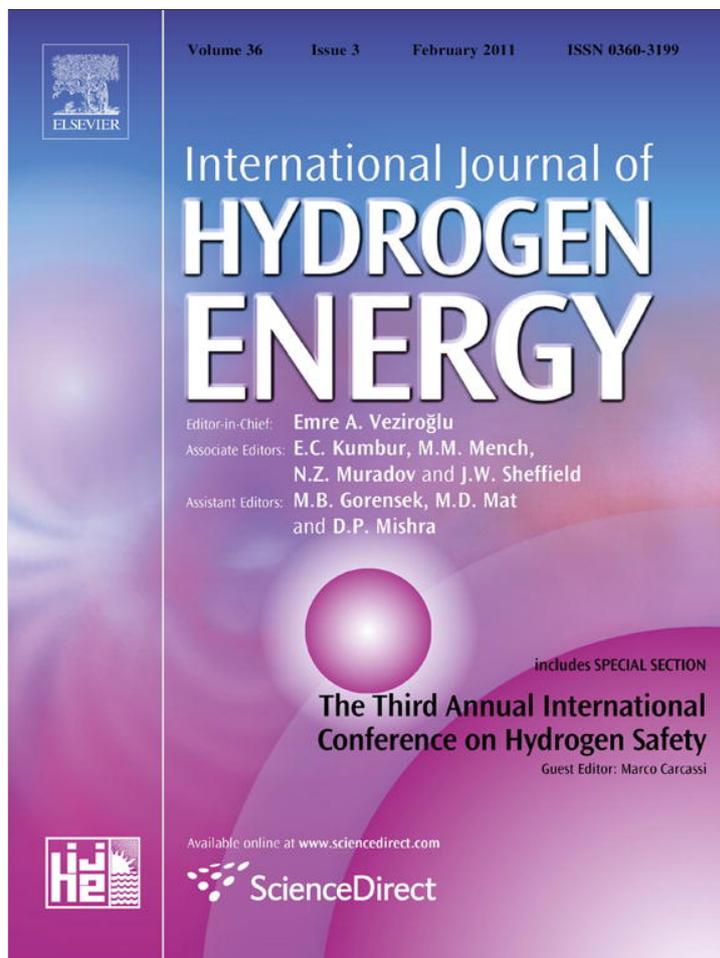


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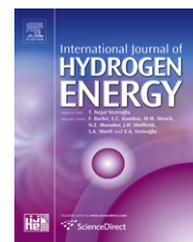


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## Calorimetric properties of C14 and C15 YMn<sub>2</sub> and YMn<sub>2</sub>(H,D)<sub>6</sub>

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### ABSTRACT

The capacity of YMn<sub>2</sub> to undergo reversible hydrogenization makes this compound a potential candidate for hydrogen storage. This report describes the successful synthesis of YMn<sub>2</sub>H<sub>6</sub> from hexagonal C14 YMn<sub>2</sub> as well as calorimetric studies of hexagonal C14 YMn<sub>2</sub>, cubic C15 YMn<sub>2</sub> and their isostructural derivatives, YMn<sub>2</sub>H<sub>6</sub> and YMn<sub>2</sub>D<sub>6</sub>. Complementary structural and physical property characterizations include X-ray diffraction, electrical resistivity, and magnetic susceptibility measurements. Of particular interest is a hysteretic first-order phase transition in C15 YMn<sub>2</sub> near 100 K, which does not occur in C14 YMn<sub>2</sub>. Analysis of a specific heat anomaly that is associated with this transition reveals a substantial latent heat of 330 J/mol. No such anomalous specific heat exists in YMn<sub>2</sub>D<sub>6</sub>, suggesting that the transition is suppressed upon deuterization.

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## 1. Introduction

Intermetallic compositions related to RM<sub>2</sub> Laves phases (R = rare earth and M = transition metal Mn, Fe, Co) have large hydrogen absorption capacity at room temperature owing to the formation of RM<sub>2</sub>H<sub>x</sub> (0 ≤ x ≤ 6) hydrides. Consequently, they are considered as promising materials for hydrogen storage [1,2]. Intermetallic YMn<sub>2</sub> crystallizes in either a cubic C15 (Fd3m) or a hexagonal C14 (P6<sub>3</sub>/mmc) Laves phase. Both phases can potentially be used to store hydrogen by forming YMn<sub>2</sub>H<sub>x</sub>. Most of the relevant literature discusses C15 YMn<sub>2</sub>, which undergoes first-order structural and antiferromagnetic (μ<sub>Mn</sub> = 2.7 μ<sub>B</sub>) transitions near 100 K, accompanied by

a significant volume change of 5% [2,3]. No such phase transformation occurs in C14 YMn<sub>2</sub>. The conventional low-pressure hydrogenation process of C15 YMn<sub>2</sub> at relatively low temperatures yields YMn<sub>2</sub>H<sub>x</sub> with an x value of less than around 4.5 [4,5]. Only recently, YMn<sub>2</sub>D<sub>6</sub> (Fm-3m) was successfully synthesized from C15 YMn<sub>2</sub> under high-pressure deuterium at elevated temperature [6]. Deuterium was used rather than hydrogen to facilitate neutron diffraction studies. This effort increased x to six [6]. Just as important is the reversibility of the deuterization process, releasing the six deuterium atoms at high temperatures, enhancing the viability of YMn<sub>2</sub> for hydrogen storage. Interestingly, isostructural Fm-3m RMn<sub>2</sub>H<sub>6</sub> hydrides (deuterides), where R = Y,

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Dy, Ho, Gd or Er, have been also synthesized from several C14  $\text{RMn}_2$  Laves [7], but not yet from C14  $\text{YMn}_2$ , which is a high-pressure modification. Therefore, one related task was to verify whether  $\text{YMn}_2\text{H}_6$  hydride can be formed not only from C15 but also from hexagonal C14  $\text{YMn}_2$  modification.

The phase transitions in C15  $\text{YMn}_2$ , which involve an interplay between magnetism and lattice stability, - and particularly the associated latent heat and deuterization effect - remain to be further elucidated. This study presents relevant results of a calorimetric study. For comparison, the investigation was extended to cover C14  $\text{YMn}_2$  and its derivative, hydrogenated  $\text{YMn}_2\text{H}_6$ . Complementary measurements of magnetization and electrical resistivity were also made.

## 2. Material and methods

A C15  $\text{YMn}_2$  sample was prepared by induction-melting a mixture of high-purity yttrium and manganese in a stoichiometric ratio. X-ray diffraction patterns in Fig. 1(a) confirm the cubic Laves phase. The General Structure Analysis System program [8] yielded the lattice constant  $a$  and coordinates of Y and Mn, following Rietveld refinement, that are listed in Table 1.

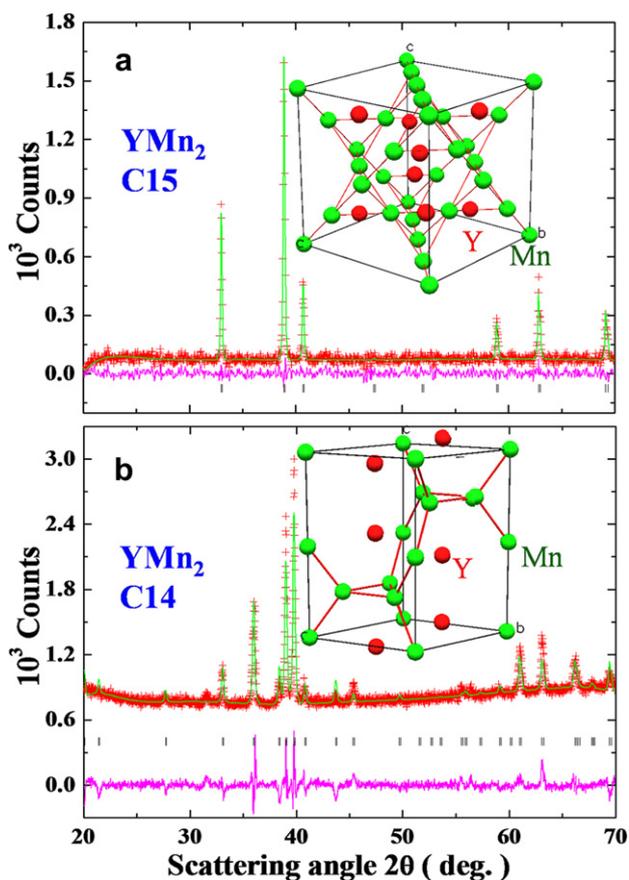


Fig. 1 – Observed (crosses) and fitted (solid lines) X-ray powder diffraction patterns of (a) C14 and (b) C15  $\text{YMn}_2$ . Short dashes represent calculated Bragg reflections of proposed structure. Bottom lines represent deviation between observed and calculated data.

$\text{YMn}_2\text{D}_6$  was prepared following a previously documented scheme [6]. Table 1 presents the X-ray diffraction data and Fig. 2(a) displays the corresponding structure with the tabulated fitting parameters.

A C14  $\text{YMn}_2$  sample was also prepared from high-purity yttrium and manganese in a stoichiometric ratio, but by high-pressure quenching from the melt, followed with annealing. The X-ray diffraction patterns in Fig. 1(b) confirm the hexagonal Laves phase. Under hydrogen at 1 GPa and 100 OC for 24 h, a hydride sample of formula  $\text{YMn}_2\text{H}_6$  was formed. Interestingly, the X-ray diffraction data and the deduced structure in Fig. 2(b) are the same as those of  $\text{YMn}_2\text{D}_6$  in Fig. 2 (a), even though the parent compounds, cubic C15 and hexagonal C14  $\text{RMn}_2$ , have different crystal structures. This result confirms that unique Fm-3m  $\text{RMn}_2\text{H}_6$  hydrides can be formed from either C14 or C15 parent  $\text{RMn}_2$  compounds, regardless of their different properties (structural, magnetic and other).

Thermal relaxation-type calorimetric measurements were made between 0.5 and 200 K for C15  $\text{YMn}_2$  and  $\text{YMn}_2\text{D}_6$ , but only above 10 K for C14  $\text{YMn}_2$  and  $\text{YMn}_2\text{H}_6$ . In each experiment, an mg-sized sample was thermally anchored with N-grease to a small sapphire disk. Thin films of  $\text{RuO}_2/\text{Al}_2\text{O}_3$  [9] and Ni–Cr were deposited on the sapphire to serve as a thermometer and heater, respectively. The relatively low heat capacity of this sample holder was separately measured for addenda corrections. The sapphire disk was suspended using four Au–Cu wires from a copper block, which was heated or cooled in steps, allowing the specific heat of the sample to be measured in both directions, revealing any thermal hysteresis. Standard adiabatic calorimetry, which involves only a heating path, does not

Table 1 – List of the fitting parameters of the crystalline structures.

$\text{YMn}_2$ , Cubic $F\bar{d}-3m$ , $a = 7.6806(8)$ Å					
Atoms	x	y	z	Multi	$U_{\text{iso}}(\text{Å}^2)$
Y	5/8	5/8	5/8	8a	0.89
Mn	0	0	0	16d	0.03
$\chi^2 = 1.758$ $R_p = 3.69\%$ $R_{\text{WP}} = 4.32\%$					
$\text{YMn}_2$ , Hexagonal $P63/mmc$ , $a = 5.4086(6)$ Å, $c = 8.8341(13)$ Å					
Atoms	x	y	Z	Site	$U_{\text{iso}}(\text{Å}^2)$
Y	1/3	2/3	0.063787	4f	0.14
Mn(1)	0	0	0	2a	0.24
Mn(2)	-0.169	-0.339	¼	6h	0.41
$\chi^2 = 1.762$ $R_p = 6.28\%$ $R_{\text{WP}} = 9.78\%$					
$\text{YMn}_2\text{D}_6$ , Cubic $F\bar{d}-3m$ , $a = 6.7096(6)$ Å					
Atoms	x	y	Z	Site	$U_{\text{iso}}(\text{Å}^2)$
Y	1/4	1/4	¼	8c	2.98
Mn(1)	1/4	1/4	¼	8c	2.98
Mn(2)	0	0	0	4a	2.95
D	0.284(3)	0	0	24e	5.98
$\chi^2 = 4.145$ $R_p = 7.30\%$ $R_{\text{WP}} = 9.59\%$					
$\text{YMn}_2\text{H}_6$ , Cubic $F\bar{d}-3m$ , $a = 6.7132(7)$ Å					
Atoms	x	y	Z	Site	$U_{\text{iso}}(\text{Å}^2)$
Y	1/4	1/4	¼	8c	2.42
Mn(1)	1/4	1/4	¼	8c	2.42
Mn(2)	0	0	0	4a	2.96
H	0.287(4)	0	0	24e	5.66
$\chi^2 = 1.026$ $R_p = 1.87\%$ $R_{\text{WP}} = 2.31\%$					

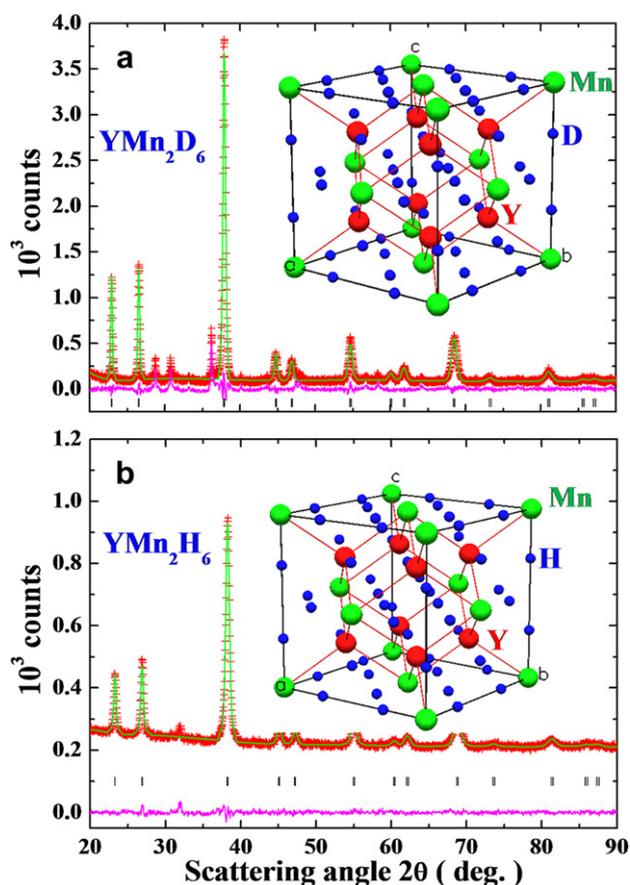


Fig. 2 – Refined XRD patterns of (a) hydrogenated C14 and (b) deuterized C15  $\text{YMn}_2$  with proposed crystal structures.

offer this capability. Before each measurement was made, the temperature of the copper block was stabilized. A small amount of Joule heat was introduced; this process was followed by rapid thermal relaxation between the sample and its holder, during which practically no heat was lost to the copper block. The temperature of the sample was fitted to an exponential dependence on the relaxation time, resulting in a time-constant  $\tau$ . The heat capacity was then calculated using the equation  $c = \kappa\tau$ , where  $\kappa$  represents the thermal conductance of Au–Cu wires as thermal links. The heat capacity of the sample holder was measured separately for addenda correction. The specific heat of sample is thus given by  $C = (c - C_{\text{addenda}}) (M/m)$  where  $m$  and  $M$  denote the mass and molar mass of the sample, respectively.

Complementary magnetic measurements, made using a superconducting quantum interference device, yielded susceptibility values  $\chi(T)$  from 2 to 300 K. Electrical resistivity  $\rho(T)$  values were obtained using the standard four-probe method.

### 3. Results and discussion

Exposing the hexagonal C14  $\text{YMn}_2$  compound to hydrogen under high-pressure and high-temperature conditions caused the formation of cubic Fm-3m  $\text{YMn}_2\text{H}_6$  - identical to cubic C15

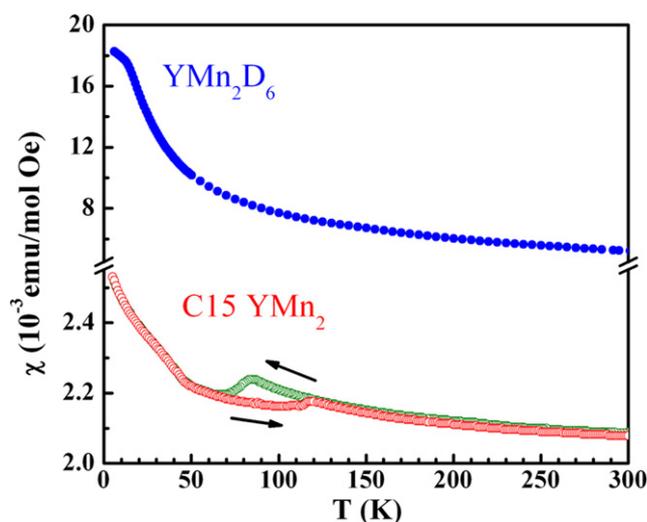
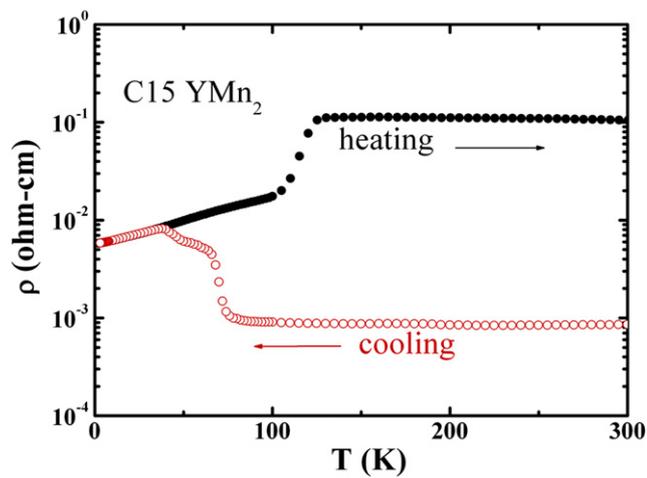


Fig. 3 – Thermal hysteresis in magnetic susceptibility of C15  $\text{YMn}_2$  reveals phase transition close to 100 K, which is suppressed in  $\text{YMn}_2\text{D}_6$ .

$\text{YMn}_2$  modification [6]. In this hydride, half of the Mn atoms occupy 4c sites and are surrounded by six deuterium atoms, while the other half are randomly distributed with the Y atoms on 8c sites.  $\text{YMn}_2\text{H}_6$  and generally  $\text{RMn}_2\text{H}_6$  are isostructural with complex metal hydrides, such as  $\text{Mg}_2\text{FeH}_6$ , but with the Mg sites replaced by randomly substituted R and Mn atoms [7]. In the present study, the mechanism by which this radical structural change can affect other properties of the two allotropic (C14 and C15) forms of  $\text{YMn}_2$  is of particular interest.

In Fig. 3, the magnetic susceptibility of C15  $\text{YMn}_2$  exhibits thermal hysteresis. It is clearly associated with the aforementioned structural and magnetic transitions near 100 K. As the temperature is lowered to around 85 K, an abrupt decline in  $\chi$  reflects antiferromagnetic ordering. Upon heating, the anomaly extends to almost 120 K. These observations are consistent with those made by Wang et al. [6]. However, Nakamura et al. [10] reported similar thermal hysteresis near 100 K, but lower susceptibility values by almost a factor of two. Moreover, they found a positive dependence of susceptibility on temperature above  $T_N$ , which differs from the negative temperature dependence in Fig. 3. These discrepancies may reflect variations in sample quality, one aspect of which is the Y/Mn off-stoichiometry, given the rather complex magnetic interactions and fluctuations of Mn moments in this compound. Fig. 3 also plots magnetic susceptibility data for  $\text{YMn}_2\text{D}_6$ . The values are almost four times those for  $\text{YMn}_2$ , and are consistent with the results of Wang et al. [6]. Most importantly, no phase transition occurs under 300 K.

Sample cracks that resulted from the large change in volume close to 100 K did not influence magnetic susceptibility, but caused serious difficulty in determining electrical resistivity. The making of the electrical resistivity measurements in Fig. 4 began with cooling of the sample from 300 to 4 K, and continued with heating back to 300 K. As the temperature declined, the resistivity remained almost constant down to 75 K, at which temperature the dramatic increase in resistivity reflected micro-cracks in the sample



**Fig. 4** – Temperature-dependence of electrical resistance of C15 YMn<sub>2</sub> close to 100 K reveals thermal hysteresis. Thermal contraction/expansion-induced micro-cracks in the sample resulted in uncertainty in absolute electrical resistivity.

that were produced by the large change in volume. Although the above mentioned anomaly was extended to close to 30 K, the absolute values of the non-reversible and difficult-to-reproduce transport property data should not be concerned for further interpretation. Indeed, another anomalous significant increase in apparent resistivity in the heating cycle began only after the temperature of the sample reached 103 K, and ended at around 125 K. Accordingly, a large difference between the resistivity values at 300 K at the beginning and the end of the thermal cycle is not surprising.

Accurately determining specific heat, one of the most basic thermodynamic quantities, is typically not difficult, especially if a bulk sample is available. At the beginning of this investigation, however, a bulk C15 YMn<sub>2</sub> sample was literally shattered as a result of the large changes in volume during the phase transitions. When such an event occurred, some unknown portions of the sample lost thermal contact, and Joule heating could not reach them. Calculations of the specific heat based on the total sample mass then become meaningless. To solve this problem, a bulk sample was crushed into powder, which was then pressed using N-grease to form a pellet for measurement. The heat capacity addenda correction included that for the added grease. Fig. 5 presents the results.

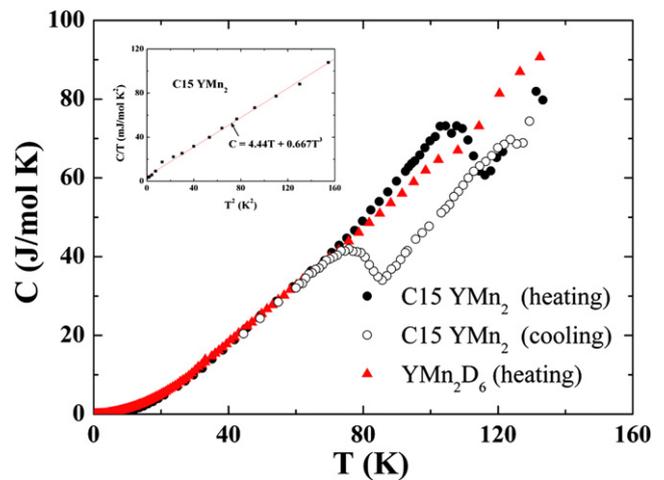
At low temperatures of 0.5–12 K, the total specific heat could be fitted to the sum of an electronic ( $C_e$ ) and a lattice ( $C_l$ ) contribution that depended on  $T$  and  $T^3$ , respectively:

$$C = C_e + C_l = \gamma T + \beta T^3, \quad (1)$$

Or

$$C/T = \gamma + \beta T^2 \quad (2)$$

The linear fit of  $C/T$  vs.  $T^2$  in the inset of Fig. 5 yields coefficients  $\gamma = 4.44$  mJ/mol K<sup>2</sup> and  $\beta = 0.667$  mJ/mol K<sup>4</sup>. The latter corresponds to a Debye temperature  $\theta_D$  of 210 K. These parameters are somewhat lower than those reported by



**Fig. 5** – Hysteretic temperature-dependence of specific heat of C15 YMn<sub>2</sub> provides a measure of latent heat of phase transition close to 100 K. This transition is clearly suppressed in YMn<sub>2</sub>D<sub>6</sub>. Inset: low-temperature data fitted to Eq. (2), yielding  $\gamma$  and  $\beta$  values.

Okamoto et al. [11] and Imai et al. [12]. The differences are understandable, considering the problem regarding thermal contact that was caused by micro-cracks arises in all samples to different degrees.

Anomalous specific heat is clearly observed herein as in earlier studies [11,12]. However, as aforementioned, relaxation-type calorimetry allows measurements to be made along both heating and cooling paths, yielding a broad thermal hysteresis between 70 and 120 K. The specific heat anomaly during heating is expected to reveal a positive latent heat  $L$ , superimposed on the background contributions ( $C_l + C_e$ ), corresponding to endothermic volume expansion. Lower specific heat values upon cooling are expected, reversing the effect that is associated with the exothermic volume contraction. A latent heat value of 330 J/mol was obtained by simple integration.

$$L = \left\{ \left[ \int (C_l + C_e) dT \right] + L \right\} - \left[ \int (C_l + C_e) dT \right] - L \Big/ 2 \\ = \left[ \int (CdT)_{heating} - \int (CdT)_{cooling} \right] / 2 \quad (3)$$

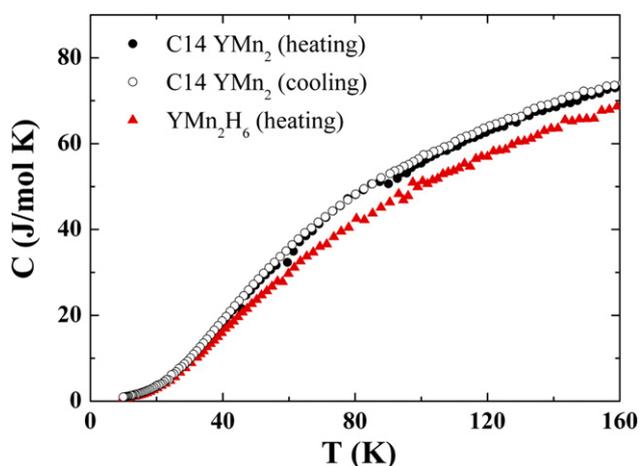
In general, low-temperature structural transformations in solids are not associated with a latent heat that is as high as this value. For example,  $L$  from cubic to tetragonal RbCaF<sub>3</sub> is only 36 J/mol at 198 K [13]. Given the excessive thermal shrinkage with spontaneous magnetostriction [3], the extra contribution could be a magnetic term  $T\Delta S_m$ , where  $\Delta S_m$  is the change in entropy that is associated with antiferromagnetic ordering.  $\Delta S_m$  is typically calculated from  $R \ln(2S + 1) = 23$  J/mol K for Mn moments with  $S = 3/2$ . However, a similar calculation does not apply here because of the itinerant nature of the Mn moments. One calorimetric study, which involved only heating, yielded  $\Delta S_m = 3.9$  J/mol K [11]. At an average transition temperature of 100 K, the magnetic-heat term would thus be 390 J/mol, which is reasonably consistent with the result in this study. This result may also explain the

broad transition in the specific heat data. Generally, low-temperature structural changes in solids occur via a lattice shear process, rather than a nucleate-and-growth mechanism that is more strongly related to high-temperature structural transformations. Therefore, low-temperature structural changes are associated with a relatively narrow range of temperatures. For example, the sharp spike anomaly in the specific heat of  $\text{RbCaF}_3$  has a half-width of only 0.5 K [13]. However, magnetic ordering typically extends over a much broader observable range of temperatures, as in the case herein.

Fig. 5 presents specific heat data for the deuteride compound  $\text{YMn}_2\text{D}_6$ . It reveals a smooth dependence of specific heat on temperature within measured range, ruling out any magnetic or structural transformation. Such a very large difference from the parent compound C15  $\text{YMn}_2$  presumably reflects the fact that  $\text{YMn}_2\text{H}_6$  hydride can be regarded not as an interstitial metal hydride but rather as a coordination compound [7]. This claim is further supported by the magnetic susceptibility data in Fig. 3, as well as by the absence of any sample cracking in the cooling/heating cycle during which the calorimetric measurements were made.

C14  $\text{YMn}_2$  has an Mn–Mn distance that is close to the critical value for the onset of a magnetic moment, but strongly temperature-enhanced spin fluctuations cause paramagnetism even at 4.2 K [14]. C14  $\text{YMn}_2$  has, having a thermal expansion coefficient that exceeds those of other C14 compounds, and so does not undergo structural transformation in the same manner as C15  $\text{RMn}_2$  [15]. Indeed, the specific heat data for C14  $\text{YMn}_2$  in Fig. 6, are consistent with those of Imai et al. [16], increasing smoothly with temperature, as expected.

The temperature-dependence of the specific heat of  $\text{YMn}_2\text{H}_6$  in Fig. 6 is almost identical to that of C14  $\text{YMn}_2$ . Apparently, hydrogenation only slightly affects the thermal or magnetic behavior of C14  $\text{YMn}_2$ , which can be related to



**Fig. 6 – Temperature-dependencies of specific heat of C14  $\text{YMn}_2$  and  $\text{YMn}_2\text{H}_6$  are similar. Both compounds are paramagnetic and do not exhibit phase transition-type thermal hysteresis.**

the paramagnetic behavior of both C14  $\text{YMn}_2$  and  $\text{YMn}_2\text{H}_6$  throughout the studied range of temperatures.

#### 4. Conclusions

$\text{YMn}_2\text{H}_6$  or  $\text{YMn}_2\text{D}_6$  can be obtained not only from cubic C15 but also from the hexagonal C14 phase of  $\text{YMn}_2$ . A latent heat of 330 J/mol was determined for the hysteretic phase transition in cubic C15  $\text{YMn}_2$  near 100 K. This transition is suppressed in  $\text{YMn}_2\text{D}_6$ , and is shown calorimetrically to be absent in hexagonal C14  $\text{YMn}_2$  and  $\text{YMn}_2\text{H}_6$ .

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