{2.39}
\]

Rewriting the formulas in the well known form of the inverse susceptibility gives

\[
\frac{1}{\chi_{\perp(001)}} = \frac{T}{C_R} - \frac{A B^0_2}{2C_R} + O\left(\frac{1}{T}\right) \tag{2.40}
\]

\[
\frac{1}{\chi_{\parallel(001)}} = \frac{T}{C_R} + \frac{A B^0_2}{C_R} + O\left(\frac{1}{T}\right) \tag{2.41}
\]

with $A = (2J - 1)(2J + 3)/5k$.

### 2.6.3 The effect of exchange interaction

In the paramagnetic regime, the magnetization of ions coupled by exchange interaction can be described, in a linear approximation, as:

\[
M = \chi_0 (\mu_i H + nM) = \chi\mu_i H \tag{2.42}
\]

$\chi_0$ is the susceptibility of the non-interacting system of $R$-ions, its inverse being given by eq. 2.40 or 2.41. $n$ is the molecular-field constant, that enters as an additional constant in the temperature dependence of the inverse susceptibility, $\chi^1 = \chi^{-1}_0 - n$. In figure 2.3 different
Theoretical description of the RNi₅ intermetallics

possibilities are sketched. The dashed lines indicate asymptotic values of χ⁻¹. Curve number one (1) gives the inverse susceptibilities of a system of rare-earth ions without exchange interaction and in a crystal field environment without a second order term. Curve two (2) is as curve one (1) but with an additional exchange interaction. The intercept of the susceptibility at zero kelvin with the y-axis is a measure for the molecular field coefficient n:

\[ n = \frac{1}{(g_J \mu_B)^2 J(J+1)} \frac{3 \theta^* k}{(J+1)} \]  \hspace{1cm} (2.43)

Here, \( \theta^* \) is the intercept of the dashed asymptote with the temperature axis. An analogous notation is used for the other curves. Curves number three (3) and four (4) give the susceptibilities of a rare-earth ion in an uniaxial (e.g. hexagonal) environment. The temperature shift, \( \Theta - \Theta \), is related to the second-order crystal field term \( B_0^2 \):

\[ B_0^2 = \frac{10k(\Theta - \Theta)}{3(2J-1)(2J+3)} \]  \hspace{1cm} (2.44)

We may apply this model as a first approximation to the RNi₅ compounds. All compounds show in the inverse susceptibility at high temperatures an almost linear behaviour. The slope found in measurements with the field in the different crystallographic directions do not differ appreciably and do correspond to the expected Curie constant. The position and the shift of the straight lines yield \( n \) and \( B_0^2 \). The anomalies at low temperature result from crystal field effects, and can be ascribed to the higher order crystal field parameters. In a more careful analysis, however, for the RNi₅ compounds, the Ni-contribution must be taken into account. Eventually, in our approach also these susceptibility measurements should be compared with the values calculated with our unique set of model parameters. We refer to section 5.4 where this programme is carried out for ErNi₅.
The inverse susceptibility versus temperature. Solid lines (1) and (2) represent rare-earth ions with and without exchange interaction in a cubic environment, respectively. The lines (3) and (4) represent the perpendicular and parallel susceptibility, respectively, of a system of rare-earth ions in a hexagonal symmetry. The temperature shift, $\theta_s - \theta_l$, is a measure for $B^s_2$ (here taken to be negative, see eq. 2.44).

2.6.4 Inelastic neutron scattering

The crystal field (CF) acts on the 4$f$ electrons of the rare-earth ions and causes a partial lifting of the degeneracy of the ground state multiplet. The overall splitting is usually ≤200 K. The number of levels and the degeneracy multiplicity are determined by the CF symmetry. In a study with inelastic neutron scattering of the hexagonal RNi$_5$ compound a number of energy differences, associated with level splittings, can be found.

Monochromatic neutrons are scattered from the sample, are detected, and analysed according to their energy and momentum. In this way the energy-transfer $\omega$ and the momentum -transfer $Q$ (scattering vector) are determined. By measuring the inelastic neutron cross-section one can find the transition energies $\varepsilon_{\nu'} = \varepsilon_{\nu} + \Delta$ between crystal field states $\nu'$ and $\nu$; the corresponding transition intensities, and the linewidths $\gamma_{\nu'}$ of the transition. In the dipole approximation the neutron scattering cross section is defined [Fulde (1979), De Gennes (1963)].

$$\frac{d^2\sigma}{dQd\omega} = \left( \frac{1.91e^2g}{2mc^2} \right) k_{\nu} e^{-2w} f^2(Q) \sum_{\nu'^{\prime}} \rho_{\nu}(T)|\langle \Gamma_{\nu'} | J_{\perp} | \Gamma_{\nu} \rangle|^2 F \left( \frac{\varepsilon_{\nu'} - \varepsilon_{\nu}}{\gamma_{\nu'}} \right)$$

Here $k_{\nu}$, $k_{\nu'}$ are the momenta of the incoming and outgoing neutrons. $f(Q)$ is the magnetic form factor of the rare earth ion and $e^{2w}$ is the Debye-Waller factor. $\rho_{\nu}$ are the Boltzmann population probabilities of the CF levels $\nu$. $J_{\perp}$ is the component of $J$ perpendicular to the scattering vector $Q$. $F(.)$ is the transition line form function, which can be approximated by a Gaussian. $\Gamma_{\nu}$ are the $2J+1$ states of the ground state multiplet.
The energy spectrum is composed of lines; the spacing of the lines gives the sequence of crystal field levels; the intensity gives the matrix elements of $J$ between the different states. The collection of transition lines found is characteristic for an energy level scheme. But it is impossible to index these transitions and connect them directly to the level scheme. A consequence of this is that other experiments in combination with inelastic neutron experiments have to be used to determine the crystal field parameters. In any calculated energy level scheme the energy separations found by neutron scattering have to be reproduced.

2.6.5 Muon Knight shift

In this paragraph a short introduction to the interpretation of muon Knight shift measurements will be given. A more elaborate treatment is given in Feyerherm [1995]. The experimental setup and an introduction to the muon technique will be given in chapter 4.

The muon behaves in many aspects as a light isotope of hydrogen. In analogy with nuclear magnetic resonance, the hyperfine field derived from the $\mu^+$ Knight shift is a manifestation of the local electronic susceptibility.

The Larmor precession of positive muons is induced when a magnetic field is applied perpendicular to the $\mu^+$ spin, see chapter 4. Implanting $\mu^+$ in any metal or metal alloy allows us to measure the Knight shift (KS) with high precision by the $\mu^+$ spin resonance ($\mu$SR) technique. In metals, the conduction electrons have nonvanishing wave functions at the $\mu^+$ site. When an electron overlaps the $\mu^+$ site, there is a direct magnetic coupling of their moments proportional to the hyperfine interaction, Fermi interaction or contact interaction. If the conduction electrons have no net moment this coupling would not yield a shift in the resonance. The applied field, of course, causes a shift directly. In paramagnetic compounds, the net moment is induced by the applied field and in fact that moment is proportional to the conduction electron spin susceptibility and the applied field. The Knight shift is defined as the relative difference between the magnetic field at the muon site and the external field $\mu_0 H$

$$\mu_0 H_{\mu} = \mu_0 H (1 + K)$$

$$K = \frac{H_{\mu}}{H} - 1 = \frac{\omega_0}{\omega} - 1$$

(2.46)

where $K$ is the Knight shift constant and $H_{\mu}$ the field at the muon site. The magnetic field is related to the Larmor precession frequency by $\omega_0 = \gamma_\mu \mu_0 H_{\mu}$, where $\gamma_\mu$ is the gyromagnetic ratio of the $\mu^+$. $\gamma_\mu = 8.5161 \times 10^8$ rads T$^{-1}$. Knight shifts for muons in metals are two to three orders of magnitude smaller than those for the nuclei of the host atoms themselves and amount to 10-100 ppm in simple metals [Karlsson 1982].

Several contributions to the Knight shift should be considered:

1. Direct Knight shift, $K_{np}$, due to Pauli paramagnetism of the conduction electrons.
2. A Knight shift, $K_{nf}$, reflecting the localized $f$ electrons moment.
3. Knight shift due to core polarization. This field is due to exchange interactions between polarized electrons at the Fermi level and those of lower energy having a finite probability at the muon site. This exchange gives rise to a contribution $\gamma_\mu$ to the susceptibility.
4. Diamagnetic screening due to the conduction electrons (Landau diamagnetism). This term is probably always very small.
5. Chemical shift which has its analogy in the chemical Knight shift in atoms and molecules. This negative shift constant is given by the Lamb expression [Gygax et al. 1984, Schenk 1985].

The local electronic structure enters the different terms to varying degrees. Altogether, all
aspects of the local electronic structure are to some extent reflected in the Knight shift. The Knight shift is compared with the bulk magnetic susceptibility as function of temperature. In $R\text{Ni}_5$ only the Knight shift due to the contributions (1) and (2) is taken into account.

In chapter 5 the results of Knight shift in Er$\text{Ni}_5$ are studied and some theoretical background is given.

2.6.6 Muon spin resonance spectroscopy
In longitudinal or zero field $\mu$SR measurement interpretation and analysis of the spectra is still in full development. The main results extracted from these $\mu$SR measurements are: the exponential damping of the muon, the initial asymmetry and the frequency of the precessing muon.

The outcome of the interpreted spectra is often not unambiguous. Mainly, the temperature dependence of the above mentioned properties have been determined.