



Specific heat of $\text{TbMn}_2(\text{H,D})_2$

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Received 11 October 2004; accepted 26 October 2004

Abstract

Specific heat (SH) measurements on $\text{TbMn}_2(\text{H,D})_2$ powders have been performed in the temperature range from 2 to 350 K, in zero magnetic field and in 9 T. Due to the low heat conductivity of the samples, the measurements were carried out on a mixed Cu- and sample-powder pellet. For TbMn_2 , the anti-ferromagnetic phase transition was manifest by a single SH peak at $T_N = 47$ K, whereas a double SH peak at 281 and 288 K and an upturn below 5 K were observed for the hydride sample. Upon applying the magnetic field of 9 T, the SH upturn was suppressed, whereas no visible influence was found on the specific heat in the whole temperature range above 10 K as well as on the double peak.

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PACS: 75.40.-s; 71.20.Lp

Keywords: Specific heat; Phase transition; Hydrides

1. Introduction

TbMn_2 crystallizes in the cubic C15-type Laves phase ($Fd\bar{3}m$ space group). It undergoes a first-order phase transition around the Néel temperature $T_N = 50$ K, below which there is antiferro-

magnetic ordering. The formation of Mn moments is accompanied by a volume increase of about 3% (with decreasing temperature) [1]. Despite considerable efforts, the exact arrangement of the magnetic moments in this compound has remained unsolved. A complicated multiphase magnetic structure with ordering of both the Mn and Tb sublattice was suggested in Ref. [2] on the basis of neutron diffraction on a single crystal. Similar to other RMn_2 compounds (R = rare earth or yttrium), TbMn_2 can easily absorb hydrogen and/or deuterium up to 4.5 atoms per formula

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unit. At room temperature, the hydrogen (or deuterium) atoms are distributed randomly at the 96g site. The hydrogen/deuterium absorption in $\text{TbMn}_2(\text{H,D})_x$ implies a modification of the crystal structure and strongly influences the magnetic properties [3]. For $x \leq 2.0$, a splitting of the uniform single cubic phase into two cubic phases, one with very low hydrogen content and the other with hydrogen content close to 2, was observed at low temperatures, with magnetic-transition temperatures ranging from 220 to 260 K [3]. For the hydrogen concentration $2.0 \leq x \leq 3.0$, a single cubic phase persists in the whole temperature range and no crystal distortion was observed.

In this work, we present a specific heat (SH) study of $\text{TbMn}_2(\text{H,D})_2$. So as to overcome difficulties related to the low heat conductivity of the powder hydride samples, the SH measurements were performed on pellets consisting of the hydride mixed with micrometer-sized Cu powder. We studied TbMn_2 samples with hydrogen, with a hydrogen–deuterium mixture in ratio 2:1, and with deuterium. The latter sample, TbMn_2D_2 , has earlier been subjected to a neutron-diffraction study, in which collinear antiferromagnetic order below $284 \text{ K} \pm 5 \text{ K}$ and a possible partial disorder within the Tb sublattice were revealed [4,5].

2. Experimental details

The standard technique for the sample preparation and the hydrogenation process has been reported elsewhere [3,6]. A room-temperature lattice parameter $a = 7.6299 \text{ \AA}$ was found for TbMn_2 , which increases to values of 7.9903 and 7.9552 Å for TbMn_2H_2 and TbMn_2D_2 , respectively. The obtained samples usually have fine-powder form, consisting of small hard grains convenient for X-ray and neutron diffraction and for magnetic measurements. However, these samples are not suitable for SH measurements due to the low heat conductivity and the difficulty in producing a bulk sample by compression. Therefore, a method of the sample preparation was developed, which is based on mixing the $\text{RMn}_2(\text{H,D})_x$ powder with micrometer-sized Cu powder (with mass ratio 1:1) and subsequent

compressing at a pressure of 2–3 kbar. The composite pellets of 6 mm diameter and thickness below 1 mm, with typical masses of 60–200 mg, exhibit suitable thermal properties for the SH measurements.

The SH measurements were performed in two different set-ups. The whole pellet was measured in a home-built set-up (AGH-Kraków) by using a quasi-adiabatic method in the temperature range 50–320 K. A small part of the pellet (7–15 mg) was measured in the temperature range 2–350 K and in an applied magnetic field of 9 T in a Quantum Design physical properties measuring system (PPMS) by means of a relaxation method (Prague). In order to specify the contribution of the addenda, a pure Cu pellet was measured under the same conditions.

3. Results and discussion

As a reference for the hydrogenated/deuterated series, the SH of $\text{TbMn}_2 + \text{Cu}$ composite was measured. Fig. 1a shows the total heat capacity of a $\text{TbMn}_2 + \text{Cu}$ pellet ($m = 7.92 \text{ mg}$) and of a Cu pellet ($m = 3.73 \text{ mg}$) with addenda, as well as of the addenda only (the sample holder) measured in the PPMS. The contribution to the heat capacity from the sample itself was found to be relatively small in comparison to the contribution from Cu and the addenda. This may imply a substantial error in the high-temperature range. However, the high-temperature data were found to be in good agreement with those measured using the whole big pellet for which the SH measurements were of a better accuracy, as shown in Fig. 1b. A distinct peak related to the antiferromagnetic phase transition appears at $T_N = (47 \pm 1) \text{ K}$. The results indicated that, by mixing the sample powder with Cu powder, the thermal conductivity was indeed improved, making the sample suitable for SH measurements. Although the peak height at T_N is in our case somewhat smaller than that reported previously in Ref. [1], the C/T vs. T^2 plot exhibits a linear dependence with a γ -value (the electronic-SH coefficient) of 100 mJ/mol K^2 , quite close to the reported value of 91 mJ/mol K^2 . The large

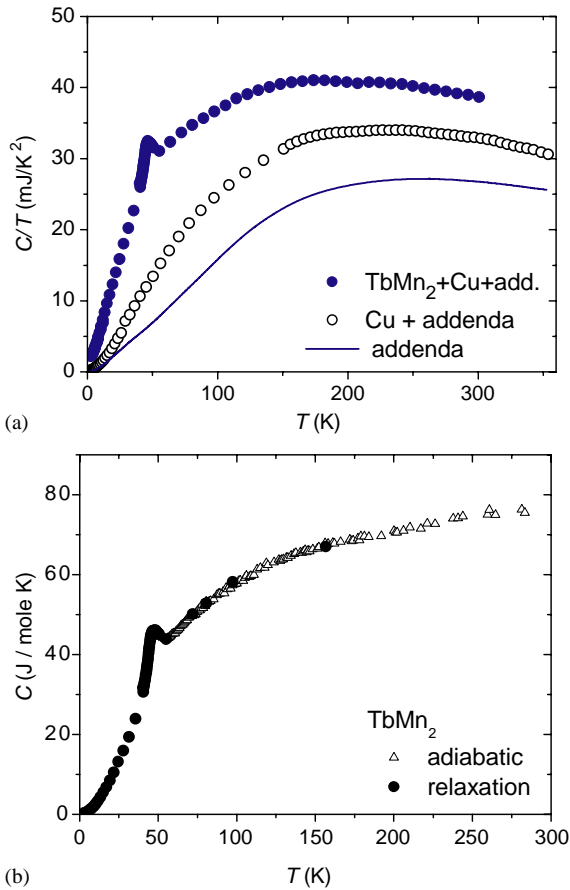


Fig. 1. (a) Total heat capacity of a $\text{TbMn}_2 + \text{Cu}$ pellet + addenda, of a Cu pellet + addenda and of the addenda (sample holder) obtained in a PPMS. (b) Comparison of the SH of TbMn_2 (after subtracting the Cu contribution and the addenda) obtained in two different set-ups. The data for the whole temperature range were obtained on a 7.92 mg sample and those at high temperatures on a 53 mg sample.

experimental γ -value is vaguely attributed to the magnetic and/or crystal field effect of Tb atoms [1].

The SH of $\text{TbMn}_2(\text{H,D})_2$, plotted as C/T vs. T , in zero magnetic field (0 T) is shown in Fig. 2a. There remains no trace of the feature at 47 K, but instead a double peak is observed with maxima at 281 and 288 K, the first one being relatively broader. As magnetic order has been found in this temperature range (depending slightly on the hydrogen contents) [3], we assume that at least one of the features is of magnetic origin. As magnetic properties of RMn_2 compounds are known to

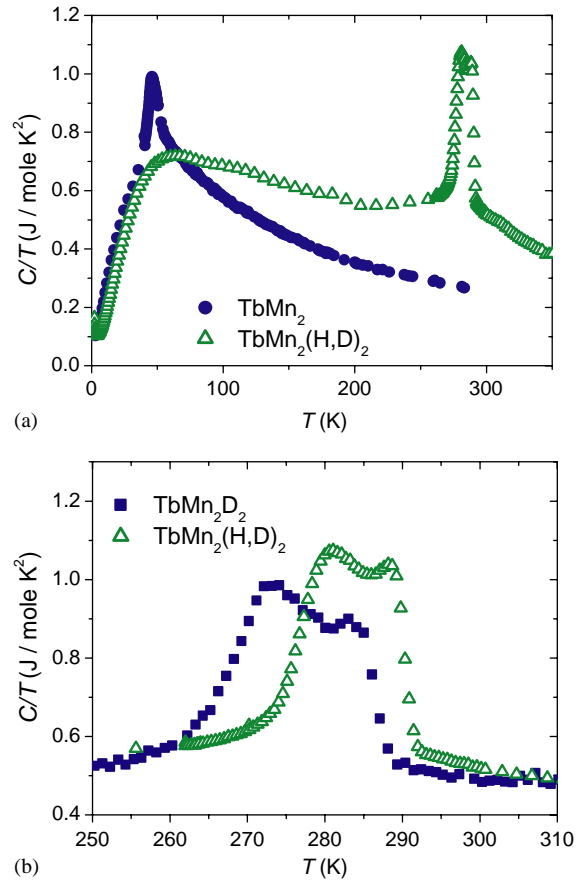


Fig. 2. (a) Specific heat of TbMn_2 and $\text{TbMn}_2(\text{H,D})_2$, plotted as C/T vs. T , in zero magnetic field. The antiferromagnetic order in the two compounds was revealed by a single SH peak at $T_N = 47$ K and a double SH peak at 281 and 288 K, respectively. (b) The enlarged double SH peak of $\text{TbMn}_2(\text{H,D})_2$ in comparison to that of TbMn_2D_2 .

depend critically on the Mn–Mn spacing, the dramatic increase of the Néel temperature (with respect to TbMn_2) can be attributed to the lattice expansion upon hydrogenation, reducing the width of the $3d$ band. Besides this, the hydrogen–deuterium absorption leads to a large excess SH for $\text{TbMn}_2(\text{H,D})_2$ in a wide temperature range of 60–350 K. This enhancement can be understood as due to vibration degrees of freedom of the hydrogen/deuterium atoms. Another source of extra SH can be a modified occupation of different interstitial sites with increasing temperature. For the ‘pure’ deuterated sample, i.e. TbMn_2D_2 , the

double SH peak was found at somewhat lower temperature, with maxima located at 272 and 284 K, as shown in Fig. 2b. The hydrogen absorption leads to a lower value of the total SH below 60 K (down to 2 K), indicating a reduction of magnetic contribution in this range (compared to that of TbMn_2), as shown in Fig. 3. An upturn in the SH was observed for $\text{TbMn}_2(\text{H,D})_2$ below 5 K in zero field. Application of a magnetic field of 9 T suppressed it completely. However, the magnetic field did not have any visible effect on the SH over the whole temperature above 10 K, including the SH peak related to the magnetic ordering.

The origin of the double peak in the SH is not clear yet. Comparison with the intensities of the magnetic reflections in neutron-diffraction patterns, shown in Fig. 4, indicates that the higher-temperature peak of both TbMn_2D_2 and $\text{TbMn}_2(\text{H,D})_2$ (at 284 and 288 K, respectively) corresponds to the temperatures where the magnetic lines appear [4,7]. This may suggest that the peak can be associated with the onset of magnetic ordering in the deuteride. Also the character of the peak with a sharp drop on the high-temperature side suggests a first-order character of the transition, as indicated by the neutron-diffraction results. The second maximum, found at a temperature which is 12 K lower for the deuteride and 7 K lower for the mixed hydride/deuteride and which carries more entropy, may tentatively be

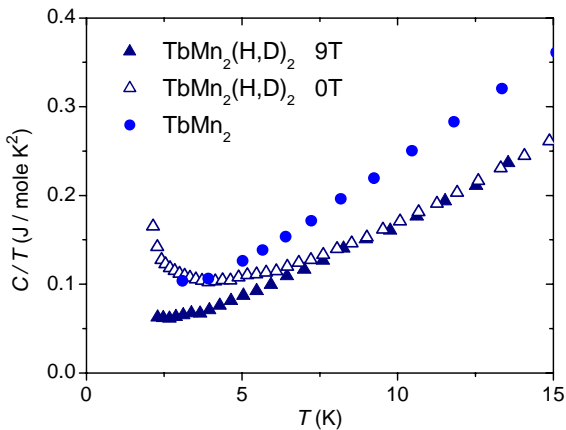


Fig. 3. Specific heat of $\text{TbMn}_2(\text{H,D})_2$ at low temperatures. A specific-heat upturn observed in 0 T below 5 K was suppressed in the magnetic field of 9 T.

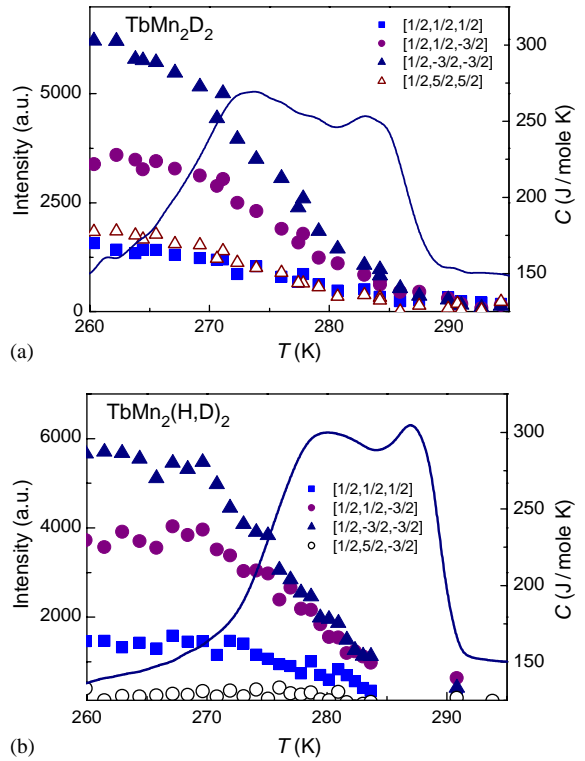


Fig. 4. Temperature dependence of intensity of the neutron-diffraction reflections and the specific-heat of (a) TbMn_2D_2 and (b) $\text{TbMn}_2(\text{H,D})_2$ in the vicinity of the magnetic and structural phase transition.

attributed to ordering of the H/D ions at certain types of crystallographic positions. It is worth noting that no sign of phase separation and/or formation of a distorted phase, which was indicated by X-ray diffraction [3] for hydrogen concentrations below 2 H atoms/f.u., was found here. The only anomaly in the temperature dependence of the lattice parameter is a small “bump” in the magnetic-transition region [7]. One should also notice that the double SH peak exists for the “pure” deuterated as well as for the mixed hydrided–deuterated sample (Fig. 2b). This excludes the possibility that the two peaks correspond to the isotope effect. The difference between the deuteride and mixed hydride/deuteride is quite likely due to a slightly different total concentration of deuterium (or hydrogen + deuterium). The study presented in Ref. [3] has shown that the magnetic properties are rather sensitive to this

concentration, and also that there is a complicated interplay of magnetic and lattice properties, which we can relate to very pronounced magnetostriction effects (due to the formation of Mn moments) interfering with the expansion due to the hydrogen absorption. The arrangement of the hydrogen atoms in the lattice can depend consequently on the magnetic state, which explains why magnetic and lattice transformations frequently occur in the TbMn_2H_x system at comparable temperatures [3]. An interesting feature of the SH of the mixed hydride/deuteride, which does not occur in pure TbMn_2 , is the pronounced upturn in C/T vs. T below 5 K, which can be suppressed by a magnetic field. We tend to relate this feature with the small magnitude of the staggered moments of the Tb sublattice, as detected by neutron diffraction. The reduction to $4.8 \mu_B/\text{Tb}$, much smaller than the value in TbMn_2 ($8.7 \mu_B$), the latter being comparable to the free-ion moment, has been attributed to some kind of magnetic disorder of the Tb sublattice, manifest as diffuse scattering [5]. The SH upturn may perhaps be related to degrees of freedom associated with this incomplete ordering, which may originate from a certain randomness in occupation of the H sublattice.

4. Summary

A new method of SH measurements of powder hydrides embedded in a metallic matrix was implemented successfully in a microcalorimetry system. An SH study of TbMn_2D_2 and $\text{TbMn}_2(\text{H,D})_2$ has revealed details of magnetic phase transitions at 284 and 288 K, which are accompanied by a second peak in the specific heat at temperatures that are a few degrees lower. An upturn in C/T , observed below 5 K in zero field, is

suppressed by an applied magnetic field of 9 T, indicating that this upturn may be related to magnetic disorder of the Tb sublattice. In order to obtain a consistent analysis of the thermodynamic properties of RMn_2 hydrides, SH measurements on samples with the same rare-earth element but with different hydrogen/deuterium contents, as well as on samples with other rare-earth elements are in progress, in combination with neutron-diffraction experiments.

Acknowledgements

This work was financially supported by the Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Kraków and by the project of bilateral cooperation between Poland and the Czech Republic. This work is a part of the research program MSM0021620834 financed by the Ministry of Education of the Czech Republic.

References

- [1] M. Shiga, H. Wada, *J. Magn. Magn. Mater.* 151 (1995) 225.
- [2] P.J. Brown, B. Ouladdiaf, R. Ballou, J. Deportes, A.S. Markosyan, *J. Phys.: Condens. Mater.* 4 (1992) 1103.
- [3] H. Figiel, A. Budziak, J. Zukrowski, G. Fischer, M.T. Kelemen, E. Dormann, *J. Alloys Compds.* 335 (2002) 48.
- [4] H. Figiel, A. Budziak, J. Zukrowski, G. Wiesinger, B. Ouladdiaf, *J. Magn. Magn. Mater.* 272–276 (2004) 585.
- [5] A. Budziak, H. Figiel, J. Zukrowski, E. Gratz, B. Ouladdiaf, *J. Phys.: Condens. Mater.* 13 (2001) L871.
- [6] H. Figiel, J. Przewoznik, V. Paul-Boncour, A. Lindbaum, E. Gratz, M. Latroche, M. Escorne, A. Percheron-Guegan, P. Mietniowski, *J. Alloys Compds.* 274 (1998) 29.
- [7] A. Budziak, Ph.D. Thesis, AGH University of Science and Technology, Kraków, 2002.