

Isotope effect on the thermodynamic and structural properties of $Y_{1-y}R_yFe_2(H,D)_{x(\gamma)}$ compounds ($R = Tb, Er, Lu; 4.0 \leq x(\gamma) \leq 4.5$)

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Abstract

Thermodynamic and structural properties of $Y_{1-y}R_yFe_2H(D)_{x(\gamma)}$ compounds ($R = Tb, Er, Lu, 4.0 \leq x(\gamma) \leq 4.5$) have been investigated using Sieverts method and X-ray diffraction (XRD) at 298 K. The D for H substitution induces a lowering of the plateau pressure, a small increase of the γ phase capacity and a decrease of about 1.7 \AA^3 of the cell volume. Additionally, the anomalous behavior of the plateau pressure *versus* cell volume observed upon Tb substitution has been explained by a change of the relative position of Y in the lanthanide series upon H(D) absorption. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Hydrogen absorption in rare earth and transition metal compounds modifies significantly their structural, magnetic and electronic properties [1]. Among these systems, RFe_2 compounds and their corresponding hydrides have been extensively studied for their magnetic properties. RFe_2 Laves phases can absorb hydrogen or deuterium up to 5 H(D)/mol [2–4]. Several structural distortions have been observed as a function of hydrogen content. The YFe_2D_x deuterides are ferromagnetic with an increase of the mean Fe moment and a decrease of T_C for $x \leq 3.5$ D/mol [5,6]. For $x = 4.2$, the monoclinic compound is ferromagnetic at low temperature then undergoes a sharp first-order magnetovolumic transition towards an antiferromagnetic structure at 84 K [7]. Thanks to complementary methods, this transition has been attributed to an itinerant electron metamagnetic behavior (IEM) of one of the Fe sites surrounded by about 5 D atoms [7]. Surprisingly this transition is very sensitive to the H for D substitution, which increases the mean Fe moment at 4.2 K and shifts the transition temperature to 130 K (by 50%) [5,8]. Since the cell volume of the hydride is 0.78% larger than the deuteride, this giant isotope effect has been related to the strong dependency of the IEM behavior on the volume [9,10]. In order to better understand the interplay between mag-

netic and elastic energies on this magnetovolumic transition, we have undertaken the study of $Y_{1-y}R_yFe_2(H,D)_{x(\gamma)}$ compounds ($R = Tb, Er, Lu$) with $x(\gamma)$ close to 4.2. In this paper, the influence of the (H,D) isotope effect on the thermodynamic and structural properties of these $Y_{1-y}R_yFe_2(H,D)_{x(\gamma)}$ compounds will be presented, whereas the magnetic properties will be the subject of a further communication. In addition to the significant (H,D) isotope effect, an unexpected behavior of the Tb substituted compounds will be presented and discussed in more details.

2. Experimental methods

The $(Y_{1-y}R_y)Fe_2$ intermetallic compounds ($R = Tb, Er, Lu$) were prepared by induction melting of the pure elements followed by three weeks annealing treatment at 1100 K. Their composition and homogeneity were checked by X-ray diffraction (XRD) and electron probe microanalysis as described in ref. [5]. The $(Y_{1-y}R_y)Fe_2$ hydrides and deuterides were prepared by solid–gas reaction using a Sieverts apparatus and their structure were checked by XRD. The samples were cooled in liquid nitrogen and opened to air before removing from their sample holder at 298 K in order to avoid H or D desorption. XRD measurements were carried out at 300 K using a Bruker D8 diffractometer (Cu K α radiation). The XRD patterns were refined using the Fullprof code [11].

3. Results

3.1. Thermodynamic properties

The pressure composition isotherms of YFe_2D_x compounds display a multiplateau behavior [12], which has been related to

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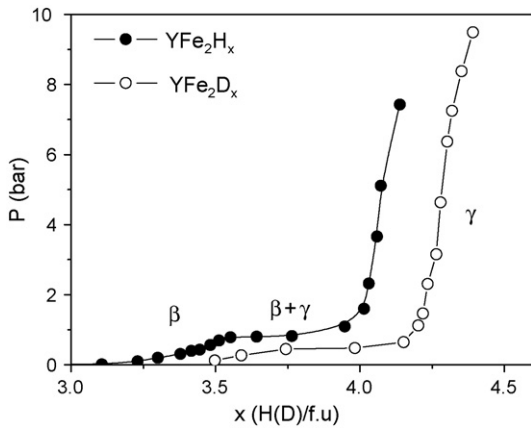


Fig. 1. Absorption isotherms at 298 K of YFe_2H_x and YFe_2D_x .

the existence of several phases with different structures. Nevertheless this work will be focused on the concentration range $3 \leq x \leq 4.6$ where two different phases, which will be denoted as β ($x \approx 3.5$) and γ ($x \approx 4.2$) in the following part of this paper, are observed. On Fig. 1 are reported the isotherms at 298 K of YFe_2H_x and YFe_2D_x . The D for H substitution leads to a decrease of the plateau pressure of 0.3 bar and an increase of the capacity of the γ phase of 0.2 mol. All the isotherms of the $(\text{Y}_{1-y}\text{R}_y)\text{Fe}_2$ compounds measured in this range of concentration display the same isotope effect: a higher plateau pressure and a lower capacity for the γ phase ($4.0 \leq x(\gamma) \leq 4.5$) of the hydrides compared to the deuterides. The equilibrium pressure versus the rare earth substitution rate y is reported on Fig. 2. Besides the larger equilibrium pressure of the hydrides, a different evolution of the pressure is observed depending of the nature of the substituted rare earth element. The equilibrium pressure increases for $\text{R}=\text{Er}$ and Lu and decreases for $\text{R}=\text{Tb}$. The evolution of the difference of pressure and capacity between the hydrides and the deuterides versus R content is reported on Fig. 3. These differences change with R content: the difference in pressure decreases down to $y=0.3$ and increases for larger R content for the Er compounds whereas the opposite variation is observed for the Tb compounds. The differences in capacity show a negative variation compared to the corresponding pressures.

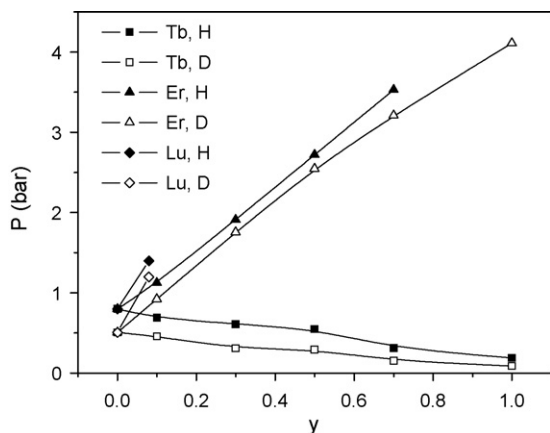


Fig. 2. Evolution of the plateau pressure at 298 K versus the R content.

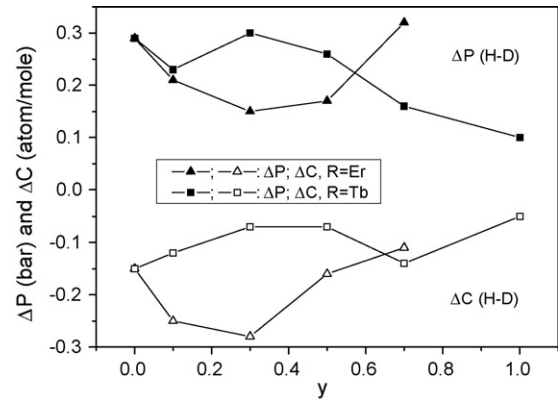


Fig. 3. Evolution of the difference in pressure and capacity between the hydrides and the deuterides versus the R content ($\text{R}=\text{Tb}, \text{Er}$).

These thermodynamic isotope effects are in agreement with those observed by Flanagan for the $\text{ErFe}_2\text{H}(\text{D})_x$ system which were measured for $x \leq 3.2$ and temperature between 273 and 403 K [13]. At room temperature the plateau pressures of the hydrides are larger than for the deuterides whereas the capacities are smaller. As the temperature increases the isotope effect decreases and disappears between 300 and 400 K depending of the x content. This has been explained with a simple model of localized oscillators for the dissolved hydrogen [13].

3.2. Structural results

All the $(\text{Y}_{1-y}\text{R}_y)\text{Fe}_2$ intermetallics crystallize in the cubic C15 structure ($Fd-3m$ space group) except TbFe_2 which displays a small rhombohedral distortion due to its magnetostrictive properties [14,15]. The cell volumes (V_{int}) follow Vegard's law, characteristic of solid solution behavior.

For all series the V_{int} decrease the faster the smaller the substituted element ($\Delta V/\Delta y = -2.12(15) \text{ \AA}^3$ for Tb, $-12.64(16) \text{ \AA}^3$ for Er and $-20.22(94) \text{ \AA}^3$ for Lu).

The corresponding γ hydrides and deuterides crystallize in a monoclinic structure (C2/m space group) which has been described in ref. [7] for $\text{YFe}_2\text{D}_{4.2}$. Their cell volume (V_{H} and V_{D}) variation versus R content is reported in Fig. 4. For Lu

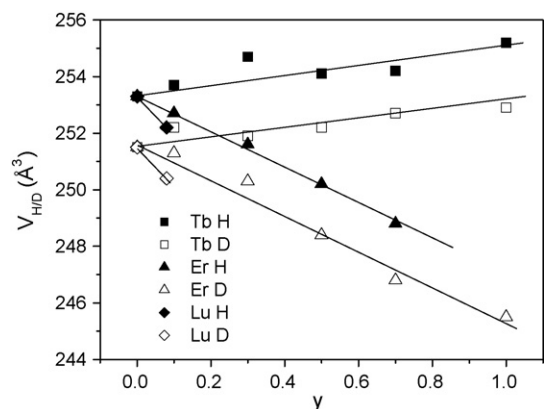


Fig. 4. Cell volumes of $\text{Y}_{1-y}\text{R}_y\text{Fe}_2$ hydrides (H) and deuterides (D) in the γ phase.

compounds, the γ phase was obtained only for the smallest Lu content ($y=0.08$), since the equilibrium pressures were too high to stabilize this phase for $y \geq 0.4$. The a , b and c monoclinic cell parameters follow also the same variation as the volumes, whereas the monoclinic angle β is almost the same ($122.4 \pm 0.2^\circ$) for all compounds.

4. Discussion

The cell volumes of the hydrides are about 1.7 \AA^3 larger than those of the corresponding deuterides. These volume differences cannot be related to a difference in capacity, since the deuterides have a larger capacity than the corresponding hydrides. Therefore, this difference should be rather attributed to the difference of the zero point amplitude of vibration of the H and D atoms which is larger for H atoms due to their smaller mass [8,16]. This means that the interstitial sites containing H atoms are more expanded than those containing D atoms and lead to a larger cell volume. The Fig. 4 also reveals that the V_H and V_D of the Tb substituted compounds both increase with y , whereas they decrease for the Er and Lu compounds. The behavior of the Tb compounds is rather surprising since the corresponding V_{int} slightly decreases with y . In addition, if the decrease of V_H and V_D for the Er and Lu compounds follows qualitatively the variation of the corresponding V_{int} , the slopes are smaller than expected for a constant cell volume enlargement by H or D atoms.

In order to explain the variation of V_H and V_D versus y for the Tb substituted compounds, it is necessary to consider that the

relative yttrium positions along a lanthanide series can change depending of the covalence of the bonding with its neighbor atoms. Siekerski [17] has calculated, with the aid of the unit cell volume, the atomic number of Y relative to that of 4f lanthanides ($Z_Y(V)$) from 52 different series of isostructural compounds taken from the literature. $Z_Y(V)$ varies from 64 for Ln metals to 67.7 for LnF_3 . Applying this method to calculate the relative position of Y in the RFe_2 compounds and in the γ deuterides we have found $Z_Y(V) = 64.4(2)$ for the intermetallics and $65.7(2)$ for the deuterides. These results are in good agreement with those obtained for RCO_2 compounds (64.6) and RH_3 compounds (65.7) [17]. This means that Y is located between Gd and Tb in the intermetallics and Tb and Dy in the deuterides. Using the $Z_Y(V)$ value calculated for the deuterides, it is possible to determine a corrected YFe_2 volume of 394.4 \AA^3 which is smaller than the experimental one of YFe_2 (398.8 \AA^3) and TbFe_2 (396.11 \AA^3). Using this new volume to calculate the corrected cell volume ($V_{\text{int-corr.}}$) variation of the $\text{Y}_{1-y}\text{R}_y\text{Fe}_2$ compounds, leads to a better agreement with the V_H and V_D variation (Figs. 4 and 5). The calculated new slopes for $V_{\text{int-corr.}}$ ($\Delta V/\Delta y = 1.19(1) \text{ \AA}^3$ for Tb, $-8.49(3) \text{ \AA}^3$ for Er and $-17.1(5) \text{ \AA}^3$ for Lu) are closer to those of the corresponding deuterides ($\Delta V/\Delta y = 1.68(5) \text{ \AA}^3$ for Tb, $-6.24(2) \text{ \AA}^3$ for Er and $-14.11(9) \text{ \AA}^3$ for Lu) than those of V_{int} .

This assumption concerning the change of the relative position of Y atoms upon H or D absorption is also useful to explain the evolution of the plateau pressure between the β and γ phases

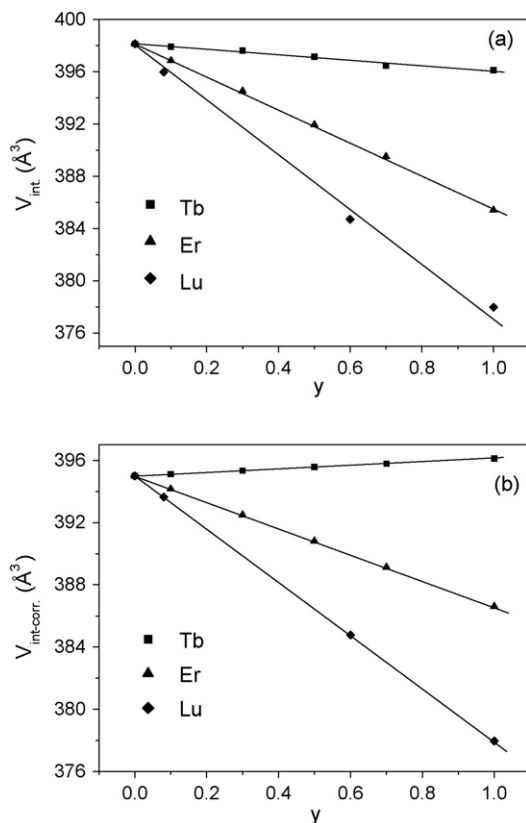


Fig. 5. (a) experimental and (b) corrected cell volumes for the $\text{Y}_{1-y}\text{R}_y\text{Fe}_2$ intermetallics (see text).

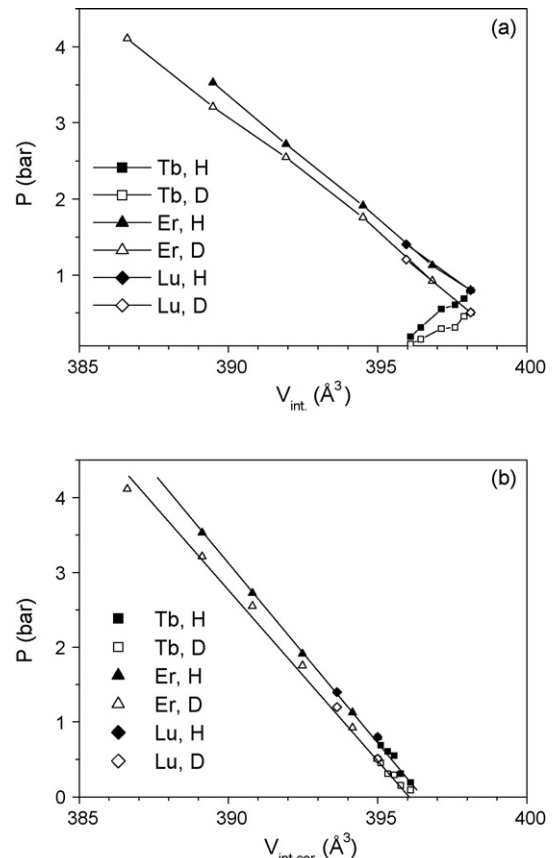


Fig. 6. Plateau pressure vs. V_{int} . (a) and $V_{\text{int-corr.}}$ with $V_{\text{YFe}_2} = 395 \text{ \AA}^3$. (b).

of the $Y_{1-y}R_yFe_2$ hydrides and deuterides at 298 K. On Fig. 6a, these plateau pressures are reported *versus* the corresponding V_{int} . The pressure decrease observed for the R = Er and Lu compounds is in agreement with the geometric rule which assumes that the stability of an hydride increases with the volume of the parent intermetallic [18]. However, an opposite behavior is observed for the Tb substituted compounds, since their plateau pressures increase with V_{int} . Using a $V_{int-corr.}$ of 395 \AA^3 for YFe_2 to calculate new volumes for the pseudobinary intermetallics, allows obtaining a linear decrease of the plateau pressure *versus* cell volume for all the $Y_{1-y}R_yFe_2$ deuterides whatever the R element ($\Delta P/\Delta V = -0.44(1) \text{ bar/\AA}^3$) (Fig. 6b). In addition the plateau pressures of the hydrides decrease also linearly *versus* $V_{int-corr.}$ with a slightly larger slope ($\Delta P/\Delta V = -0.47(1) \text{ bar/\AA}^3$). The $V_{int-corr.}$ of 395 \AA^3 , is slightly larger than that calculated by the interpolation between the $RFe_2D_{x(\gamma)}$ deuterides (R = Tb and Er) and corresponds to $Z_Y(V) = 65.5$. This difference can be either attributed to the experimental error on the $Z_Y(V)$ calculation, which was done using only two experimental data points, or to the fact that for the β phase the relative change of cell volume for Y is smaller than for the γ phase due to a smaller D content. The relationship between plateau pressures and cell volumes has been extensively studied in $LaNi_{5-y}M_y$ compounds (M = Al, Si, Mn, Fe, Co, Cu) [19]. It was generally observed that $Ln(P)$ decreases linearly with V_{int} for a given temperature. In the present study the plateau pressure of the γ phase is related to $V_{int-corr.}$ In most of the $LaNi_{5-y}M_y$ compounds there is only one plateau and the hydride is in equilibrium with the α phase, which contains only a small amount of hydrogen. The relative volume of the M atoms compared to the Ni atoms should therefore not be affected by hydrogen absorption. On the contrary, in the $Y_{1-y}R_yFe_2$ compounds the γ phase is in equilibrium with a β phase which contains already about 3.5 H(D) atoms/mol and in addition the relative Y volume is sensitive to a change of the covalence of the bonding.

5. Conclusion

The D for H substitution in $Y_{1-y}R_yFe_2$ deuterides leads to a lowering of the $\beta \rightarrow \gamma$ plateau pressure, an increase of the

γ phase capacity and an expansion of the cell volume, which was attributed to the difference in the zero point amplitude of vibration of H and D atoms in the matrix. In addition, the Tb for Y substitution was found to have an opposite effect compared to the Er and Lu substitution: a decrease of the plateau pressure *versus* y and V_{int} , and an increase of V_H and V_D *versus* y . This anomalous behavior has been attributed to a change of the relative position of Y in the 4f lanthanide series upon H(D) absorption which modifies the covalence of the bonding.

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