Magnetic and Thermodynamic properties of RNi5 compounds

Kayzel, F. E.

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5 Results for ErNi₅

5.1 Introduction

Different ErNi₅ characteristics were studied with the experimental methods discussed in chapter 4. We performed high-field magnetization measurements on monocrystalline material and determined the heat capacity, also in applied magnetic fields. On powdered ErNi₅, inelastic neutron scattering measurements were carried out. In different geometries, muon spin resonance (µSR) measurements were performed on monocrystalline ErNi₅.

In specific-heat measurements on ErNi₅, Sankar et al. [1974] have shown the important influence of crystal field effects on the low-temperature energy. A magnetic ordering temperature of 8 K was found. Magnetization measurement by Escudier et al. [1977] on monocrystalline ErNi₅ revealed a ferrimagnetic ordering below 9 K. On the basis of these magnetization measurements a set of crystal field (CF) parameters was proposed by Escudier et al. [1977], leading to a dominant $|\pm 13/2\rangle$ ground state. For an overview of the parameters used by Escudier and other authors see table 5.3. Naït Saada [1980] introduced a slightly different set of parameters with the same ground state. A different ground state was proposed by Goremychkin et al. [1984]. From inelastic neutron scattering a dominant $|\pm 15/2\rangle$ ground state was deduced. Performing Mössbauer spectroscopy, Gubbens et al. [1988] came to the same conclusion. From high-field magnetization measurements along the [001] direction in combination with specific heat data, Radwański et al. [1992a, 1992b] derived a set of CF parameters that lead to a truly dominant $|\pm 15/2\rangle$ ground state. To resolve the controversy concerning the ground state of the Er ion, magnetization studies of ErNi₅ have been undertaken. On the basis of high-field magnetization measurements along the [120] direction, a different set of CF parameters was proposed by Zhang et al. [1994]. These CF parameters lead to the same ground state as proposed by Radwański et al. [1992a, 1992b], but yield a better description of the low-temperature magnetization along the difficult [120] direction. With the Zhang CF parameters a smooth metamagnetic transition at about 16 T was calculated. The set of CF parameters of Radwański et al. [1992a, 1992b] predicted a curve with a very sharp transition around 20 T along the [120] direction. In the present work we have refined the Zhang parameter set. Our parameters differ only slightly from the parameters reported by Zhang.

The description of the ErNi₅ system involves seven parameters. The complete set of parameters is seldom published as an entity. Most authors give only part of the parameters they have used to describe the system. The essential parameters used by us are (see chapter 2):

- four CF parameters $B_2^0, B_4^0, B_6^0, B_6^0$,
- the interaction between the Er atoms within their own sublattice, given by the intra-sublattice molecular-field coefficient $n_{\text{ intra}}$,
- the interaction between the erbium and nickel sublattices given by the inter-sublattice molecular-field coefficient $n_{\text{ inter}}$,
- the magnetic response of the Ni sublattice, described as a Pauli paramagnetic system with a temperature independent susceptibility, $\chi_{\text{ Ni}}$.

We determined these parameters carefully using the information of all the experiments we
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performed: magnetization in high-magnetic fields, paramagnetic susceptibility, specific heat on monocrystalline samples and inelastic neutron scattering on polycrystalline ErNi₅. Each of these experiments gives the possibility to extract a new piece of information that is not accessible from the other.

In addition, µSR measurements are reported. These experiments were not used in the determination of the CF parameters. However, they give a good picture of the magnetic behaviour of ErNi₅. The temperature dependence of the muon depolarization was measured on monocrystalline plates and on a large monocrystalline sample. The muon position in the hexagonal structure is provisionally determined with reasonable probability by muon Knight shift measurements.

5.2 Specific heat

5.2.1 The magnetic contribution to the specific heat

We have measured the specific heat of ErNi₅ on a 190 mg monocrystalline sample (#Q5802), semi-adiabatically in the temperature range from 1.5 to 250 K. These heat capacity measurements have been published in Radwański et al. [1992a, 1992b]. The measured specific heat of ErNi₅ is shown in figure 5.1. The data points of ErNi₅ above 200 K are less accurate due to measurement errors. The occurrence of the $\lambda$-type peak in ErNi₅ is associated with long-range magnetic order. It has its maximum at 8.9 K. For $T_\text{c}$ a value of 9.2 K is taken from the midpoint temperature between the peak and the lower end of the righthand side of the curve. Additional measurements of the specific heat on a second sample (see paragraph 5.5) lead to an unchanged peak position but to a more pronounced peak.

The specific heat has been analysed by considering the nuclear ($c_n$), electronic ($c_d$), lattice (or phonon) ($c_{ph}$) and the magnetic ($c_m$) contributions to the specific heat, see equation 2.31 in chapter 2.5.1.

The nuclear contribution, related to the hyperfine interaction of the 4$f$ shell with the nuclear moment of the 4$f$ ion, is not observed. In the case of the fully polarized 4$f$ shell of the Er ion, this specific heat adds significantly to the heat capacity below 1 K only.

The specific heat of the isomorphous non-magnetic compounds LaNi₅ and YNi₅ is shown as a reference in figure 5.1. In chapter 6 we discuss the specific heat of the two compounds in more detail. As expected from the difference in molar masses, the specific heat of YNi₅ is smaller than the specific heat of LaNi₅ at a certain temperature. The temperatures belonging to the LaNi₅ specific heat values have been multiplied by a correction factor of 0.959 to account for the difference in molar mass with respect to the magnetic compound ErNi₅, resulting in the dashed line in figure 5.1. Using the same procedure, with a correction factor 0.888 for YNi₅, resulted in the full line in figure 5.1, which appears to coincide with the corrected LaNi₅ curve in a large temperature region. These correction factors are calculated with equation 2.36 of paragraph 2.5.1. When subtracting the corrected lattice contribution of the non-magnetic equivalent from the ErNi₅ data, the so-determined magnetic contribution to the specific heat becomes negative above 70 K. This indicates that the corrected lattice contribution was overestimated. We therefore have kept the results of LaNi₅ as the lattice contribution of ErNi₅, so the difference of the (molar) specific heats of ErNi₅ and LaNi₅.
Figure 5.1 Heat capacity curves of monocrystalline ErNi$_5$ (#AF016 ♦) between 1.5 K and 200 K. As reference the heat capacity of the non-magnetic equivalent LaNi$_5$ (▲) and YNi$_5$ (▼) is shown. Additional lines are the LaNi$_5$ (dashed) and YNi$_5$ (full) specific heat corrected for the difference in molar mass.

Figure 5.2 The temperature variation of the magnetic contribution of ErNi$_5$ derived as the difference of the measured molar specific heat of ErNi$_5$ and that of LaNi$_5$ (see text). The full points are measured on sample #AF016 and the open data points are measured on sample #LM9203 (see section 2.2). The solid curve shows the ErNi$_5$ contribution calculated with the parameters in table 5.3.
measured at the same temperature, is taken as the magnetic contribution in ErNi$_5$. The resulting magnetic contribution is shown in figure 5.2. Above 100 K the derived values are less accurate. We have to subtract two large numbers finding a small value. Also the relative error in the measured specific heat at higher temperatures is considerable.

The magnetic contribution to the specific heat has been calculated using formula 2.30 and our parameter set (see table 5.3). The calculated curve is shown in figure 5.2 as the full line. The general behaviour is in good agreement with the experimentally derived magnetic contribution to the specific heat. It perfectly reproduces the position of the $\lambda$-type peak at 8.9 K associated with the occurrence of long-range order, as well as the broad maximum near 35 K.

The involved entropy up to 200 K is determined by integrating the experimental magnetic contribution to the $c_m/T$ (see figure 5.3). We calculated the theoretical entropy with our parameter set (solid line figure 5.3). There is little difference between these two. At 150 K it reaches a value of 21.5±1 JK$^{-1}$mol$^{-1}$ (assuming zero entropy at 1.3 K). This is close to the value expected for the $(2J+1)$-fold degeneracy of the ground state multiplet, i.e. $R\ln(16) = 23.04$ JK$^{-1}$mol$^{-1}$. This shows that at 200 K almost all levels are involved in the specific heat.

Measurements of the specific heat of ErNi$_5$ have been reported before by Sankar et al. [1974]. Above 50 K their specific heat of ErNi$_5$ is lower than our observation. The magnetic contribution to the specific heat derived by this author is thus smaller than our present result. Their magnetic entropy values, evaluated up to 300 K, are $R\ln 2$ short of $R\ln(2J+1)$ (in this case $R\ln 16$). This deficit is attributed to the presence of two states with a small energy

![Figure 5.3](image)

**Figure 5.3** Temperature variation of the experimental entropy of ErNi$_5$ (samples #AF016 ◆ and #LM9203 ○) after substraction of the LaNi$_5$ contribution. The calculated entropy is given as a full line. Also indicated is the entropy associated with the degeneracy of the $4f$ $J = 5/2$ multiplet amounting to $R\ln 16 = 23.04$ JK$^{-1}$mol$^{-1}$. 

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difference (about 1 K). Fitting the specific heat with point charge calculations they find a ground state \([13/2]\) and indeed another state 0.9 K separated. This situation, of course, is not reproduced by our calculations (see e.g. figure 5.18).

### 5.2.2 Specific heat in magnetic fields

In this paragraph, we present specific-heat measurements on ErNi\(_5\) ( #LM9203) in applied fields along the easy [001] axis \((\mu_0H= 0, 0.3, 1, 2, 5 \text{ T})\). We could not fix the sample strongly enough to the substrate to measure the heat capacity along the hard direction. We calculate the influence of the field on the specific heat using the CF parameters in table 5.3.

The specific heat of ErNi\(_5\) has been measured in the temperature range from 1.4 K to 200 K in zero field, and up to 80 K in the above mentioned fields. Vacuum grease (Apiezon N) was used to fix the sample in position on a sapphire plate. A cryostat with a superconducting coil capable of generating steady fields up to 8 T was used. Into this cryostat the specific heat cell, described earlier in chapter 4, was inserted. The thermometers, Ru-oxide and Pt, were corrected for their field dependent resistance.

The magnetic contribution to the specific heat of ErNi\(_5\) with fields applied along the [001] direction is shown in figure 5.4. Again, the magnetic contribution to the measured specific heat of ErNi\(_5\) is obtained by subtracting the LaNi\(_5\) values. The height of the zero field \(\lambda\)-like peak amounts to 20 JK\(^{-1}\)mol\(^{-1}\), slightly larger than the value measured on the previous sample (#AF016, see figure 5.2). Also the broad peak at 30 K is higher. It suggests a better quality of the newly grown sample.

Applying a relatively small field along the easy magnetization axis leads to a collapse of the \(\lambda\)-peak. This can be observed in the measurement with a field of 0.3 T (symbols \(\square\) in fig. 5.4). The position of the top of the peak shifts to a lower temperature (8 K). The peak value is reduced to 14 Jmol\(^{-1}\)K\(^{-1}\). At temperatures above 17 K, the 0.3 T curve (measured up to 22 K) coincides with the zero-field measurement. An applied field of 1 T completely removes the \(\lambda\)-peak and only a broad transition is left with the top at a temperature of 12 K. The peak amounts to a value of 10 Jmol\(^{-1}\)K\(^{-1}\). In higher applied fields a broadening of this peak and a gradual shift to higher temperatures is observed. The 2 T curve (measured up to 45 K) approaches the zero-field specific heat at higher temperatures.

The specific heat in field has been calculated using the set of parameters of table 5.3. The results are presented in fig. 5.5. Note that the calculated specific heat takes into account only the internal fields. From the irregularly shaped sample, the form factor \(N\) could only be estimated up to a limited extent. To overcome this problem, the internal field is taken as an adjustable parameter in the calculations. The magnetization curves were calculated for different assumed fields. In this way we get a mapping of the applied field on the ‘assumed’ field. As a first approximation, the internal field was taken to be independent of the temperature. As the measure of the best fit we took the position of the \(\lambda\)-peak. We find in this way that an internal field of 0.01 T coincides best with an applied field of 0.3 T. If we make use of the equation for the demagnetizing factor \(N = (\mu_0H_{\text{app}} - \mu_0H_I) / (\mu_0\rho M)\), with \(M = M_s = 104.49 \text{ Am}^2\text{kg}^{-1}\) (8.62 \(\mu_\text{f.u.}^{-1}\)), \(\rho = 9442.5 \text{ kgm}^{-3}\), this result implies a demagnetizing factor \(N\) of approximately 0.6. For our irregularly shaped sample this value is reasonable. The demagnetizing factor should be between \(N = 0\) and \(N = 1\). At higher temperatures the influence

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Figure 5.4  The magnetic contribution to the specific heat of ErNi$_5$, derived as the difference between the molar specific heat of ErNi$_5$ and the zero-field values observed on LaNi$_5$, in fields applied along the [001] direction. The symbols (◊) 0.0 T, (□) 0.3 T, (○) 1.0 T, (△) 2.0 T and (▽) 5.0 T represent the results at the indicated applied field values.

Figure 5.5  The calculated Er contribution to the specific heat of ErNi$_5$ for different internal fields. The lines with the symbols (◊) 0.0 T, (□) 0.01 T, (○) 0.7 T, (△) 2.0 T and (▽) 5.0 T represent the curves, calculated at the indicated internal field values.

of the demagnetizing field must decrease. In our calculations, we ignored this effect

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(a possible source for a deformation of the calculated curve). The calculated curve for the 0.05 T internal field (not displayed) shows that the top of the λ-peak does not shift for such a low field. Experimental points at these fields display a greater steepness after the λ-peak than the calculated curve.

The specific heat measured in an applied field of 1 T can be best fitted with an internal field of 0.7 T corresponding to the same demagnetizing factor \( N \) as in the 0.01 T internal field case. It fits well the 1 T applied-field curve up to 15 K. At higher temperature this calculation does not follow the tendency of the 1 T curve and fails to describe the extra increase in heat capacity. One explanation for this behaviour is the change of the internal field, already mentioned above. The magnetization decreases with temperature and the contribution of the demagnetization to the internal field decreases. At higher temperatures, above the ordering temperature, the internal field will be almost equal to the applied field.

For the other calculated curves the relative contribution of the demagnetizing field becomes increasingly smaller at higher applied fields. We note that for these higher field values the agreement between calculated and experimental curves is satisfactory.

In conclusion, the calculated curves reproduce the shape of the experimentally observed curves. The λ-peak calculated at zero field is in fair agreement with the experimental data, although the observed points show a sharper peak.

5.3 High-field magnetization

The first reported magnetic measurement showed ErNi₅ to be ferromagnetic with a magnetization that is lower than the full rare-earth moment of 9.5 \( \mu_B \) per Er³⁺ ion. Bleaney [1963] concludes from the structure and the crystal field involved that ErNi₅ should have a spontaneous magnetization along the [001] axis. This magnetic moment formation was later confirmed in neutron diffraction measurements by Corliss [1964]. The magnetization along the three hexagonal axes up to 15 T has been measured by Escudier et al. [1977]. The [001] axis was shown to be the easy axis and a small difference between the [100] and [120] axis at 15 T was found. Our magnetization studies along the [001] and [120] axis up to 35 T were published in Radwański et al. [1992]. In addition, we performed measurements along the [100] axis. These measurements were performed to complete the high-field magnetization studies and to clarify the difference between the two directions in the basal plane.

The monocrystalline sample of ErNi₅ (#Q5802) for the magnetization experiment has been grown at the FOM-ALMOS centre of the University of Amsterdam. A sphere of 3 mm diameter has been spark-eroded from the as-grown monocrystalline rod. The magnetization measurements were performed in the High-field installation at the University of Amsterdam. At a temperature of 1.5 K, fields were applied along the [100] direction, [120] direction and [001] direction (see fig. 5.6). The magnetization has been measured with step-like pulses up to 35 T and with a linear decreasing pulse from 38 T down to 1.2 T. The results obtained in increasing and decreasing fields showed no difference, i.e. no hysteresis was found.

Figure 5.6 shows the magnetization of ErNi₅ measured along the main crystallographic directions, and that of a free-to-rotate sphere. Extrapolating the magnetic moment measured along the easy [001] axis down to zero field, we find a value of 8.62 \( \mu_B \text{f.u.} \). This is significantly higher than the value of 7.2 \( \mu_B \text{f.u.} \) reported by Escudier et al. [1977]. This experimental fact gives an unquestioned argument for a dominant \(|±15/2\rangle\) ground state, supporting the conclusions of Goremychkin et al. [1984]. The magnetization value increases
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Figure 5.6  High-field magnetization of ErNi$_5$ (#Q5802) at 1.5 K, measured along the principal hexagonal directions, used symbols [100]-axis ($\bigcirc$), [120]-axis ($\Delta$), free sphere ($\blacklozenge$) and [001]-axis ($\bigodot$). Points with open symbols are experimental values determined in stepped field pulses and full symbols are experimental values measured in continuous field pulses (shown are the values in decreasing fields). Solid lines are calculated curves.

linearly in higher fields and leads to a high-field susceptibility of $4.2 \times 10^{-3} \mu_B$ f.u.$^{-1}$. This high-field susceptibility of the easy magnetization axis equals the variation of the induced nickel moment, i.e. the nickel susceptibility, $\chi_{Ni}$. Taking for the Er magnetic moment a value of $9 \mu_B$ we derive an opposite average nickel moment of $0.076 \mu_B$ per Ni atom in zero applied field.

Up to 12 T, the magnetization along the [100] axis and [120] axis increases monotonously. At that point the two curves start to diverge. The magnetization along the [100] axis continues to increase whereas along the [120] axis a metamagnetic transition starts. Along the [100] axis the magnetization reaches a value of $7.10 \mu_B$ f.u.$^{-1}$ at 38 T. At this field along the [120] axis, the value for the magnetization amounts to $8.25 \mu_B$ f.u.$^{-1}$.

The high-field magnetization process along the different axes has been calculated with the total hamiltonian written in equation 2.28. and with values of our parameter set given in table 5.3. The results are shown in figure 5.6 as solid lines. The calculations and the experimental results for the magnetization along the three crystallographic axes are in good agreement. In particular, the magnetization along the easy [001] axis and the smooth variations along the two basal plane axes are reproduced accurately. The high-field induced anisotropy between the [100] and [120] axis is very well represented. The amplitude of the moments as well as their angle, $\theta$, with the [001] axis as a function of the applied field at 1.4 K are shown in figure 5.7. The angle $\theta$ first decreases gradually and similarly along the [100] and [120] axes. Above 14 T, with the field applied along the [120] axis, $\theta$ exhibits a sharp transition and reaches 90°.
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around 20 T. With the field applied along the [100] axis a somewhat less sharp transition occurs around 20 T. The amplitude of the Er moment decreases for both axes and reaches a minimum when it is forced into the [001] plane. For higher fields it increases again. Thick lines show the calculated moments along the [120] or the [100] magnetization axes. These curves, that must be compared to the experimental data, pass through zero in zero internal field and continue to increase monotonously above the minimum in the moments’ amplitude. Note that, in accordance with our observations, the calculated variation of the magnetic moment with the applied field along the [120] direction is much larger than that with the field along the [100] direction, although in the detailed calculation for both directions a rather sharp ‘metamagnetic’ transition does occur.

![Graph showing magnetic field dependence](image)

**Figure 5.7** Calculated field dependence of the amplitude of the magnetic moment (thin lines) and its projection on the field direction (thick line) (righthand scale) and of the angle between the moment and the [001] direction, when the field is applied along either the [120] axis or the [100] axis (lefthand side). The dashed lines represent the [120] axis and the full lines the [100] axis.

5.4 Susceptibility

On the same sample that was used to measure the high-field magnetization, the temperature dependence of the susceptibility was measured in the Louis Neél Laboratory in Grenoble. The resulting inverse susceptibility perpendicular and parallel to the [001] axis is shown in figure 5.8.

The susceptibility measured along the [001] axis diverges around 9 K. This is the critical temperature, $T_C$, where the system shows a spontaneous magnetization. The inverse susceptibility perpendicular to the [001] axis shows an upturn below 50 K.

Lines can be fitted through the reciprocal susceptibilities at higher temperatures assuming a linear temperature dependence. This is based on the simplified model $\chi = T/C - n$ ($C: \text{Curie constant}; n: \text{molecular-field constant}; see \text{section 2.6.2}$). However, at higher temperatures the

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Figure 5.8. Temperature dependent inverse molar susceptibility of ErNi$_5$ measured parallel and perpendicular to the easy [001] axis. The calculated susceptibility is given as a solid line. The average slope of the high-temperature part of the inverse susceptibility is given as a dashed line. The dashed-dot line is a theoretical line, see discussion in paragraph 5.4.

The parallel ($\chi_{\parallel}$) and the perpendicular ($\chi_{\perp}$) reciprocal susceptibilities are shifted with regard to each other. This shift varies from 71 K (at 100 K) to 62 K (at 300 K), with an average value of 67 K. From this anisotropy of the paramagnetic susceptibility between the basal plane and the sixfold axis [001], the second order CF parameter was estimated to be $-0.89$ K. This can be derived from the temperature shift $\theta_{\parallel} - \theta_{\perp}$ ($= -67$ K) (see figure 5.8), by using equation 2.44 of chapter 2.6.3: $B_2^0 = 10k(\theta_{\parallel} - \theta_{\perp})/3(2J-1)(2J+3)$ with $J = 15/2$, the total angular momentum of erbium; $k$ is the Boltzmann constant.

In paragraph 2.6.2, we introduced a simple model to estimate the molecular-field constant. Applying this model to our data we would derive a negative value, $n = -0.98$ T.f.u.$\mu_B^{-1}$. In a more careful analysis, the nickel contribution has to be taken into account. Using eq. 2.28, the susceptibility along the [001] axis and that in the hexagonal plane have been calculated on the basis of the set of parameters given in table 5.3. (with e.g. $n = 0.17$ T.f.u.$\mu_B^{-1} > 0$). The good agreement is visible in fig. 5.8 (solid lines). In order to show the influence of the Ni contribution more clearly, we calculated the susceptibility in a larger temperature interval (see fig. 5.9) The negative curvature, the apparently reduced values for the Curie constant and...
most striking- the wrong sign of the molecular-field constant in the first approximation originate from the nickel contribution.

\[
\chi^{-1}(T) \text{ (Tf.u./}\mu_B) \quad \text{calculated inverse susceptibility of ErNi}_5
\]

\[
\begin{array}{c}
0 \\
20 \\
40 \\
\end{array}
\]

\[
\begin{array}{c}
T(K) \\
0 \\
200 \\
400 \\
600 \\
800 \\
\end{array}
\]

**Figure 5.9** The calculated inverse susceptibility over a wide temperature range up to 1000 K; $\chi^{-1}$ is calculated using equation 2.28. A negative curvature over the whole temperature region is observable; the calculated curves for $T< 300$ K are shown in figure 5.8 as well, together with the experimental results.

### 5.5 Inelastic Neutron Scattering

The inelastic neutron scattering technique provides spectroscopic information on crystal fields (CF) in rare-earth compounds. The transition energy between CF levels is determined directly. This is different from measurements of magnetization, susceptibility, specific heat, thermal and electrical transport properties where one collects only indirect or integrated information.

Inelastic neutron scattering measurements have been performed on polycrystalline ErNi$_5$ powder. The sample has been prepared at the FOM-ALMOS facility. Erbium of purity 3N (99.9%) and nickel of 5N purity has been arc-melted on a water cooled copper crucible in an argon atmosphere in a stoichiometric composition. The melt was broken and crushed to powder. This powder was kept under argon atmosphere. Inelastic neutron scattering experiments were carried out above the ordering temperature, at 15 K and 60 K, with a time-of-flight (TOF) detector at the Interfacultair Reactor Instituut (IRI) in Delft.

In figure 5.10 and 5.11, the inelastic neutron scattering pattern is shown, for ErNi$_5$ at 15 K and 60 K respectively. These curves remain after subtraction of the measured background. In the experimental setup it is possible to measure the angle dependence of the scattered
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Figure 5.10  Inelastic neutron scattering spectrum of ErNi$_5$ at a temperature of 15 K obtained by the TOF spectrometer. Relative counts are plotted versus the energy transfer of the neutrons. The full line curve represents the experimental quasi-elastic line in the energy region from about $-1.5$ meV to 1.5 meV. These values must be multiplied by the indicated factor.

Figure 5.11  Inelastic neutron scattering spectrum of ErNi$_5$ at a temperature of 60 K obtained by the TOF spectrometer. Relative counts are plotted versus the energy transfer of the neutrons. The full line curve represents the experimental quasi-elastic line in the energy region from about $-1.5$ meV to 1.5 meV. These values must be multiplied by the indicated factor.

neutrons over 90°. As our sample was polycrystalline, it was not necessary to use the whole angle range. The resulting curve is an average of the first thirteen channels. We found that at
higher channels the background caused spurious results. The data are plotted as relative counts, i.e. as fractions of the central peak value. The neutron absorption side in figures 5.10 and 5.11 gives the clearest results.

Fitting the data at 60 K with a summation of coupled gaussian distributions, i.e. fitting simultaneously the position (but not the amplitudes) of the absorption and emission peaks, we find three distinct transitions, at energies $\epsilon_1 = 1.9(1)$ meV, $\epsilon_2 = 4.0(1)$ meV and $\epsilon_3 = 6.2(1)$ meV. These transitions were also found by Goremychkin et al. [1984] (see table 5.2). The fitting of data at 15 K gives a less clear result, i.e. the error was larger. At this temperature, distinct transitions are found at $\epsilon_1 = 1.8(2)$ meV and $\epsilon_2 = 4.0(2)$ meV. If we fit the data with three gaussian functions, an additional weak peak is indicated, at 5.7 meV. Goremychkin argues that $\epsilon_1$ is connected with a transition from the ground state to a first excited level. Transitions between higher excited levels will strongly depend on temperature due to the temperature induced occupancy of these levels. The intensities of the peaks connected to the excited levels initially grow with increasing temperature, whereas the intensity of the peaks connected to the ground state decrease. The absorption peak belonging to the transition energy $\epsilon_1$ hardly changes, pointing to a fully occupied level already at low temperatures. The occupancy of the lower level and the emission-to-absorption ratio is calculated (as the fraction $E_j^{0/1}$), with our parameter set (see table 5.3), and given in table 5.2. Here, we identify $\epsilon_1$ with the 21 K transition from the ground state to the first excited level, and $\epsilon_2$ with the transition from the first to the second excited level. One should bear in mind, however, that the first peak ($\epsilon_1$) is largely masked by the central peak. This might cause the apparent increase in intensity from 15 K to 60 K, whereas a decrease (by 50%) is expected. Focussing attention to the most reliable peak data, i.e. the absorption peak $\epsilon_2$ at 15 K and both the absorption and emission peak at 60 K, we find the agreement rather satisfactory.

The position of $\epsilon_1$ changes from 1.8 meV to 1.9 meV and the position of $\epsilon_2$ shifts from 5.7 meV to 6.2 meV. These shifts could be caused by almost identical transitions, with slightly

Table 5.1 Transition energy between crystal-field levels, $\epsilon_j$ in meV, the relative intensity of the absorption peak, $I_j^{ab}/I_0$, and the ratio of the intensity of the absorption and emission peak, $I_j^{em}/I_j^{ab}$, determined by fitting the experimental data with gaussian functions. Calculated is also $P_j$, the occupancy of level $j$. The first column gives the measuring temperature. The 90 K row gives the transition energy found by Goremychkin [1984].

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<th>$I_1^{ab}/I_0$ (%)</th>
<th>$I_1^{em}/I_1^{ab}$</th>
<th>$\epsilon_2$ (meV)</th>
<th>$I_2^{ab}/I_0$ (%)</th>
<th>$I_2^{em}/I_2^{ab}$</th>
<th>$\epsilon_3$ (meV)</th>
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<td>4.0(2)</td>
<td>1.9</td>
<td>0.12</td>
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<td>8.2</td>
<td>0.73</td>
<td>4.0(1)</td>
<td>3.2</td>
<td>0.50</td>
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<td>1.1</td>
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<td>90</td>
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<td></td>
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<td>calculated</td>
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<td>0.79</td>
<td>0.24</td>
<td>4.0</td>
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<td>5.7</td>
<td>0.008</td>
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<td>0.70</td>
<td>4.0</td>
<td>0.27</td>
<td>0.47</td>
<td>6.2</td>
<td>0.12</td>
</tr>
</tbody>
</table>

$R$Ni$_5$ Compounds
Results for ErNi$_5$

higher transition energy, contributing to these peaks at higher temperatures. Concluding, the first and second peak can be ascribed to transitions from a low lying level including the ground state. The peak, $e_3$, is connected to a transition from a level that is stronger populated at higher temperature, i.e. from a higher excited level. Some possibilities are indicated in figure 5.18.

5.6 Muon measurements

5.6.1 Muon spin rotation

In the muon spin rotation measurements, a field perpendicular to the incoming beam, i.e. to the muon polarisation is applied. This is called the transverse field (TF) geometry (see chapter 4.4.3), which is used for Knight shift measurements. Fast muons are used (see chapter 4.4.2). A. Schenk and co-workers at the Paul Scherrer Institute (PSI) performed such measurements on an ErNi$_5$ monocrystalline sample with an average diameter 6 mm and about 50 mm long, grown by us at the FOM-ALMOS facility of the Van der Waals-Zeeman Institute. An oriented seed was used as the start of this crystal growth experiment. The crystal growth direction was approximately along the [120] axis (see fig 5.14). This large piece of monocrystalline material was oriented, within 1°, along the [120] axis, and cut in three parts of 15 mm length. In order to obtain a sufficiently large measuring volume, these oriented cylinders were packed. In this way a “monocrystalline” sample was constructed with an effective diameter of 8 mm and a length of 15 mm. The µSR Knight shift of this sample has been measured and an analysis of these measurements is presented in what follows.

At 300 K, an angular scan with a transverse field of 0.5043(7) T has been made. The incoming beam and the muon polarization are directed along the [120] axis. That axis is also the rotation axis of the sample during the angular scan. A single signal was observed, (see figure 5.12) with the relaxation rate $\lambda$ of 2.9×10$^{-6}$ s$^{-1}$, independent of the orientation. This value is the same as in zero-field measurements (see fig 5.16). The Larmor precession frequency due to the field only would be $\nu^0_\mu = \mu_\mu H_{app} \gamma_\mu / 2\pi = 68.36$ MHz $\gamma_\mu / 2\pi = 135.55342$ MHz T$^{-1}$, the gyromagnetic ratio see chapter 2.6.5 and 4.4.1).

Temperature scans were performed by measuring at four different temperatures between 100 K and 250 K. Two different geometrical setups were used. One setup had the incoming muon beam along the [120] direction of the sample and the applied field along the [001] axis. In the other setup the incoming beam was aligned as above and the field was applied along the [100] axis. In the latter case, at lower temperatures a splitted signal appeared (see figure 5.13). To fit the data in this configuration, it was assumed that the relaxation rates for both signals are equal and are given by the results for the field applied parallel to the [001] axis (for $\omega < 1$). The amplitudes of these two signals have a ratio of 2:1.

Going from 250 to 300 K the splitting disappears. This must be due to the onset of rapid muon diffusion. We can conclude that the Larmor precession frequency measured in the angular scan at 300 K reflects an average value for the Knight shift.

The appearance of the split signal together with the amplitude ratio for the split signal of
Figure 5.12  Muon spin rotation measurement showing the angular dependence of the Larmor precession frequency, $v_\mu$, with the field (of 0.5043 T) perpendicular to the [120] axis and the sample rotating around the [120] axis. The position of the [100] and the [001] axes are indicated. The full line is a fit to the equation $v_\mu(\theta) = a' + b'\cos(2\theta)$ (eq. 5.2), with fitting parameters $a' = 68.16$ MHz and $b' = -0.475$ MHz.

Figure 5.13  The observed frequencies with the applied field parallel to the [001] axis ($\vartriangle$). In the other setup the field was applied parallel to the [100] axis. Then, two frequencies are observed ($\vartriangle$) and (□). The lines are guides to the eye. $f^{(1)}$, $2f^{(2)}$, $3f^{(j)}$ refer to the different sites occupied by the muons, see text.
2:1 is only consistent with the assumption that the $\mu^+$ is residing at an interstitial site with at least three (or $3n$, with $n = 1, 2, 4$) equivalent positions, and which become inequivalent under the influence of a field along the [100] axis. That means any site not located on an ‘internal’ three fold axis. The 3f-site (positions [1/2,0,0], [0,1/2,0], [1/2,1/2,0]), see figure 5.14, is one of the five possible sites given by a study of hydrogen absorption in LaNi$_5$ [Percheron-Guégen et al 1980]. In PrNi$_5$ the 6i site, of which the projection on the hexagonal plane gives the 3f-site, is determined as the muon location [Feyerherm 1996].

At a particular site $j$ the Larmor frequency $\nu^{t}_{\mu}$ is given by (see sections 2.6.5 and 4.4.3, eq. 4.17)

$$2\pi \nu^{t}_{\mu} = \gamma_\mu \mu_0 H^t_{\text{eff},\mu}$$

The effective field $H^t_{\text{eff},\mu}$ is the vector sum of the actual (local) field at site $j$ and the field representing the contact interaction, by assumption proportional to the local electron spin-polarization (conduction electrons and presumably in particular the 3d-electrons). The Knight shift is the relative deviation of the observed frequency from the frequency in the applied field only, i.e. $K^{t,\beta} = (H^t_{\text{eff},\mu} - H_{\text{app}})/ H_{\text{app}}$ (see eq. 2.46, and the discussion in section 4.4). In the following derivation, we use the magnetic induction ($\mu_0 H$, SI units tesla) and the magnetic moment per unit of matter ($M_d$, $M_f$, SI unit Am$^2$mol$^{-1}$f.u.$^{-1}$, or -equivalently- expressed in $\mu_B$/f.u. = 5.85 Am$^2$mol$^{-1}$f.u.$^{-1}$), rather than magnetic field and magnetization ($H$, $M_d/V$, SI units Am$^{-1}$), respectively.

In this notation the actual field (induction) at site $j$ is the sum of:
- the applied field $\mu_0 H_{\text{app}}$,
- the dipolar field exerted by the Er-moments, written as $\{A^t_{\mu} + (\mu_0/V)(1/3 - N)\} M_j$,
- the dipolar field exerted by the Ni-moments (3d mainly), taken to be $-N(\mu_0/V) M_d$.

The local electron spin-polarization (giving rise to the contact interaction) is the sum of the local response to the (averaged) internal field and the response to the exchange interaction with the Er-moments. We assume that the latter contribution is equal to the response to an (averaged) internal field $n_{d\mu} M_j$ (i.e. the molecular field), keeping in mind that deviations are conceivable. In short, in first instance, the contact interaction is assumed to be proportional to $M_d = \chi_d (\mu_0 H_{\text{app}} - N M_j + n_{d\mu} M_j)$, where the Ni-susceptibility $\chi_d$ as well as the molecular field parameters $n_{d\mu}$ are assumed to be scalars.

In order to be explicit, we choose a coordinate system fixed to the crystal, with x||[100], y||[120] and z||[001] (see figure 5.14). The applied field lies in the (x, z) plane: $H^x_{\text{app}} = H \cos \vartheta$, $H^z_{\text{app}} = H \sin \vartheta$. Having in mind the geometrical form and orientation of our artificial sample, we state that components in the y-direction do occur, neither of field nor of magnetic moments. Moreover, we assume that our artificial sample has rotational symmetry around the [120]-axis, so that the tensor $N$ can be replaced by a scalar $N (=N_{xx} = N_{zz})$. For ErNi$_5$, with density $\rho = 9442.5$ kgm$^{-3}$ and molar mass 0.46081 kgmol$^{-1}$, so with molar volume $V = 48.8 \times 10^6$ m$^3$mol$^{-1}$, the factor $\mu_0/\rho V = 0.02575$ TmolAm$^{-3}$ = 0.1438 T.f.u.$\mu_B^{-1}$. At a maximum susceptibility $\chi$ of 0.3 $\mu_B$/f.u.$^{-1}$, the “direct” Knight shift $-N(\chi/(\chi_{\mu} V))$ would be about -0.8% (with $N \approx 0.2$) or even 2% (with $N \approx 0.5$), so not negligible with respect to the experimentally observed values of a few percent. Notice, however, that deviations of the rotational symmetry, leading to strong variation in the effective demagnetizing fields, would have caused strong variations in the observed frequency in the angular scan (fig. 5.12). Such variations obviously are absent or relatively small. In passing, we remark that the rotational axis is slightly tilted, but that we ignore this fact here because we expect the influence to be at least one order of magnitude.
smaller, and hence negligible. We conclude that the $x$- and $z$-component of the magnetic moment can be regarded to be independent, being the response to applied fields $H\sin \theta$ and $H\cos \theta$ in the $x$- and $z$-direction, respectively. The same conclusion applies for the effective fields $H_{\text{eff}, \mu}^{(j)}$. For the site $f^{(1)}$ (see fig. 5.14), this follows directly from the fact that the tensor $A^{(1)}_f$ is diagonal in the coordinate system chosen, because of the local symmetry of the site. In table 5.2, we give as an example the result of a rigid lattice calculation of the dipole field exerted by the 4f-moment [A. Schenk 1993]. For the $f^{(2)}$ site, the corresponding components can be obtained from those for the $f^{(1)}$ site by performing a rotation over 60°: $A^{(2)}_f = \frac{1}{4}(A^{(1)}_f \alpha \beta + 3A^{(1)}_f \gamma \gamma)$, and so on (see table 5.2). The components perpendicular to the applied field, however, can be neglected in first approximation, since they contribute only in second order. Then, in linear approximation, the Knight shift $K$ can be written as

$$K = K_{[001]} \cos^2 \theta + K_{[100]} \sin^2 \theta = \frac{K_{[001]} + K_{[100]}}{2} + \frac{K_{[001]} - K_{[100]}}{2} \cos 2 \theta$$  \hspace{1cm} (5.1)$$

In order to discuss the observed Knight shift further, we recall (see e.g. eq. 2.21)

$$M_d = \chi_d \left( \mu_0 H + n_{f,0} M_f \right)$$  \hspace{1cm} (5.1)$$

Here $H$ is considered to be the applied field $H_{\text{app}}$. The corrections due to the demagnetizing field can be neglected (or can be incorporated in the susceptibility and the molecular field constant). Now, we expect $M_f$ to depend strongly on the temperature, of course leading also to a strong temperature dependence of the total magnetic moment.

Figure 5.14  Probable muon positions in the hexagonal plane, i.e. 3f site. The principal axes are indicated and the direction of the applied field at which the 3f sites are broken up into 2f$^{(2)}$ and one f$^{(1)}$ site.

In section 5.3, we showed that the experimentally observed susceptibility can be calculated rather accurately in our model, with the parameters given in table 5.3. Consequently, we may assume that the calculated Er-moment represents the actual moment also quite satisfactorily. For that reason we split the Knight shift in a part which does not depend on the Er-moment and a part proportional to the effective 4f- susceptibility $\chi_{\text{eff}}^4$, defined as the calculated Er-moment divided by the applied field taken in the calculation, in the direction $\alpha = x, z$.

Assembling the different contributions, we find

$$K^{(j)\alpha} = K^{(j)\alpha}_d + K^{(j)\alpha}_f$$
$$K^{(j)\alpha}_d = -N^{\alpha\alpha}(\mu_0 V) \chi^\alpha_d + A^{(j)\alpha}_d \chi^\alpha_d$$
$$K^{(j)\alpha}_f = \left\{ A^{(j)\alpha}_f + (\mu_0 V) \left(1/3 - N^{\alpha\alpha}(1 + n_{f,0} \chi^\alpha_f)\right) \right\} \chi^\alpha_{f,\text{eff}}$$

For generality, the 3d-contribution is allowed to be anisotropic, either because of the form of
the sample ($N^x \neq N^y$) or because the local spin density has an anisotropic response. Here, $A_{d}^{(j)\alpha\alpha}$ is a measure for the contact interaction at site $j$, i.e. in the presence of a Ni-moment with components $M_{d}^{\beta}$ the corresponding effective field is given by $\sum_{\beta} A_{d}^{(j)\alpha\beta}M_{d}^{\beta}$. In fact, taking $\chi_{d}$ equal to $\chi_{Ni} \approx 4.2 \times 10^{3} \mu_{B}T^{-1}$f.u. (see table 5.3) we can neglect the contribution in $K_{d}^{(j)zz}$ due to the demagnetizing field. Also $n_{id}\chi_{d}$, estimated to be about $-27 \times 10^{-3}$, can be neglected with respect to unity. Writing down the expressions for the sites $f^{(1)}$ and $f^{(2)}$ explicitly, for the field directions $[100]$ and $[001]$, we have

$$K_{t}^{(1)[100]} = \{ A_{t}^{(1)xx} + (\mu_{o}/V)\left(1/3 - N^{xx}\right) + A_{c}^{(1)xx} \} \chi_{t,eff}^{[100]}$$

$$K_{t}^{(2)[100]} = \{ 1/4\{ A_{t}^{(1)xx} + 3A_{t}^{(1)yy} \} + (\mu_{o}/V)\left(1/3 - N^{xx}\right) + A_{c}^{(2)xx} \} \chi_{t,eff}^{[100]}$$

$$K_{t}^{(j)[001]} = \{ A_{t}^{(1)zz} + (\mu_{o}/V)\left(1/3 - N^{zz}\right) + A_{c}^{(j)zz} \} \chi_{t,eff}^{[001]} \quad (j = 1, 2)$$

Here $A_{c}^{(j)zz} = A_{d}^{(j)zz}\chi_{d}n_{id}$.

At high temperatures, rapid diffusion would leave $K_{t}^{[001]}$ unchanged and would yield an average, $\overline{K}_{t}^{[100]}$, over the $2f^{(2)}$ and the $f^{(1)}$ site:

$$\overline{K}_{t}^{[100]} = 1/3 (2K_{t}^{(2)[100]} + K_{t}^{(1)[100]})$$

$$= \{ -1/2(A_{t}^{(1)xx} + A_{t}^{(1)yy}) + (\mu_{o}/V)(1/3 - N^{xx}) + 1/2(A_{c}^{(1)xx} + A_{c}^{(1)yy}) \} \chi_{t,eff}^{[100]}$$

(5.1)

Here $\delta A_{c}^{(1)zz}$ represents a possible anisotropic contribution to the contact interaction. Fig. 5.15 shows a plot of the observed Knight shift, observed at different temperatures, versus the calculated effective 4f-susceptibility $\chi_{t,eff}$. For the direction $\alpha = [001]$ a satisfactory linear dependence is found, yielding a slope $dK_{t}^{[001]}/d\chi_{t,eff}^{[001]} = -0.086$ T.f.u. $\mu_{B}^{-1}$. From this result, we want to derive a value for $A_{t}^{(j)zz}$, using the third line in eq. 5.5. We start by estimating the other contributions. Extrapolation down to $\chi_{t,eff}^{[001]} = 0$ yields $K_{d}^{(j)zz} = -0.25\%$ (independent of the site $j$, of course). With $\chi_{d} = 4.2 \times 10^{3} \mu_{B}T^{-1}$f.u.^{-1}, we have, from eq 5.4,

$$A_{d}^{(j)zz} = K_{d}^{(j)zz} / \chi_{d} = -0.6$ T.f.u. $\mu_{B}^{-1}$. Consequently, with $n_{id} = -6.4$ T.f.u. $\mu_{B}$ (see table 5.3), we find thus $A_{c}^{(j)zz} = A_{c}^{(j)zz} = A_{d}^{(j)zz} \chi_{d}n_{id} = n_{id} K_{d}^{(j)zz} = 0.017$ T.f.u. $\mu_{B}^{-1}$. The contribution $(\mu_{o}/V)(1/3 - N^{xx})$ is also of the magnitude of about 0.01 T.f.u. $\mu_{B}^{-1}$, of either sign (depending on whether one assumes $N^{xx} = 0.2$ or $N^{xx} = 0.5$ to be the better choice). Anyway, from this analysis $A_{t}^{(j)zz}$ is expected to be near to $-0.086 - 0.017 = -0.1 \pm 0.01$ T.f.u. $\mu_{B}^{-1}$.

For the direction $\alpha = [100]$, the picture is much less clear. Let us first consider the result at 300 K, where the signal is not split anymore. Ignoring the possible anisotropies in the demagnetizing field and in the contact interaction, the difference in slope (indicated in fig. 5.15) gives $3/2A_{t}^{(1)zz}$ instantly, or more in detail

$$\frac{dK_{t}^{(j)[001]}}{d\chi_{t,eff}^{[001]}} = \overline{K}_{t}^{[100]} - \frac{K_{t}^{(j)[001]}}{\chi_{t,eff}[001]} = \frac{3/2A_{t}^{(1)zz}}{\chi_{t,eff}[300K]}$$

(5.1)
Results for ErNi$_5$

Figure 5.15  The relative Knight shift in two different configurations plotted against the calculated $f$ electron susceptibility, $\chi^f_{\text{eff}} M_f / H_{\text{app}}$. $\chi^f_{\text{eff}}$ gives the Knight shift with the field parallel to the [001] axis, $K^{(2)[100]}$ (□) and $K^{(1)[100]}$ (▲) are the Knight shifts with the field in the [100] direction. The slope of the dashed lines gives the $\chi^f_{\text{eff}} = -0.086$ T.f.u/$\mu_B^{-1}$ and $\chi^f_{\text{eff}} = +0.095$ T.f.u/$\mu_B^{-1}$, respectively.

This leads to the estimate $A_{\text{f}}^{(1)zz} = 2/3(-0.086 - 0.095) = -0.121$ T.f.u/$\mu_B^{-1}$, in quite satisfactory agreement with the estimate above. We may infer from the rather consistently low values for $K^{(1)[100]}$ (see figure 5.15), that the anisotropies are not large, indeed. We conclude, that a rather reliable value for $A_{\text{f}}^{(1)zz}$ has been deduced.

Now comparing this value with the calculated values for the 3f-sites and the 6i-sites, respectively, given in table 5.2, we find that the f-site is the most probable muon stopping centre. Of course, the other Knight shift measurements should be consistent with this picture. For the Knight shift at site f$^{(2)}$, with the field in the [100] direction, very low values are expected (the negative value $A_{\text{f}}^{(2)xx} = -0.024$ T.f.u/$\mu_B^{-1}$ just about being compensated by the other contributions), again in accordance with experiment. (Note: also for the 6i-sites, in this configuration very low Knight shift values are expected.) Finally, for the f$^{(1)}$-site, in this configuration, rather large positive Knight shifts are expected ($A_{\text{f}}^{(1)xx} = +0.215$ T.f.u/$\mu_B^{-1}$). Such large values were found at temperatures between 150 K and 250 K, indeed. Apparently, large deviations do occur, preventing a systematic derivation of the slope, at low temperature, leading to an experimental result for which we have no explanation at the moment. We hope, that more accurate measurements can give a clue for the solution, in future.

So, from this analysis, we conclude that the 3f site is the preferential muon site in ErNi$_5$. 
Results for ErNi$_3$

Table 5.2

In this table the estimated slope $dK_f^{(001)}/d\chi_d^{(001)}$ along the [001]-axis and the [100]-axis are given. In the second part the experimental and calculated dipole coupling tensor for the muon sites 3f and 6i in Tf.u.$\mu$$_B$ are given. The site found in PrNi$_3$ [Feyerherm 1996] is the 6i ($z = 0.21$) position.

<table>
<thead>
<tr>
<th>experiment:</th>
<th>Tf.u.$\mu$$_B$</th>
<th>theory:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$dK_f^{(001)}/d\chi_d^{(001)}$</td>
<td>-0.087</td>
<td>$dK_f^{(1)(100)}/d\chi_d^{(100)}$</td>
</tr>
<tr>
<td>$d\overline{K}_f^{(001)}/d\chi_d^{(001)}$</td>
<td>+0.095</td>
<td>$dK_f^{(2)(100)}/d\chi_d^{(100)}$</td>
</tr>
</tbody>
</table>

| $A_i^{xx}$ (Tf.u.$\mu$$_B$) | $A_i^{yy}$ | $A_i^{zz}$ | $A_i^{xy}$ |
| experimental | -0.121 | |
| calculated $A_i^{xx}$ at site | |
| f$^{(1)}$ | +0.215 | -0.103 | -0.112 |
| 2f$^{(2)}$ | -0.024 | +0.136 | -0.112 | -0.048 |
| 6i ($z=0.21$) | +0.149 | -0.092 | -0.058 |

The 6i site found in PrNi$_3$ [Feyerherm et al. 1996] is less likely. The $\mu^+$ may be regarded as a ‘light isotope’ of hydrogen when it is residing at an interstitial site in a metal.Muon spin rotation experiments are equivalent with hydrogen-NMR Knight shift measurements in the limit of zero hydrogen concentration. We can not compare our results with deuterium studies of LaNi$_3$ [Norëus et al. 1983]. There the crystal structure of LaNi$_3$D$_6$ (space group P31m) is different, due to the uptake of 6 hydrogen/deuterium atoms. Dalmas de Reotier [1990] finds in LaNi$_3$, with muon measurements at 18 K in zero field, a depolarization time 0.100(2) $\mu$s$^{-1}$ and a decay time of 17(5) $\mu$s of the muon. He arrives at the conclusion that the 3f site is occupied by the muon.

5.6.2 Muon spin relaxation

We performed muon spin relaxation experiments with a beam of slow muons (surface muons, see section 4.4), that do not penetrate far into the sample. Hence, flat samples covering a big surface are needed. We performed $\mu$SR measurements on a mosaic of monocrystalline slabs. Two orientations of monocrystalline slabs are used, hereafter called sample 1 and 2. Each sample consists of about 15 monocrystalline slabs (thickness ~0.5 mm) sparc-eroded from one monocrystal with a diameter ~6 mm and a lengh of 20 mm. The slabs are fixed with vacuum grease on a silver plate. The slabs cover a square cross section of about 33×33 mm$^2$. The slabs of sample 1 are cut with their surface perpendicular to the [001] axis. After fixing the slabs onto the silver plate their orientation in the hexagonal plane ([100]-[120] plane) is arbitrary. Sample 2 is oriented with the surface of the slabs perpendicular to the [100] axis. Again their orientation in the [001]-[120] plane, perpendicular to the [100] axis, is arbitrary.

Measurements have been performed at ISIS and PSI. The samples have been measured with a longitudinal geometry and have been analysed using the muon depolarization function.

RNi$_3$ Compounds
In muon spin relaxation measurements, the relaxation rates are determined without external field, so above $T_c (= 9.2 \, \text{K})$ no corrections for demagnetizing fields have to be taken into account. At 300 K, a measurement with a longitudinal field of 0.2 T showed the same results as the measurement without field. The measurements were done in a temperature range from 2.5 to 300 K. In figure 5.16, the spectrum of ErNi$_5$ is shown as registered at 70 K at zero field. The muon depolarization function is well described by an exponential function. The solid line is the exponential fit for the depolarization damping.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{spectrum.png}
\caption{Time dependence of the muon polarization in zero field. The solid line is the exponential fit for the depolarization damping.}
\end{figure}

The first measurements were performed at ISIS where the two samples were used to determine the depolarization function along the [001] and [100] axes (figure 5.17). The depolarization, $\lambda$, is higher than in other RNi$_5$ compounds. For $T > 200 \, \text{K}$, $\lambda$ does not depend on the orientation of the initial muon polarization. At these high temperatures the muon diffusion is fast (the diffusion correlation time is $< 1 \, \mu\text{s}$). Starting at 200 K the damping rate with the polarization along the [100] axis, $\lambda_{[100]}$, increases with decreasing temperature. At ISIS it was impossible to measure signals with a damping rate above 15 MHz. At PSI it is possible to measure up to 60 MHz. For this muon beam geometry, the damping rate below $T \approx 55 \, \text{K}$ in the [100] direction is too large to be measured, even at the PSI facility.

Below $T_c = 9.2 \, \text{K}$ we could only find a signal in the geometry with the initial polarization along the [001] direction. At the lowest temperatures the signal for sample 1 (muon spin $P_{[001]}$) entered again within the measuring window at ISIS (open circles in figure 5.17). We acquired measurement time at PSI and we could extend the measurement to higher damping rates (full circles in figure 5.17). At PSI, the spin rotator makes it possible to use only one sample for the two different geometries, i.e. with the initial polarization parallel and perpendicular to the [001]-axis. The $\mu$SR damping rate recorded on sample 1 and 2 at ISIS and the damping rate recorded at PSI give the same result.

From these muon measurements we see that the damping is strongly anisotropic even at $T \sim 20 \times T_c (180 \, \text{K})$. The increase of $\lambda_{[001]}$ for $T < 50 \, \text{K}$ is probably due to the fact that the...
Results for ErNi$_5$

Figure 5.17  Temperature dependence of the $\mu$SR relaxation rate measured on ErNi$_5$. With the initial polarization ($P_i$) parallel and perpendicular to the [001]-axis. The open circles refer to measurements at ISIS with sample 1 and open circles with a triangle are measurements on sample 2 (see text). The solid circles have been measured at PSI and are independent of sample 1 or sample 2.

Magnetic fluctuations are quasi-static as indicated by the $^{166}$Er Mössbauer spectroscopy measurements of Gubbens [1993]. From 2.5 K to up about 7 K the spectra could easily be fitted with one damping rate. At about 12 K a maximum of $\lambda_{P_i\parallel[001]}$ has been observed. Below 12 K we observe a drop of the total asymmetry, $a$, from 0.212 to 0.159.

5.7 Discussion

Using the total hamiltonian given in chapter 2 (eq. 2.28) different physical properties have been calculated. In an iterative process the calculated specific heat, susceptibility, magnetization and the level scheme are compared with the experimental data, in order to find an optimal set of parameters.

The low temperature magnetization curve in the basal plane, especially the smooth metamagnetic transition along the [120] direction and the field induced anisotropy between [120] and [100] in fields above 14 T give the opportunity to determine the parameters precisely. Considering the inelastic scattering peaks and the magnetization along the easy axis [001] we adopt the assumption, proposed previously, of a dominant $|\pm15/2\rangle$ state as the ground state. The first excited state is a dominant $|\pm13/2\rangle$ level. This state is located at 21 K (1.8 meV) above the ground state. All these experimental facts give us the opportunity to select eventually the best parameter set. Our parameter set is given in table 5.3 in a bold typeface. Additionally, in table 5.3 the parameters used by different authors are given.
Table 5.3  Crystal field parameters $B_{ij}$ of the Er$^{3+}$ ion and the nickel susceptibility, as well as the molecular-field constants according to different authors, for ErNi$_5$.

<table>
<thead>
<tr>
<th></th>
<th>$B_{ij}$ (K)</th>
<th>$B_{ij}$ (10$^3$ K)</th>
<th>$B_{ij}$ (10$^5$ K)</th>
<th>$x_m$ ($10^5$ $\mu_B$/T)</th>
<th>$n_{pp}$ (Tf.u./$\mu_B$)</th>
<th>$n_{as}$ (Tf.u./$\mu_B$)</th>
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<td>14.4</td>
<td>329</td>
<td>4.8</td>
<td>0.04</td>
<td>-5.2</td>
</tr>
<tr>
<td>this work</td>
<td><strong>-0.88</strong></td>
<td><strong>-1.07</strong></td>
<td><strong>14.4</strong></td>
<td><strong>329</strong></td>
<td><strong>4.2</strong></td>
<td><strong>0.01</strong></td>
<td><strong>-6.4</strong></td>
</tr>
</tbody>
</table>

Compared to the parameter set of Zhang we changed the nickel susceptibility and the $B_{2}^{0}$ crystal field parameter slightly to obtain a better agreement with the magnetization with the field applied along the easy axis. In particular, the magnetization along the easy [001] axis and the smooth variations along the two basal plane axes are reproduced accurately. The high-field induced anisotropy between the [100] and [120] axis is very well represented.

The calculated susceptibilities are reported as the curves in figure 5.8 and 5.9. The temperature dependence of the inverse susceptibility along the hard axis and that of the easy axis are in excellent agreement with the experimental results. The calculated specific heat is reported in figure 5.5. Again, the calculated curve and the experimental data agree very well. The discrepancies found in the curves can be associated to inaccuracies in the determination of the non-magnetic contribution. Experimental data with the field applied along the [001] direction matches well the calculated specific heat in the same fields (apart from the uncertainty in the demagnetizing field). The calculated CF splitting of the ground state multiplet $^4I_{15/2}$ of the Er$^{3+}$ ion is given in an energy level scheme, see figure 5.18, together with the corresponding eigenfunctions. The observed INS transition energies agree well with the calculated crystal field splitting.

Muon Knight shift observations could well be explained with direct dipolar-field calculations. This analysis promises the use of muons as probe to observe ‘directly’ the magnetic structure at low temperatures (i.e. material with magnetic order) and high fields (i.e. in the hard direction).

The calculations and our analysis indicate that a collection of measurements is needed to
get a single set of parameters that describe all phenomena in a satisfactory way. Adaptation of a parameter set to one kind of measurement is always possible, leading to a better fit for that particular kind of experiment. We prefer, however, to consider one set of parameters, simultaneously adjusted to as many different kinds of measurements as possible, at the expense of not being able to match all separate phenomena as well as would be possible in a “dedicated” analysis.

**Figure 5.18** Scheme of the splitting of the ground multiplet of the ion Er$^{3+}$ by the crystal field between 1.5 K and 30 K (on the left). Arrows are indicating the main transitions. The energies observed by neutron spectroscopy are indicated by ε. On the right the level scheme with a field applied along the [120] direction.