PHYSICAL REVIEW B **68**, 214418 (2003)

Pressure-induced magnetic collapse and hydrogen segregation in the frustrated Laves hydrides $\mathbf{Tb(Mn_{0.88}Al_{0.12})_2H_x}$

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(Received 7 August 2003; published 15 December 2003)

We have studied magnetic and crystal properties of the frustrated Laves hydrides $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H}_x$ ($x = 1-3$) and $\mathrm{HoFe_2H_{1.5}}$ by x-ray diffraction up to 45 GPa and neutron diffraction up to 16 GPa. We found magnetostructural transitions. When the lattice constant approaches some critical value, the hydrogen atoms diffuse in the crystal lattice and form hydrogen-rich and hydrogen-poor domains. The chemical segregation drastically affects the magnetic properties. In $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_1}$, the hydrogen-rich domains show short-range antiferromagnetic correlations, whereas hydrogen-poor domains show long-range ferromagnetic order. We discuss the coupling between magnetic and structural phenomena and the possibility of a magnetically induced chemical segregation.

DOI: 10.1103/PhysRevB.68.214418 PACS number(s): 75.25.+z, 61.12.Ld, 75.50.Ee, 61.10.Nz

I. INTRODUCTION

The Laves hydrides $RT_2\mathrm{H}_x$ ($R = \mathrm{Y}$ or a rare-earth ion, T = transition metal) recently attracted much attention because of an unusual coupling between the structural and magnetic properties.[1–6] The T sublattice in these compounds is topologically frustrated for first-neighbor antiferromagnetic interactions, so that no one spin structure can minimize the Heisenberg energy, which results in a fully degenerated magnetic ground state.[3–6] The topological frustration leads to a very intricate coupling between the magnetic and structural properties. Hydrogen atoms occupy interstitial sites in the metal sublattice and can form ordered superstructures at low temperatures. In the cubic hydride $R\mathrm{Mn_2H_{4.4}}$ ($R = \mathrm{Y,Gd,Tb,Dy,Ho}$), the magnetic and hydrogen sublattices order at the same temperature through a first-order magnetostructural transition.[7,8] The symmetries of the hydrogen and antiferromagnetic orders are closely related. Hydrogen disorder (induced by a chemical doping in the Mn sublattice) suppresses the long-range magnetic order and stabilizes short-range antiferromagnetic correlations down to $T = 0$.[9] In the hexagonal hydrides $R\mathrm{Mn_2H}_x$ ($R = \mathrm{Er,Tm,Lu}; 2 < x < 4.6$), different long-range or short-range ordered magnetic structures are stabilized depending on the symmetries of the hydrogen superstructures.[10,11] The strong coupling between the chemical (hydrogen) and magnetic sublattices raises an intricate question about the microscopic origin of the interplay between the two sublattices. It was argued that the formation of a hydrogen superstructure can release the topological frustration by changing the local symmetry of the magnetic atoms and therefore can stabilize some particular magnetic structure.[8] In this model, hydrogen order works as a key parameter which governs the magnetic order.

The magnetic properties of the Laves phases $R\mathrm{Mn_2}$ and their hydrides are very sensitive to the values of interatomic distances. The Mn magnetic moments are close to the instability limit between the localized and itinerant states and lose their intrinsic magnetic moments when first-neighbor Mn-Mn distances become smaller than some critical distance $d_c \sim 2.7$ Å.[1] In the cubic compounds, the critical distance corresponds to the lattice constant $a_{\mathrm{Mn}} = 2\sqrt{3}d_{\mathrm{Mn}} = 7.6$ Å. In contrast, the well-localized magnetic moments of the rare-earth ions are not expected to be affected by pressure (at least at pressures < 100 GPa). Therefore, one can change the state of the Mn magnetic moments and the balance between the rare-earth sublattices and the Mn sublattices by applying hydrostatic pressure. The rare-earth ions form a simple diamondlike sublattice which is not topologically frustrated. Therefore, by changing the balance between frustrated and nonfrustrated magnetic sublattices, the high-pressure studies can give insight into the role of topological frustration in the magnetostructural phenomena.

Recently, we studied the effect of pressure on the magnetic ordering in the Laves hydride $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_1}$.[12] The small amount of Al was used to destroy hydrogen order and to stabilize short-range magnetic correlations at $P = 0$. At $P = 6$ GPa, we observed a first-order transition with a pronounced volume effect ($\Delta V/V = -8\%$). Pressure suppresses magnetic moments in the Mn sublattice and stabilizes simple long-range ferromagnetic order in the nonfrustrated rare-earth sublattice. These results support the idea about the dominant role of the topological frustration in the formation of unusual short-range orders at $P = 0$.

The high-pressure transition in $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_1}$ is very interesting, first of all because of the huge volume anomaly. This anomaly can be assigned to a difference between the ionic radii of the magnetic and nonmagnetic Mn ions. Nevertheless, studies of the nonhydrogenated Laves compound $\mathrm{Ho(Mn_{0.9}Al_{0.1})_2}$, where a similar pressure-induced magnetic transition from short-range to long-range magnetic order was found, did not reveal any substantial anomaly in the volume-pressure dependence.[13] If the magnetostructural transition is associated with some critical interatomic distance in the Mn sublattice, it should also depend on the hydrogen content. Interstitial hydrogen expands the metal lattice and acts as ‘‘negative pressure,’’ therefore similar transitions may occur in the higher-content hydrides $Tb(Mn_{0.88}Al_{0.12})_2H_x$ ($x>1$) at pressures above 6 GPa. To get all the information on the origin of the magnetostructural phenomena, one should study different hydrogen concentrations in an extended pressure range and use neutron diffraction to characterize both magnetic and hydrogen sublattices. It would also be useful to change the balance between the magnetic and the hydrogen sublattices by replacing Mn by another transition element, for example Fe.

Here we present a systematic high-pressure study of the Laves hydrides $Tb(Mn_{0.9}Al_{0.1})_2H_x$ ($x=1,2,3$) and $HoFe_2H_{1.5}$ in pressure ranges up to 45 GPa by x-ray diffraction and up to 16 GPa by neutron diffraction. The combination of synchrotron and neutron techniques under such high pressures is unique.

II. SAMPLE SYNTHESIS AND EXPERIMENTAL DETAILS

The starting intermetallic compounds were prepared by arc melting from Mn and Al of 99.99% purity and rare-earth metals of 99.9% purity. We substituted 12% of Mn by Al. Due to the very different chemical affinities of Al and Mn to hydrogen, the substitution is expected to suppress possible hydrogen order.[9,12] We used the Al substitution to avoid possible differences in hydrogen superstructures in the hydrides with different hydrogen contents. Otherwise it would be impossible to compare high-pressure data obtained for different hydrogen concentrations.

The hydrides were prepared by a reaction of the intermetallic compounds with a fixed volume of hydrogen gas at $T=300$ K and hydrogen pressure 0.2–0.5 bar. The hydrogen content was estimated by measuring the volume of the absorbed gas. In order to get a homogeneous hydrogen distribution across the sample, we used additional annealing at $T=400-450$ K. The sample quality and symmetry of the metal lattice were checked by x-ray diffraction at ambient temperature.

Neutrons are sensitive to light elements and magnetic moments and therefore were used to characterize hydrogen sublattices and magnetic orderings. We used the deuterium isotope to decrease incoherent scattering in neutron-diffraction patterns. The neutron experiments at $P=0$ and high pressures were performed on the high-intensity diffractometer G6.1 at the Laboratoire Léon Brillouin.[14] The incident neutron wavelength was 4.74 Å. We used the "Kurchatov-LLB" pressure cells to generate pressure up to 16 GPa in neutron experiments.[15] Sapphire anvils were used in the pressure range up to 10 GPa and diamond anvils were used at higher pressures. Pressure was measured by ruby fluorescence. We used a solid NaCl pressure-transmitting medium. A pressure cell was inserted in a standard ILL-type cryostat and temperature was varied from 1.4 K to 300 K.

High-pressure x-ray experiments were carried out at the beamline ID30 at the European Synchrotron Research Facility (ESRF). We used the Le Toullec membrane diamond anvil cells and the N_2 pressure-transmitting medium. Because of the higher intensity of synchrotron radiation, we could use smaller sample volumes and therefore reach higher pressures (up to 45 GPa). The monochromatic x-ray beam ($\lambda=0.3738$ Å) was focused to the sample and the diffraction pattern was recorded by an image-plate detector. The experiments were carried out at room temperature.

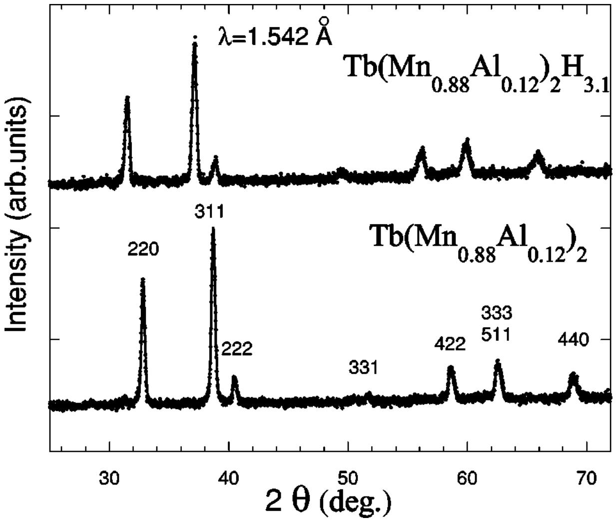

FIG. 1. X-ray-diffraction patterns of $Tb(Mn_{0.88}Al_{0.12})_2$ and $Tb(Mn_{0.88}Al_{0.12})_2H_{3.1}$ measured at ambient pressure and temperature.

The data were treated by the FULLPROF program.[16] We used x-ray data for high-precision measurements of lattice parameters, whereas neutron data were used to characterize magnetic and hydrogen sublattices.

III. MAGNETIC AND CRYSTAL STRUCTURE AT $P=0$

At $P=0$, all the $Tb(Mn_{0.88}Al_{0.12})_2H_x$ ($1<x<3.8$) samples have the same cubic symmetry of the unit cell as the nonhydrogenated $Tb(Mn_{0.88}Al_{0.12})_2$ (Fig. 1). The lattice constant increases linearly with hydrogen concentration (Fig. 2). Neutron diffraction did not detect any traces of hydrogen order. We observed neither anomalies in temperature dependences of the lattice constants nor any superstructural peaks which might be associated with a lowered symmetry of the

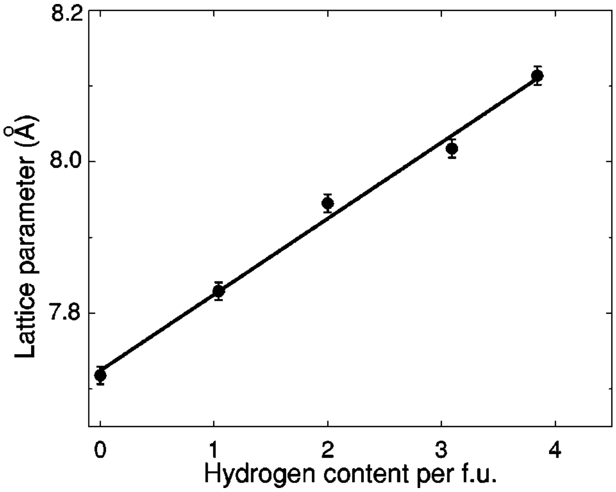

FIG. 2. Lattice parameter at $T=300$ K vs hydrogen content in $Tb(Mn_{0.88}Al_{0.12})_2H_x$.

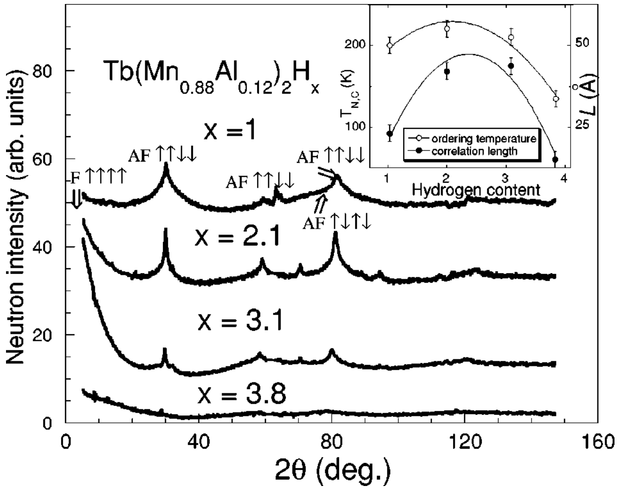

FIG. 3. Magnetic neutron scattering in $Tb(Mn_{0.88}Al_{0.12})_2H_x$ at $T = 10$ K and $P = 0$. Spectra measured in the paramagnetic range were subtracted to separate the magnetic contribution. Inset: magnetic ordering temperature and magnetic correlation length vs hydrogen content.

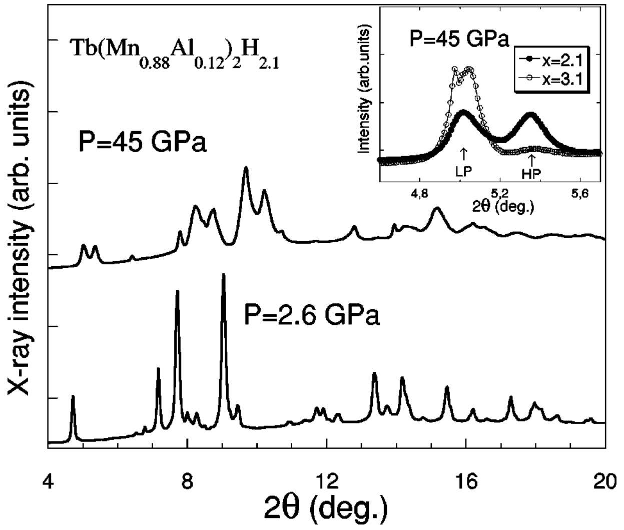

FIG. 4. X-ray-diffraction patterns in $Tb(Mn_{0.88}Al_{0.12})_2H_x$ at 2.6 GPa and 45 GPa. $T = 300$ K. Inset: (111) reflection in $Tb(Mn_{0.88}Al_{0.12})_2H_{2.1}$ and $Tb(Mn_{0.88}Al_{0.12})_2H_{3.1}$ at 45 GPa.

unit cell due to formation of a hydrogen superstructure. The relative intensities of the diffraction lines are in good agreement with a model assuming a random distribution of the hydrogen atoms among the R_2Mn_2 interstitial sites.

When temperature decreases, additional broad diffuse peaks appear on the diffraction patterns (Fig. 3). These peaks develop below $T_N = 150-220$ K and are attributed to a short-range magnetic ordering. The positions of the strongest peaks correspond to the propagation vector $\mathbf{k} = 1/2\ 1/2\ 1/2$ ($\uparrow\uparrow\downarrow\downarrow$ stacking of the ferromagnetic planes along the cubic diagonal), i.e., to the same type of antiferromagnetic order as found in the hydrogen-ordered samples $RMn_2H_{4.4}$.[8] The samples with an intermediate hydrogen content ($x = 2,3$) show some additional scattering at small angles. This scattering is attributed to ferromagnetic correlations which probably come from the Tb-Tb ferromagnetic interactions. Finally, in the sample with the lowest hydrogen content $x = 1$, a contribution from $\uparrow\downarrow\uparrow\downarrow$-type antiferromagnetic correlations was observed (Fig. 3).

In contrast with the hydrogen-ordered cubic hydrides, where the long-range antiferromagnetic structures were observed,[7,8,17,18] the diffuse character of the diffraction peaks in hydrogen-disordered $Tb(Mn_{0.88}Al_{0.12})_2H_x$ samples indicates the short-range nature of the magnetic correlations in both Tb and Mn sublattices. The correlation lengths in the magnetic sublattice vary from 10 to 40 Å. It is difficult to determine the exact values of the ordered magnetic moments in the short-range ordered samples. We estimated the magnetic moments in $Tb(Mn_{0.88}Al_{0.12})_2H_1$ at $T = 10$ K, and obtained $2.5\mu_B$ on the Mn sites and $7.4\mu_B$ on the Tb sites. These values are only slightly lower than the corresponding values measured in the hydrogen-ordered hydride $TbMn_2H_{4.4}$ (3.6 and $9\mu_B$ on the Mn and Tb sites, respectively[8]). It shows that at $P = 0$, the Mn moments are stable in the whole concentration range $1 < x < 4$. In nonhydrogenated $TbMn_2$, the Mn moments close to the instability limit and the Mn magnetism are stabilized by the exchange field induced by the Tb sublattice.[6] Details on the magnetic properties of the hydrogen-disordered $R(Mn_{1-y}Al_y)_2H_x$ will be published in a forthcoming paper.

Similar to $Tb(Mn_{0.88}Al_{0.12})_2H_x$, $HoFe_2H_{1.5}$ did not show any clear evidence for a hydrogen order. Nevertheless, the magnetic properties of $HoFe_2H_{1.5}$ and $Tb(Mn_{0.88}Al_{0.12})_2H_x$ are very different. In $HoFe_2H_{1.5}$, we observe narrow magnetic peaks located at the positions of the structural peaks. In contrast with the Mn-based hydrides, the magnetic order is long-range and is not substantially different from the magnetic order in the nonhydrogenated compounds RFe_2.[19] The magnetic structure of $HoFe_2H_{1.5}$ is ferrimagnetic. It consists of two antiparallel ferromagnetic sublattices formed by Ho and Fe moments.

IV. $Tb(Mn_{0.88}Al_{0.12})_2H_x$ ($0<x<4$): CRYSTAL STRUCTURE UNDER HIGH PRESSURE

The x-ray-diffraction spectra collected at high pressures are shown in Fig. 4. The nonhydrogenated compound $Tb(Mn_{0.88}Al_{0.12})_2$ shows a smooth variation of the unit-cell volume without any volume anomaly or structural distortion. In $Tb(Mn_{0.88}Al_{0.12})_2H_1$ and $Tb(Mn_{0.88}Al_{0.12})_2H_{2.1}$, we observe a pressure-induced transition. When the lattice constant approaches some critical value $a_c = 7.6$ Å, the structural peaks split and new sets of diffraction peaks appear. These diffraction peaks should be attributed to a new phase having the same cubic symmetry as the low-pressure phase but a smaller lattice parameter. The low-pressure (LP) and the high-pressure (HP) phases coexist in a wide range of pressures (Fig. 5). The transition is reversible when pressure decreases. In $Tb(Mn_{0.88}Al_{0.12})_2H_{3.1}$, the transition does not occur or is shifted to much higher pressures. At 45 GPa, we observed only minor traces of the HP phase in $Tb(Mn_{0.88}Al_{0.12})_2H_{3.1}$. As was shown in Ref. 12, the LP phase (at least for $x = 1$) retains the short-range antiferromagnetic correlations both in Mn and Tb sublattices,

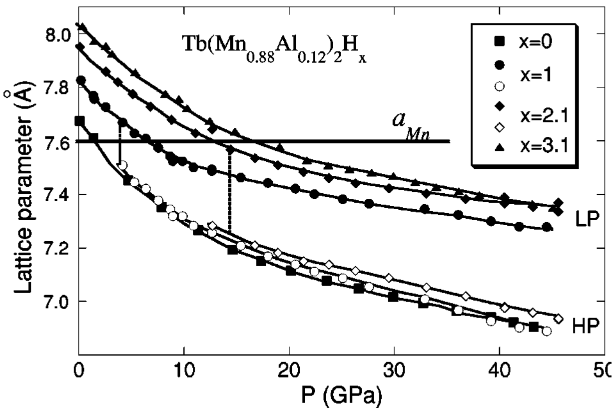

FIG. 5. Lattice parameter vs pressure in $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_x}$. Filled symbols correspond to the LP phases while open symbols correspond to HP phases. The dotted lines show the onsets of the LP-HP transition.

whereas in the HP phases the Mn moments vanish and the Tb moments order in a long-range ferromagnetic structure.

Comparison of the compressibility curves measured for different hydrogen contents leads to very intricate observations. At small pressures, the differences in lattice constants (a) measured at the same pressure for different hydrogen contents are almost pressure-independent, that is, the $a(P)$ curves are almost parallel to each other (Fig. 5). The differences in the lattice parameters should be attributed to an additional "hydrogen volume" occupied by hydrogen atoms in the unit cell. As was shown for many other metal hydrides,[15,20–22] this "hydrogen volume" depends only weakly on pressure. In contrast, at pressures above the transition, the $a(P)$ curves are not parallel anymore. This is true for both HP and LP phases. The LP phase in $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_{2.1}}$ is more compressible than the LP phase in the lower-content hydride $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_1}$ but less compressible than the higher-content hydride $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_{3.1}}$. At very high pressures ~ 40 GPa, the lattice parameters of these three compounds approach the same value. In the same way, the lattice parameters of the HP phases in $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_1}$ and $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_{2.1}}$ approach the value of the lattice parameter of the nonhydrogenated compound $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2}$ (Fig. 5). It means that under very high pressures, there is no additional volume assigned to hydrogen atoms in the HP phases.

In order to search for the possible origins of this highly unusual behavior, we studied hydrogen sublattices in the HP and LP phases in $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_1}$ at $P = 7.2$ GPa by powder neutron diffraction. As seen in Fig. 6, the relative intensities of the (111) and (200) peaks in the LP and HP phases are very different. We refined the hydrogen contents in the HP and LP phases using our neutron data. We obtained $x = 1.6(3)$ for the HP phase and $x = 0.1(3)$ for the LP phase at $P = 7.2$ GPa.

Our neutron data unambiguously show that the high-pressure transitions in the $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_x}$ are associated with a chemical segregation in the hydrogen sublattice. The hydrogen segregation naturally explains the unusual volume-pressure dependences at high pressures. As pressure increases, the hydrogen gradually transfers from the LP phase to the HP phase. Under very high pressures, the hydrogen contents in the LP and HP phases approach the extreme concentrations $x = 0$ and $x > 3$, respectively. Therefore, samples having different hydrogen concentrations in the initial homogeneous phases under very high pressures will consist essentially of the same hydrogen-rich and hydrogen-poor phases. The only difference will be in the relative proportions of the HP and the LP phases.

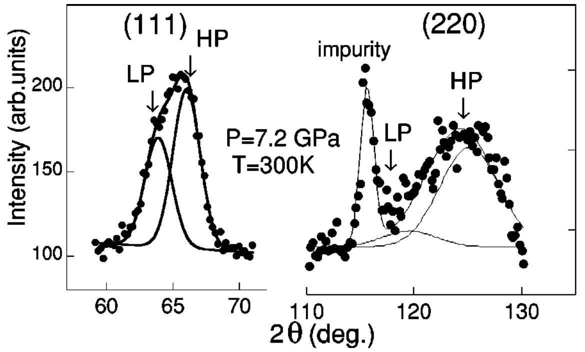

FIG. 6. Structural reflections (111) and (220) in $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_1}$ measured in the paramagnetic range ($T = 300$ K) at $P = 7.2$ GPa. The solid lines are the fits of the LP and the HP phases assuming that hydrogen atoms diffuse from the LP phase to the HP phase.

V. DISCUSSION: MAGNETIC AND CRYSTAL STRUCTURES OF $\mathrm{HoFe_2H_{1.5}}$

The high-pressure transition affects both hydrogen and magnetic sublattices (Figs. 6 and 7). Moreover, the segregation occurs exactly when the lattice constant approaches the region of magnetic instability $a_c \approx a_{\mathrm{Mn}} = 2\sqrt{3} d_c = 7.6$ Å where the Mn moments are expected to vanish. This raises a very interesting question about the possible magnetic origin of the hydrogen segregation. To our knowledge, it would be

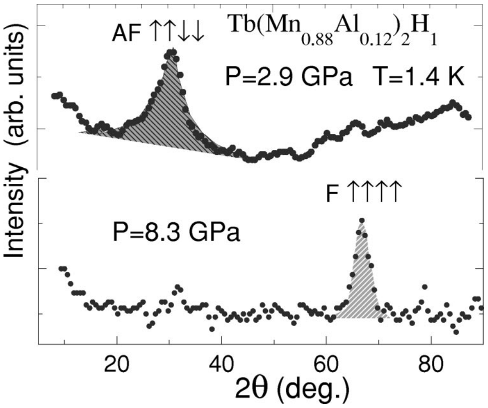

FIG. 7. Magnetic neutron scattering in $\mathrm{Tb(Mn_{0.88}Al_{0.12})_2H_x}$ measured at $T = 1.4$ K and pressures 2.9 and 8.3 GPa. Spectra measured in the paramagnetic range were subtracted to separate the magnetic contribution At $P = 5.9$ GPa, magnetic moments in the Mn sublattice vanish and the initial short-range antiferromagnetic order transforms to long-range ferromagnetic order.

the only case where magnetic order would affect the chemical composition.

Although this scenario is very unusual, this possibility should not be ruled out. In general, the nonmagnetic ions are expected to occupy smaller volumes in crystal structures than the magnetic ones. The transformation from a magnetic to a nonmagnetic state could occur through a sharp first-order transition (as in YMn_2, see Ref. 21) or through a continuous step-by-step variation of the magnetic moment [as seems to occur in $Ho(Mn_{0.9}Al_{0.1})_2$, see Ref. 13]. In the first case, one should expect a volume decrease through the magnetic transition, whereas in the second case one can expect an enhanced compressibility in the pressure range of the continuous transition. In both cases, the volume decrease (jumplike or continuous) will influence the ground state of the system through the PV term in the free energy at $T=0$. If ΔV_M is the difference in volumes between the magnetic and nonmagnetic states of the Mn ion, the gain in energy per Mn ion will be equal to $-P\Delta V_M$. Below, we will show that the hydrogen sublattice can interfere with the magnetic sublattice through the magnetovolume effects.

In the case of a linear variation of the sample volume with hydrogen content, every hydrogen atom brings an additional volume V_{H} to the total volume of the hydride. Without considering the magnetic phenomena, the volume increase in the HP phase is exactly compensated by the volume decrease in the LP phase. In this case, the change in the free energy of the system due to chemical segregation will be equal to $\Delta F=NPV_{\mathrm{H}}-NPV_{\mathrm{H}}+N\mu=N\mu$, and the "high-pressure" PV term will not play any role in the stabilization of the chemically segregated state. Here N is the number of atoms transferred to the hydrogen-rich phase and μ is the chemical potential (per transferred atom) associated with the transfer. Finally, the only condition for the stability of the initial homogeneous state is $\mu>0$. This is the trivial condition for a phase stability.

Bringing the magnetovolume phenomena into consideration changes the situation drastically. If the lattice parameter of the initial homogeneous phase a_{homog} is only slightly larger than the critical parameter of the magnetic instability $a_{\mathrm{homog}}>a_{\mathrm{Mn}}$, the hydrogen segregation can move part of the sample through the magnetic instability limit: $a_{\mathrm{LP}}>a_{\mathrm{Mn}}$, $a_{\mathrm{HP}}<a_{\mathrm{Mn}}$. Although the chemical segregation itself is not expected to change the total volume of the system, the additional volume effect associated with the magnetic $\rightarrow$nonmagnetic transition could bring about some gain in the free energy. In this case, every hydrogen atom transferred from the homogeneous phase to the HP phase will transform $2N/\Delta x$ Mn atoms to the nonmagnetic state, and the change in the free energy due to chemical segregation will be $\Delta F=N\mu-2NP\Delta V_M/\Delta x$. Here Δx is the difference in hydrogen contents in the homogeneous and the hydrogen-poor phases $\Delta x=x-x_{\mathrm{HP}}$. As seen from the above expression, under some conditions on μ, ΔV_M, and Δx, the segregation will help to minimize the energy of the system.

Finally, we propose two possible scenarios for the high-pressure transition in $Tb(Mn_{0.88}Al_{0.12})_2H_x$.

(i) Pressure changes the sign of the chemical potential μ and therefore makes the homogenous phase unstable upon chemical segregation.

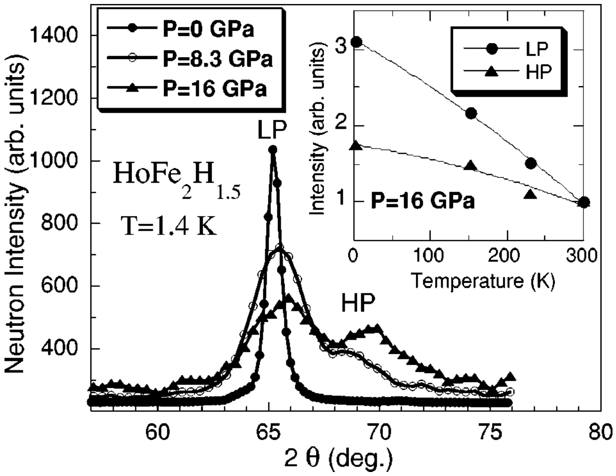

FIG. 8. Neutron diffraction patterns in $HoFe_2H_{1.5}$ measured at $T=1.4$ K and pressures 0, 8.3, and 16 GPa. Inset: integrated intensities of (111) reflections in the HP and LP phases at $P=16$ GPa vs temperature. The intensities are normalized to their values at $T=300$ K.

(ii) μ does not change sign under pressure and the chemical segregation is driven by the magnetovolume phenomena.

One can think about the possible experimental ways to verify the above scenarios. For example, one could try to decouple the magnetic and hydrogen sublattices in RT_2H_x by choosing another T element that would be less sensitive to applied pressure. RFe_2 compounds are expected to keep magnetic moments on the Fe sites up to pressures as high as 50 GPa.[23] We studied the magnetic and structural transitions in $HoFe_2H_{1.5}$ under pressures up to 16 GPa using powder neutron diffraction. In Fig. 8, we show neutron-diffraction spectra collected at ambient pressure, 8.3 GPa and 16 GPa. At 8.3 GPa, we observe the first traces of a structural transition. At 16 GPa, we clearly observe the same split of the diffraction peaks as in the Mn-based compounds, which shows that the hydrogen segregation also occurs in $HoFe_2H_{1.5}$. Both LP and HP phases are long-range magnetically ordered and ferro(ferri)magnetic, so the magnetic and structural sublattices contribute to the same diffraction peaks. In the inset of Fig. 8, one can see the temperature variations of the diffraction peaks at 16 GPa. The decrease in intensity is associated with the decrease of values of the ordered magnetic moments with temperature. The Curie temperature is well above room temperature, therefore we could not separate the magnetic and structural contributions by measuring spectra in the paramagnetic range. Consequently, we did not measure the exact values of the magnetic moments in the Ho and Fe sublattices. One can notice that the magnetic contribution at $T=1.4$ K in the diffraction peaks of the HP phase is considerably smaller than in the LP phase.

The chemical segregation in $HoFe_2H_{1.5}$ supports scenario (i). Assuming this scenario, one should search for a possible physical reason why under high pressures the homogeneous states become systematically unstable. As was shown above, when neglecting magnetovolume effects, the specific "high pressure'' does not produce any gain in the free energy with the hydrogen segregation. At $P=0$, the AB_2H_x Laves hydrides form many different phases which have different hydrogen contents $0<x<x_{\max}$ and different values of lattice parameters.[24,25] There is no trivial explanation why these intermediate-concentration phases should be unstable under high pressures.

We notice that the possible influence of magnetovolume effects [and therefore the scenario (ii)] in $HoFe_2H_{1.5}$ is not completely impossible. Although the Fe sublattice is more stable magnetically than the Mn sublattice, it is not fully independent of the values of interatomic distances. From high-pressure data obtained in RFe_2 (Ref. 23), we estimated the magnetic moments on the Fe sites in the HP phase. We found that the volume change due to the hydrogen segregation may induce a significant decrease of the Fe moment of about 20–30%. Therefore, scenario (ii) cannot be fully ruled out.

In conclusion, we observed an unusual magnetostructural transition in the frustrated Laves hydrides $Tb(Mn_{0.88}Al_{0.12})_2H_x$ $(x=1,2)$. The unique combination of neutron and x-ray diffraction under very high pressures allowed us to obtain complete information about the structural and magnetic properties of the high-pressure phases. At high pressures, the hydrogen sublattice segregates into hydrogen-rich and hydrogen-poor regions. This transition is accompanied by a magnetic collapse in the Mn sublattice and the formation of a long-range ordered ferromagnetic state. We speculate about the possible influence of the magnetovolume effect in the chemical segregation. Our results show that high pressure is a powerful tool to study exotic phenomena in magnetically unstable systems.

ACKNOWLEDGMENTS

We thank A.V. Irodova for help with the sample characterization. This work was supported in part by the Russian State Program MPNT NS-2037.2003.02.

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