Neutron crystal-field spectroscopy of $\text{RNi}_2^{11}\text{B}_2\text{C}$ ($\text{R} = \text{Ho}, \text{Er}, \text{Tm}$)

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Abstract. Inelastic neutron scattering experiments of the crystal-field (CEF) splitting of the R^{3+} ions ($\text{R} = \text{Ho}, \text{Er}, \text{Tm}$) in the superconductor $\text{RNi}_2^{11}\text{B}_2\text{C}$ have been performed in the paramagnetic as well as in the magnetically ordered state in order to deduce the CEF parameters which in turn determine the thermodynamic magnetic properties of these systems. The calculated ordered magnetic moments are in agreement with magnetic neutron diffraction results, i.e. both the easy axis and the size of the zero-field moments are correctly reproduced. In addition, the entropy involved in the magnetic ordering obtained from specific heat measurements is in correspondence with the number of low-lying CEF states observed in this study. Our CEF parameter set also reproduces both the behavior and the anisotropy in M/H measured for single crystals.

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1. Introduction

The recently discovered quaternary intermetallic superconducting compounds $\text{RNi}_2\text{B}_2\text{C}$ [1] (where $\text{R} = \text{Sc}, \text{Y}$, rare earth, Th, U [2]) turn out to be ideal for studies concerning the interaction between superconductivity and magnetism, if a magnetic ion is inserted at the R-site. Since the magnetic ordering temperature T_m of the R sublattice and the superconducting critical temperature T_c are of the same order of magnitude (Table 1), the energy scales of these two effects are of similar size (in contrast e.g. to the corresponding values in $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$). A result of this interplay is the almost reentrant behavior into the normal state for $\text{HoNi}_2\text{B}_2\text{C}$ and to a lesser extent for $\text{ErNi}_2\text{B}_2\text{C}$ and $\text{TmNi}_2\text{B}_2\text{C}$ [3,4]. In addition, both T_m and the degradation of T_c scale roughly with the de Gennes factor $(g_J - 1)^2 \cdot J(J + 1)$, where g_J is the Landé factor and J the total angular momentum [5]. Since preparation of large single crystals of these compounds

is much easier compared to other (high-temperature) superconductors, bulk magnetic properties were measured on such crystals [6–8]. The magnetic structures were determined by neutron powder [9–11] and single-crystal [12–14] diffraction. With neutron diffraction for $\text{R} = \text{Ho}$ and Er the magnetic moments were found to lie in the **ab**-plane, whereas the Tm moments are aligned along **c**. This is in full agreement with the anisotropies obtained in the single-crystal susceptibility measurements. The mechanism for superconductivity in these compounds is still disputed. While some authors favor a BCS-type of interaction (weak and strong coupling limit) based on tunnelling [15], pressure [16], and phonon measurements [17] or based on band structure calculations [18], other authors found arguments for a two-fluid model (specific heat data [19]) or at least against a BCS model, since localized moments on the Ni-atoms (proposed by neutron diffraction [11] and μSR measurements [20]) would be difficult to reconcile with an s-wave pairing [21].

For an understanding of the magnetism in these compounds on a microscopic scale, knowledge of the magnetic ground state is indispensable. The determination of the CEF interaction provides this information for magnetically non-interacting magnetic ions. Therefore, the exact knowledge of this interaction serves as a starting point towards the real system. Soon after the discovery of these compounds CEF splittings have been measured by several groups with the help of neutron spectroscopy [22], but the analysis of the data turned out to be a formidable problem. For high- T_c materials like $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ the almost cubic nearest neighbor coordination around the rare-earth ion made it possible to start in the analysis with only two independent CEF parameters (A_{40} and A_{60}) and then to proceed stepwise from tetragonal with five ($A_{20}, A_{40}, A_{44}, A_{60}, A_{64}$) to orthorhombic with nine ($A_{20}, A_{22}, A_{40}, A_{42}, A_{44}, A_{60}, A_{62}, A_{64}, A_{66}$). Such an approach is not possible for the present (tetragonal) compounds. Therefore, we used a modified point-charge model to obtain reasonable starting parameters. We succeeded in finding consistent sets of CEF parameters for $\text{HoNi}_2\text{B}_2\text{C}$, $\text{ErNi}_2\text{B}_2\text{C}$, and $\text{TmNi}_2\text{B}_2\text{C}$, which reproduce our neutron spectroscopy data. From these parameters thermodynamic magnetic properties as well as size and direction of the or-

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Table 1. Lattice constants, T_c , T_m and saturated magnetic moments μ for $\text{RNi}_2\text{B}_2\text{C}$ ($R = \text{Ho, Er, Tm}$)

	$\text{HoNi}_2\text{B}_2\text{C}$	$\text{ErNi}_2\text{B}_2\text{C}$	$\text{TmNi}_2\text{B}_2\text{C}$	Refs.
a (Å)	3.51097(5)	3.49601(6)	3.48044(4)	
c (Å)	10.5376(2)	10.5666(2)	10.5955(2)	
T_c (K)	8	10	11	
T_m (K) incomm.	8	5.8	1.5	[9,33,8]
T_N (K) AF	5	—	?	[6]
μ_{obs} (μ_B)	8.7 (AF)	7.8		[10,11]
μ_{calc} (μ_B)	6.8	7.8	4.7

Fig. 1. SQUID-measurement of the superconducting transition of $\text{HoNi}_2\text{B}_2\text{C}$. The spin reorientation at 5 K clearly weakens superconductivity

dered magnetic moments were calculated and found to be in good agreement with corresponding measurements.

2. Experiments

Our polycrystalline samples were prepared by ordinary arc-melt technique [23], but in order to reduce the very high neutron absorption of natural Boron the isotope ^{11}B (Cambridge Isotope Laboratories, 99%) was used. The resulting annealed buttons were ground to fine powder and analyzed by susceptibility measurements, X-ray and neutron diffraction (see Figs. 1 and 2, respectively) which proved the high quality of the samples.

The inelastic neutron scattering (INS) measurements were performed on the triple-axis instruments IN3 (ILL, Grenoble, France), and FLEX (HMI, Berlin, Germany) as well as on the time-of-flight (TOF) instrument MARI (ISIS, UK) at temperatures between 1.4 and 150 K. Final energies E_f were fixed on IN3 to 4.2, 4.8, and 14.7 meV with the moduli of the scattering vector Q in the range between 1.0 and $2.72 \text{ \AA}^{-1}$. For $E_f < 5 \text{ meV}$ a beryllium filter was placed in the scattered neutron beam in order to reduce higher-order contaminations, while for $E_f = 14.7 \text{ meV}$ a pyrolytic graphite filter was used for the same reason. In order to increase intensity a horizontally and vertically focussing monochromator and a horizontally focussing analyzer were used. The energy resolution at the elastic peak turned out to be $\delta E = 0.16 \text{ meV}$ for $E_f = 4.8 \text{ meV}$. On FLEX $E_f = 2.98 \text{ meV}$ and $0.7 \leq Q \leq 1.2 \text{ \AA}^{-1}$ was used together with a beryllium filter (vertically focussing monochromator, horizontally focussing analyzer, $\delta E = 0.05 \text{ meV}$). The TOF

Fig. 2. Neutron diffraction pattern of $\text{HoNi}_2\text{B}_2\text{C}$. Impurity phases contribute less than 1.5 % **Fig. 3.** Neutron spectra of $\text{HoNi}_2^{11}\text{B}_2\text{C}$ taken on the TOF instrument MARI in the paramagnetic state for two different moduli of the scattering vector Q at $\hbar\omega = 0 \text{ meV}$ (top and middle) and their difference (bottom). The lines are guides to the eye

experiments were performed with an incident energy E_i of 120 meV and $1.3 \leq Q \leq 4.7 \text{ \AA}^{-1}$ at the elastic peak position ($\delta E = 1.4 \text{ meV}$). All experiments were performed in the neutron energy-loss configuration. The powder samples were enclosed in aluminum containers with following shapes: hollow cylinders (with 4/5 mm radius and 50 mm height) for both IN3 and FLEX and hollow cylinders (radius: 1.8/2.0 cm; height: 50 mm) for MARI.

3. Results

3.A. $\text{HoNi}_2^{11}\text{B}_2\text{C}$

The energy spectra obtained for two different detector banks on MARI are shown in Fig. 3 together with a difference

Fig. 4. Neutron spectra of $\text{HoNi}_2^{11}\text{B}_2\text{C}$ taken on the triple-axis instrument IN3 in the paramagnetic state. The full line represents the result of our CEF profile fit, whereas the dashed line was obtained from the CEF parameters published recently in [29]

Fig. 5. Neutron spectra of $\text{HoNi}_2^{11}\text{B}_2\text{C}$ taken on the triple-axis instrument IN3 for the three different magnetic regimes

plot. Since inelastic magnetic intensities are proportional to the square of the magnetic form factor, intensities from CEF transitions should decrease for larger Q (in contrast to phonons whose intensities increase). Therefore, we readily conclude from Fig. 3 that there are either no CEF levels above 20 meV or that their transition matrix elements out of the low-lying states have to be close to zero. In Fig. 4 inelas-

Fig. 6. C/T -data obtained for $\text{HoNi}_2\text{B}_2\text{C}$ [6] and the calculated entropy ΔS

Fig. 7. Low-energy neutron spectra of $\text{HoNi}_2^{11}\text{B}_2\text{C}$ taken on the triple-axis instrument IN3 for the three different magnetic regimes

tic features between 8 and 18 meV (which are in agreement with measurements by Grigereit et al. [22]) and around the elastic line are displayed for the paramagnetic state (between 2 and 8 meV no magnetic intensity was found in low resolution/high intensity scans). The sharp peak at 14.4 meV (3 times E_f) corresponds to a higher-order contamination (despite the use of a Be filter) which was checked by changing E_f by just a small amount to 4.2 meV. Whereas for low temperatures (Fig. 5) the peaks were found to be rather sharp (indicative for a single thermally occupied low-lying state), at 15 K only broad transitions were observed which is very likely due to a larger number of low-lying states. This is in agreement with specific heat measurements where the entropy at the magnetic phase transition turns out to be close to $R \cdot \ln 4$ (Fig. 6) which supports a model of four low-lying states involved in the magnetic ordering. These presumably four states could not be resolved with the resolution of IN3 for 15 and 6.1 K, but clearly magnetic quasi-elastic like scattering was observed (Fig. 7). For 1.8 K the internal magnetic field in the ordered state splits up these states, and no quasi-elastic scattering but an inelastic transition at 1.7 meV was found.

3.B. $\text{ErNi}_2^{11}\text{B}_2\text{C}$

Again, inelastic neutron data taken on MARI for $\text{ErNi}_2^{11}\text{B}_2\text{C}$ do not show any ground-state transitions higher than 20 meV

Fig. 8. Neutron spectra of $\text{ErNi}_2^{11}\text{B}_2\text{C}$ taken on the TOF instrument MARI in the paramagnetic state for two different moduli of the scattering vector Q at $\hbar\omega = 0$ meV (top and middle) and their difference (bottom). The lines are guides to the eye

Fig. 9. Neutron spectra of $\text{ErNi}_2^{11}\text{B}_2\text{C}$ taken on the triple-axis instrument IN3 in the paramagnetic state. The line represents the result of a CEF profile fit

Fig. 10. Low-energy neutron spectrum of $\text{ErNi}_2^{11}\text{B}_2\text{C}$ taken on the triple-axis instrument FLEX in the magnetically ordered state

Fig. 11. Neutron spectra of $\text{TmNi}_2^{11}\text{B}_2\text{C}$ taken on the triple-axis instrument IN3 in the paramagnetic state. The line represents the result of a CEF profile fit

Fig. 12. Neutron spectra of $\text{TmNi}_2^{11}\text{B}_2\text{C}$ taken on the triple-axis instrument IN3 in the paramagnetic and the magnetically ordered state. The lines represent the results of a CEF profile fit (with a molecular field of 0.54 T along the c -direction for the data set taken at 0.1 K)

(Fig. 8). Between 0 and 20 meV clearly two ground-state transitions are visible (6 and 18 meV, the corresponding excited transition at 12 meV was observed at higher temperatures). No additional peaks could be resolved with better resolution at 15 K except for a small asymmetry in the 6 meV peak (Fig. 9). The internal magnetic field at 1.5 K clearly splits up the ground state doublets (visible as quasi-elastic intensity at 15 K), and two inelastic peaks were observed at low energies (Fig. 10).

3.C. $\text{TmNi}_2^{11}\text{B}_2\text{C}$

For $\text{TmNi}_2^{11}\text{B}_2\text{C}$ four ground-state transitions were found at 3, 5.4, 10.2, and 12.5 meV, respectively (Fig. 11). In addition, quasi-elastic scattering was observed which was absent below the magnetic transition temperature at 1.5 K [24]. For the peak at 3 meV a slight asymmetry was observed at 0.1 K (Fig. 12) which could be reproduced by calculating the CEF splitting in an internal field of $B_{mf} = 0.54\text{ T}$ obtained by the mean-field approach presented in Chap. 5.

4. Analysis

Since the spectroscopic information for the individual samples are not sufficient to deduce all CEF parameters inde-

Table 2. CEF parameters A_{nm} for $\text{RNi}_2\text{B}_2\text{C}$ ($\text{R} = \text{Ho}, \text{Er}, \text{Tm}$)

	PCM	$\text{HoNi}_2\text{B}_2\text{C}$	$\text{ErNi}_2\text{B}_2\text{C}$	$\text{TmNi}_2\text{B}_2\text{C}$
A_{20} (meV)	-79.0	-14.5 $\pm$ 6	-6.3 $\pm$ 1.3	-13.0 $\pm$ 0.3
A_{40} (meV)	2.89	2.3 $\pm$ 0.8	3.3 $\pm$ 0.3	2.16 $\pm$ 0.14
A_{44} (meV)	-86.6	-71.4 $\pm$ 3.3	-73.9 $\pm$ 1.3	-63.1 $\pm$ 1.2
A_{60} (meV)	0.01	-0.42 $\pm$ 0.3	-0.61 $\pm$ 0.12	-1.32 $\pm$ 0.05
A_{64} (meV)	3.87	11.7 $\pm$ 1.4	10.1 $\pm$ 3.1	15.6 $\pm$ 1.1

pendently, reasonable starting parameters and consistency checks between the different samples are indispensable to reach a satisfactory description of the CEF. For high-temperature superconductors with almost cubic surrounding as e.g. found for $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [25] starting parameters could be obtained by using cubic symmetry with its correlation between the four non-zero CEF parameters. This approach is not feasible for $\text{RNi}_2\text{B}_2\text{C}$ for the following reasons: the surrounding of the rare-earth ions is not cubic but square planar, additional coordination shells are important, and the system tends more towards metallic behavior. Therefore, we started from an extended point-charge model (PCM). The ordinary PCM [26] is given by:

$$V_{\text{CEF}}(\mathbf{r}) = \sum_i \frac{e^2 Z_i}{|\mathbf{r} - \mathbf{R}_i|} \quad (1)$$

(where the sum runs over all the surrounding ions with charge $Z_i e$ and position vector $\mathbf{R}_i$). The corresponding CEF parameters are given by:

$$\begin{aligned} A_{nm} &= \sum_i Z_i \frac{\langle r^n \rangle}{R_i^{n+1}} \frac{4\pi}{2n+1} (-1)^m Y_n^{-m}(\theta_i, \varphi_i) \\ &= \sum_i a_n^m(i), \end{aligned} \quad (2)$$

with $\langle r^n \rangle$ the n -th moment of the radial distribution of the 4f-electrons and Y_n^{-m} the spherical harmonics.

The extended PCM includes the following corrections:

- Due to screening of the 4f-electrons by the outer shells, a shielding parameter $(1 - \sigma_n)$ enters Eq. (2) [27].
- $\langle r^n \rangle$ is replaced by $\frac{\langle r^n \rangle}{\tau^n}$ since the calculated Hartree-Fock wave functions of the 4f-electrons differ from the observed ones. τ is a phenomenological parameter [28].
- Screening effects of the charge carriers are taken into account extending (1) to a Yukawa-type of potential:

$$V_{\text{CEF}}(\mathbf{r}) = \frac{e^2 Z_i \cdot e^{-K|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r} - \mathbf{R}_i|} \quad (3)$$

with K as the inverse screening length.

With all these corrections the CEF Hamiltonian can be written in the following form [29]:

$$H_{\text{CEF}} = \sum_{nm} A_{nm} Y_n^m \quad (4)$$

and the CEF parameters are defined as:

$$A_{nm}(K) = \sum_i a_n^m(i) \cdot b_{n+1/2}(K|\mathbf{r} - \mathbf{R}_i|). \quad (5)$$

$b_{n+1/2}(x)$ are modified spherical Bessel functions, normalized to one for $x = 0$. The only free parameters in the extended PCM are then the positions $\mathbf{R}_i$, the ionic charges Z_i of the surrounding ions and the inverse screening length K . For $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ the model provides CEF parameters which are in very good agreement with the experiment [30]. For $\text{RNi}_2\text{B}_2\text{C}$ we included all ions within a sphere of 5 Å radius around the rare-earth ion to obtain starting parameters (Table 2) for a CEF fit to the neutron spectroscopy data. The calculated CEF splitting turned out to be in good agreement with the measurements by taking following effective charges $Z_i \cdot e$ from band-structure calculations [31], an infinite screening length (since already effective charges are used), and $\sigma_2 = 0.6846 - 0.00854N$, $\sigma_4 = 0.02356 + 0.00182N$, $\sigma_6 = -0.04238 + 0.00014N$ (N : number of 4f-electrons) taken from [28]:

$$\begin{aligned} R : & \quad 0.4e \\ Ni : & \quad 0.3e \\ B : & \quad -0.3e \\ C : & \quad -0.4e \end{aligned}$$

Starting with the parameters obtained by this procedure (Table 2, first row) the fits to the experimental data (including J-mixing and intermediate coupling) finally converged for the three compounds to the consistent set of parameters given in Table 2. The spectra resulting from our CEF parameters are displayed in Figs. 4, 9, 11, and 12 as full lines. The CEF level scheme and the intensity of the transitions out of the low-lying states are listed in Table 3.

The dashed line in Fig. 4 results from CEF parameters obtained by Cho et al. [32] by fitting single-crystal magnetization data. Obviously, their set of CEF parameters cannot reproduce the spectroscopy data, since macroscopic properties are far too insensitive to details of the CEF level structure. Instead, thermodynamic magnetic properties should be used to verify the CEF parameters obtained by direct spectroscopic experiments.

5. Magnetic properties

With the parameters obtained in Chap. 4 the magnetic moments, calculated self-consistently in a mean-field approach, turned out to be in good agreement with experimentally obtained values in size and direction (see Table 1). In contrast, the CEF parameters given by Gardner et al. [22] predict for $\text{ErNi}_2\text{B}_2\text{C}$ an easy axis of magnetization which is not in agreement with the experiment (parallel instead of perpendicular to $\mathbf{c}$). Using the molecular field obtained in this way ($B_{mf} = 2.5$ T; perpendicular to $\mathbf{c}$), the CEF splitting in the antiferromagnetically ordered state of $\text{HoNi}_2\text{B}_2\text{C}$ was calculated and turned out to be in good qualitative agreement with the measurement: Singlet-singlet transitions at 11.2, 12.3, 12.8, and 16.6 meV with transition probabilities 5.1, 0.8, 0.3, and 1.6, respectively (all the other transitions are much weaker). The incommensurate magnetic ordering in $\text{ErNi}_2\text{B}_2\text{C}$ makes such a calculation less reliable, since the spatial distribution of the internal magnetic field is inhomogeneous. Nevertheless, a calculation for the simple antifer-

Table 3. Eigenstates Γ_i (doublets are marked by an asterisk), eigenvalues E_i and transition probabilities ($|\langle \Gamma_i | J_{\perp} | \Gamma_j \rangle|^2$) calculated from the CEF parameters listed in Table 2. (a) R = Ho; (b) R = Er; (c) R = Tm

	Γ_4	Γ_5^*	Γ_1	Γ_2	Γ_5^*	Γ_3	Γ_5^*	Γ_4	Γ_1	Γ_2	Γ_3	Γ_5^*	Γ_1
E (meV) 0	0.15	0.32	10.40	11.14	11.65	11.86	11.96	12.75	13.56	15.99	16.59	17.17	
Γ_4	0.00	60.25	0.00	0.00	0.95	0.82	2.00	0.00	0.00	0.00	3.13	0.07	0.00
Γ_5^*	60.25	0.11	57.57	3.74	5.64	1.76	1.24	0.04	0.18	0.69	0.69	1.43	0.09
Γ_1	0.00	57.57	0.00	5.15	2.66	0.00	0.89	0.00	0.00	0.37	0.00	0.57	0.00

	Γ_6^*	Γ_7^*	Γ_6^*	Γ_7^*	Γ_6^*	Γ_7^*	Γ_6^*	Γ_7^*
E (meV) 0	0.69	5.78	6.79	8.18	8.55	18.77	18.85	
Γ_6	47.66	49.15	21.59	1.82	0.09	0.09	1.23	0.01
Γ_7	49.15	50.69	3.28	8.23	1.15	1.50	1.23	6.33

	Γ_5^*	Γ_1	Γ_3	Γ_4	Γ_2	Γ_5^*	Γ_3	Γ_1	Γ_5^*	Γ_4
E (meV) 0	2.88	3.28	5.31	10.28	12.57	16.14	24.82	24.93	25.64	
Γ_5	29.08	18.93	9.74	5.30	4.56	6.58	1.00	0.06	0.65	0.19

Fig. 13. Specific heat data measured for $\text{Ho}_{0.02}\text{Lu}_{0.98}\text{Ni}_2\text{B}_2\text{C}$ [33]. The line is the calculated Schottky specific heat

romagnetic case ($B_{mf} = 2.0$ T; perpendicular to c) results in four levels at 0, 1.0, 1.2, and 2.2 meV (originating from the two lowest doublets) with transition probabilities of 3.7, 4.0, and 0.4, respectively. Keeping in mind the fact that these levels are expected to be dispersive, the agreement with the experiment (Fig. 10) is excellent (at 2.2 meV no intensity was found within statistical errors).

As an additional verification of our CEF parameter sets bulk magnetic properties were calculated and compared with measurements presented in the literature. The Schottky specific heat can be calculated directly from the CEF eigenvalues obtained in Chap. 4. Another more reliable method to probe the CEF parameters is to calculate the susceptibility or magnetization, since both eigenvalues and eigenfunctions are involved in the calculation.

5.A. $\text{HoNi}_2\text{B}_2\text{C}$

In order to overcome the problem that levels involved in the magnetic ordering cannot be tested by ordinary specific

heat measurements, a diluted system ($\text{Ho}_{0.02}\text{Lu}_{0.98}\text{Ni}_2\text{B}_2\text{C}$) was used to measure the magnetic specific heat [33]. At a Ho concentration of 2 % more than 90 % of the Ho-ions are isolated from other Ho-ions which is far beyond the percolation limit for long-range magnetic ordering, and pair interactions are negligible. Therefore, the magnetic specific heat will be dominated by the single-ion properties and a Schottky calculation is valid for the low-lying states (0, 0.15, 0.15, and 0.32 meV). Such a calculation with a non-magnetic (fitted) background ($C_{BG}[\text{J/mol}\{\text{Ho}\} \cdot \text{K}] = 2.3 \cdot T + 9.7 \cdot 10^{-2}T^3$) is displayed together with the specific heat data in Fig. 13.

While there is reasonable agreement between the calculated and observed specific heat data, the calculated magnetizations parallel and perpendicular to c (Fig. 14.a) actually coincide with the data [6] above the magnetic ordering and the critical temperature (the calculation was only performed for the paramagnetic state).

5.B. $\text{ErNi}_2\text{B}_2\text{C}$

The CEF levels at energies higher than 1 meV obtained in our study for Er^{3+} in $\text{ErNi}_2\text{B}_2\text{C}$ create a broad feature in the magnetic specific heat with a maximum at 20 K (Fig. 15). Such an anomaly was also found in measurements [34]. While there is good agreement in the position and size of the maximum, there seems to be a problem of the non-magnetic background subtraction in the measured data (plotted is only the supposedly magnetic part ΔC directly taken from [24]). Again, the calculated magnetization of the two directions (Fig. 14b) practically coincides with the single-crystal data [7].

5.C. $\text{TmNi}_2\text{B}_2\text{C}$

The specific heat data of $\text{TmNi}_2\text{B}_2\text{C}$ published by Movshovich et al. [35] show below 5 K an upturn due to magnetic ordering ($T_m = 1.5$ K) as well as a small anomaly

Fig. 14. Measured (symbols) and calculated (lines) M/H -data for **a** $\text{HoNi}_2\text{B}_2\text{C}$ [6], **b** $\text{ErNi}_2\text{B}_2\text{C}$ [7], and **c** $\text{TmNi}_2\text{B}_2\text{C}$ [8]

Fig. 15. $\Delta C/T$ -data obtained for $\text{ErNi}_2\text{B}_2\text{C}$ [34]. The line results from the CEF splitting presented in Table 3b

Fig. 16. C/T -data obtained for $\text{TmNi}_2\text{B}_2\text{C}$ [35]. The line results from the CEF splitting presented in Table 3c and a Debye-temperature of 200 K

Fig. 17. Extrapolated CEF splittings for R^{3+} in $\text{RNi}_2\text{B}_2\text{C}$. For $R = \text{Ho}, \text{Er}, \text{Tm}$ the splittings obtained in this paper are shown (the states are given in Table 3). All Γ_5 , Γ_6 , and Γ_7 are doublets. Where multiple indices are given the state with the leftmost index is lowest

at $T_c = 10$ K on top of a broad feature between 5 and 20 K (Fig. 16). This feature originates essentially from the three CEF levels between 2 and 6 meV and from (non-magnetic) electronic and phononic contributions. For the calculation only the CEF levels and the phononic part was taken into account by using a Debye-temperature of 200 K (compared to 320 K obtained by Movshovich et al. [35] by fitting two excited CEF levels). The electronic contribution γ is expected to be much smaller than the $35 \text{ mJ}/(\text{mol} \cdot \text{K}^2)$ given by Movshovich as a result of their fit. The reliability of our CEF parameter set is again demonstrated by the perfect agreement of the calculated and measured magnetization data (Fig. 14c).

6. Conclusion

We succeeded in determining CEF-parameter sets of the R^{3+} ions in $\text{HoNi}_2\text{B}_2\text{C}$, $\text{ErNi}_2\text{B}_2\text{C}$, and $\text{TmNi}_2\text{B}_2\text{C}$ with the use of inelastic neutron scattering in the paramagnetic state. The obtained parameters were used to calculate direction and size of the saturated magnetic moments and the CEF splittings in the magnetically ordered state, which turned out to be in good agreement with measurements. In addition, we could show that our parameter sets are able to reproduce magnetic specific heat and susceptibility measurements.

CEF parameters of one rare-earth ion x can be extrapolated to another rare-earth ion y in the same chemical struc-

ture, since the CEF parameters then essentially scale with the ratios of $\langle r^n \rangle$ (tabulated in [28]):

$$A_{nm}^y = \frac{\langle r^n \rangle^y}{\langle r^n \rangle^x} \cdot A_{nm}^x. \quad (6)$$

Such extrapolations of the Tm^{3+} CEF-parameter set to other R^{3+} ions in $\text{RNi}_2\text{B}_2\text{C}$ yields the CEF splittings displayed in Fig. 17. While the details may vary for the individual cases, the overall splitting and the qualitative distribution in energy is reliable.

For further investigations of the microscopic magnetic properties of these compounds clearly inelastic neutron measurements on single crystals are essential. The single-ion results presented here will then be a good starting point for an explanation of collective magnetic phenomena and their interplay with superconductivity.

Note added in proof. The easy-directions of magnetization obtained in our mean-field calculations are $\langle 110 \rangle$ for Ho and $\langle 100 \rangle$ for Er which is in agreement with recent single-crystal measurements [36].

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