

Synthesis of Single-Phase YMn_2D_2 Studied by *in situ* Neutron Diffraction

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Hydrogen absorption at room temperature in YMn_2 leads to a mixture of several phases with various hydrogen contents. A thermal treatment at 473 K allows single-phase YMn_2H_x hydrides with $0 < x \leq 3.5$ to be obtained. The hydride synthesis has been studied in the case of single-phase YMn_2D_2 by *in situ* thermal-dependent neutron diffraction experiments. The different steps for the formation of the single-phase deuteride are described and discussed. © 2000 Academic Press

Key Words: deuteride; thermal treatment; Laves phases; neutron diffraction.

1. INTRODUCTION

YMn_2 has been widely studied for its unusual magnetic properties (1, 2) which can be modified by applying external pressure or by chemical substitution (3, 4). Since hydrogen absorption in YMn_2 leads to a large volume increase and therefore to an increase in Mn–Mn distances, it can be considered as a negative chemical pressure effect that induces interesting changes in magnetic properties. To study the evolution of the magnetic properties as a function of H content and to determine the $\text{YMn}_2\text{–H}_2$ phase diagram (5) it is necessary to prepare single-phase YMn_2H_x hydrides. However, hydrogen absorption at room temperature leads to a mixture of several phases with different hydrogen contents. It was found that thermal treatment at 473 K allows us to obtain single-phase cubic hydrides for $0.1 \leq x \leq 3.5$ with a continuous increase in the cell parameter as a function of hydrogen content (6). For $3.5 < x < 4$ a mixture of cubic $\text{YMn}_2\text{H}_{3.5}$ and rhombohedral YMn_2H_4 is formed. For $x \geq 4$, YMn_2H_x hydrides display a rhombohedral distortion (7, 8). To understand the mechanism behind the preparation of single-phase hydrides or deuterides, we studied the influence of the thermal treatment on the synthesis of YMn_2D_2 by *in situ* neutron diffraction (ND).

2. EXPERIMENTAL

The preparation and characterization of the YMn_2 intermetallic compound are described in Ref. (6). The synthesis of

YMn_2D_2 deuteride was attempted at 300 K by exposing about 8 g of powdered YMn_2 to a pressure of 9 bar of deuterium. X-Ray diffraction (XRD) analysis showed that a mixture of several phases was obtained after hydrogen absorption. The two main phases are cubic $\text{YMn}_2\text{D}_{0.1}$ and rhombohedral $\text{YMn}_2\text{D}_{4.3}$. A weak contribution of deuterides with small deuterium content ($0.1 < x < 0.5$) can also be observed in the XRD pattern, in agreement with previous results (6).

This sample was then introduced into a silica tube, which was connected to a volumetric device to measure the evolution of D_2 pressure and, consequently, D_2 content in the sample as a function of time. The *in situ* powder neutron diffraction experiments were performed on the position-sensitive detector (PSD) diffractometer D1B at the Institut Laue Langevin (ILL). The wavelength was 2.52 Å and the diffraction patterns were recorded every 5 min from 28° to 108° in 2θ with a step of 0.05° while heating or cooling the samples. During the neutron experiment the silica sample holder was placed in a furnace, operating under a vacuum, equipped with vanadium heating elements and shields. The sample was heated from room temperature up to 473 K at the rate of 0.3 K/min, kept at 473 K for 85 min, and cooled down to 315 K at the rate of 0.8 K/min. The patterns were refined with the Rietveld method, using the Fullprof program (9). The shape of the peaks was fitted using a pseudo-Voigt function.

3. RESULTS

The evolution of the ND patterns during the heat treatment from 300 to 473 K is presented as a three-dimensional plot in Fig. 1 and the patterns at $T = 300, 405,$ and 473 K are reported in Fig. 2.

At 300 K the ND pattern (Fig. 2A) corresponds to a mixture of two phases: 55% YMn_2D_x , which is cubic with $a = 7.70(1)$ Å and a refined deuterium content of about 0.10(2) D/f.u. and 45% rhombohedral phase with $a = 5.85(1)$ Å and $c = 14.05(1)$ Å and a deuterium content of

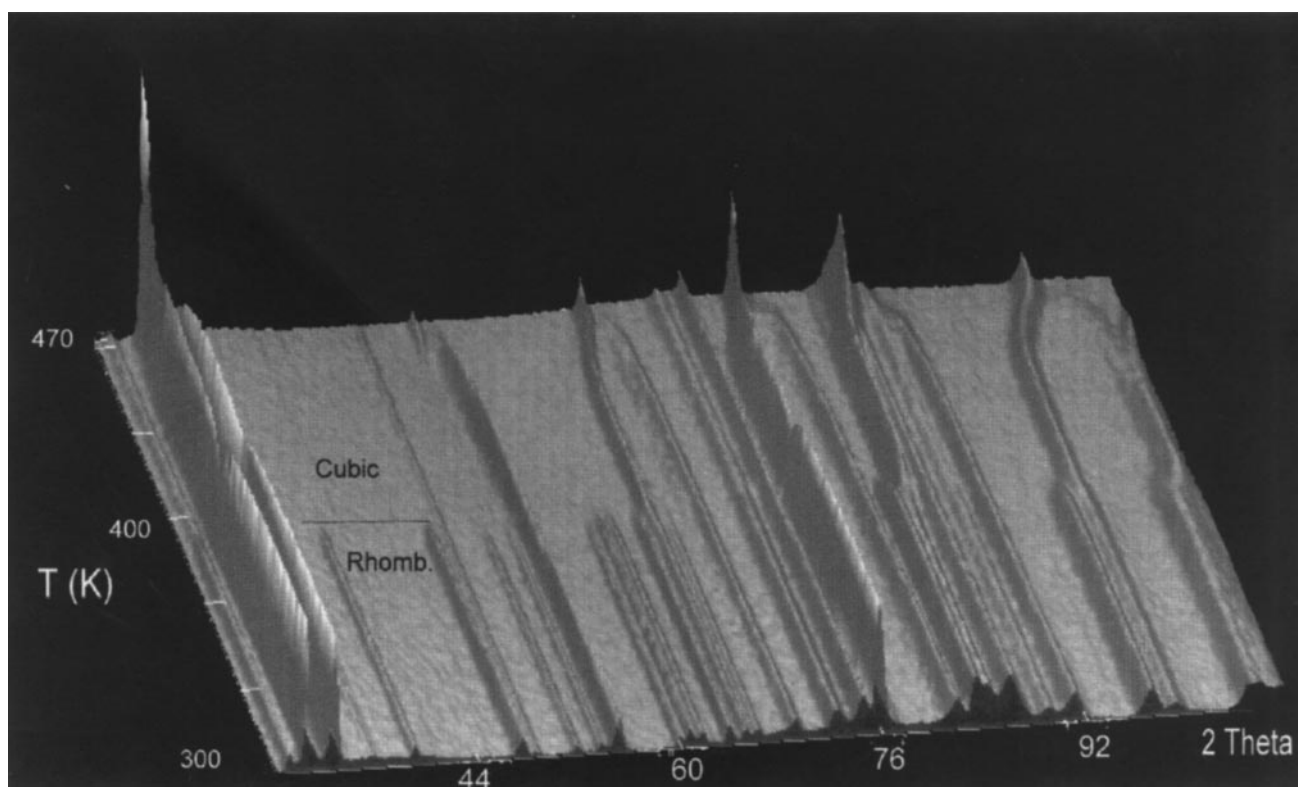


FIG. 1. Evolution of the neutron diffraction patterns of YMn_2D_2 as a function of temperature during the heating treatment.

4.30(5) D/f.u. This corresponds to about 2 D/f.u., in agreement with the total amount of deuterium absorbed by the sample. $\text{YMn}_2\text{D}_{0.1}$ has a larger linewidth compared with $\text{YMn}_2\text{D}_{4.3}$; this reflects the wider distribution of deuterium content, which was also observed in the X-ray diffraction pattern.

The structure of the rhombohedral phase was refined in agreement with Ref. (8) with a preferential occupation of D atoms in A2B2 sites and an antiferromagnetic structure with a fixed magnetic moment of $3.2 \mu\text{B}/\text{Mn}$.

The evolution of the amount of phases, the evolution of cell volume, and the evolution of deuterium content of the two deuteride phases and of deuterium pressure as a function of temperature are reported respectively in Figs. 3, 4, and 5. The evolution of linewidth (full width at half-maximum) is reported as a function of time and temperature in Fig. 6. Three different domains can be observed.

The first domain is between 300 and 392 K. Heating up to 392 K leads only to a small cell volume increase in the two phases, due to the thermal expansion, whereas the amount of each phase remains nearly constant. At 392 K, the rhombohedral phase transforms into a cubic phase with the C15 type cubic structure [$a = 8.19(1) \text{ \AA}$], a statistical distribution of deuterium atoms in tetrahedral interstitial A2B2 sites (Fig. 2B) and no magnetic moment. This transition is ac-

companied by a sharp increase in linewidth. In agreement with previous neutron diffraction studies (7, 8) the jump in cell volume can be attributed to a magnetovolume effect corresponding to the transition from an antiferromagnetic state to a paramagnetic state (Néel temperature).

The second domain is between 392 and 435 K. As the temperature increases, the cell volume of $\text{YMn}_2\text{D}_{0.1}$ increases whereas its amount slightly decreases. For $\text{YMn}_2\text{D}_{4.3}$ the opposite variation in cell volume and amount of phases is observed. The cell volume decrease of $\text{YMn}_2\text{D}_{4.3-y}$ can be related to the decrease in deuterium content from 4.3 to 3.8 D/f.u. Taking into account the amount of $\text{YMn}_2\text{D}_{4.3-y}$ this corresponds to 0.22 D/f.u. desorbed by the sample. The increase in pressure corresponds to about 0.1 D/f.u., which is of the same order of magnitude and indicates that the deuterium desorption remains quite small. Then above 415 K the pressure decrease shows that the deuterium is absorbed again by the sample.

In the third domain from 435 to 473 K important changes can be observed:

— There is a large decrease in the amount of $\text{YMn}_2\text{D}_{0.1}$ (Fig. 3) which disappears at 473 K, accompanied by an increase in its cell parameter ($\Delta a/a = 1.2\%$) (Fig. 4). The refined deuterium content remains constant within 0.1 D/f.u. but the increase in linewidth indicates a wide

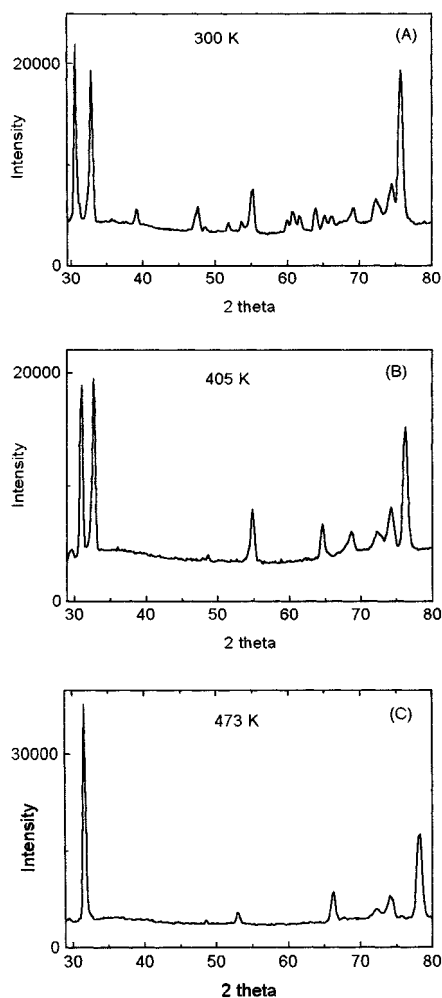


FIG. 2. Neutron diffraction patterns for YMn_2D_2 at 300 K (A), 405 K (B), and 473 K (C).

distribution of deuterium content. Moreover, due to the small quantity of this phase and its low D content, the errors bars are quite large (± 0.1 D/f.u.).

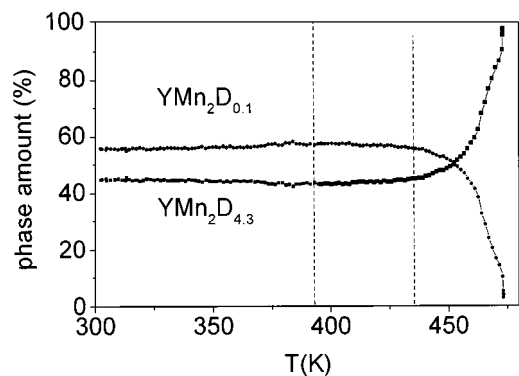


FIG. 3. Evolution of the amount of phases as a function of temperature.

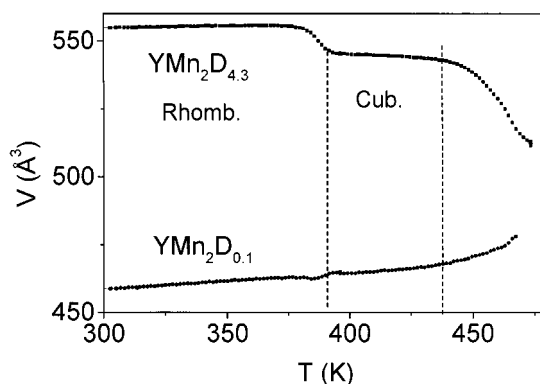


FIG. 4. Evolution of the cell volume of the $\text{YMn}_2\text{D}_{0.1}$ and $\text{YMn}_2\text{D}_{4.3}$ phases as a function of temperature. For the rhombohedral phase the cell volume was multiplied by 4/3 to correspond to the same amount of formula unit than in the cubic phase ($Z = 8$).

— There are an increase in the amount of phase $\text{YMn}_2\text{D}_{4.3-y}$ (Fig. 3) and a decrease in its cell parameter ($\Delta a/a = -2.3\%$) (Fig. 4). The deuterium content decreases progressively from 3.8 to 2.1 D/f.u. However, the increase in linewidth indicates also a broad distribution of deuterium content (Fig. 6).

— The D_2 pressure decreases, reaching 0.02 bar at 473 K; this indicates that all the deuterium is absorbed by the sample (Fig. 5).

After 25 min at 473 K there is only one cubic phase (Fig. 2C) with the C15 structure ($a = 8.01 \text{ \AA}$) and a refined amount of deuterium, 2.1(1) D/f.u. The progressive decrease in linewidth at 473 K indicates the homogenization of deuterium concentration (Fig. 6). However, after 85 min at 473 K, the linewidth is still larger than below 435 K. Then when cooling down to 315 K the cell parameter of this phase decreases to 7.97(1) \AA due to thermal contraction ($\Delta a/a = -0.4\%$), whereas the linewidth remains constant.

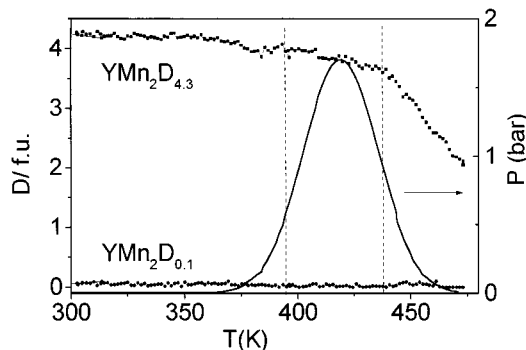


FIG. 5. Evolution of refined deuterium content and of deuterium pressure in the container as a function of temperature.

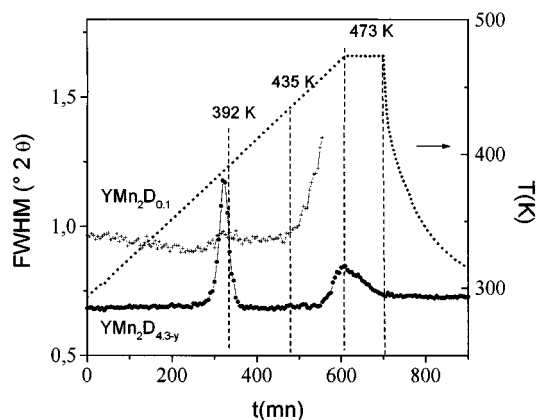


FIG. 6. Evolution of linewidth at half-maximum (FWHM) of $\text{YMn}_2\text{D}_{4.3-y}$ and $\text{YMn}_2\text{D}_{0.1}$ at $2\theta = 76^\circ$ as a function of time. The temperature (\cdots) is scaled on the right axis.

4. DISCUSSION

The synthesis of single-phase YMn_2D_2 occurs in three different steps. From room temperature to 392 K the amount of each phase remains constant and there is no deuterium desorption or diffusion.

The structural transition observed at 392 K for $\text{YMn}_2\text{D}_{4.3}$ is in agreement with that previously observed (8) and corresponds to a first-order magnetostructural transition. The sharp increase in linewidth observed at the transition for $\text{YMn}_2\text{D}_{4.3}$ can be explained by the coexistence of the rhombohedral and cubic phases, which have different cell volumes and therefore different peak positions. The temperature at which this transition occurs depends on the hydrogen content of the sample and its thermal history. In Ref. (7) the transition took place at about 330 K whereas in Ref. (8) the transition occurred at 398 K on heating and 380 K upon cooling. These differences can be related to the change in cell volume and therefore in Mn–Mn distances. In Ref. (7) the cell volume of the rhombohedral phase measured at 300 K was 411.2 \AA^3 , whereas it was 417.7 \AA^3 in Ref. (8) and is 416.4 \AA^3 in this paper. This sensitivity of the magnetic ordering temperature to Mn–Mn interatomic distances in such a compound was also observed by applying external pressure (7): the magnetic ordering temperature decreases progressively with applied pressure.

In the rhombohedral structure, the deuterium atoms are located preferentially in specific tetrahedral A2B2 sites, with two sites fully occupied and one-half occupied over six possible sites. The physical origin of this deuterium order is related to the repulsive interaction of deuterium atoms which cannot be located at distances closer than 2.1 \AA and is favored by the lowering of the symmetry in the rhombohed-

ral structure. Above 392 K, the phase transforms into a cubic structure with a random occupation of the deuterium atoms in the A2B2 sites. This allows the deuterium atoms to move more freely from one site to another. This can explain why it is necessary to heat above this structural transition to observe deuterium desorption and diffusion.

In the range 392–435 K, the pressure increase and decrease indicate that the deuterium-rich phase desorbs a small amount of deuterium which is reabsorbed by the $\text{YMn}_2\text{D}_{0.1}$ phase. This is confirmed by the significant increase in cell volume of the phase $\text{YMn}_2\text{D}_{0.1}$ (Fig. 4), though it is not clearly observed in the deuterium content variation (Fig. 5). However, one must keep in mind that in the present experiment, cell parameter variations are more reliable than deuterium content, which is obtained with relatively poor accuracy ($\pm 0.1 \text{ D/f.u.}$).

From 435 to 473 K, the amount of $\text{YMn}_2\text{D}_{4.3-y}$ increases sharply whereas that of $\text{YMn}_2\text{D}_{0.1}$ decreases until complete disappearance. For both phases, the increase in linewidths indicates a large distribution of deuterium content during the diffusion process. Such linewidth evolution is related not only to the absorption–desorption process but also to the diffusion of deuterium within the particles.

After 40 min at 473 K the mean deuterium concentration of the cubic phase is 2.1 D/f.u. with $a = 8.00(1) \text{ \AA}$. The main evolution is a diminution of the linewidth versus temperature, indicating homogenization of the sample around 2.1 D/f.u. Then, when the sample is cooled down, the cell parameter decreases linearly as a function of temperature whereas the linewidth remains constant. The larger linewidth of YMn_2D_2 compared with that of $\text{YMn}_2\text{D}_{4.3}$ reflects a larger distribution of deuterium concentration and we can expect that prolonged thermal treatment at 473 K would lead to a more homogeneous sample.

5. CONCLUSION

In this work we have studied the influence of thermal treatment on the synthesis of single-phase YMn_2D_2 deuteride. After hydrogenation at 300 K the sample contains mainly a mixture of $\text{YMn}_2\text{D}_{0.1}$ and $\text{YMn}_2\text{D}_{4.3}$. On heating, the evolution of the ND patterns shows that the rhombohedral $\text{YMn}_2\text{D}_{4.3}$ phase undergoes a structural transition at 392 K and becomes cubic above this temperature due to a magnetostructural transition which has been previously observed. From 392 to 435 K, a small deuterium desorption from the deuterium-rich phase followed by a reabsorption by the deuterium-poor phase is observed. Above 435 K the evolution of cell volume and amount of both phases indicates that the deuterium content is redistributed until a single-phase YMn_2D_2 deuteride with the C15-type cubic structure is obtained.

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