PHYSICAL REVIEW B VOLUME 56, NUMBER 5 1 AUGUST 1997-I

Interplay of magnetic and hydrogen orders in the laves hydride $YMn_2H_{4.3}$

I. N. Goncharenko*
Laboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay, 91191 Gif sur Yvette, France
and Russian Research Center "Kurchatov Institut," 123182 Moscow, Russia

I. Mirebeau
Laboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay, 91191 Gif sur Yvette, France

A. V. Irodova
Russian Research Center "Kurchatov Institut," 123182 Moscow, Russia

E. Suard
Institut Laue-Langevin, 156X, 38042 Grenoble, France

(Received 26 February 1997)

We have performed a neutron-diffraction study of the Laves hydride $YMn_2H_{4.3}$ to investigate the interplay between the atomic order in the hydrogen sublattice and the magnetic structure. We find that structural order in the H sublattice and antiferromagnetic order in the Mn sublattice have the same rhombohedral symmetry. At ambient pressure we observe a first-order magnetostructural transition, where the magnetic sublattice transforms from a paramagnetic state to an antiferromagnetic one, as the hydrogen atoms form the ordered superstructure. An applied pressure decouples the two types of order, which then occur at different temperatures. It allows us to separate the effects of structural order from those related to the average Mn-Mn distance. [S0163-1829(97)01430-6]

Magnetic instability in the Laves compounds $R\mathrm{Mn}_2$ (where R is rare earth or Y) has attracted much interest in recent years. Their magnetic properties are strongly sensitive to Mn-Mn distances, with a suppression of the magnetic moment below some critical distance ($d_c = 2.7$ Å).[1] Compounds like YMn_2, where the first-neighbor Mn-Mn distance d_{Mn} is slightly above d_c, show complicated types of magnetic order and a large magnetovolume anomaly. This sensitivity to interatomic distances has stimulated many studies of the influence of an applied pressure or chemical substitution. Together with modification of the electronic band structure,[2] hydrogen doping increases the lattice parameter by filling the interstitial sites in the metal lattice,[3] so that it could be considered as a "negative pressure." In YMn_2H_x, Mössbauer and magnetization experiments show the increase of the magnetic ordering temperature as x increases from 0 to 4.3, in agreement with the general behavior expected in $R\mathrm{Mn}_2$ compounds with increasing d_{Mn}.[4,5] In the concentration range $1<x<3.5$, a ferromagneticlike behavior was observed, with a few different magnetic phases still not characterized up to now. In contrast, the compound with maximal H content $YMn_2H_{4.3}$ shows a rhombohedral distortion of the original cubic cell and seems to be antiferromagnetic.[5] It is important to note that hydrogen not only changes the lattice parameter, but could also form an ordered sublattice in the metal host, with different superstructures depending on the concentration. Therefore, it could influence the magnetic order not only by varying the lattice constant but also by changing the local environment of the Mn atoms and by inducing distortions in the metal lattice. Neutron diffraction is the most suitable tool to study hydrogen chemical ordering and its interplay with magnetism, since neutrons have both a magnetic moment and a high scattering length for hydrogen (or deuterium). A high-pressure experiment could bring important information since they allow the lattice parameter to vary without any change of the chemical content and therefore to separate both effects. We studied both magnetic and crystal structure in $YMn_2H_{4.3}$ by neutron diffraction at ambient and high pressure, using isotopic substitution H/D to identify ordering processes in the magnetic and hydrogen sublattices.

Samples of $YMn_2(H,D)_{4.3}$ were prepared by absorption of hydrogen (deuterium). The crystal structure was checked by x-ray diffraction at room temperature, showing a rhombohedral distortion in agreement with Ref. 6. We studied a completely deuterated sample $YMn_2D_{4.3}$ and a sample $YMn_2H_{2.8}D_{1.5}$, having a zero neutron-scattering length for the (H,D) sublattice. High-resolution neutron-diffraction experiments were carried out in ILL on the D2B spectrometer at room temperature. High-intensity measurements were performed on diffractometers D1B in ILL and G6.1 in LLB in the temperature ranges 1.5–300 and 8–400 K, respectively. High-pressure experiments up to the pressure of 6.6 GPa were performed on G6.1, using a sapphire anvil cell and a specific neutron setup,[7,8] both at ambient temperature and down to 4.5 K. Data were analyzed using the FULLPROF refinement program.[9] Neutron-diffraction spectra of both deuterated and "zero matrix" samples are shown in Fig. 1. In contrast to x-ray measurements, we observe strong superstructure lines corresponding to a doubling of the chemical cell. Since these lines are strong in both samples, they should be attributed to antiferromagnetic (AF) order rather than to hydrogen order. At the same time, the two spectra exhibit strong differences in the intensities of the lines which can be indexed in the chemical

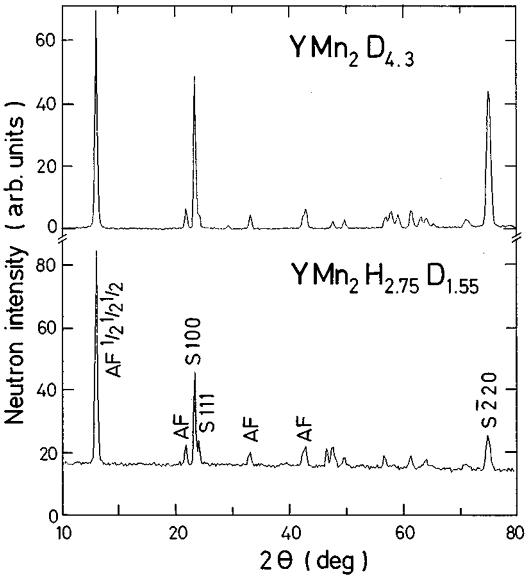

FIG. 1. Neutron-diffraction spectra of the deuterated and ''zero matrix'' samples, measured at 1.5 K (wavelength $\lambda = 2.523$ Å). The Miller indices of the most intense reflections are shown. The structural (S) peaks are strongly affected by H/D substitution, whereas the antiferromagnetic (AF) peaks remain unchanged.

cell, showing that the hydrogen contribution is located at the positions of the structural peaks. The observed superstructure reflections could be indexed assuming an AF propagation vector $\mathbf{k} = 1/2\ 1/2\ 1/2$. The relative intensities of the AF peaks suggest that the magnetic moments lie in the plane perpendicular to **k**. This can be seen in Fig. 1 by the strong enhancement of the 1/2 1/2 1/2 peak. Assuming the same magnitude of magnetic moment for all Mn atoms, there is only one type of collinear magnetic arrangement. It corresponds to the stacking sequence $+ + - -$ of ferromagnetic 111 planes. The magnetic structure was refined with the above assumptions together with the crystal structure (see below). The value of the Mn moment ($3.2\mu_B$/Mn at 1.5 K) agrees quite well with the value expected in RMn$_2$ compounds when d_{Mn} is close to 2.9 Å.

As in most hydrides of Laves phases,[3] hydrogen is expected to occupy tetrahedral interstices (2Y+2Mn) of the metal lattice (positions 12i and two kinds of positions 6h of the space group $R3m$). The total number of positions is 24 per unit cell, containing 8.6 hydrogens. A random distribution of the hydrogen atoms in the 24 positions yielded a significant discrepancy between the calculated profile and the experimental data ($R_F = 16\%$). In addition, we did not observe the intense diffuse scattering, which is usual for disordered hydrides. Therefore, we searched for a model involving some order in the hydrogen sublattice. The physical reason for this ordering is the interaction between hydrogen atoms through the local distortions of the metal lattice. For the Laves hydrides, short-range interactions yield a minimal distance $d_H \sim 2$ Å between neighboring hydrogens.[3] This explains why in the fully hydrogenated sample, hydrogen atoms occupy only 35% of the total number of allowed positions. Since we do not observe any superstructure peaks, the ordered superstructure is characterized by the propagation vector $\mathbf{k} = 0$. In the rhombohedral space group of the lowest symmetry $R3$, we checked all variants of hydrogen distributions allowed by the blocking distance d_H. We found only one model which completely satisfied the blocking conditions and yielded a better fit than the disordered variant ($R_F = 10\%$). In this model, nine allowed interstices are almost fully occupied with hydrogens. Within these nine positions, six interstices (two kinds of 3b positions) are fixed whereas a third kind of 3b interstices may be chosen in different ways among the 6c positions of a higher symmetry space group $R3m$. The best fit ($R_F = 5.5\%$) corresponds to a model described in the space group $R3m$, with two kinds of 3b positions fully occupied and 6c positions only half-occupied (Fig 2). The calculated profile and the final parameters combining both magnetic and crystal structures are shown in Fig 3 and Table I.

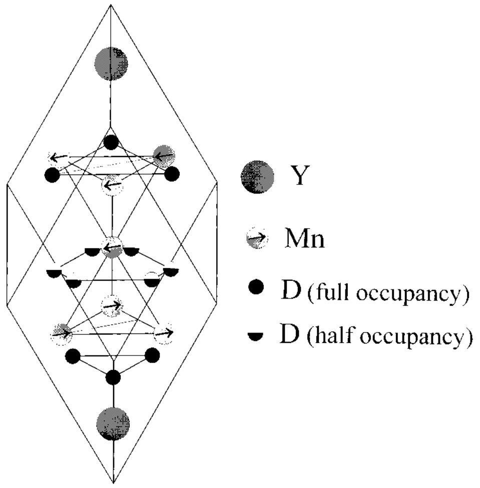

FIG. 2. Schematic drawing of the magnetic and crystal structure.

Between 1.5 and 373 K we observed only *one* transition, around 330 K. Here, both rhombohedral splitting and antiferromagnetic peaks disappear by a first-order transition (Fig. 4). This suggests that at ambient pressure hydrogen and magnetic orders occur at the same temperature. Under high pressure we could expect a decoupling of these two transitions if they are sensitive to interatomic distances in different ways. We observed two different phenomena at high pressure. First of all, even a small applied pressure (of about 0.5 GPa) strongly modifies the relative intensities of the neutron-diffraction lines. The intensities strongly depend on the respective orientations of the pressure cell, incident and scattering beams. We attribute this effect to a change in the domain distribution within the sample. At ambient pressure, the rhombohedral distortion of the unit cell could occur along any cubic diagonal 1 1 1, all of them being equivalent. Small pressure inhomogeneities (usually the pressure is higher of about 0.1 GPa along the axis of the cell) will make the diagonals unequivalent. The observed variation of the intensities corresponds to a preferable domain population when the rhombohedral axes 111 are along the axis of the pressure cell. In the experiments at room temperature, we used this effect to get a maximal intensity by varying the position of the cell. When measured in the optimal position of the cell, the relative intensity of the magnetic and structural reflections is the same at 0.5 GPa and at ambient pressure. At higher pressures, the intensity of the antiferromagnetic reflection 1/2 1/2 1/2 rapidly decreases with pressure, whereas the rhombohedral splitting of the unit cell gradually increases [Fig. 5(a)]. This effect cannot be attributed to a

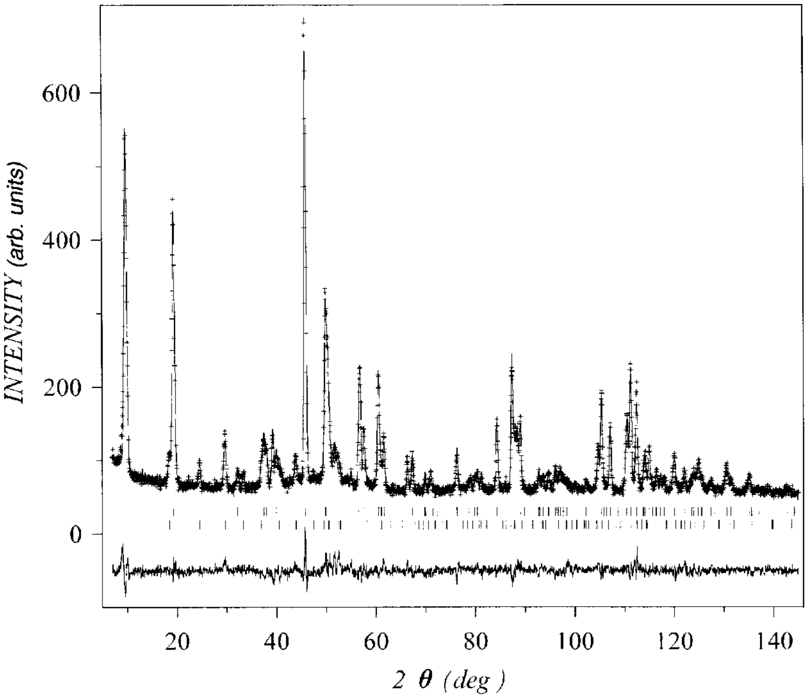

FIG. 3. Neutron-diffraction spectrum and profile refinement of $YMn_2D_{4.3}$, measured at 300 K ($\lambda = 1.5932$ Å). Tick marks correspond to the positions of the structural (top) and the magnetic (bottom) peaks.

change in the domain population. As shown by the temperature dependences of the magnetic intensities [Fig. 5(b)] the Néel temperature T_N rapidly decreases with pressure [inset, Fig 5(b)]. Since the rhombohedral splitting clearly persists above T_N, we conclude that high pressure *decouples* the structural and magnetic transitions. At high pressure hydrogen order should contribute alone to the cubic-rhombohedral transition, which occurs in the paramagnetic state. The magnetic transition which occurs at a lower temperature, seems to be closer to a second-order type, in contrast with the data at ambient pressure.

The most interesting phenomenon is the interplay of magnetic and hydrogen orders. From the coincidence of the structural and magnetic transitions at ambient pressure, we could expect some interaction between hydrogen and magnetic sublattices. This could also explain why both hydrogen and magnetic orders have the same rhombohedral symmetry. Applying a pressure helps to understand the relation between these two types of orders. The observed decoupling of the magnetic and structural transitions at high pressure could be understood as follows. Since hydrogen atoms interact through the local distortions of the cell, decreasing the size of interstices under applied pressure should enhance H-H interactions and could favor a *higher* hydrogen ordering temperature. In contrast, from the general trends of the magnetic order in RMn_2 compounds, we expect a *decrease* of the ordering temperature with decreasing d_{Mn} under pressure. The change of the balance between the energy scales of the two sublattices results in a decoupling of the unique magnetostructural transition above some critical pressure (about 2 GPa from our data).

Since at high pressure the structural transition occurs in the paramagnetic state, we could suggest that the rhombohedral splitting is an intrinsic feature of the order in hydrogen sublattice. Under pressure, T_N varies as a function of the Mn-Mn distances in the same way as with changing hydrogen content. Nevertheless, the type of magnetic order remains antiferromagnetic, whereas hydrides with smaller hydrogen content, having at ambient pressure the same Mn-Mn distances but a cubic structure, show ferromagnetic proper-

TABLE I. Crystal and magnetic structure parameters of $YMn_2D_{4.3}$, $T = 300$ K. Crystal structure: space group $R3m$, $a = 5.5713(13)$ Å, $\alpha = 60.845(16)°$, $Z = 2$. In the cubic phase ($\alpha = 60°$), the atoms Y(1) and Y(2) will occupy the special positions 0.125 0.125 0.125 and −0.125 −0.125 −0.125, whereas Mn(1) and Mn(2) will occupy positions 0.5 0.5 0.5 and 0.5 0.5 0, respectively. Magnetic structure with propagation vector **k** = 1/2 1/2 1/2. The parameters for which the errors are not given were fixed in the refinement.

Atom	Site	p	x	y	z	B (Å^2)	μ_x (μ_B)	μ_y (μ_B)	μ_z (μ_B)
Y(1)	1a	1	0.1240(3)	0.1240(3)	0.1240(3)	0.1			
Y(2)	1a	1	−0.1240(3)	−0.1240(3)	−0.1240(3)	0.1			
Mn(1)	1a	1	0.4927(7)	0.4927(7)	0.4927(7)	0.35	3.44(3)	−1.72(3)	−1.72(3)
Mn(2)	3b	1	0.4945(8)	0.4945(8)	0.0033(13)	0.35	−3.44(3)	1.72(3)	1.72(3)
D(1)	3b	0.94	0.1247(6)	0.1247(6)	0.5042(9)	1.34(5)			
D(2)	3b	0.94	−0.1422(6)	−0.1422(6)	0.2867(9)	1.34(5)			
D(3)	6c	0.5	−0.2985(12)	0.1437(12)	0.5150(12)	1.34(5)			

$R_{\mathrm{wp}} = 16.4\%$, $R_{\mathrm{expt}} = 29.4\%$, $R_{\mathrm{F}} = 5.5\%$, $R_{\mathrm{Bragg}} = 6.2\%$, $R_{\mathrm{magn}} = 9.2\%$

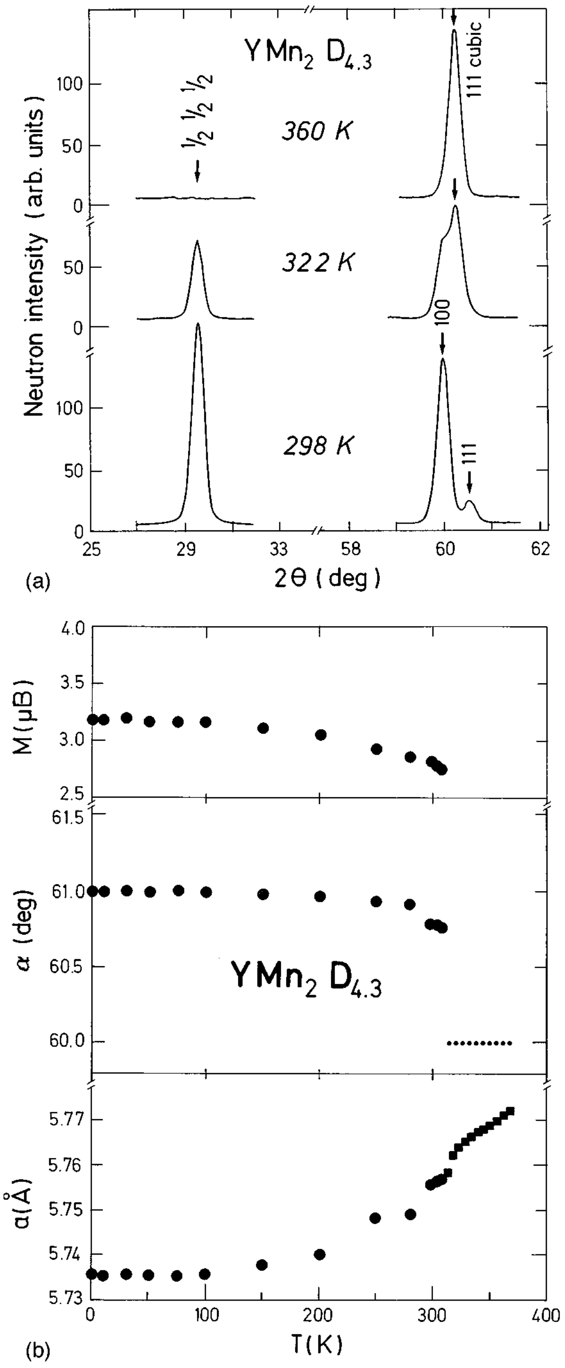

FIG. 4. (a) Temperature evolution of the structural and magnetic peaks, measured in $YMn_2D_{4.3}$ with $\lambda = 4.743$ Å in the region of the magnetostructural transition. (b) Lattice parameter a, rhombohedral splitting α, and Mn magnetic moment M vs temperature. Large dots refer to the rhombohedral phase, squares and small dots to the cubic phase.

ties. Therefore, we conclude that antiferromagnetic order with rhombohedral propagation vector $\mathbf{k} = 1/2\ 1/2\ 1/2$ is closely related with the symmetry of distortion of the unit cell and with the distribution of hydrogen atoms in the structurally ordered phase.

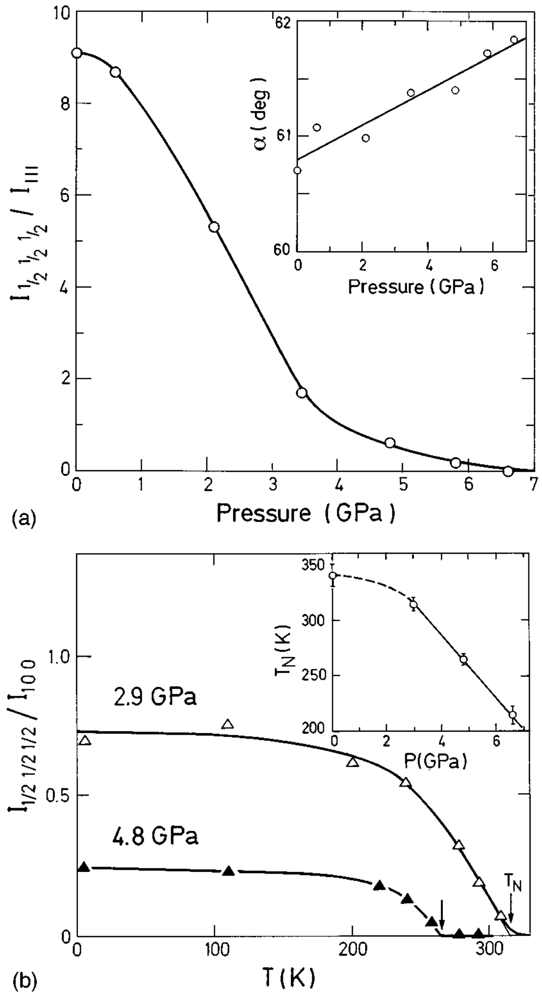

FIG. 5. (a) Integrated intensity of the magnetic peak 1/2 1/2 1/2 (divided by the intensity of the structural peak 111) vs pressure at 300 K. In the inset, evolution of the rhombohedral splitting α with pressure. (b) Temperature dependence of the intensity of the magnetic peak 1/2 1/2 1/2 at 2.9 and 4.8 GPa. In the inset, the Néel temperature T_N vs pressure.

In conclusion, we found that in the hydrogen-rich compound $YMn_2H_{4.3}$, magnetic and hydrogen orders occur at ambient pressure at the same temperature. To understand the interplay between the two sublattices, we could consider an interaction through two types of crystallographic distortions, either induced by hydrogens, or by Mn moments themselves to reduce the topological frustration in the magnetic sublattice.[10] The two types of order have the same rhombohedral symmetry (antiferromagnetic order with wave vector $\mathbf{k} = 1/2\ 1/2\ 1/2$ corresponding to a stacking of ferromagnetic planes perpendicular to a rhombohedral axis 1 1 1, and hydrogen order with $\mathbf{k} = 0$ and rhombohedral $R3m$ space group). An applied pressure decouples these two transitions, showing that the rhombohedral splitting is related with the hydrogen order which favors an antiferromagnetic structure. Studies of other Laves hydrides are now in progress. In RMn_2H_x where R is a magnetic rare earth, we could expect a decoupling of the two transitions even at ambient pressure due to the shortening of Mn-Mn distances. Moreover, the magnetic order of the rare earth could also affect orders in both Mn and hydrogen sublattices.

This work was partly supported by the Russian Foundation for Basic Research, Grant No. 96-02-19775.

[*] FAX: (33)-1-69-08-82-61. Electronic address: gonch@bali.saclay.cea.fr

[1] For a review, see M. Shiga, Physica B **149**, 298 (1988).

[2] For a review, see M. Gupta and L. Schlapbach, in *Hydrogen in Intermetallic Compounds I*, edited by L. Schlapbach, Topics in Applied Physics Vol. 63 (Springer-Verlag, Berlin, 1988), p. 139.

[3] For a review, see K. Yvon and P. Fischer, in *Hydrogen in Intermetallic Compounds I* (Ref. 2), p. 87.

[4] H. Fujii, M. Saga, and T. Okamoto, J. Less-Common Met. **130**, 25 (1987).

[5] J. Przewoznik, J. Zukrowski, and K. Krop, J. Magn. Magn. Mater. **140-144**, 807 (1995).

[6] J. Przewoznik, V. Paul-Boncour, M. Latroche, and A. Percheron-Guegan, J. Alloys Compd. **232**, 107 (1996).

[7] I. N. Goncharenko, J. M. Mignot, G. André, O. A. Lavrova, I. Mirebeau, and V. A. Somenkov, High Press. Res. **14**, 41 (1995).

[8] I. N. Goncharenko, J. M. Mignot, and I. Mirebeau, Neutron News **7**, 29 (1996).

[9] J. Rodriguez-Carvajal, Physica B **192**, 55 (1993).

[10] R. Ballou, J. Deportes, R. Lemaire, and B. Ouladdiaf, J. Appl. Phys. **63**, 3487 (1988); R. Ballou, C. Lacroix, and M. D. Nunez Regueiro, Phys. Rev. Lett. **66**, 1910 (1991).