The specific heat of ErNi$_5$ and LaNi$_5$

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Received 26 June 1992

Abstract. The specific heat of ErNi$_5$ and LaNi$_5$ has been measured on single-crystalline specimens in the temperature interval from 1.5 K to 250 K. By comparison, the contribution of the Er subsystem to the specific heat has been determined. This contribution is well accounted for within a single-ion Hamiltonian that includes the CEF and exchange interactions of the Er$^{3+}$ ions. The CEF interactions of the Er$^{3+}$ ion have been compared with those found in other RNi$_5$ compounds and the remarkable constancy of CEF interactions through the 4f series is discussed.

1. Introduction

ErNi$_5$ crystallizes in a hexagonal crystallographic structure and orders ferrimagnetically below 9 K [1]. Magnetization studies performed in fields up to 35 T along the $c$ and $a$ axes of ErNi$_5$ [2] have resulted in the $\Gamma_9$ doublet with a dominant $|\pm 15/2\rangle$ component as the ground state of the Er$^{3+}$ ion in agreement with inelastic neutron scattering (INS) experiments performed by Goremychkin $et\ al$ [3]. Specific heat studies of ErNi$_5$ have been undertaken in order to resolve the controversy concerning the magnetic/CEF contribution to the specific heat of the Er subsystem in this compound. The single-ion contribution due to the presence of the Er$^{3+}$ ion in ErNi$_5$ calculated in [2] has been found to be significantly larger than derived experimentally in [4]. This discrepancy has been attributed to uncertainties in the experimental evaluation of the Er-subsystem specific heat probably associated with the approximations used in the determination of the phonon contribution. In this paper, we present our results of specific heat measurements on ErNi$_5$ and LaNi$_5$. This latter compound serves as the reference system, having the same crystallographic structure and containing a non-magnetic rare-earth element.

2. Experimental details

The specific heat of ErNi$_5$ has been measured on a single-crystalline specimen with a mass of 190 mg in the temperature range from 1.5 K to 250 K by an adiabatic

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method. This single-crystalline specimen is part of a single-crystalline batch that has been grown by the arc-melting technique in a purified argon atmosphere at the Material Centre ALMOS of the University of Amsterdam. The quality of the sample is found to be high—the presence of erbium oxide is not detectable. Er₂O₃ is manifest in the specific heat by a peak at the magnetic ordering temperature of 3.2 K. In the present measurement no anomaly at this temperature is observed. For LaNi₅, the specimen consists of three pieces of single-crystalline material with a total mass of 253 mg.

3. Results and discussion

The specific heat of ErNi₅ is shown in figure 1, together with that of LaNi₅. The specific heat of ErNi₅ is much larger than that of LaNi₅. The λ-type of peak of the ErNi₅ with its maximum at 8.9 K is associated with the occurrence of long-range magnetic order. The value of 9.2 K for Tₘₕ is taken from the mid-point temperature of the λ-peak. The specific heat is analysed by taking into account the nuclear (c_N), electronic (c_el), lattice (phonon) (c_ph) and magnetic (c_m) contributions to the specific heat:

\[ c = c_N + c_{el} + c_{ph} + c_m. \]  

The nuclear contribution, related to hyperfine interactions of the 4f shell with the nuclear moment of the 4f ion, is not observed. This is not surprising as even in the case of a fully polarized 4f shell of the Er ion, the nuclear specific heat contributes significantly only below 1 K.

![Figure 1. Specific heat of single-crystalline ErNi₅ and LaNi₅.](image-url)

Information about the electronic and lattice contributions is provided by the specific heat of LaNi₅, a compound that is Pauli paramagnetic. The specific heat
of this compound is shown in figure 2. It shows a smooth behaviour, resembling the Debye function. At a temperature of 220 K it reaches the value of $18R$, $R$ being the gas constant. The behaviour at low temperatures is presented in more detail in figure 3 in a plot of $c/T$ versus $T^2$. This plot clearly does not follow a linear variation, implying that the phonon contribution does not follow the Debye function temperature dependence in detail. Apparently, the dynamics of the lattice cannot be described over the full temperature range by one single parameter, the Debye temperature. We have correlated this fact with a complex energy structure of the phonon spectrum that has been revealed by point-contact spectroscopy measurements performed by Akimenko et al [5]. In fact, the specific heat of LaNi$_5$ can be represented by a straight line in temperature up to 10 K only. The low-temperature variation shown in figure 3 leads to a Sommerfeld coefficient $\gamma$ of 36 mJ K$^{-2}$ mol$^{-1}$ and $\theta_D$ of 322 K. The specific heat for LaNi$_5$ has been measured before by Nait-Saada [6] and Sahling et al [7] who reported values of 33 and 39 mJ K$^{-2}$ mol$^{-1}$ for $\gamma$ and values of 322 and 393 K for the Debye temperature $\theta_D$, respectively. Values of 36 mJ K$^{-2}$ mol$^{-1}$ and 296 K for $\gamma$ and $\theta_D$ have been found by Szewczyk et al [8] from specific heat measurements of GdNi$_5$. From a detailed analysis over different temperature regions of the specific heat of LaNi$_5$, we deduced a variation of the Debye temperature with temperature. This variation is shown in the inset of figure 3. The value reported in [8], which has been derived within the temperature region between 35 and 45 K falls well in this variation. Apparently, there is a significant phonon softening at 22 K. We have correlated this variation of $\theta_D$ with the non-standard phonon spectrum revealed by point-contact spectroscopy measurements.

![Graph](image)

**Figure 2.** Experimental specific heat of single-crystalline LaNi$_5$, together with an approximation made with a Debye temperature $\theta_D$ of 322 K and $\gamma$ of 36 mJ K$^{-2}$ mol$^{-1}$ (chain curve). The horizontal line represents a value of $18R$.

Leaving the problem of the detailed analysis of the phonon contribution in LaNi$_5$ out of the present discussion, the contribution of the Er subsystem in ErNi$_5$ has been derived as the difference of the measured (molar) specific heats of ErNi$_5$ and LaNi$_5$. 
This contribution is shown in figure 4. Already, at a first glance, this contribution (i) is much larger than that derived in [4] (see also figure 3 of [2]) and (ii) resembles well the calculated specific heat that has been presented in [2]. This confirms the suggestion that the lattice contribution was not subtracted correctly in [4]. We have calculated the entropy that is involved in this extra specific heat. Its temperature variation is shown in figure 5. At 150 K it reaches a value of 21.5 ± 1 J K⁻¹ mol⁻¹ with zero entropy at 1.3 K. This value is close to that expected for the (2J + 1)-fold degeneracy of the ground multiplet, i.e. $R \ln 16 = 23.04$ J K⁻¹ mol⁻¹. It indicates that (i) this extra specific heat observed in ErNi₅ is associated with the electronic excitations of the Er³⁺ ions, and (ii) that the magnitude of the CEF interactions in ErNi₅ is of the order of 150 K.

The rare-earth specific heat is calculated by making use of the general formula:

$$c_m = -T \delta^2 F / \delta T^2.$$  \hspace{1cm} (2)

$F$ is the free energy of the rare-earth subsystem over the available energy states resulting from the consideration of the Hamiltonian of the Er³⁺ ion in the form:

$$\mathcal{H}_R = \sum B_n^m O_n^m + n g^2 \mu_B^2 (-J(J) + \frac{1}{2}(J)²).$$  \hspace{1cm} (3)

The first term is the CEF Hamiltonian written for the lowest multiplet given by Hund's rules: $^4I_{15/2}$ with $J = 15/2$, $S = 3/2$, $L = 6$ and the Landé factor $g = 6/5$. The second term represents the exchange interactions between the Er ions written in the mean-field approximation. The calculated contribution of the Er³⁺ ions to the specific heat of ErNi₅ is shown in figure 4. The overall behaviour is in very good agreement with the experimentally derived magnetic contribution to the specific heat. It perfectly reproduces (i) the $\lambda$-type of peak at 8.9 K associated with the occurrence
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Figure 4. Temperature variation of the contribution of the Er subsystem to the specific heat of ErNi$_5$ derived as the difference of the molar specific heats of ErNi$_5$ and LaNi$_5$. The broken curve shows the Er-subsystem contribution calculated with the CEF parameters shown in table 1 under [2]. The value for the effective molecular field coefficient $\eta_{RR}$ between the Er moments of 0.17 T f.u./$\mu_B$ determines the position of the $\lambda$-type of peak with $T_\lambda = 9.2$ K.

Figure 5. Temperature variation of the experimental entropy of the Er subsystem. The entropy associated with the excitations of the 4f electrons over the Hund's ground-state multiplet amounts to 23.04 J K$^{-1}$ mol$^{-1}$.

of long-range magnetic order and (ii) the broad Schottky-type of maximum in the vicinity of 30 K. The calculated value of the maximum amounts to 8.3 J K$^{-1}$ mol$^{-1}$, whereas the experimental results point to a broader maximum with a maximal value of 7.3 J K$^{-1}$ mol$^{-1}$. In principle, the better fit could be obtained by relatively
small variations of the energy separations. This has not been done, however, owing to the fact that the specific heat is insensitive to the eigenfunctions of the states. Detailed magnetic measurements and high-resolution inelastic neutron scattering on well characterized single-crystalline specimens are planned.

The set of CEF parameters, relevant to the hexagonal symmetry that has been used in these calculations, has been taken from [2]. This set of parameters describes well

(i) the energy separations to the three lowest levels (i.e. the INS results of [3]);
(ii) the spontaneous moment of the Er ion close to 9 \( \mu_B \);
(iii) the ground state of the Er\(^{3+} \) ion;
(iv) the anisotropy of the susceptibility;
(v) the temperature dependence of the susceptibility with a 'bump' at 20 K for the direction perpendicular to the hexagonal axis (figure 4 of [2]);
(vi) the magnetization in high fields; and
(vii) the temperature dependence of the specific heat of the Er subsystem.

This set of CEF parameters is shown in table 1, together with those obtained in [1] and [3]. In principle, one can see that for all the sets there is a general agreement over the size of the CEF interactions and the parameters themselves are quite similar. The set from [1] leads, however, to the ground state \( \Gamma_7 \), that must be excluded on the basis of the magnetization measurements in high fields [2] as well as of INS experiments [3].

<table>
<thead>
<tr>
<th>( B_{\alpha}^m ) (K)</th>
<th>[1]</th>
<th>[3]</th>
<th>[2]</th>
</tr>
</thead>
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<tr>
<td>( B_{2}^0 )</td>
<td>-0.7</td>
<td>-0.64</td>
<td>-0.615</td>
</tr>
<tr>
<td>( B_{2}^2 )</td>
<td>-1</td>
<td>-2.3</td>
<td>-2.5</td>
</tr>
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<td>( B_{2}^4 ) (x 10^{-3} K)</td>
<td>+50</td>
<td>+23.2</td>
<td>+23.2</td>
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<tr>
<td>( B_{2}^6 ) (x 10^{-6} K)</td>
<td>+300</td>
<td>+132</td>
<td>+132</td>
</tr>
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<td>Ground state</td>
<td>( \Gamma_7 )</td>
<td>( \Gamma_9 )</td>
<td>( \Gamma_9 )</td>
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<td>CEF splitting (K)</td>
<td>183</td>
<td>151</td>
<td>152</td>
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The anisotropic behaviour of the paramagnetic susceptibility of the Er subsystem has been calculated in [2]. The temperature dependences of the inverse susceptibility along the hard and easy axes above 100 K follow the Curie–Weiss law very well. Both curves show nearly the same value of the paramagnetic moment \( \langle \mu \rangle = 9.62 \mu_B, \mu_{\perp} = 9.71 \mu_B \) but the paramagnetic Curie temperatures differ by 54 K (\( \theta_{||} = +28 \) K and \( \theta_{\perp} = -26 \) K). The contribution of the Er subsystem accounts for most of the susceptibility of ErNi\(_5\). Even at 300 K the Er subsystem susceptibility largely exceeds that associated with the conduction electrons, which predominantly originate from the Ni subsystem. The anticipated 'bump' in the vicinity of 20 K in the susceptibility for the \( c \perp \) direction seen in figure 4 of [2], that has not been observed in measurements reported in [1] and [6], has been found in recent susceptibility measurements [9].

The energy level scheme of the Er\(^{3+} \) ion, calculated with the present set of CEF parameters, is shown in figure 6, together with the associated eigenfunctions. The CEF interactions of the hexagonal symmetry split the \( ^4I_{15/2} \) multiplet into eight doublets as
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Figure 6. The energy level scheme of the Er$^{3+}$ ion in ErNi$_5$ under the action of the CEF interactions, the CEF parameters are shown in table 1 under [2], together with the associated eigenfunctions. All the levels are doublets, as the Er$^{3+}$ ion with $J = 15/2$ is a Kramers ion. The arrows show the transitions observed in inelastic neutron scattering experiments.

the Er$^{3+}$ ion, with $J = 15/2$, is a Kramers ion. The eigenfunction of the ground-state doublet $\Gamma_0$ is given by:

$$\psi = +0.999|\pm 15/2\rangle - 0.04|\pm 3/2\rangle + 0.0004|\mp 9/2\rangle.$$  (4)

The quantization axis is taken along the hexagonal axis. The largest component is given by the maximal value of $J_z$. This ground state results from predominant second-order CEF interactions. The energy level scheme with eigenfunctions as shown in figure 6 provides excitations observable in INS experiments at energies of 21.0 K ($1 \rightarrow 2$), 46.0 K ($2 \rightarrow 3$) and 72.6 K ($2 \rightarrow 5$). These excitations have been observed [3].

In the ordered state all the levels are split by the exchange interactions but their splitting is small. In figure 7 the temperature dependence of the energy level scheme is presented. The exchange interactions do not cause a mixing of the levels. The effective molecular field coefficient between the Er-ion moments, $n$, has been found to be 0.17 T f.u./$\mu_B$ [2]. This is 15% lower than the value of 0.20 T f.u./$\mu_B$ that can be derived from the molecular field expression

$$n = 3k_B T_c / g^2 \mu_B^2 J(J + 1).$$  (5)
Exchange interactions of this size produce a molecular field of 1.5 T experienced by the Er$^{3+}$-ion moment at the lowest temperatures.

It is interesting to compare the CEF interactions in ErNi$_5$ with those evaluated on the basis of numerous magnetic, neutron and specific heat studies, for other R$^{3+}$ ions within the RNi$_5$ series. This comparison is made in table 2, where the values for CEF coefficients, $A_n = B_n / \theta_n (r_{d4}^n)$, are collected. $\theta_n$ is the $n$th-order Stevens factor, whereas $(r_{d4}^n)$ is the $n$th power of the radius of the 4f shell. Values for the multipolar charge moments of the 4f electron cloud $\theta_n (r_{d4}^n)$ have been collected in [10]. Inspecting the results shown in table 2, one can notice, on the one hand, a substantial difference between the coefficients in different compounds but, on the other hand, remarkable systematics can be found. Except for the coefficient $A_6^0$ of the Tm ion, there is full agreement in the sign of the CEF coefficients across the series. The nearly constant CEF interactions in the RNi$_5$ series independently on the R ion involved result in (i) a systematic uniaxial/planar alternation of the easy magnetic direction (EMD) (governed by the sign of the second-order Stevens factor $\alpha_J$) and (ii) a systematic $\alpha/b$ axis alternation of the EMD within the hexagonal plane (governed by the sign of the sixth-order Stevens factor $\gamma_J$). These systematic alternations are also found in other series like the hexagonal R$_2$Co$_{17}$ and R$_2$Fe$_{17}$, and the cubic RFe$_2$ compounds, and have been discussed in [19].

4. Conclusions

The temperature dependence of the specific heat of ErNi$_5$ is well understood by considering two independent electronic subsystems. The conduction electron subsystem is described by a value for the Sommerfeld coefficient $\gamma$ of 36 mJ K$^{-2}$ mol$^{-1}$. The substantial departure of the lattice contribution to the specific heat from that
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Table 2. CEF coefficients, in units of $K_a^{-1}$, of the trivalent R ions in the RNi₅ compounds. PCM denotes a point charge model result.

<table>
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<tr>
<th>Compound</th>
<th>$T_a$ (K)</th>
<th>$A_2^0$</th>
<th>$A_4^0$</th>
<th>$A_6^0$</th>
<th>$A_8^0$</th>
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given by the Debye function has been deduced from measurements on LaNi₅. The 4f electronic subsystem of the Er ions is well accounted for by the CEF and effective Er–Er exchange interactions. The CEF interactions of the R³⁺ ions in RNi₅ derived from a large number of magnetic, neutron and specific heat studies are found to be remarkably similar and independent of the R³⁺ ion involved.

Acknowledgments

This work has been partly supported by the European Commission within its BRITE/EURAM Research and Development Programme, BREU-0068.

References

[9] Gignoux D *et al* to be published