Two energy scales in the specific heat of the bimetallic ferromagnetically coupled chain compound $MnNi(NO_2)_4(en)_2$ (en = ethylenediamine)

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(Dated: October 23, 2005)

We present a detailed study of the field dependent specific heat of the bimetallic ferromagnetically coupled chain compound $MnNi(NO_2)_4(en)_2$, en = ethylenediamine. For this material, which in zero field orders antiferromagnetically below $T_N = 2.45$ K, small fields suppress magnetic order. Instead, in such fields a double-peak like structure in the temperature dependence of the specific heat is observed. We attribute this behavior to the existence of an acoustic and an optical mode in the spin wave dispersion as result of the existence of two different spins per unit cell. We compare our experimental data to calculations for a $S_1 = 1$, $S_2 = 5/2$ mixed spin chain. Our calculations on a finite chain of five S_1 plus five S_2 spins in external fields incorporate the finite ionic zero-field splitting and fully reproduce the double-peak like structure as well as its field dependence.

PACS numbers: 75.40.Cx, 75.40.Mg, 75.50.Ee, 75.50.Xx

Alternation in spin systems, be it of the magnetic coupling, the local symmetry or the spin value, induces new and exotic types of magnetic ground states and excitations [1–6]. In particular, this is exemplified in novel bimetallic chain systems, *viz.*, molecule-based chain systems with alternately arranged magnetic units carrying quantum spins S_1 and S_2 of different size. The ability to synthesize mixed-spin chain materials [3, 7, 8] has stimulated theoretical investigations [4–6, 9], with special emphasis on the case of a $S_1 = 1$, $S_2 = 1/2$ spin chain. The magnon dispersion relation of such chains splits into an optical and an acoustical mode because of the two differently sized quantum spins S_1 and S_2 per unit cell, both for antiferromagnetic coupling along the chain [4, 5] as well as ferromagnetic coupling [6, 9]. Although ground state and fundamental excitations of a Heisenberg ferromagnet are simple, thermodynamic properties are very sensitive to interactions of the magnon excitations, as is evidenced by the ferromagnetic uniform spin-1/2 Heisenberg chain (compare chapter 11.3 of [10] and references therein). Computations for bimetallic Heisenberg chains show that the two energy scales associated to the acoustic and the optical spin excitation modes are reflected by "double-peak" kind of features in the specific heat $c_p(T)$ for both antiferro- [4, 5] and ferromagnetic [6, 9] coupling.

Similar predictions had been made for chains of mixed classical and quantum spins as far back as 1975 [11]. In spite of this long history, experimental verifications of the features expected in the specific heat are lacking. In fact, experimental tests of mixed-spin chain models are scarce [12], since most materials available contain elements with larger spins [8, 13], which are difficult to be treated adequately in theoretical calculations [4, 5].

In this Letter, we will present a verification of the two energy scale prediction via a detailed study of the specific heat c_p of $MnNi(NO_2)_4(en)_2$, en = ethylenediamine = $C_2N_2H_4$, in zero and applied fields. After the field-induced suppression of long-range antiferromagnetic order we observe a double-peak like structure in the temperature dependence of c_p for $MnNi(NO_2)_4(en)_2$. We compare our findings with the results of numerical calculations for a finite size $S_1 = 1$, $S_2 = 5/2$ mixed spin chain, which fully reproduce the essential features of the experimentally observed specific heat.

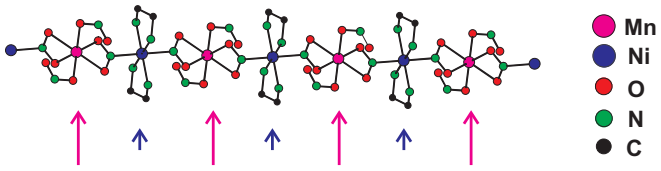

FIG. 1: (Color online) One chain segment of the structure of $MnNi(NO_2)_4(en)_2$ showing the alternating arrangement of Mn and Ni ions. For clarity, the hydrogen atoms are omitted. A full description of the structure is presented in Ref. [15].

$MnNi(NO_2)_4(en)_2$ is one of the best characterized mixed spin chain compound [14, 15], crystallizing in an orthorhombic structure, space group *Pccn* (lattice parameters $a = 14.675$ Å, $b = 7.774$ Å, $c = 12.401$ Å). It contains chains of alternately arranged Ni and Mn ions linked by NO_2 ligands, which carry magnetic moments with spin $S_1 = 1$ and $S_2 = 5/2$, respectively (Fig. 1). The magnetic coupling along the chain, J, is ferromagnetic, with $J = 2.8$ K [9]. A finite ionic zero-field splitting D of 0.36 K is derived from the anisotropy of the susceptibility. Because of an effective antiferromagnetic interchain coupling of $J_\perp = 0.036$ K, the system undergoes a transition into an antiferromagnetically (AFM) ordered state below $T_N = 2.45$ K in zero magnetic field [9, 15]. The long-range magnetically ordered state is suppressed by rather small magnetic fields [15].

For our study we have used crystals $MnNi(NO_2)_4(en)_2$ investigated previously [15]. Here, we will present the easy axis data $B\|c$, for which AFM ordering is suppressed in less than ~ 0.4 T. The heat capacity was measured using commercial calorimeters in magnetic fields $B\|c$ up to 1.6 T at temperatures T down to 0.4 K. As will be discussed below, these c axis data allow a comparison to more accurate numerical calculations than the data $\|a$. Further details will be given elsewhere [16].

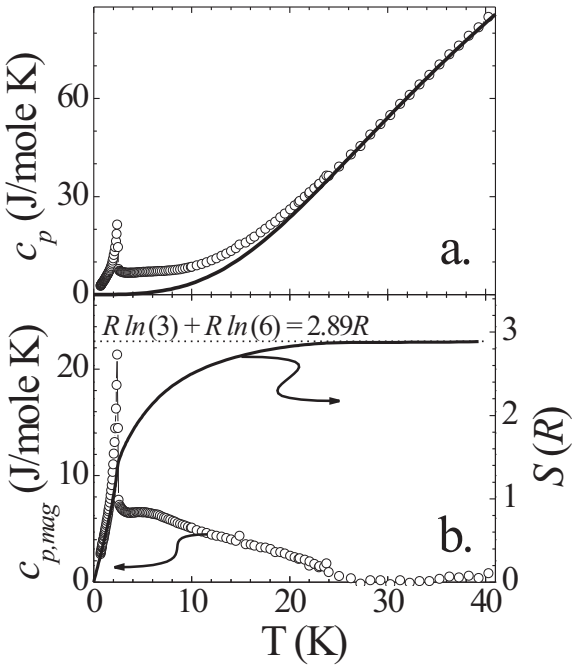

FIG. 2: (a) The zero-field specific heat c_p of $MnNi(NO_2)_4(en)_2$ as function of temperature T. (b) The zero field magnetic specific heat $c_{p,mag}$ and associated entropy S of $MnNi(NO_2)_4(en)_2$ as function of temperature.

In Fig. 2(a) we depict the zero-field specific heat c_p of $MnNi(NO_2)_4(en)_2$ as function of T. The AFM anomaly at $T_N = 2.45$ K is clearly discernible. To derive the magnetic specific heat we determine the lattice contribution $c_{p,lat}$. Since a single T^3-term does not reproduce the experimental data above T_N, we use two Debye-contributions, each calculated via the full Debye-integral, to parameterize $c_{p,lat}$. $MnNi(NO_2)_4(en)_2$ is built up by chain segments -Mn-NO_2-Ni-NO_2-, with two ethylendiamine molecules and two NO_2 groups attached to the Mn and Ni ions, respectively (Fig. 1). Intramolecular oscillations of ethylendiamine or NO_2, because of the light atoms involved, yield Einstein contributions, which are irrelevant for the temperatures considered here. The chain segment units Mn, Ni and NO_2 are similar in atomic weight. Therefore, to parameterize the lattice contribution of these units we choose one Debye-temperature Θ_D with $3 \times 4 = 12$ modes. Analogously, the four attached molecules ethylendiamine and NO_2 per chain segment are parameterized by a second Debye-temperature contributing with 12 modes. This way, we reproduce the lattice specific heat of $MnNi(NO_2)_4(en)_2$ with Debye-temperatures $\Theta_{D1} = 138$ K and $\Theta_{D2} = 249$ K (solid line in Fig. 2(a)).

We obtain the magnetic specific heat contribution $c_{p,mag}$ by subtracting $c_{p,lat}$ from the total c_p (Fig. 2(b)). Further, by numerically integrating $c_{p,mag}/T$ we obtain the magnetic entropy S included in Fig. 2(b). Both quantities indicate that above T_N there are magnetic fluctuations present over a wide temperature range. In $c_{p,mag}$ there is a broad anomaly ranging up to $\sim 10\,T_N$. The associated entropy reaches only $1.4\,R\,\ln(2)$ at T_N, which is less than half of the value expected for the sum of the magnetic entropies of Ni ($S = 1$) and Mn ($S = 5/2$), $R\ln(3)+R\ln(6) = 2.89\,R$ (dotted line in Fig. 2(b)). This value is reached only at $10\,T_N$. Conversely, the saturation of S at $2.89\,R$ demonstrates the adequacy of our derivation of the lattice specific heat.

AFM order in $MnNi(NO_2)_4(en)_2$ is suppressed by small magnetic fields [15]. This enables us to study magnetic fluctuations in $MnNi(NO_2)_4(en)_2$, as they appear in c_p. In Fig. 3 we plot $c_{p,mag}$ as function of field. We observe a rapid suppression of the AFM state, in agreement with Ref. [15]. Moreover, after suppression of the AFM state the broad specific heat anomaly above T_N becomes more pronounced in magnetic fields.

The temperature T_{up} of the maximum in $c_{p,mag}$ represents a measure for an energy scale characteristic for the magnetic fluctuation spectrum (indicated for the 1.6 T data in Fig. 3). In the inset of Fig. 3 we record its field dependence up to 1.6 T, with a modest increase of T_{up} by about 1 K/T. Further, after suppression of AFM order in the T dependence of c_p there is additional structure. This is most clearly seen for $c_{p,mag}/T$, where one now observes a double-peak like structure (see Fig. 3). We take as measure for a second characteristic energy scale T_{low} the maximum in $c_{p,mag}/T$ and include its field dependence in Fig. 3. Again, we find a modest increase of T_{low} by about 1 K between 0.4 and 1.6 T.

T_{up} and T_{low} are clearly distinct temperatures and increase at a similar rate. Therefore, they do not stem from ionic states Zeeman split in an external field. Further, extrapolating T_{low} to zero field yields a finite value of about 0.7 K, implying that T_{low} does not arise from Zeeman splitting of ionic degenerate states. Therefore, we associate both characteristic energy scales T_{up} and T_{low} with collective excitation modes of the magnetic fluctuation spectrum of $MnNi(NO_2)_4(en)_2$ as result of the existence of an acoustic and an optical magnon mode.

An accurate computation of the specific heat for ferromagnetic mixed $S_1 = 1$, $S_2 = 1/2$ chains already is a

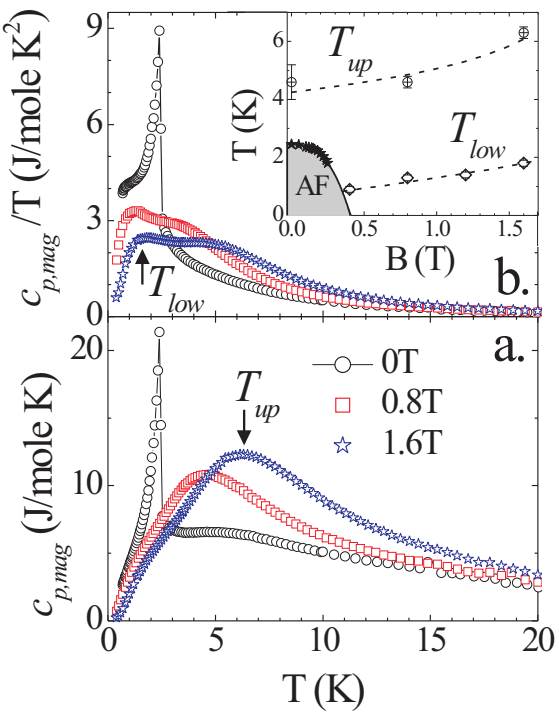

FIG. 3: (Color online) (a) The field dependence of $c_{p,mag}$ of $MnNi(NO_2)_4(en)_2$ for fields $B\|c$. (b) The same data plotted as $c_{p,mag}/T$. Inset: The magnetic phase diagram of $MnNi(NO_2)_4(en)_2$ for $B\|c$: T_N from Ref. [15] ($\star$), T_{up} from the maximum in $c_{p,mag}$ ($\oplus$), T_{low} from the maximum in $c_{p,mag}/T$ ($\diamond$); lines are guides to the eye.

challenging task [9], and no results for $S_1 = 1$, $S_2 = 5/2$ are available even within approximate schemes such as modified spin-wave theory [6]. Furthermore, these calculations did neither include an external field nor the ionic zero-field splitting. Therefore, we compute the specific heat by full diagonalization of the chain Hamiltonian

$$\mathcal{H} = -J \sum_{i=1}^{N/2} \left(\vec{S}_i \cdot \vec{s}_i + \vec{s}_i \cdot \vec{S}_{i+1} \right) - D \sum_{i=1}^{N/2} \left(S_i^z\right)^2 - h \sum_{i=1}^{N/2} \left(S_i^z + s_i^z\right) . \qquad (1)$$

Here, the $\vec{s}_i$ ($\vec{S}_i$) correspond to the spins of the Ni-ions (Mn-ions) and have $S_1 = 1$ ($S_2 = 5/2$). Following Refs. [9, 15], we take a single-ion anisotropy into account only for the Mn-sites. h is expressed in terms of the external magnetic field B through $h = g_{\rm av}\, \mu_B\, B$.

Note that conservation of total S^z by the Hamiltonian (1) is technically very important. Exploiting all symmetries, *i.e.*, S^z-conservation, translations and reflection if appropriate, matrices with dimensions as large as 34 585 have to be diagonalized for a chain with a total of $N = 10$ spins. Generic directions of the magnetic field break the conservation of S^z in which case we would be able to treat systems with at most $4 + 4 = 8$ spins. Therefore we restrict the present analysis to fields $B\|c$. In order to obtain results for different magnetic fields from one diagonalization, we approximate the two distinct g-factors on the Mn- and Ni-sites [15] by an average $g_{\rm av}$. We adopt the parameters $J = 2.8$ K and $D = 0.36$ K determined previously from the high-temperature behavior of the magnetic susceptibility [9]. The small interchain coupling $J_\perp$ is not included.

In the absence of a magnetic field $h = 0$, finite-size effects occur in the specific heat for $T \lesssim 3\,J$ (≈ 8 K) on the largest available chains with five spins $S_1 = 1$ and five spins $S_2 = 5/2$. Fortunately, it turns out that a magnetic field stabilizes the computation such that finite-size effects can be neglected for the other two cases of interest, $h = 0.4\,J$ ($B = 0.8$ T) and $0.8\,J$ (1.6 T) over the entire temperature range (for details see Ref. [16]).

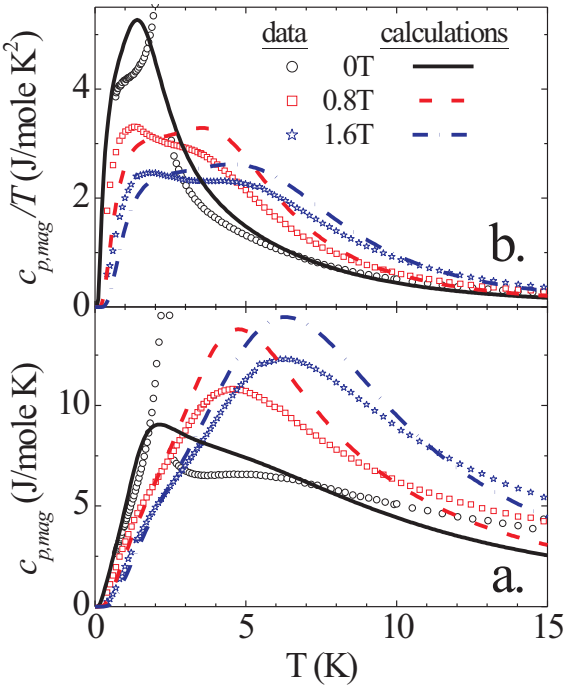

FIG. 4: (Color online) (a) The magnetic specific heat $c_{p,mag}$ of $MnNi(NO_2)_4(en)_2$, calculated for a finite chain with five spins $S_1 = 1$ and five spins $S_2 = 5/2$ in external magnetic fields $B\|c$ of 0, 0.8, and 1.6 T. We include the corresponding experimental data; for details see text. (b) The data from (a) plotted as $c_{p,mag}/T$.

In Fig. 4 we plot the specific heat $c_{p,mag}$ and $c_{p,mag}/T$,

as obtained in our calculations, as function of temperature in external magnetic fields $B\|c$ of 0, 0.8, and 1.6 T. For comparison, in the figure we include the corresponding experimental data.

Since an interchain coupling is not introduced in the calculations we do not reproduce the antiferromagnetic ordering in zero magnetic field. Instead, we observe a finite-size maximum in $c_{p,mag}/T$ at $T_{low} = 1.4$ K. The finite-size data does not exhibit a second maximum in $c_{p,mag}$, but instead there is a shoulder at $T_{up} \approx 5$ K. These temperatures compare well to those obtained experimentally in zero field ($T_{up} = 4.6(6)$ K and an extrapolated $T_{low} = 0.7(3)$ K), even though finite-size effects are relevant in this temperature range. Moreover, a double-peak like structure clearly is visible in the numerical results for $c_{p,mag}/T$ at $B = 0.8$ T and 1.6 T, which can be considered to be free of finite-size effects. These findings fully agreee with general expectations [6, 9], and the positions of these maxima are very close to the experimental values for $T_{up} = 4.8/6.4$ K and $T_{low} = 1.5(2)/1.9(3)$ K in 0.8/1.6 T. Thus, the basic energy scales of the magnetic fluctuation spectrum of $MnNi(NO_2)_4(en)_2$ are fully reproduced by our calculations.

According to a recent analysis [17] of the ferromagnetic $S = 1$ chain, a single-ion anisotropy D alone can give rise to a double-peak structure in the specific heat, but for this to happen much bigger values of D are required than realized in $MnNi(NO_2)_4(en)_2$. Further computations performed by the present authors [16] show that the magnetic fields used in this Letter do not yield a double-peak structure in a homogenous $S = 1$ chain either. Thus, we conclude that our observation of a double-peak like structure in the specific heat directly reflects the alternating spins $S_1 = 1$, $S_2 = 5/2$ along the chains.

Beyond the very close resemblance on a qualitative level, there are some quantitative differences. For instance, while in the calculations the maximum of $c_{p,mag}/T$ is found close to T_{up}, in the experiments it is observed at T_{low}, *i.e.*, in the range of the antiferromagnetic transition temperature. Apart from other idealizations inherent to the model (1), these differences are most likely due to an effective antiferromagnetic interchain coupling $J_\perp \approx 0.014\,J$ [9]. On the one hand, such an interchain coupling is necessary to account for the magnetic order observed at $B = 0$, on the other hand within an RPA treatment [9] it does lead to corrections of a few percent to the magnetic susceptibility at $B = 0.8$ T and 1.6 T.

In summary, we have carried out specific heat measurement in zero and applied field on the bimetallic chain compound $MnNi(NO_2)_4(en)_2$. By determining the lattice contribution of the specific heat we have extracted the magnetic specific heat $c_{p,mag}$. For the first time, in its temperature dependence we verify a long-predicted double-peak like structure. Comparison with numerical calculations for a finite bimetallic $S_1 = 1$, $S_2 = 5/2$ ferromagnetic spin chain yields a very close resemblance on a semi-quantitative level. Hence, our experimental observation of a double-peak like structure in the specific heat directly reflects the alternating spins $S_1 = 1$ and $S_2 = 5/2$ along the chains.

This work has been supported by the DFG under contract no. SU229/6-1. We are indebted to the Rechenzentrum of the TU Braunschweig for allocation of CPU time on the compute-server `cfgauss` and to J. Schüle for technical support. We would like to thank N. Fukushima, S. Grossjohann, S. Wessel, and A.U.B. Wolter for useful discussions, and M. Meissner for support with the heat capacity measurements..

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