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Journal of Alloys and Compounds 217 (1995) 157–160

Journal of ALLOYS AND COMPOUNDS

Thermal expansion of YMn_2H_x compounds

H. Figiel [a], A. Lindbaum [b,*], Cs. Kapusta [a], E. Gratz [b]

[a] *Department of Solid State Physics, University of Mining and Metallurgy, Krakow, Al. Mickiewicza 30, 30-059 Krakow, Poland*

[b] *Institute for Experimental Physics, Technical University of Vienna, Wiedner Hauptstr. 8–10, A-1040 Vienna, Austria*

Received 12 May 1994

Abstract

The thermal expansion of YMn_2H_x compounds ($x=0.5$, 2, 3) has been studied by means of low temperature X-ray powder diffraction. Both the magnetic ordering temperature and the lattice parameter a of the cubic Laves phase increase with increasing x. The volume anomalies at the magnetic ordering temperatures decrease with increasing hydrogen content x. This is attributed to the increasing localization of the Mn moments. Spin fluctuations in the paramagnetic state, which are successively suppressed with increasing x, are responsible for an enhanced thermal expansion in the paramagnetic range.

Very interesting results were observed for $x=0.5$. In this compound there is a huge tetragonal distortion which changes its sign at 105 K. This outstanding behaviour may be due to a highly anisotropic magnetoelastic interaction caused by a possible ordering of the hydrogen atoms within the cubic C15-Laves phase structure.

Keywords: Thermal expansion; Spontaneous magnetostriction; Spin fluctuations

1. Introduction

It has been shown by neutron diffraction that YMn_2 is an antiferromagnet with a complicated incommensurate arrangement of the Mn moments [1,2]. The onset of the magnetic order at 100 K is accompanied by a huge volume anomaly $\Delta V/V \simeq 0.05$ and a tetragonal distortion of the cubic symmetry [3]. The volume anomaly is connected with a collapse of the Mn moment by more than 30% at T_N, which recovers again with increasing temperature [4]. Magnetic investigations of the YMn_2 hydrides revealed the appearance of a ferromagnetic component in the magnetization and an increase of the ordering temperature depending on the amount of hydrogen [5]. Furthermore, the hydrogen causes an increase of the cubic lattice constant at room temperature [6].

It has been observed that the magnetic order becomes stabilized and hardly pressure dependent by hydrogenation [7]. In pure YMn_2 the critical pressure at which T_N is shifted below 4 K is only 3.8 kbar [8].

In our previous paper [9] we showed that in YMn_2H_1 the magnetic transition is also accompanied by a volume anomaly at $T_c=200$ K, but the magnitude is only five percent of that in pure YMn_2. Within the paramagnetic region the thermal expansion coefficient $1/a(da/dT)$ of YMn_2H_1 is almost two times smaller than for YMn_2. In the discussion of this previous paper we attributed this deviating behaviour of YMn_2H_1 as compared with the pure compound YMn_2 to the suppression of the spin fluctuations as a result of the hydrogenation. The hydrogen atoms cause an increase of the Mn–Mn distances and thus the formation of more localized and stable Mn moments. In the present paper we extend our investigations to samples with higher and lower hydrogen concentrations (YMn_2H_x with $x=0.5$, 2 and 3). For the investigation of the thermal expansion we used temperature dependent X-ray diffraction applied to powdered polycrystalline samples.

2. Results

The temperature variation of the lattice constants was monitored through the (222) and (440) reflections. Fig. 1 shows the variation of the cubic lattice constant at room temperature with increasing hydrogen content. In Figs. 2–4 the measured temperature variations of the lattice constants are depicted. For the sample with the largest hydrogen content ($x=3$, Fig. 2), the magnetic ordering temperature estimated from our measurement is 300 K (arrow in Fig. 2). This is in agreement with the magnetization measurements reported in [5]. However, the anomaly found in the temperature variation

* Corresponding author.

SSDI 0925-8388(94)01320-9

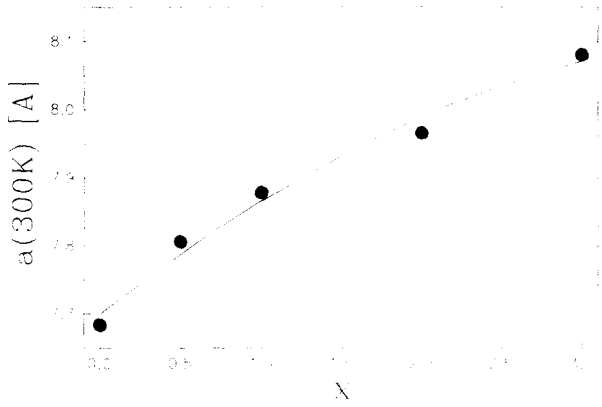

Fig. 1. Cubic lattice parameter a of the YMn_2H_x compounds at 300 K.

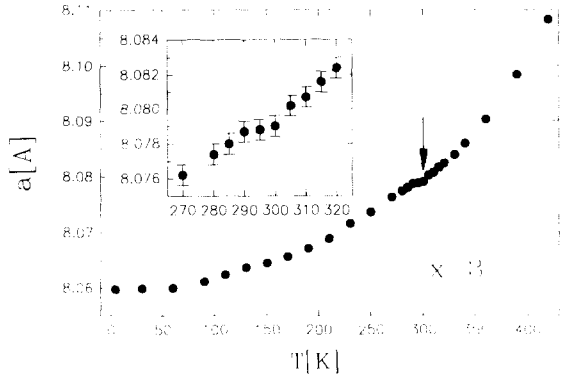

Fig. 2. Temperature dependence of the cubic lattice parameter of YMn_2H_3 (the arrow indicates the magnetic ordering temperature).

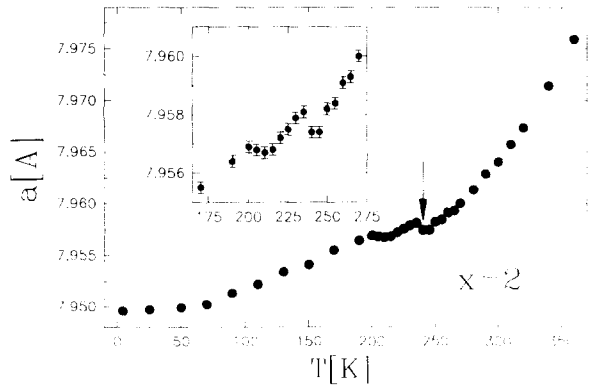

Fig. 3. Temperature dependence of the cubic lattice parameter of YMn_2H_2 (the arrow indicates the magnetic ordering temperature).

of the lattice constant is very weak. With decreasing x the discontinuity in a vs. T increases remarkably. For $x=2$ shown in Fig. 3 we see two anomalies. The upper discontinuity which indicates the magnetic ordering temperature is at 240 K (arrow in Fig. 3), the low lying anomaly appears at 205 K. The inset in Fig. 3 shows this in more detail. In our previous investigation [9] of the sample with $x=1$ we did not pay so much attention to the details concerning a vs. T. However, a closer inspection, especially in the light of the present results, reveals that for $x=1$ also two anomalies exist at 160 and 200 K, the latter again corresponding to the ordering temperature.

However, the most interesting results concerning thermal expansion are observed for the sample with $x=0.5$ (Fig. 4). Our measurement revealed two step-like anomalies in the volume at 245 and 105 K. At the lower transition (105 K) there is an hysteresis of about 5 K. The relative volume change at the lower transition is smaller by about one third compared with the upper one. The volume changes are accompanied by a huge tetragonal distortion of the cubic unit cell which is about two times larger below the lower transition. Note that the sign of the tetragonal distortion changes at the lower transition. In Fig. 5 the parameter of the tetragonal distortion $(\Delta l/l)_{tet}=(2/3)(c-a)/a$ is shown as a function of temperature. In our experiment we determined the kind and the magnitude of the distortion from the analysis of the split (440) reflection and the fact that there was no splitting of the (222) reflection. For illustration of the clearness of the situation (especially concerning the distortion) the (440) and the (222) reflections for three temperatures above, between and below the two transitions are shown in Fig. 6. It

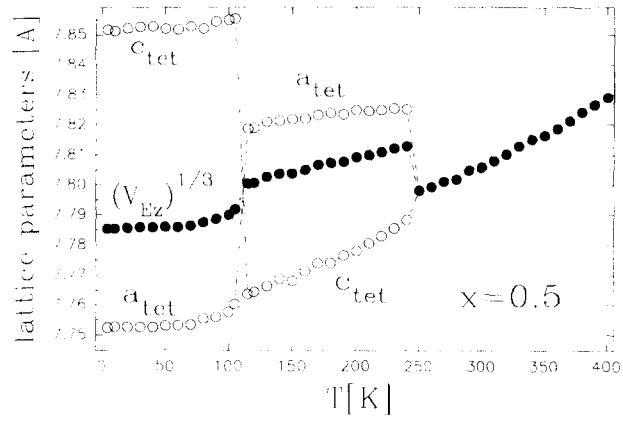

Fig. 4. Temperature dependence of the cubic and tetragonal lattice parameters of $YMn_2H_{0.5}$.

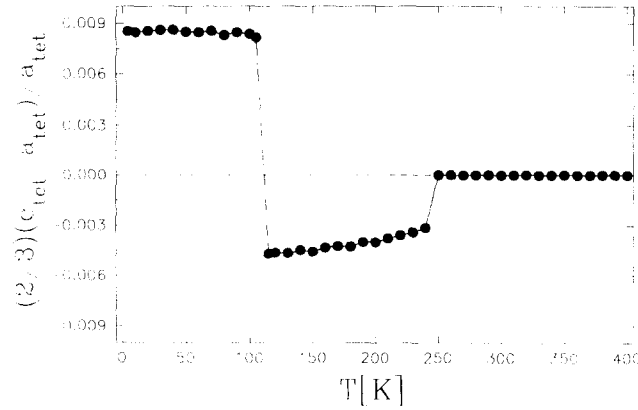

Fig. 5. Temperature dependence of the tetragonal distortion of $YMn_2H_{0.5}$.

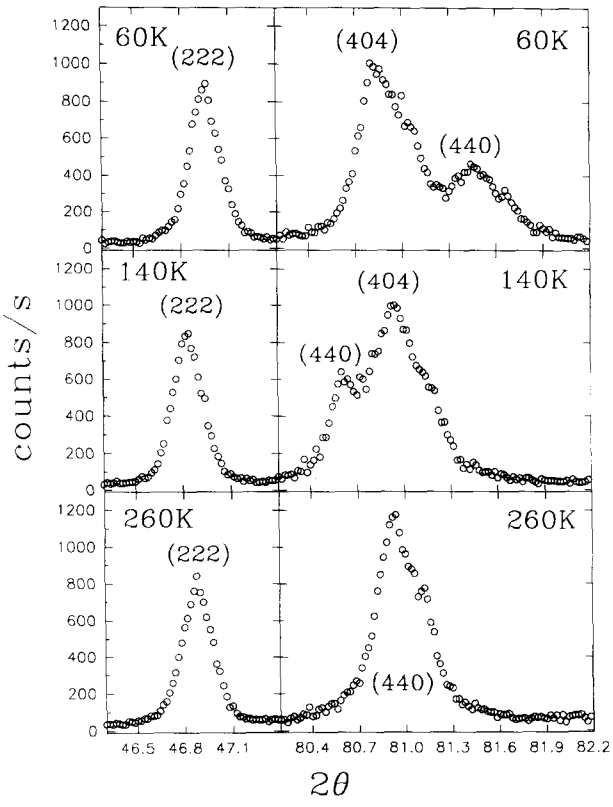

Fig. 6. The X-ray reflections (222) and (440) of $YMn_2H_{0.5}$ at 60, 140 and 260 K.

should be pointed out that Ge was used as an internal standard, therefore we can exclude any systematic errors resulting from the equipment.

For $x=1$, 2 and 3 we could not find any distortion of the cubic unit cell within the accuracy of the X-ray measurement, i.e. if any, it could be $\Delta l/l \simeq 10^{-4}$ at the most.

3. Discussion

Volume anomalies are in general observable at the onset of magnetic ordering in itinerant electron systems. As an example we refer to the $RECo_2$- systems, in which large volume anomalies are observed due to the magnetic ordering of the itinerant Co subsystem [10]. As already mentioned, the enormous volume anomaly in pure YMn_2 is connected with the fractional collapse of the Mn moments at T_N. Since we observe almost no volume anomaly for $x=3$, we conclude that the Mn moments are not changed when passing the ordering temperature, which means that the Mn moments are highly localized. This has been confirmed by NMR experiments [6,7]. The volume anomalies increase towards lower hydrogen concentrations, i.e. the degree of the localization of the Mn moments decreases.

Following the decrease of the hydrogen content x we additionally observe the appearance of a second transition below the ordering temperature. The lower transition is obviously of magnetic origin, since there are some anomalies observable in the temperature variation of the corresponding magnetization curves [5]. For example we note that the M vs. T curve for $x=1$ shows a kink at around 160 K – just where the thermal expansion reveals a drop of the unit cell volume [9]. This feature seems to become strongly enhanced in the sample with $x=0.5$. The concentration dependence of the two transition temperatures is summarized in Table 1.

The extremely large distortion of the unit cell observed in $YMn_2H_{0.5}$ may be related to the combined influence of the crystal field- and spin-orbit- interaction, which are possibly of comparable size in the investigated systems. The anisotropy of this magnetic interaction may depend on the occupation of the interstitial sites by the H atoms. As was confirmed by recent neutron diffraction studies, the interstitial sites which can be occupied are primarily the 96g sites (24 in the primitive unit cell) of the cubic $Fd3m$ space group [11]. These sites are denoted as the A_2B_2 sites. In our case the hydrogen atom is surrounded by two Y and two Mn atoms. The higher anomaly in a vs. T corresponds to the onset of the magnetic order, as was confirmed by recent Mössbauer measurements [12] and by measurements of the a.c. susceptibility as well as magnetization measurements performed on our sample. The lower anomaly at 105 K may be due to a rearrangement of the Mn moments. A similar distortion of the unit cell, because of the presence of a small amount of hydrogen, has been reported for $Sm(Fe, Co)_2H_{0.1}$ [13]. This indicates that the presence of hydrogen in the lattice leads to anisotropic effects. The hydrogen at the A_2B_2 interstitial sites causes a rhombohedral deformation of the local environment. At high temperatures there is a diffusion of hydrogen and the anisotropic effect vanishes. At lower temperatures, where there is practically no diffusion, one expects a distortion of the

Table 1
Transition temperatures of the YMn_2H_x compounds. T_1 denotes the magnetic ordering temperature

x	T_1 (K)	T_2 (K)
3	300	–
2	240	205
1	200	160
0.5	245	110 (105)

Table 2
Thermal expansion coefficients at 300 K for the YMn_2H_x compounds

x	0	0.5	1	2	3
$\frac{1}{a}\frac{da}{dT} \cdot 10^5$ K	5.1	2.9	2.8	2.6	2.1

lattice. Thus, for $x=0.5$ where on average exactly one hydrogen atom is built into the primitive unit cell of YMn_2 (2Y, 4Mn, 1H) the huge tetragonal distortion observed at the magnetic ordering temperature may be caused by an ordering of the hydrogen atoms at this temperature.

Comparing the thermal expansion coefficient in the paramagnetic state at 300 K (Table 2) we may conclude that they are not very different and are relatively small in all the investigated hydrides ($x=0.5, 1, 2, 3$), especially if we compare them with the value 2–3 times larger in the pure YMn_2 compound. However, we see that they decrease with increasing x, which can be understood by the suppression of the spin fluctuations due to the increasing degree of hydrogenation. This is in agreement with the vanishing volume anomaly at the ordering temperature with increasing hydrogen content.

Acknowledgement

We are grateful to Dr. J. Zukrowsky and Dr J. Przewoznik for the preparation of the hydrides. This work was supported by the Austrian Science Foundation (FWF-Project P-8913), the 'Hochschuljubilaeumsstiftung der Stadt Wien' and the Polish State Committee for Scientific Research (grant No. 203409101).

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