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Specific heat anomalies in $RMn_2(H,D)_x$ hydrides

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Abstract

Specific heat (SH) measurements of $RMn_2(H,D)_x$ (R = Gd, Tb, Er, Nd; $x = 0$–3.0) powders have been performed in the temperature range of 50–320 K by a quasi-adiabatic technique. The hydrogenation implies a large increase of the Néel temperature (T_N), an enormous enhancement of the SH peak at T_N, and a large excessive specific heat in the whole temperature range studied. Structured SH anomalies were observed around the temperature of the antiferromagnetic phase transition.

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Keywords: Specific heat; Phase transition; Hydrides

1. Introduction

$GdMn_2$ and $TbMn_2$ crystallize in the cubic C15 type Laves phase ($Fd3m$ space group). They undergo a magnetic first-order transition around 100 and 50 K, respectively. The transition is driven by an antiferromagnetic order of the Mn sublattice and is accompanied by the volume increase of about 1.5% for $GdMn_2$ and 3% for $TbMn_2$ (with decreasing temperature) [1]. $ErMn_2$ and $NdMn_2$ crystallize in the hexagonal C14 Laves phase ($P6_3/mmc$ space group). $NdMn_2$ orders antiferromagnetically at 104 K with the volume change of about 1% [2,3], while for $ErMn_2$ only the erbium sublattice orders at 15 K, because the Mn–Mn spacing is below a critical value [4]. All existing RMn_2 compounds (R = rare earth with exception of La, Ce, Eu and Yb) can easily absorb hydrogen and/or deuterium up to 4.5 atoms per formula unit. At room temperature the hydrogen and deuterium atoms are distributed randomly at the 96 g site in the cubic compounds, and in sites with a similar coordination in the hexagonal ones. The hydrogen/deuterium absorption in $RMn_2(H,D)_x$ leads to a modification of the crystal structure and strongly influences magnetic properties [5,6].

In this work, we present the specific heat (SH) measurements of $RMn_2(H,D)_x$ (R = Gd, Tb, Er, Nd; $x =0$–3). We have studied the hydrogenated samples with hydrogen, with hydrogen–deuterium mixture in a ratio 2:1, and with deuterium.

2. Experimental details

The standard technique for the sample preparation and hydrogenation process was reported elsewhere [5,7]. A new method for the sample preparation was developed, which is based on mixing the powder of $RMn_2(H,D)_x$ with micron-size Cu powder (with the mass-ratio of 1:1) and then compressing using the pressure of 2–3 kbar. The composite pellet of 6 mm-diameter and thickness below 1 mm, with a typical mass of 60–200 mg, exhibits proper thermal properties required for the SH measurements [8]. The specific heat measurements have been performed on the whole pellet

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by using a quasi-adiabatic method in a home-built set-up (AGH-Kraków) in the temperature range of 50–320 K. The $TbMn_2 + Cu$ composite has been also measured as a reference for the hydrogenated/deuterated series. Moreover, a small part of such a pellet was measured in the temperature range of 2 –350 K in quantum design physical properties measuring system (PPMS) by means of a relaxation method in Prague [9]. A good agreement was obtained for the high-temperature data from the two different measurements.

3. Results and discussions

The specific heat of $GdMn_2H_{1.5}$ is shown in Fig. 1. The onset of antiferromagnetic order can be associated with a wide SH peak at 280 K, which exhibits a shoulder on the high-temperature side. At 100 K, a small peak was found indicating the presence of a small amount of pure $GdMn_2$ phase. In addition, a broad bump can be distinguished around $T = 180$ K. Fig. 2 shows the specific heat of $TbMn_2(H,D)_x$. A large asymmetric SH peak with maximum at $T_N = 248$ K and an additional broad one at 186 K were observed for $TbMn_2H_{0.5}$ (Fig. 2a) in the temperature range, where separation into two phases, with low and high hydrogen content, was observed by X-ray crystallographic study for both samples. Except for the difference in the Néel temperature T_N, the data could be taken as qualitatively similar. This may indicate that for the compounds with the cubic C15 structure, irrespective of the R-element and hydrogen concentration, the absorption of ‘pure’ hydrogen would lead to an analogous effect in the specific heat. For these two samples, a large increase of T_N and an enormous enhancement of the SH peak at T_N were observed upon hydrogenation. For instance a small SH peak at T_N of 47 K was observed in $TbMn_2$ (Fig. 2a, inset), while the much larger one was found at 248 K for the concentration of 0.5 hydrogen/f.u. in $TbMn_2$. For the samples with the hydrogen–deuterium mixture and with the pure deuterium, a double SH peak in the antiferromagnetic phase transition region was always observed. For $TbMn_2(H,D)_2$ the double SH peak was revealed by a broad maximum located at 281 K and a sharper one at 288 K (Fig. 2b). For the ‘pure’ deuterated sample, i.e. $TbMn_2D_2$, it was found at lower temperatures: the broad and shaper maximum located at 272 and 284 K, respectively. The drastic increase of the Néel temperature is generally attributed to the lattice expansion upon hydrogenation. The lattice parameter $a = 7.6299$ Å was found for $TbMn_2$, while it increased to 7.9483 and 7.9552 Å, respectively for $TbMn_2H_2$ and $TbMn_2D_2$. Moreover, the hydrogen absorption implied a large excessive specific heat in the whole temperature range of 50–300 K.

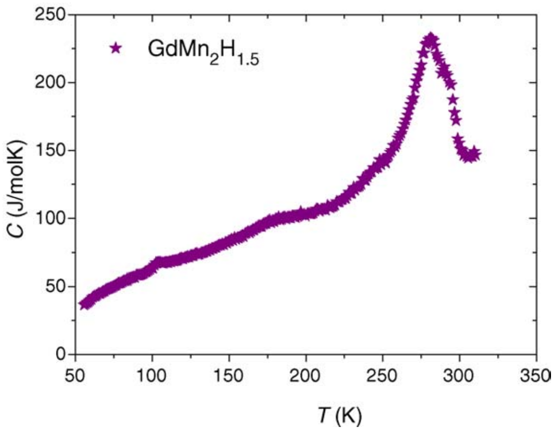

Fig. 1. Specific heat of $GdMn_2H_{1.5}$. The antiferromagnetic order was revealed by a large single SH peak at 280 K.

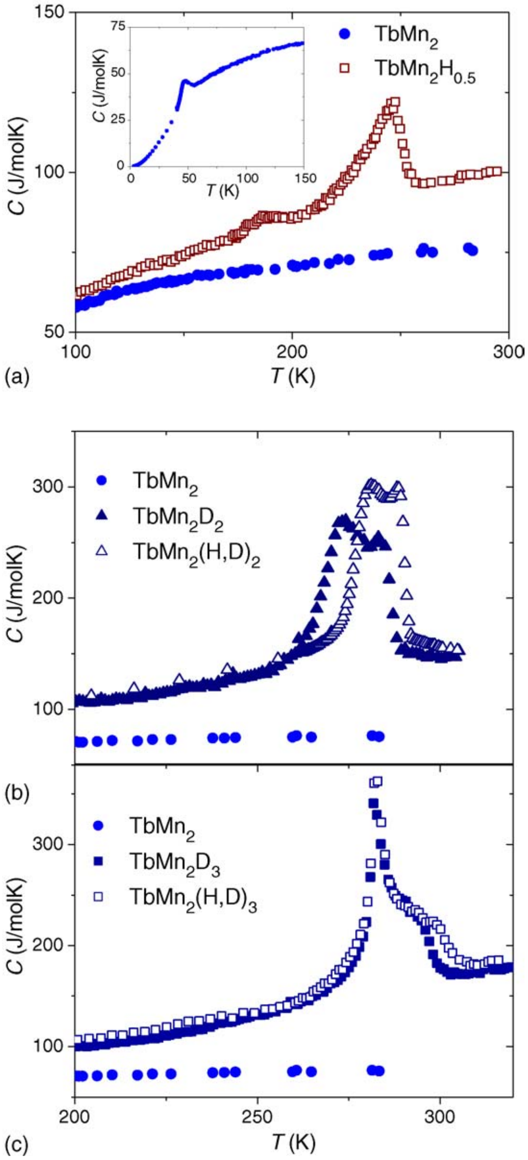

Fig. 2. Specific heat of $TbMn_2$ hydrides/deuterides. (a) A large single SH peak at 248 K in $TbMn_2H_{0.5}$ in a comparison with that at T_N of 47 K in $TbMn_2$ (insert). (b) The double SH peak with two maxima in $TbMn_2D_2$ (at 272 and 284 K) and in $TbMn_2(H,D)_2$ (at 281 and 288 K). (c) The double SH peak with a sharp peak and a shoulder in $TbMn_2D_3$ (at 282 and 292 K) and in $TbMn_2(H,D)_3$ (at 283 and 295 K).

The origin of the double-peak character of the anomaly in the specific heat is not clear yet. We notice that the broad SH maximum at 281 K in $TbMn_2(H,D)_2$ is consistent with the temperature where the fast increase of the magnetic-line intensity was observed [9]. Thus, the broad maximum for the two samples (with $x = 2.0$) was attributed to T_N, whereas the sharp maximum at T several K higher may be related to the hydrogen/deuterium order–disorder transition [8]. In order to check the correlation between the double SH peak and the absorbed H concentration, the SH measurements were also performed on the samples with $x = 3.0$. The SH for data for $TbMn_2D_3$ and $TbMn_2(H,D)_3$ are shown in Fig. 2c. The double SH peak does exist also for these two samples. In both cases a similar feature of the double SH peak was observed: a sharp peak at 282 and 283 K, respectively, and a well-developed bump, respectively, at 292 and 295 K. Increasing the absorbed concentration from $x = 2.0$ to 3.0 does not shift much the transition temperature. However, it significantly affects the shape of the double SH peak, i.e. from the two well-defined maxima into one sharp peak and a shoulder. With the same concentration, on the other hand, the absorption with the hydrogen–deuterium mixture and with the pure deuterium provides no visible difference. Namely, at the same x-value, the “pure” deuterated and the mixed hydrided-deuterated sample revealed a similar overall shape for the double SH peak, except for a small difference in the peak-separation and peak-height ratio. A large excessive specific heat in the temperature range of 50–300 K was also found for those samples.

In $ErMn_2$, the Mn ions do not have, due to a small Mn–Mn spacing, magnetic moments. Upon hydrogenation, the lattice expansion leads to the Mn-moment formation For instance, for $x = 2.0$ the linear lattice expansion of about 5% is sufficient to stabilize moments in the Mn sublattice, which order at about 200 K. In Fig. 3, the specific heat of $ErMn_2D_2$ and $ErMn_2(H,D)_2$ is shown. Two sharp peaks, at 190 and 202 K, are present for the sample with hydrogen–deuterium mixture, whereas a λ-type single peak, twice as high, was observed at 206 K for the pure deuterated sample. The results showed that the H–D composition has large influence on the SH peak in this case. Unlike the case of $TbMn_2$ hydrides/deuterides (cubic C15 structure), the hexagonal C14 structure may be the important factor at $ErMn_2$ hydrides/deuterides. A certain difference can be also seen in the fact that the X-ray diffraction on $ErMn_2H_2$ has revealed a clear distortion for the single-phase hydride accompanying the onset of magnetic order, not visible for the cubic hydrides [6].

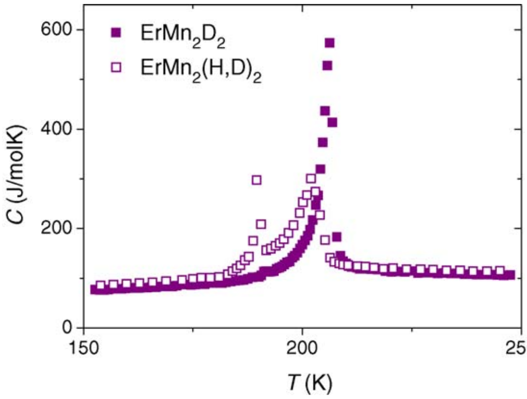

Fig. 3. Specific heat of $ErMn_2$ hydride/deuteride ($x = 2.0$). $ErMn_2D_2$ exhibits a λ-type single SH peak at 206 K, while $ErMn_2(H,D)_2$ reveals a double SH peak at 190 and 202 K.

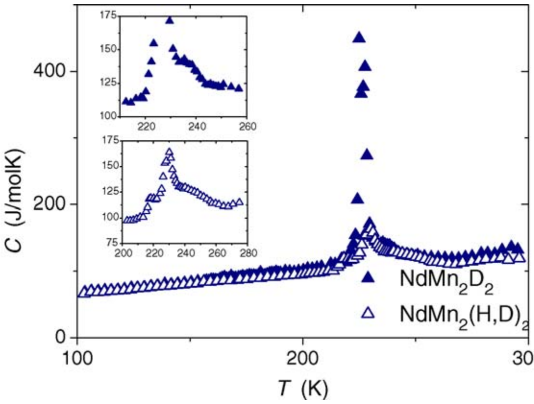

Fig. 4. Specific heat of $NdMn_2D_2$ and $NdMn_2(H,D)_2$. A sharp SH peak is, respectively, at 225 and 230 K and a shoulder, respectively, around 238 and 246 K.

Thus, the low-temperature peak (at 190 K) in $ErMn_2(H,D)_2$ can be attributed to the presence of hydrogen. In fact a visible peak at 191 K existing in $ErMn_2D_2$ can be seen as due to a small admixture of hydrogen in deuterium. SH of $ErMn_2H_2$ still remains to be studied, and a question remains whether, e.g. a phase separation of the hydride and deuteride can be considered.

In order to check whether such a composition dependence of the SH features would be related the difference in crystal structure, the SH studies have been extended to $NdMn_2D_2$ and $NdMn_2(H,D)_2$, having the C14 structure, as well. The results are shown in Fig. 4. For $NdMn_2D_2$ a sharp single peak at 225 K and a shoulder at 238 K are observed. A much smaller peak located at 230 K and a less visible shoulder around 246 K were revealed for $NdMn_2(H,D)_2$. Besides, a small additional peak was observed at 218 K. Despite of the large difference in the peak-height, the peak-shape for both samples is quite similar. In this case the hydrogen–deuterium mixture and the pure deuterium does not lead to a large influence on the structure of the SH peak, only on the peak-intensity.

4. Summary

A large influence of the hydrogen and deuterium absorption on the thermodynamic properties of RMn_2H_x (with both cubic C15 (R = Gd and Tb) and hexagonal C14 structures (R = Er and Nd)) was demonstrated in our specific heat study. A various development of specific-heat anomalies was found. A large single SH peak was observed at T_N for the pure hydrogenated samples $GdMn_2H_{1.5}$ and $TbMn_2H_{0.5}$. For $TbMn_2(H,D)_x$ ($x = 2.0$, 3.0) a double SH peak was present. A large change of the peak-shape was observed with increasing the absorbed concentration, with the same concentration, a very similar shape of the peak was found indicating that there is no impact of the hydrogen–deuterium composition. But the hydrogen–deuterium ratio was found to play a certain significant role for hydrided/deuterated $ErMn_2$. Namely the sample with the hydrogen–deuterium mixture $ErMn_2(H,D)_2$ exhibits two sharp peaks, whereas two-times larger λ-type single peak was found for $ErMn_2D_x$. No influence of the H/D ratio on SH was detected in $NdMn_2$ hydrides/deuterides: a single SH peak was observed for both $NdMn_2D_2$ and $NdMn_2(H,D)_2$.

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