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Magnetic properties of $TbMn_2(H,D)_x$

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Abstract

The aim of this paper is to investigate the influence of hydrogenation on thermodynamic properties of intermetallic compound $TbMn_2$. Specific heat, ac susceptibility and magnetization of three samples: $TbMn_2$, $TbMn_2H_{0.5}$ and $TbMn_2(H,D)_2$ have been measured. For the sample with $x = 0$ and 2.0, at the Néel temperature (T_N), where a single and/or double specific heat peak was observed, an anomaly was also revealed in the susceptibility (respectively at 47 K, and at 281 K and 288 K).

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Keywords: Interstitial alloys; Specific heat; Magnetic properties; Phase transition

1. Introduction

The cubic C15 type Laves-phase $TbMn_2$ undergoes a first-order phase transition at the Néel temperature $T_N = 47$ K. The formation of Mn moments below T_N is accompanied by a volume increase of 1.6% [1]. The neutron diffraction study on a single crystal of $TbMn_2$ suggested a complicated multiphase magnetic structure in both the Mn and Tb sublattice [2]. $TbMn_2$ can easily absorb hydrogen and/or deuterium up to 4.5 atoms per formula unit. At room temperature, the hydrogen (or deuterium) atoms are distributed randomly at the 96g site (i.e. the hollow type A2B2). A drastic increase of the Néel temperature, a strong influence the magnetic properties and a large modification of the crystal structure by the hydrogen/deuterium absorption has been revealed [3,4]. The specific heat measurement have revealed a single peak respectively at 47 K and 248 K for the sample with $x = 0$ and 0.5, while a double peak was observed in the temperature range 270–300 K for $x = 2.0$ and 3.0 [5]. Increasing the hydrogen concentration from $x = 2.0$ to 3.0 significantly affects the shape of the double SH peak, i.e. from the two well-defined maxima into one sharp peak and a shoulder.

In this work we present the AC susceptibility and magnetization measurements on three chosen hydrides samples: $TbMn_2$, $TbMn_2H_{0.5}$ and $TbMn_2(H,D)_2$. We focus our investigations in the temperature range where the specific heat peaks were present.

2. Experimental details

The hydrides samples (the deuterated (D) and the mixed hydrided-deuterated (H,D) ones) have been prepared by a standard technique for the hydrogenation process [3,4].

The ac susceptibility measurements were performed using a ac susceptometer/dc magnetometer (Lake Shore 7225). Magnetization measurements were performed on a Quantum Design Physical Properties Measuring System (PPMS) magnetometer in applied external magnetic field up to 9 T. The specific heat measurements have been carried out on two different set-ups as reported previously [5].

3. Results and discussion

Fig. 1 shows the temperature dependence of dc susceptibility for $TbMn_2$ measured at an external field H_0 of 100 Oe cooled

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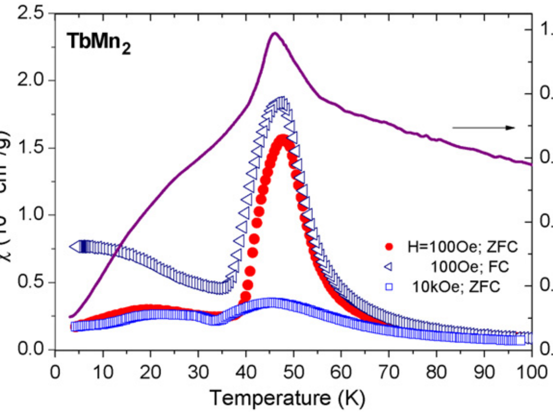

Fig. 1. The dc susceptibility of $TbMn_2$ measured at an external field H_0 of 100 Oe, in zero field cooled (ZFC) and in field cooled (FC), and at 10 kOe in ZFC condition. For a comparison the specific heat data at the phase-transition peak was also shown.

in zero field (ZFC) as well as in the external field (FC) and at external field of 10 kOe. A large maximum was revealed at the temperature T_N, where a specific heat peak was observed, attributed to the phase transition to an antiferromagnetic order. However, a small shift of T_N with increasing magnetic field was found; a value for the phase-transition temperature T_N of 47.75 K, and 45.5 K was estimated respectively at $H_0 = 100$ Oe and 10 kOe. A broad bump was observed in ZFC, respectively at 22.25 K and 19.85 K, i.e. it shifted to lower temperatures with increasing magnetic field, similar to T_N. For $H_0 = 100$ Oe, the maximum at T_N was found to be amplified by cooling in field. Moreover, field cooling implies a large enhancement of the susceptibility at low temperatures. It was attributed to some extra contribution from orientation of Mn magnetic moment in external field.

The temperature dependence of the first- and third harmonic of the real (χ') and imaginary part (χ'') of susceptibility was measured for $TbMn_2$ and $TbMn_2H_{0.5}$. Namely the first harmonic was measured at a frequency $f = 125$ Hz and at $H_{ac} = 1$ Oe, and the third harmonic ($\chi'_3(T)$, $\chi''_3(T)$) was at $f = 125$ Hz and at $H_{ac} = 5$ Oe. The data for $TbMn_2$ were shown in Fig. 2. The first harmonic of the real part revealed a single maximum at 49.9 K (T_N) and a broad bump at 23.8 K, while the third harmonic χ'_3 exhibited a small maximum at 51 K (above T_N) and a deep asymmetric minimum at 46 K (below T_N). Moreover, the extra broad bump around 25 K was only revealed in the $\chi'(T)$ curve, whereas no anomaly in $\chi''_3(T)$ was observed in this temperature range. For the imaginary part, a single peak was observed at T_N in both the $\chi''(T)$ and $\chi''_3(T)$ curve. A distinguished broad maximum was also revealed around 25 K in the $\chi''(T)$ curve, while there was no anomaly in the $\chi''_3(T)$ curve. The hydrogenation implies a large suppression of AC susceptibility in $TbMn_2H_{0.5}$, as shown in Fig. 3. However, the $\chi'(T)$ revealed a similar feature as that for $TbMn_2$ with a broad maximum at T_N and low-temperature anomaly. Such an anomaly was shifted to lower temperature, at 20 K and with a large enhanced (relative) intensity with respect to the anomaly at T_N. Hydrogenation implies a large enhancement of χ'' below 30 K and also a disappearance of the small max-

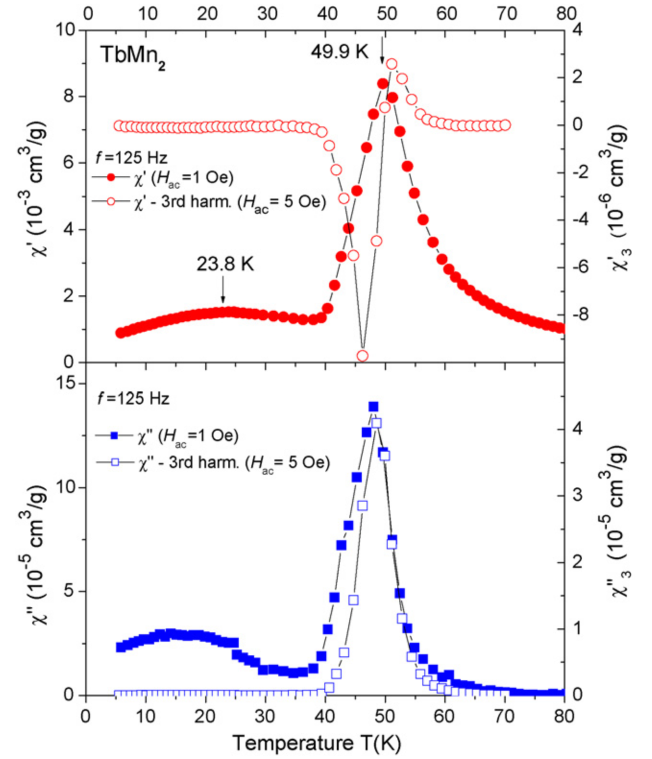

Fig. 2. The real (χ') and imaginary part (χ'') of the first (closed markers) and third harmonic (open markers) of ac susceptibility for $TbMn_2$. The first harmonic was measured at a frequency $f = 125$ Hz and at $H_{ac} = 1$ Oe, and the third harmonic was at $f = 125$ Hz and at $H_{ac} = 5$ Oe.

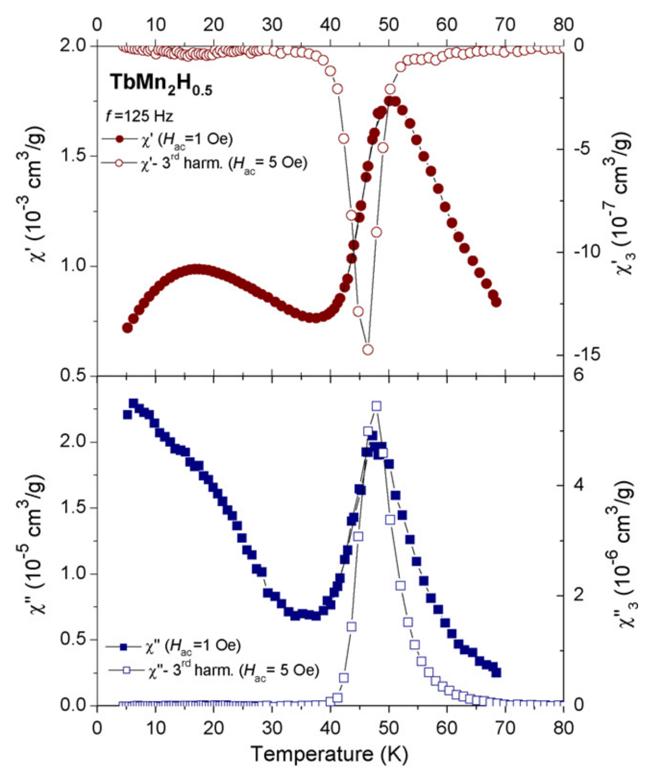

Fig. 3. The real (χ') and imaginary part (χ'') of the first (closed markers) and third harmonic (open markers) of AC susceptibility for $TbMn_2H_{0.5}$. The first harmonic was measured at a frequency $f = 125$ Hz and at $H_{ac} = 1$ Oe, and the third harmonic was at $f = 125$ Hz and at $H_{ac} = 5$ Oe.

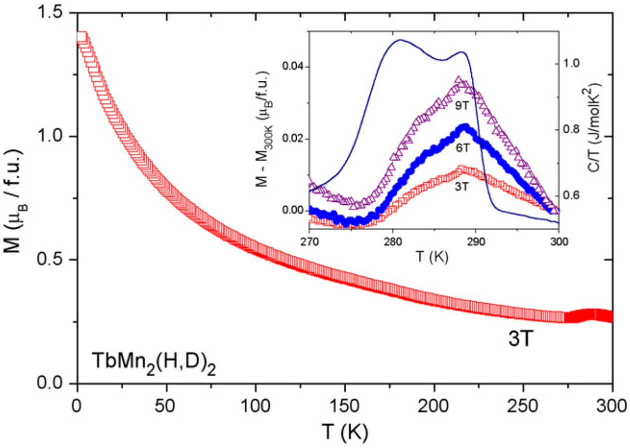

Fig. 4. Temperature dependence of magnetization, $M(T)$ of $TbMn_2(H,D)_2$ in an external magnetic field of 3 T. Inset: the enlarged phase-transition anomalies in the magnetization measured at 3 T, 6 T and 9 T. For a clarity, the curves was normalized to 1 at 300 K, i.e. the values $M(T) - M_{300\,K}$ were shown. The double specific heat peak was shown for a comparison.

imum at 51 K in the $\chi_3''(T)$ curve. This enhancement suggests more freedom for Tb magnetic moments in the distorted lattice. The similarity in both pure- and hydrogenated sample with $x = 0.5$ indicate that a big part of $TbMn_2H_{0.5}$ sample behave as a hydrogen-free $TbMn_2$ material. These results support the suggestion that in $TbMn_2H_{0.5}$ two phases were co-existed; one is almost free from hydrogen ($x = 0$), and the other one with $x \cong 2.0$ [3].

No anomaly was revealed (PPMS) in the magnetization curve $M(T)$, for $TbMn_2(H,D)_2$ at low temperatures. A large change, however, was observed at T_N, in applied high external magnetic field. The magnetization measurements of $TbMn_2(H,D)_2$ at 3 T, 6 T and 9 T were shown in Fig. 4. In all cases the magnetization continuously decreases with increasing temperature and reveals an anomaly around 275–300 K. For clarity we showed (in inset of Fig. 4) the temperature dependence of the normalized magnetization, i.e. with the subtracted value at 300 K ($M_{300\,K}$). The room temperature or the subtracted value respectively was $0.27\mu_B$/f.u. ($B = 3$ T), $0.53\mu_B$/f.u. (6 T) and $0.8\mu_B$/f.u. (9 T). A sharp peak was observed at $T_C = 288$ K, i.e. at the high-temperature maximum of the double peak in the $C(T)$ curve, and a shoulder around 280 K, i.e. around the low-temperature maximum of the double peak. The sharp peak at 288 K is attributed to the phase transition to the antiferromagnetic state, whereas the wider shoulder at 281 K may be related to thermally activated diffusion of hydrogen.

4. Summary

Our investigations showed that the hydrogenation has a strong influence on the ac susceptibility, magnetization and specific heat of $TbMn_2(H,D)_x$ system. The phase separation for $x = 0.5$ was shown to be not perfect from the viewpoint of magnetic properties; the hydrogen-free phase is less than 75%. For $TbMn_2(H,D)_2$ the transition to antiferromagnetic state at 288 K was observed, both in the specific heat and magnetization measurements, whereas the peak at 280 K is considered to be connected with the hydrogen (re)ordering.

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