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On the origin of the giant isotopic effect of hydrogen on the magnetic properties of $YFe_2A_{4.2}$ (A = H, D): A high pressure study

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In order to identify the origin of the giant isotope effect observed on the magnetic properties of $YFe_2A_{4.2}$ compounds (A = H, D) and probe the role of the cell volume difference, we have compared the effect of hydrostatic pressure up to 1.0 GPa on the ferro-antiferromagnetic transition temperatures $T_{F\text{-}AF}$ and spontaneous magnetization of $YFe_2D_{4.2}$ and $YFe_2H_{4.2}$. Using compressibility value of 0.013 GPa^{-1} and the remarkably different negative pressure slopes of $T_{F\text{-}AF}$, the existence of critical volume where the ferromagnetism is suppressed at 0 K, $V_C = 501.7 \pm 0.3$ Å^3, was demonstrated. This consequently established the crucial role of volume on the huge isotope effect observed on the magnetic properties. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4798260]

The effect of hydrogen and/or deuterium insertion on the physical properties of intermetallic containing iron and rare-earth elements has attracted much interest during the last years. Indeed, these alloys exhibit interesting properties from both fundamental and applied point of view. The magnetic properties of some iron rich compounds (like Nd-Fe-B) have been shown to be very sensitive to the hydrogen content.[1] More recently, the intensive research for efficient magnetocaloric materials has led to the discovery of so called giant magnetocaloric effect materials like $La(Fe,Si)_{13}$, whose magnetic performance can be optimized by hydrogen insertion into the lattice.[2–4] As a consequence, spectacular upsurge of interest in room-temperature magnetic refrigeration has appeared, which promises several advantages over conventional refrigeration techniques, including lower environmental impact. Among other hydrogen containing materials, the potential of YFe_2 hydrides (deuterides) for magnetic refrigeration application has also been recently revealed.[5] $YFe_2D_{4.2}$ undergoes a structural transition from cubic towards monoclinic structure around room temperature. Upon cooling, a paramagnetic-antiferromagnetic ($T_N = 131$ K) occurs, and then an antiferromagnetic-ferromagnetic (F-AF) transition ($T_{F\text{-}AF} = 84$ K) is observed.[6] The latter is a first-order magnetic phase transition and shows a significant magnetocaloric effect around the transition temperature.[5]

When studying the influence of light elements insertion on the physical properties of intermetallic compounds, two types of mechanisms are often discussed: on one hand, the negative pressure effects related to the interstitial elements into the lattice usually leading to unit cell volume expansion and sometime change of crystal symmetry, on the other hand, the electronic effects due to the bonding of the interstitial elements with the surrounding atoms and the modification of the Density of State (DOS). Obviously, the two types of effects are simultaneously present in the studied compounds, but their relative importance is difficult to predict.

Another interesting point is the possible influence of the isotopic nature of light atoms on the physical properties of a material. The influence of the nature of the (H, D, T) isotope on the thermodynamic properties of hydrides has been widely investigated due to the isotope separation process.[7–10] But, the influence of the nature of hydrogen isotope on the magnetic or electronic properties of interstitial compounds is often neglected. This question is not trivial since the electrons are known to play the major role in bonding and, therefore, on the physical properties, and the isotopes have the same electron number.

In order to investigate this issue, we propose here a study of isostructural $YFe_2A_{4.2}$ compounds, the A atoms being either hydrogen or deuterium. The chosen system offers the advantage of being obviously isoelectronic and to present the same crystal structure. In addition, a large change of the magnetic properties under applied pressure has been observed for $YFe_2D_{4.2}$, and it is interesting to follow the behaviour of the corresponding hydride.[11]

Detailed structural studies[11,12] showed that as a consequence of the ordering of deuterium atoms in $YFe_2D_{4.2}$, the crystal structure changes from the cubic (*Fd-3m* space group) to monoclinic (*Pc* space group) symmetry during cooling at temperature around 320 K. The lowering of the crystal symmetry due to the deuterium order occurs at much higher temperature than the magnetic ordering and can be at the origin of the magnetic transitions at lower temperatures. In the low temperature monoclinic phase, the Fe atoms occupy eight different sites and are surrounded by 4 or 5 D atoms.[11] This induces a wide Fe-Fe distance distribution, which is responsible of a broad hyperfine field distribution at low temperature.[6] Then, the first order ferromagnetic-antiferromagnetic transition has been attributed to the loss of magnetic moment of one Fe site through an itinerant electron metamagnetic (IEM) behavior.[6]

Concerning the isotope effect, it has been shown previously that the hydride compound exhibits a larger unit cell volume than the isostructural $YFe_2D_{4.2}$ deuteride and that there exists a linear increase of the cell volume reaching 0.75% between the hydride and the deuteride.[6] This volume difference

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has been explained by the difference of the zero point amplitude of vibration of the interstitial atoms inside the lattice.

At ambient pressure, an exceptionally large shift of 47 K corresponding to 50% of the F-AF transition temperature ($T_{F\text{-}AF}$ or T_{M0} in previous work) is observed between the $YFe_2D_{4.2}$ and $YFe_2H_{4.2}$ compounds. Values of $T_{F\text{-}AF} = 131(2)$ K vs. $T_{F\text{-}AF} = 84(2)$ K at zero field are found for the hydride and the deuteride, respectively.[6] The second magnetic transition from antiferro to paramagnetic state observed by Neutron Powder Diffraction (NPD) is also sensitive to isotope effect as it is shifted from $T_N = 131$ K to 165 K for $A = D$ and H, respectively. This may be an indication that the magnetism of Fe is of exceptionally high sensitivity in the $YFe_2A_{4.2}$ compounds. This interpretation is corroborated by an enormous composition dependence of both magnetization and hyperfine field parameters have been reported between 3.5 and 5 interstitial atoms per formula unit, which exhibit a spectacular suppression of magnetic order.[13,14] Such effect has been assigned to a competition between magnetovolume and electronic effects, in particular, a strong Fe-H bonding observed for large H content.[15] According to such hypothesis, it is important to check the behavior under applied pressure in order to investigate the volume dependence of the physical properties. Recent investigation demonstrated huge effect of pressure on magnetic transition temperature of $YFe_2D_{4.2}$ deuteride: the transition temperature is shifted to zero Kelvin for $P = 0.5$ GPa, which corresponds to the volume decrease of only about 0.6%.[12] For higher pressures, the antiferromagnetic structure remains stable at low temperature. Having in mind only 0.75% cell volume difference at room temperature and about 50% higher value of $T_{F\text{-}AF}$ of hydride compared to deuteride, one can speculate about the existence of one similar critical volume V_C for both compounds, where the ferromagnetic ground state is suppressed at 0 K.

We will now present the results of studies of the pressure/volume evolution of magnetic transition temperature and spontaneous magnetization in $YFe_2H_{4.2}$ hydride to get complementary results with those obtained on $YFe_2D_{4.2}$ deuteride.[12] The role of the strong interplay between magnetic and elastic energy will be studied and estimated.

The preparation of interstitial compounds by solid gas reaction and their characterization are described in Refs. 6 and 16. The magnetization measurements at high hydrostatic pressure up to 1.0 GPa were performed on a powder sample in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design Co.) using a miniature piston-cylinder CuBe pressure cell.[17] The studies were performed at magnetic fields up to 7 T in the temperature range from 2 K to 300 K. The evolution of the magnetic ordering temperature $T_{F\text{-}AF}$ under different pressures was determined from temperature dependence of the low field magnetization measured in a magnetic field of 0.03 T at a heating rate of 1 K min^{-1}. It was defined as inflexion point on magnetization vs. temperature curves. The saturation magnetization and critical magnetic fields at different pressures were determined from the isothermal magnetization curves.

Temperature dependencies of the low-field magnetization measured at magnetic field of 0.03 T under different pressure values are displayed for $YFe_2H_{4.2}$ in Figure 1.

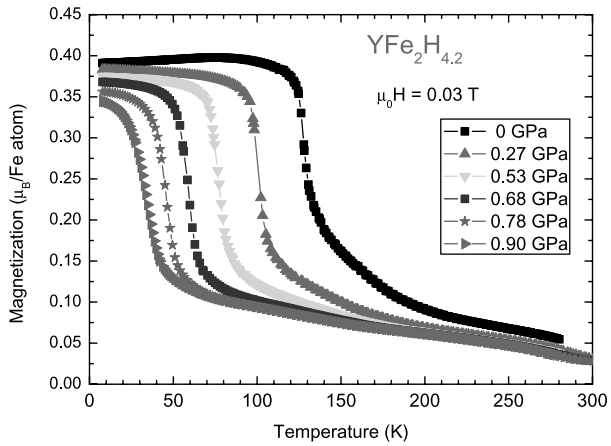

FIG. 1. Thermal evolution of the low field magnetization recorded for several applied pressures on $YFe_2H_{4.2}$.

It is easy to see that $T_{F\text{-}AF}$ dramatically decreases with increasing pressure. This decrease is linear but contrary to the results obtained recently on $YFe_2D_{4.2}$ we were not able to suppress completely the ferromagnetic ground state by the maximum pressure of 0.9 GPa. The remarkable lower pressure slope of $T_{F\text{-}AF}$, $dT_{F\text{-}AF}/dP = -105$ K GPa^{-1} for the hydride ($dT_{F\text{-}AF}/dP = -156$ K GPa^{-1} for deuteride[12]) together with its significantly higher $T_{F\text{-}AF}$ means that double external pressure is necessary for suppression of its ferromagnetic ground state.

Pressure dependence of the $T_{F\text{-}AF}$ temperature as derived from isofield magnetization curves of both $YFe_2H_{4.2}$ and $YFe_2D_{4.2}$ is presented on Figure 2. The difference in pressure behavior represents again an isotope dependant behavior. We extrapolate the suppression of the ferromagnetic order to disappear at about 1.25 GPa for the hydride against 0.56 GPa for the deuteride.

A set of magnetization isotherms as a function of magnetic field at maximum pressure of 0.9 GPa is visualized on Figure 3. This set of isotherms confirmed that $T_{F\text{-}AF}$ is close to 40 K at this pressure. The critical field (H_C) rapidly increases with temperature, with slope $dH_C/dT = 0.17$ T/K, same value as was observed for $YFe_2D_{4.2}$.[12]

The spontaneous magnetization significantly decreases with pressure. This decrease is non-linear but the initial

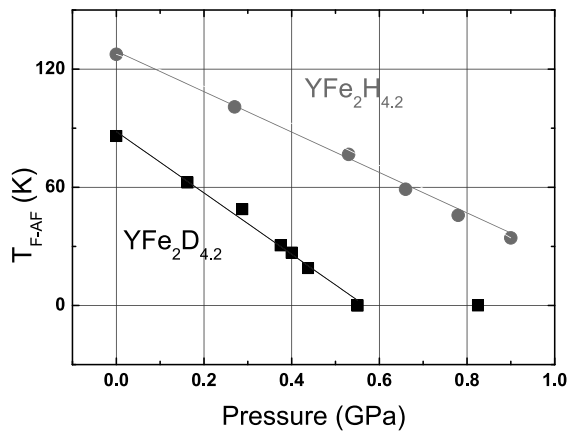

FIG. 2. Pressure dependence of $T_{F\text{-}AF}$ temperature as derived from isofield magnetization curves of $YFe_2H_{4.2}$ (●) and $YFe_2D_{4.2}$ (■).

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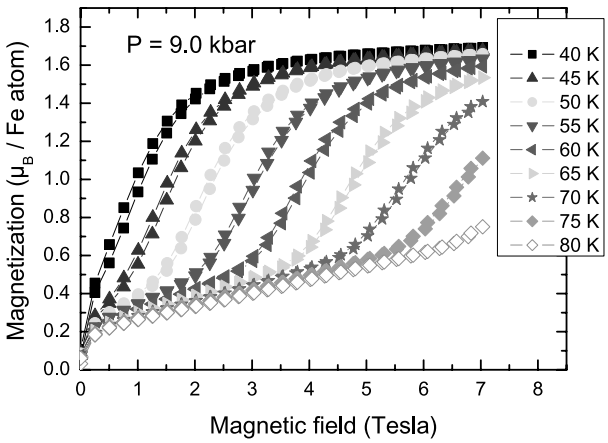

FIG. 3. Magnetic isotherms recorded for $YFe_2H_{4.2}$ at the indicated temperatures in the high pressure cell for the maximum pressure of 0.9 GPa.

pressure slope of the relative values of spontaneous magnetization $d\ln(M_S)/dP = -7.3 \times 10^{-2}\,GPa^{-1}$ is similar to that of deuteride $YFe_2D_{4.2}$ (Ref. 12) as seen on Figure 4, where the pressure dependencies of the relative values of spontaneous magnetization for both the $YFe_2H_{4.2}$ and $YFe_2D_{4.2}$ are presented.

Using the compressibility value of $0.013\,GPa^{-1}$ determined in Ref. 12 for deuteride, we can deduce the volume dependence of the transition temperature $T_{F\text{-}AF}$. It is noteworthy that the compressibility is very close in both YFe_2 ($\kappa = 0.011\,GPa^{-1}$) and $YFe_2D_{4.2}$. That is why we have assumed the same values of compressibility for both hydride and deuteride. The evolution of the transition temperature $T_{F\text{-}AF}$ versus the cell volume is plotted in Figure 5. The elementary cell calculated here corresponds to 8 YFe_2/formula units as in the original cubic structure of the intermetallic. It is found that the ferromagnetism disappears at the same value of cubic equivalent elementary cell for both compounds reaching the value of 501.7 ± 0.3 Å^3. This observation is the clear evidence about the crucial role of volume for the stability of ferromagnetic ground state for both hydride and deuteride.

The complex interplay of number of nearest Fe-Fe neighbors and sensitivity of exchange interactions to the Fe-Fe interatomic distances is the main reason of the complex

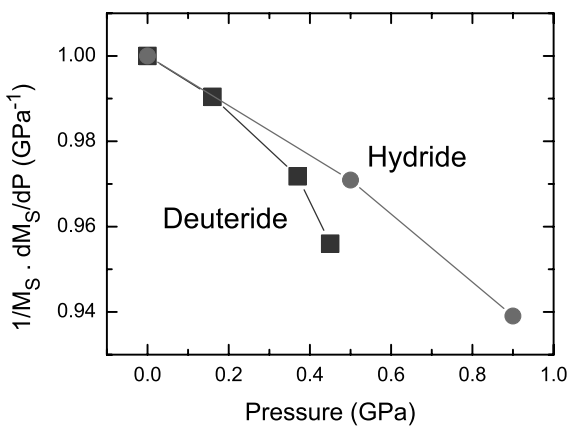

FIG. 4. Relative values of spontaneous magnetization for both the $YFe_2H_{4.2}$ (●) and $YFe_2D_{4.2}$ (■) at different pressures.

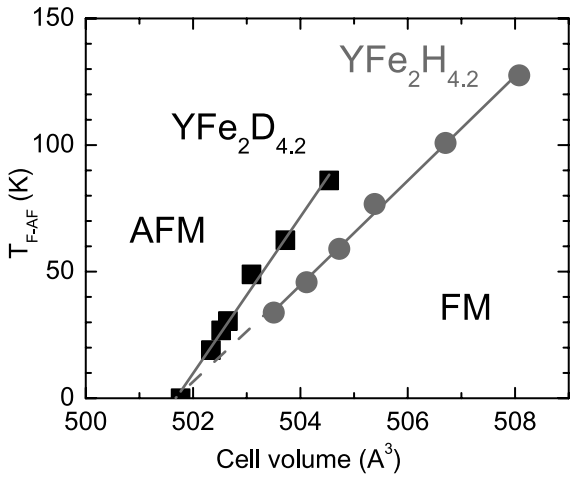

FIG. 5. Volume dependence of the $T_{F\text{-}AF}$ temperature as derived from isofield magnetization curves of $YFe_2H_{4.2}$ (●) and $YFe_2D_{4.2}$ (■) demonstrating the existence of a critical volume where ferromagnetism disappears.

magnetic phase diagrams of many Fe-based intermetallic compounds and their corresponding hydrides/deuterides, carbides, and nitrides.[18] The theoretical calculation of hydrogen rich YFe_2 based hydrides confirmed the existence of substantial differences between electronic structures of the hydride YFe_2H_4 and the parent compound YFe_2.[15,19] Concerning the total magnetization, the main effect is due to the lattice expansion, which yields an increase of the magnetic moment of about $0.36\,\mu_B$ per Fe atom. The consequence of insertion of hydrogen is the weakening of the exchange interactions and consequently lowering of the magnetic ordering temperatures even though the total magnetic moment increases.[15]

From the point of view of the high value of Fe magnetic moment and relatively weak exchange interaction, the magnetic behavior of hydrogen rich compounds is substantially different than that of RFe_2 compounds that exhibit rather high stability of both Fe magnetic moments and Curie temperatures and that can be taken as strong itinerant ferromagnets. Moreover, the magnetic order of $YFe_2H_{4.2}$ is on the verge of stability, as it was showed by both experimental studies and theoretical calculations, indicating that there is no magnetic order for the YFe_2H_5 hydride.[13,15] From this point of view, the magnetic behavior of hydrogen rich $YFe_2H_{4.2}$ like hydrides resembles some of the R_2Fe_{17} compounds that simultaneously exhibit high values of magnetic moment of Fe and low ordering temperatures and are rather sensitive to external conditions. Another similarity is the suppression of ferromagnetic ground state by rather low pressures of a few tenths of GPa and existence of relatively stable pressure induced antiferromagnetic ground state for Y_2Fe_{17},[20] Lu_2Fe_{17},[21] and Ce_2Fe_{17} ($dT_{F\text{-}AF}/dP = -380\,K\,GPa^{-1}$ for Ce_2Fe_{17} (Ref. 22)) One of the characteristic properties of R_2Fe_{17} compounds is also the anisotropic behavior of their lattice parameters and anisotropic compressibility below room temperature.[20] Consequently, the anisotropic variations of exchange interactions are one of the reasons for the low stability of ferromagnetic ground state in these compounds as shown in Ref. 23. Anisotropic thermal expansion of the monoclinic phase below the room temperature has been observed also on $YFe_2D_{4.2}$ where both the thermal

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expansion and magnetoelastic effect at $T_{F\text{-}AF}$ have been observed significantly weaker along the monoclinic *b*-axis.[16] Having in mind that we are on the verge of magnetism for these compounds, the possible anisotropic behavior under pressure can contribute to the observed huge pressure effects.

Larger cell parameters for the hydrides compared to deuterides have been already observed for other compounds and are mostly related to quantum effect. Light atoms like hydrogen have large amplitude of the zero point vibration in their condensed phases. The root mean square amplitude of vibration of the hydrogen isotope in the host metal is sensitive to the mass and can vary from 0.43 Å for ($\mu+$) to 0.19 Å for T.[24] The observed 0.75% larger cell volume of the hydride is in our case is rather high. Ordering of interstitial elements at low temperatures can also play a role, as they induce a different magnetic behavior of the various Fe sites as it was also observed in $Hf_{1-x}Ta_xFe_2$ compounds.[25]

To conclude, we proved that the volume of the elementary cell is the crucial parameter that is responsible for the different values of magnetic ordering temperature $T_{F\text{-}AF}$ and also significantly affects the different values of magnetization in both the $YFe_2H_{4.2}$ and $YFe_2D_{4.2}$. By our high pressure studies, we found the existence of one critical volume V_C for disappearance of the ferromagnetic ground state for both compounds. These results demonstrate that the strong interplay between magnetic and elastic energies is the origin of the giant isotopic effect. We also showed that one should be very careful in deducing the physical properties of hydrides from the study of isostructural deuterides compounds since we demonstrated above that, in some cases, even pure electronic properties can be dramatically affected. The authors hope that the obtained results will motivate theoretical studies in spite of the rather complex crystal structure of these compounds, namely theoretical investigation of the electronic band structure evolution versus composition and pressure in the YFe_2A_x series of compounds.

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