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Specific heat of YMn_2H_x and $HoMn_2H_x$

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Abstract

Specific heat (SH) measurements of RMn_2H_x (R = Y, Ho; x = 0–4.3) powders have been performed by a quasi-adiabatic (in the temperature range of 50–320 K) and relaxation (2–400 K) methods. The hydrogenation causes a large increase of the transition temperature T_N with the enhancement of both SH peaks at T_N and the specific heat background. Various features of the double specific-heat anomaly were observed close to T_N. The possible correlations between the hydrogen vibration modes, hydrogen migration, and the specific heat anomalies have been discussed.

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Keywords: Specific heat; Magnetic properties; Phase transition; Hydrides

1. Introduction

Recently, the intermetallic compounds RMn_2 have attracted a large interest due to their potential application as hydrogen-storage materials which store up to 4.5 H atoms per formula unit at relatively low pressures and temperatures [1]. Besides, in those compounds the Mn–Mn distance plays a crucial role in inducing a Mn magnetic moment. The hydrogenation is considered as the application of a negative chemical pressure leading to a large increase of lattice parameters and the Mn–Mn distance. Thus, it is expected that $RMn_2(H)_x$ system would exhibit a variety of physical properties. With respect to the hydrogen-storage process, a good understanding of those physical properties, especially around the phase transitions, is of tremendous importance.

RMn_2H_x with Y and Ho crystallize in the cubic C15 type Laves phase (*Fd*3*m* space group). For the hydrogen content $x \leq 4.5$ the hydrogen atoms are distributed at the 96*g* A2B2 sites [2]. For $HoMn_2H_x$ for $x < 2.0$, a splitting of the uniform single cubic phase into two phases, one with very low hydrogen content and the other one with hydrogen content close to 2, was generally observed at low temperatures. For the higher hydrogen concentration less apparent crystal distortion for Ho-based hydrides was observed. The YMn_2H_x compounds are single phase and cubic between 1.15 and 3.5 H/f.u.

RMn_2H_x undergo a phase transition to the antiferromagnetic phase below T_N. The neutron scattering data of some Tb- and Er-based hydrides showed that T_N increases largely with increasing H-content [3,4]. Magnetization and specific-heat measurements have been performed on $RMn_2(H,D)_x$ samples [5,6]. In this paper, we present the specific-heat results for Y- and Ho-based hydrides especially those with a large hydrogen concentration $x > 2.0$.

2. Experimental details

The standard technique for sample preparation, hydrogenation process and the sample-preparation procedure for SH measurements were reported elsewhere [3,5]. The SH measurements were performed on two different equipments. The whole pellet was measured by using a standard quasi-adiabatic method in the temperature range 50–320 K and a small part of the pellet (10–30 mg) was measured by a relaxation method in the temperature range of 2–400 K in Quantum Design Physical Properties Measuring System (PPMS). Magnetic $M(H)$ and $M(T)$ measurements were performed by PPMS magnetometer, T = 2–350 K and B = 0–9 T.

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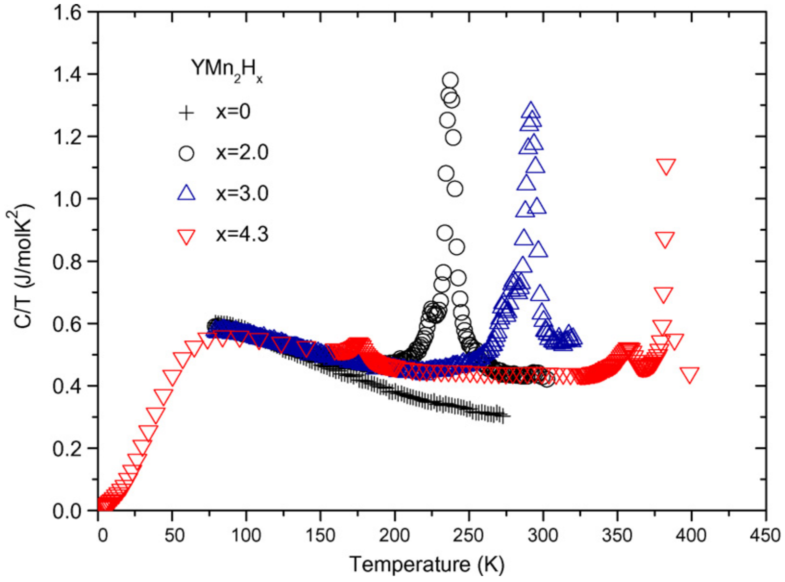

Fig. 1. Temperature dependence of specific heat for YMn_2H_x compounds plotted as *C*/*T* vs. *T*.

3. Results and discussion

Temperature dependence of the specific heat plotted as *C*/*T* versus *T* for YMn_2H_x ($x = 0$, 2.0, 3.0, 4.3) is shown in Fig. 1. For all hydrides samples ($x > 0$) a double peak was observed; one sharp and big peak and one small peak at lower temperature. An additional small peak appeared at 175 K for $x = 4.3$. The results suggest that there would be two transitions, one with magnetic-transition origin and the other one possibly related to order–disorder transition of hydrogen.

The *C*/*T* versus *T* curves for $HoMn_2H_x$ ($x = 1.0$, 1.65, 2.0, 2.5, 3.0, 3.5 and 4.3) in the phase transition region are shown in Fig. 2. A triple anomaly was observed for the samples with low hydrogen content. A similar peak-structure with a sharp peak centered between two broad peaks was observed for two samples with $x = 1.0$ and 1.65. The sharp peak was always at 215 K. The broad peak at lower temperature was found at 200 K for both two samples. A small broadening of the peak was observed with increasing H-content. Increasing H-content, however, implied a large enhancement and a visible shift of the peak at the higher temperature side. Namely, it was located at 230 K for $x = 1.0$, while it shifted to 240 K for $x = 1.65$. The triple anomaly was still revealed for $x = 2.0$, but with a much different feature which consists of a single sharp peak at 215 K and a large double peak with two maxima at 250 and 260 K, respectively. For the higher H-content, the single peak at 215 K disappeared and only the double peak was observed. With increasing H-content, the double peak was largely shifted to higher temperature. For $x > 3.0$,

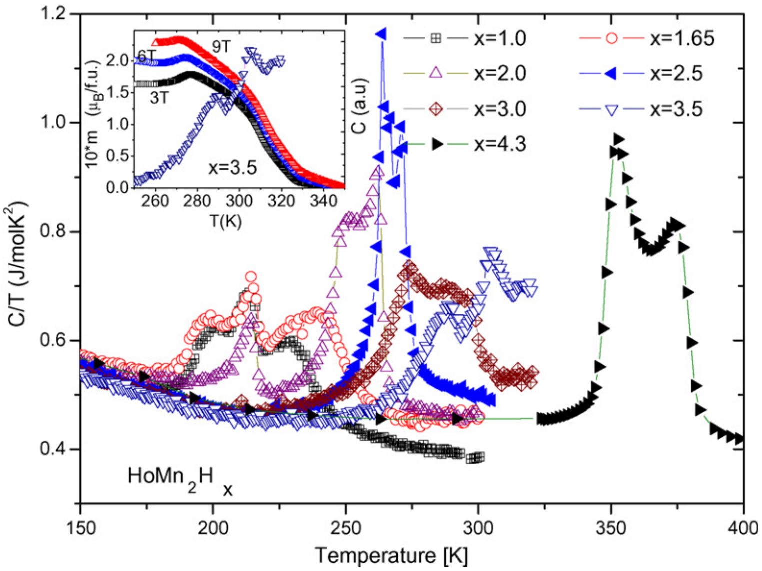

Fig. 2. Temperature dependence of specific heat for $HoMn_2H_x$ compounds in the transition temperature region. Inset: The temperature dependence of reduced magnetization ($m = M(T) - M(350\,K)$) and the specific heat anomalies for $x = 3.5$.

the double peak is much wider and the two maxima of the double peak are well separated from each other. We notice here that for $x \leq 1.5$ $HoMn_2H_x$ hydrides undergo a structural transition—a spinoidal decomposition revealed by X-ray diffraction study at around 235 K [7], i.e. around the temperature where the high-temperature broad peak exists. For $x = 2.0$, no drastic change of structure was observed and only non-monotonic increase of volume cell was observed at 250 K, i.e. at the temperature where the double SH peak appeared. On the other hand, a similar structural transition again observed for $x = 2.5$ and 3.0 at $T = 265 \pm 5$ K, which coincide with the lower-temperature maximum of the double SH peak at 264 and 272 K, respectively. The results suggest that, although there is a correlation between the structural transition and the SH anomaly in these compounds, the SH peak is caused by the entropy release, rather related to the hydrogen migration itself, than to the structural changes.

Almost all anomalies in the reported data for both types of materials have peculiar double-peak (or even triple-peak) structure.

In comparison, the SH data with the magnetization data in the phase transition region, both the reduced magnetization versus temperature $M(T)$ and the $C(T)$ curves were shown for $HoMn_2H_{3.5}$ sample in the inset of Fig. 2. The magnetization increased largely below 330 K. The SH peak at 304 K coincides with the knee-type anomaly in the $M(T)$ curve. However, at 287 K, i.e. at the temperature where the low-temperature maximum of the double SH peak was revealed, only a smooth increase in $M(T)$ was observed. At $T = 278$ K, yet another (and most pronounced) anomaly exists in the $M(T)$ curves. It may be related to a reorientation of magnetic moments.

In RMn_2H_x hydrides the small kinks on the $M(T)$ curves always coincide at least with one feature on the $C(T)$ curves, proving that at relevant temperatures the magnetic phase transitions take place. However, the entropy values ΔS released at the transition in hydrides exceed considerably those for non-hydrogenated materials (e.g. for YMn_2 $\Delta S = 3.9$ J/mol K). Thus, the antiferromagnetic–paramagnetic transition alone may not explain all large anomalies in the specific heat observed in our experiments. In other words, we consider that quite a portion of ΔS may be related to hydrogen atoms vibration degrees of freedom that are released at the antiferromagnetic–paramagnetic transition due to possible strong magnetic–phonon interactions. Such interactions are conceivable since the Mn–Mn exchange interactions strongly depend on hydrogen presence via, e.g. the increased mean Mn–Mn distance. Another source of excess entropy may be from hydrogen migration between A2B2 sites, i.e. transition between low temperature ordered state and high temperature random distribution of hydrogen atoms. For high deuterium content $x = 4.3$ and 4.5 the interplay between magnetic and hydrogen ordering was thoroughly investigated by means of neutron diffraction study [2,8,9] and it was found that at ambient pressure both transitions occur at the same temperature for $YMn_2H_{4.3}$, $YMn_2H_{4.5}$, and $HoMn_2H_{4.5}$. We have therefore estimated the excess entropy released at the transition. For that we have first subtracted the specific heat background of non-hydrogenated samples from the hydrogenated ones. The resultant entropy released at the transition was then subtracted by a value of 3.9 J/mol K (the entropy for non-hydrogenated sample) and evaluated for 1 mol hydrogen (ΔS_H). The results are shown on Fig. 3. The relevant data from Tb- and Er-hydrides [6,10] are also included. Although no straightforward explanation is apparent for the x dependence, the data showed a breaking up at $x = 2.0$ into two hydrogen concentration regions. It may be connected with the fact that below ca. $x = 2.0$ the materials tend to break into two hydride phases with the existence of some additional vibration mode for hydrogen, while such a vibration mode is suppressed at higher x-values. In the inset of Fig. 3 the mean temperatures of heat capacity anomalies in those hydrides are plotted as a function of hydrogen concentration. A smooth increase of the transition temperature with increasing H-content was shown, in contrary to the entropy ΔS_H. It is apparent that the in both types of structure-symmetry (C15 for Ho-, Tb-, Y-based and C14 for Er-based compounds) the H sites are similar. The H vibration spectrum should also be universal as well as the energy barrier responsible for migration. Further direct studies of hydrogen atoms vibration spectrum are needed to verify this important point.

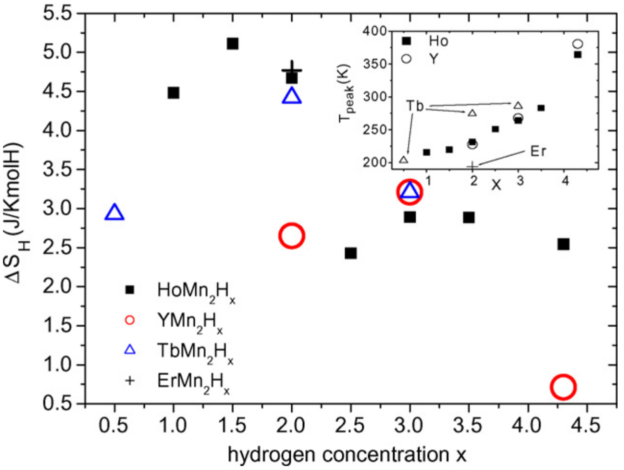

Fig. 3. Hydrogen content dependence of the entropy released at the antiferromagnetic–paramegnetic transition (calculated per hydrogen mol and after subtraction of the magnetic transition entropy for YMn_2). Inset: The hydrogen content dependence of the mean temperature of the specific-heat anomalies.

4. Summary

A variety of specific-heat feature have been observed at the vicinity of the magnetic phase transition for the hydrides RMn_2H_x with a double peak (R = Y) and/or triple peak (R = Ho). While only a shift of the SH peaks to higher temperatures for the Y-based hydrides with increasing the H-content was observed, such hydrogenation implied a large change of the specific heat features of Ho-based hydrides. It was argued that at least part of those anomalies and part of the entropy released at the phase transition is due to hydrogen migration and vibration degrees of freedom.

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