

## Specific heat and magnetization of $\text{RMn}_2(\text{H,D})_2$

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### Abstract

The effect of hydrogen absorption on magnetic and thermodynamic properties of hydrides compounds  $\text{RMn}_2(\text{H,D})_2$  ( $\text{R} = \text{Y, Nd, Tb, Ho, and Er}$ ) have been investigated by performing specific heat and magnetization measurements in the temperature range of 2–320 K and in magnetic fields up to 9 T. The phase transition to the antiferromagnetic order accompanying a crystal structure transformation have been revealed by complicated-structure anomalies in specific heat and weak anomalies in magnetization.

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### 1. Introduction

In recent years the intermetallic compounds  $\text{RMn}_2$  have attracted a large interest. Apart from their particular physical properties especially with a large volume change of 1–5% at the magnetic phase transition temperature, they are thought to be potential materials for technical applications due to their ability to absorb a large amount of hydrogen [1]. A hydrogen-absorption up to 6 at.H/f.u. can be realized at high pressure [2]. Reversible absorption process with relative large hydrogen absorption up to 4.5 at.H/f.u. can be realized easily at low pressures and temperatures [3]. Moreover, the hydrogen absorption is considered as applying a negative chemical pressure leading to a large increase of lattice parameters. In the  $\text{RMn}_2$  compounds, the Mn–Mn distance plays a crucial role in inducing a Mn magnetic moment and thus it largely influences the thermal and magnetic properties [4]. An increase of the atomic distance by hydrogen absorption in the  $\text{RMn}_2(\text{H,D})_x$  implies a strong influence on their physical properties [5].

We have investigated the  $\text{RMn}_2(\text{H,D})_2$  system, with  $\text{R} = \text{Ho}$  crystallizing in the cubic C15 type Laves phase ( $Fd\bar{3}m$  space group) ( $P63/mmc$  space group), and with  $\text{R} = \text{Nd, Er}$  crystallizing in hexagonal C14 structure. In this work we focus our investigation on the hydrides samples  $\text{RMn}_2(\text{H,D})_2$ . For the investigated compounds, the phase separation observed for  $x < 2$  does not occur in the whole temperature range of 2–350 K, except of the  $\text{NdMn}_2(\text{H,D})_2$ , and thus the characteristics of the observed anomalies at  $T_N$  can be underlined.

### 2. Experimental details

The hydride samples were prepared by a standard hydrogen-absorption technique reported elsewhere [3,5]. We have used  $\text{RMn}_2(\text{H}_y\text{D}_{1-y})_2$  samples containing ‘pure’ hydrogen ( $y = 1$ ), with hydrogen–deuterium mixture ( $y = 0.66$ ) and with ‘pure’ deuterium ( $y = 0$ ). At room temperature, the hydrogen (or deuterium) atoms are distributed randomly at the 96g site (i.e. the hollow type A2B2).

For specific heat measurements the composite pellets of sample material mixed with micron-size copper or silver powder were prepared and measured by using a standard quasi-adiabatic method in the temperature range 50–300 K and by a relaxation method in Quantum Design Physical Properties Measuring System (PPMS) [6]. The magnetic field and temperature dependence of magnetization,  $M(H)$  and  $M(T)$ , was measured by using PPMS magnetometer ( $T = 5$  K,  $B = 0$ –9 T for  $M(H)$ , and  $T = 1.5$ –350 K,  $B = 3, 6$  and 9 T for  $M(T)$ ).

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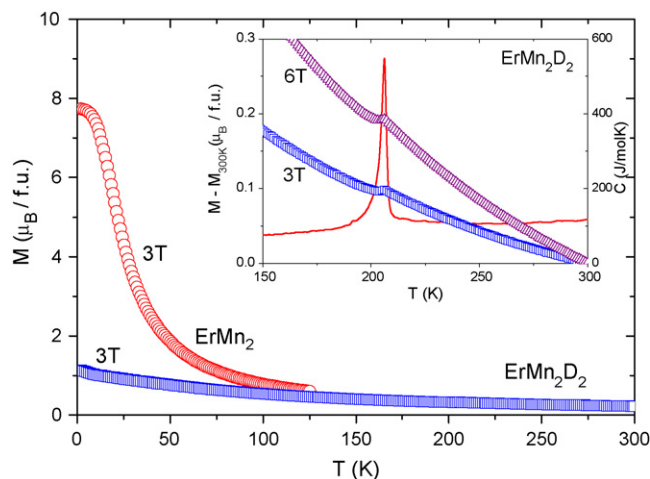


Fig. 1. Temperature dependence of magnetization for  $\text{ErMn}_2$  and  $\text{ErMn}_2\text{D}_2$  measured in an external magnetic field of 3 T. Inset shows the specific heat and the magnetization (in magnetic field 3 and 6 T) in the phase transition region for  $\text{ErMn}_2\text{D}_2$  revealed anomaly at  $T_N$  of 205 K. For a clarity the ‘normalized’ magnetization curves,  $M(T) - M_{300\text{K}}$ , were presented.

### 3. Results and discussion

The temperature dependence of magnetization of  $\text{ErMn}_2\text{D}_2$ , measured at an external magnetic field of 3 T, is shown in Fig. 1. For a comparison the data for  $\text{ErMn}_2$  are shown in the same figure. Deuterium absorption leads to a large suppression of the magnetization at low temperatures. Namely, a value of  $7.73\mu_B/\text{f.u.}$  was found for  $\text{ErMn}_2$  (at 2 K and at 3 T), whereas it decreases to a value of  $1.13\mu_B/\text{f.u.}$  for  $\text{ErMn}_2\text{D}_2$ . Due to lattice expansion, the Mn–Mn distance was larger than the critical Mn–Mn distance, and Mn magnetic moment was induced in the hydride compound  $\text{ErMn}_2\text{D}_2$ . An antiferromagnetic order suppresses the magnetization of Er sublattice below 125 K. The existence of a magnetic order in this hydride sample was confirmed by specific heat  $C(T)$  and magnetization  $M(T)$  results. A very sharp  $\lambda$ -shape peak in the specific heat, attributed to the antiferro-paramagnetic phase transition, was observed at 205 K (the inset of Fig. 1). At this temperature, a small but sharp feature on the magnetization curve was revealed. The anomaly becomes more visible at a higher magnetic field of 6 T. For a clarity the ‘normalized’ magnetization curve,  $M(T) - M_{300\text{K}}$  was presented, i.e. by subtracting the room temperature value respectively of 0.024 and  $0.436\mu_B/\text{f.u.}$  at 3 and at 6 T (Fig. 1, inset). It was claimed [7], that the hexagonal compound  $\text{ErMn}_2\text{D}_2$  undergoes structural transition to monoclinic  $C2/m$  at temperatures range 150–210 K with a possible coexistence of two crystallographic structures. Thus the phase transition observed at  $T_N$  of 205 K can be expected to be accompanied by a structural transition in this compound. However, in our experiments, no additional anomaly was observed in temperature dependences of magnetization and specific heat from 205 up to 300 K indicating no structural phase transition or hydrogen re-ordering in this temperature range.

$\text{NdMn}_2\text{D}_2$  and  $\text{NdMn}_2(\text{H,D})_2$  have revealed a more complicated behavior, as shown in Fig. 2a and b. For  $\text{NdMn}_2\text{D}_2$

a double peak in the specific heat with a large intensity was found at  $224.5 \pm 0.1\text{ K}$  ( $T_{N1}$ , low-temperature SH peak) and  $227.8 \pm 0.1\text{ K}$  ( $T_{N2}$ , high-temperature SH peak). Existence of this double peak was confirmed in several runs. In addition a broad bump at  $238 \pm 1\text{ K}$  ( $T_S$ ) was observed. Such a broad SH bump at  $T_S$  appeared at the temperatures at which a rapid increase of magnetization occurred (with decreasing temperature). The high-temperature SH peak ( $T_{N2}$ ) coincides with the magnetization maximal value after revealing a plateau-type feature, while the low-temperature one coincides with an abrupt decrease in the magnetization at  $T_{N1}$ . The anomaly at  $T_S$  ( $=238\text{ K}$ ) presumably corresponded to a separation of the sample into two phases, found for this compound from X-ray measurements [8]. One phase may undergo an antiferromagnetic–paramagnetic order at  $T_{N1}$ . With respect to the rapid increase of magnetization down to  $T_{N2}$  ( $=227.8\text{ K}$ ), it was expected that in the second phase a small ferromagnetic component or a canted-antiferromagnetic component exists down to  $T_{N2}$ . The magnetization abruptly drops at  $T_{N1}$  ( $=224.5\text{ K}$ ) down to an equivalent value as that at 238 K at 3 T and/or to a lower value with increasing magnetic field to 6 and 9 T. Thus the temperature  $T_{N1}$  is also considered to be related to a reorientation of magnetic moments in the second phase. Nevertheless,  $T_{N2}$  was attributed to a magnetic structure change in the antiferromagnetic phase of the sample, and a perfect and homogeneous antiferromagnetic arrangement of magnetic moments in  $\text{NdMn}_2\text{D}_2$  was expected below  $T_{N1}$ .

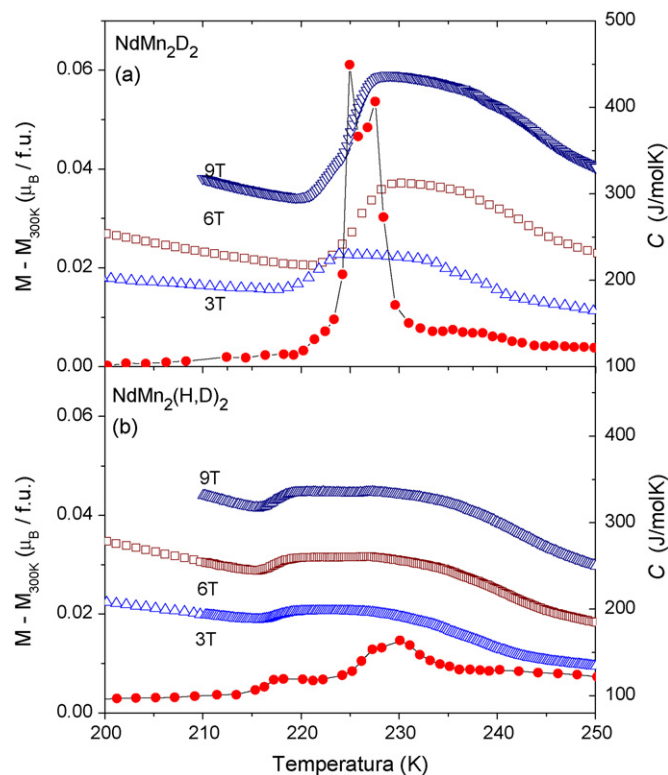


Fig. 2. Temperature dependence of normalized magnetization,  $M(T) - M_{300\text{K}}$ , measured in a magnetic field of 3, 6 and 9 T and specific heat of  $\text{NdMn}_2\text{D}_2$  (a) and  $\text{NdMn}_2(\text{H,D})_2$  (b) in the phase transition region. Solid line is a guide for eye.

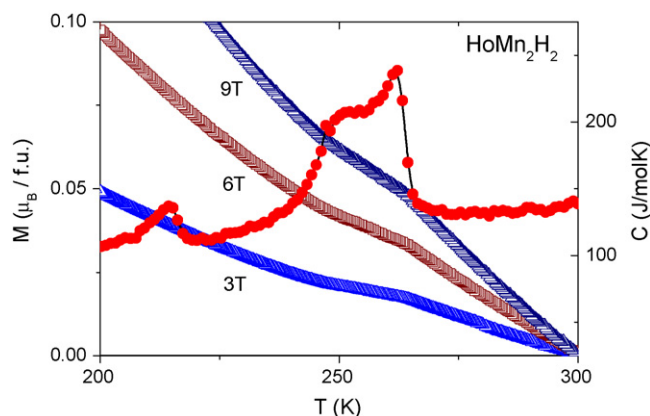


Fig. 3. Temperature dependence of normalized magnetization,  $M(T) - M_{300\text{K}}$ , measured in a magnetic field of 3, 6 and 9 T and specific heat of  $\text{HoMn}_2\text{H}_2$ .

A similar feature in the specific heat, however much less pronounced, with a distinguished double peak and a broad bump at higher temperature was revealed for  $\text{NdMn}_2(\text{H,D})_2$  (Fig. 2b). Observed differences were rather attributed to the sample quality, i.e. they were related to the inhomogeneity of the hydrogen/deuterium atoms distribution within the lattice.

In Fig. 3 the magnetization and specific heat data for  $\text{HoMn}_2\text{H}_2$  were shown. The  $C(T)$  curve revealed a small peak at  $214.5 \pm 0.5$  K and a double specific heat anomaly composed of a broad maximum at  $252.5 \pm 0.5$  K and a sharp peak at  $262.5 \pm 0.2$  K. At higher temperature side of the sharp peak it drops back to the background value. A change in the slope of the  $M(T)$  curve was found at 252.5 and at 262.5 K, i.e. in a good coincidence with the double specific heat anomaly. With increasing magnetic field, the slope-changes become more visible. However, no any visible anomaly in the magnetization curve  $M(T)$  was observed at 215 K. The complicated character of specific heat temperature dependence is surprising due to the fact, that  $\text{HoMn}_2\text{H}_2$  shows a cubic structure in the whole temperature range and does not show any structural transition or phase separation. The high-temperature sharp SH peak is attributed to magnetic phase transition to antiferromagnetic state. The broad component of double specific heat peak is considered to be related to a reorientation of magnetic moments possibly accompanied with a hydrogen migration. The small SH peak at 214.5 K indicates that the hydrogen distribution may not be homogenous and thus a small fraction with lower hydrogen content exists in the sample which undergoes a phase transition to the antiferro-

magnetic state at this temperature. With respect to a very small change in the magnetization of the major part of the sample in the phase transition region 250–260 K, it was expected that the phase transition of such a small fraction would not be reflected in the magnetization curve.

#### 4. Summary

Distinguished anomalies in the specific heat and much weaker in magnetization have been observed at the phase transition to the antiferromagnetic order in  $\text{RMn}_2(\text{H,D})_2$ . A complicated structure of the SH feature and magnetization was obtained. Namely, a single SH peak and a sharp anomaly was found for Er-hydrides (i.e.  $\text{RMn}_2(\text{H,D})_2$  with  $\text{R} = \text{Er}$ ). Also a double SH peak was observed for Nd- and Ho-hydrides, a large change in magnetization (with a rapid increase, a plateau-type, and then an abrupt drop) was observed for Nd-hydrides, whereas only a small slope-change was obtained for Ho-hydrides. In some cases an additional anomaly is attributed to inhomogeneous distribution of hydrogen in the sample.

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