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Synthesis of novel deuterides in several Laves phases by using gaseous deuterium under high pressure

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Abstract

New deuterides of Laves phases: ErFe_2D_5 , YFe_2D_5 , $\text{ZrFe}_2\text{D}_{3.5}$ and ZrCo_2D_2 , have been obtained by using of gaseous deuterium at high pressure. A new orthorhombic structure was found for ErFe_2D_5 and YFe_2D_5 , while $\text{ZrFe}_2\text{D}_{3.5}$ and ZrCo_2D_2 were formed with a large expansion of the initial C15 cubic lattice. Formation of hydrides with high hydrogen concentration substantially changes the magnetic properties of ErFe_2 and YFe_2 but has no significant influence on the magnetization of ZrFe_2 . The possibility of the formation of new deuterides (hydrides) in ZrCr_2 and YMn_2 has also been confirmed.

1. Introduction

During the last decade, hydrogen absorption and its influence on the structural, magnetic and electronic properties of Laves phase intermetallic compounds have been intensively studied (for example [1–3]). A large number of these intermetallics, especially those in which a rare-earth element is one of the components, have a high hydrogen absorption capacity even at pressures lower than 1 MPa. The zirconium-based intermetallics such as ZrV_2 , ZrCr_2 and ZrMn_2 show a similar behaviour but ZrCo_2 and ZrFe_2 [4] behave differently.

The application of high hydrogen (deuterium) pressure in research on hydrogen absorption in Laves phases seems interesting for several reasons:

- The possible formation of hydride phases in systems (such as ZrCo_2 or ZrFe_2) which under low-pressure conditions (at low hydrogen fugacities) do not absorb hydrogen in amounts sufficient for hydride phase formation. Results of our preliminary experiments confirmed the formation of hydrides in ZrFe_2 and ZrCo_2 [5] at a suitable hydrogen pressure.

- The possible formation of new hydrides with higher hydrogen content in systems for which the hydrides containing as many as four H atoms per formula unit are already known. For instance, Shashikala *et al* [6] have reported that ErFe_2 at high hydrogen pressure can form an orthorhombic hydride containing up to five H atoms per formula unit.
- The role of pressure is not yet clear in such processes as hydrogen-induced amorphization (HIA) and hydrogen-induced decomposition (HID); the appropriate application of pressure can control amorphization or decomposition of hydrides formed in intermetallic compounds.

In recently performed high-pressure experiments we succeed in synthesizing the new orthorhombic phases ErFe_2D_5 and YFe_2H_5 [7]. This encouraged us to extend our studies to other systems.

2. Experimental details

The samples were prepared by induction melting of the appropriate amounts of metals under vacuum or in an argon atmosphere. The quality of the samples was checked by XRD and microprobe analysis. Samples were located in a high-pressure apparatus described elsewhere [8] and treated at 100 °C in vacuum before the hydrogen charging. Without this treatment the hydrogen absorption in all Laves phases investigated was very small in spite of the high hydrogen (deuterium) pressure applied. It seems that the surface phenomena related to the presence of thin water layers on the metallic planes are responsible for the reduction of hydrogen penetration into the metal bulk. Therefore the vacuum pretreatment followed by exposure to high hydrogen pressure is crucial for obtaining new hydrides in Laves phases.

The hydrogenation was usually performed at pressures up to 1.7 GPa and temperatures not exceeding 150 °C. The exposure of samples to given hydrogen pressure and temperature conditions ranged from several hours to more than one month. In order to avoid possible hydrogen desorption the apparatus was cooled down to minus 60 °C, then the pressure was reduced to the atmospheric value, and samples were discharged and immediately placed in liquid nitrogen where they were stored for further investigations.

The XRD measurements were performed at room temperature by using a D8 Brucker diffractometer between 10° and 120°2 θ in steps of 0.02° (Cu K α wavelength). It was proved that with the exception of ZrCo_2D_2 no samples decomposed during the time of the diffraction measurement. The magnetic measurements were performed on a DSM8 magnetosusceptometer with applied fields up to 1.6 T. The magnetization was measured as a function of temperature (from 4.2 to 300 K) with an applied field of 1 T. Measurements at temperature higher than 300 K could not be made due to the desorption of hydrogen from the sample.

3. Results and discussion

At 1.1 GPa deuterium pressure and 373 K temperature conditions the new hydrides ErFe_2D_x , YFe_2D_x , ZrFe_2D_4 and ZrCo_2D_2 were synthesized.

However, ZrFe_2 transforms into deuteride even at 0.33 GPa. The diffraction data are summarized in figure 1.

ErFe_2 and YFe_2 with a C15 cubic structure and cell parameters $a = 7.36$ and 7.28 Å respectively transformed into centred orthorhombic deuterides which could be described in the space group *Imm*2. Formation of deuterides in ZrFe_2 and ZrCo_2 does not change the symmetry of the cubic C15 structure but is accompanied by a large increase of the lattice constant (8% for $\text{ZrFe}_2\text{D}_{3.5}$ and 4.5% for ZrCo_2D_2). Also, in the case of hexagonal ZrCr_2

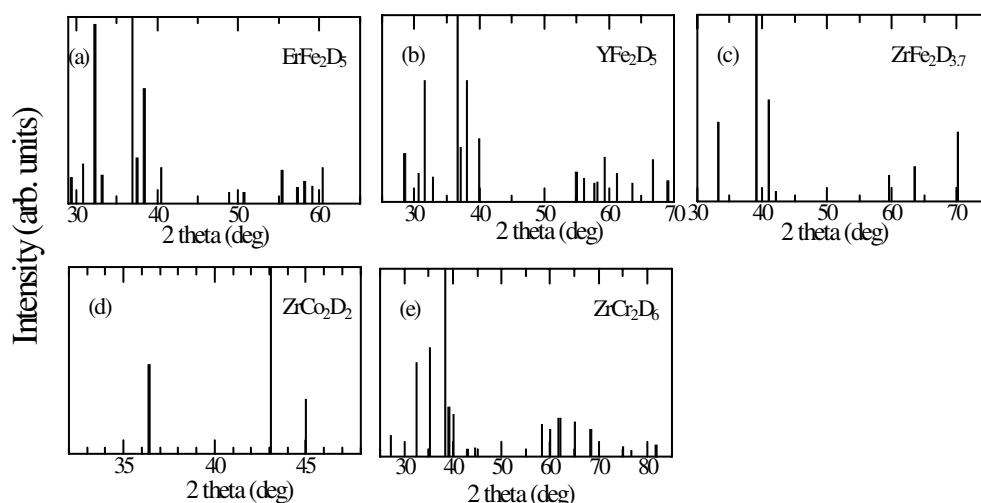


Figure 1. X-ray diffraction patterns of the new Laves phase deuterides.

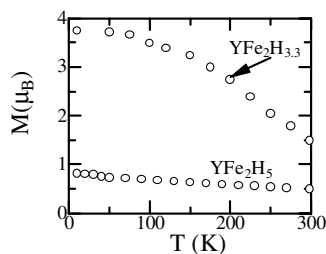


Figure 2. The temperature-dependent magnetization of $\text{YFe}_2\text{H}_{3.3}$ and YFe_2H_5 .

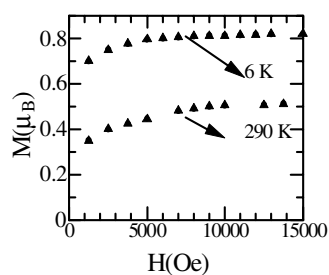


Figure 3. Magnetization versus field for YFe_2H_5 at 6 and 290 K.

the transformation into ZrCr_2D_6 occurs with a large expansion of the lattice (7.7% for a and 8.46% for c) but its crystal structure remains unchanged. We also found a new hydride in the YMn_2 Laves phase. According to chemical analysis the concentration of hydrogen corresponds to the formula $\text{YMn}_2\text{H}_{6.4}$. The properties of this hydride are currently under investigation.

The magnetic properties of YFe_2H_5 and $\text{ZrFe}_2\text{D}_{3.5}$ are shown in figures 2–4.

The saturation magnetization M_s of YFe_2 initially increases with hydrogen (deuterium) content and reaches a maximum value at 3.3 H/fu [9]. The sharp decrease of M_s observed at 5 H/fu can be attributed to a reduction or to a non-collinear orientation of the Fe moments.

The magnetization of $\text{ZrFe}_2\text{D}_{3.5}$ does not differ much from that of deuterium-free material (figure 4). At 4.5 K, the deuteride displays a moment of $1.88 \mu_B/\text{Fe}$ compared to $1.78 \mu_B/\text{Fe}$ for ZrFe_2 . At 290 K, the magnetic moments are $1.7 \mu_B/\text{Fe}$ for both ZrFe_2 and $\text{ZrFe}_2\text{D}_{3.5}$. This

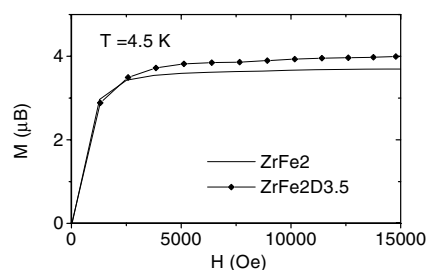


Figure 4. Magnetization versus field for ZrFe₂ and ZrFe₂D_{3.5}.

development is similar to that for YFe₂ hydride up to 3.5 H/fu where an increase of the saturation magnetization at 4.5 K but a decrease of T_c was observed [9]. However, at higher hydrogen concentration orthorhombic YFe₂D₅ shows a weak ferromagnetic behaviour almost independent of temperature [7]; on the other hand, ErFe₂H₅ is weakly ferromagnetic at high temperature but sharply increases its magnetization below 20 K due to magnetic ordering of erbium.

4. Conclusions

High pressure of gaseous deuterium (hydrogen) was successfully applied to synthesize new deuterides (hydrides). Exposure of RFe₂ (R = Y, Er, Mn) or ZrT₂ (where T = Fe, Co, Cr) to gaseous deuterium (hydrogen) at 1.1 GPa pressure leads to the formation of new deuterides (hydrides). YFe₂ and ErFe₂ deuterides (with >5 D/fu) have orthorhombic structure of space group *Imm2* with two different R and Fe sites. The deuterium (hydrogen) concentration corresponding to formula RFe₂D₅ can be reached when all types of A2B2, AB3 and B4 interstitial site are occupied. All three ZrT₂ deuterides investigated were formed without change of the crystal structure but with a large increase of the lattice parameters.

In contrast to the case for ErFe₂D₅ and YFe₂D₅ deuterides, where a strong reduction of the bulk magnetization at room temperature was observed, the formation of the deuteride phase in ZrFe₂ (with 3.5 D/fu) only slightly influences the magnetic properties.

The YMn₂H_{6.4} phase was also synthesized under high hydrogen pressure. This phase seems to have a different structure from those which were so far found in the YMn₂-H system. Detailed data on its structural and magnetic properties will be published elsewhere.

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