ELSEVIER

Journal of Alloys and Compounds 356–357 (2003) 32–35

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Pressure induced phase transitions and EOS of several Laves phase hydrides

H. Sugiura[a], I. Marchuk[b], V. Paul-Boncour[c], A. Percheron-Guégan[c], T. Kitazawa[d,1], S.M. Filipek[b,]*

[a]Graduate School of Integrated Science, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236-0027, Japan
[b]Institute of Phys. Chem., Polish Academy of Science, 01-224 Warsaw, Poland
[c]LCMTR, CNRS, 2–8 Rue H. Dunant, 94320 Thiais, France
[d]Toho University Faculty of Science, Funabashi, Chiba 274, Japan

Received 24 September 2002; accepted 15 November 2002

Abstract

Two C15 Laves phases YFe_2, $ErFe_2$ and their hydrides $YFe_2H_{5.6}$ and $ErFe_2H_{5.6}$ were compressed up to 31 GPa by using a diamond anvil cell. Pressure induced phase transitions were found in both $YFe_2H_{5.6}$ and $ErFe_2H_{5.6}$. Parameters of equation of state were derived for all the phases investigated.

Keywords: Intermetallics; Hydrogen storage materials; Crystal structure and symmetry; X-Ray diffraction

1. Introduction

The Laves phase intermetallics and their hydrides belong to the most investigated systems. Among others their structural and magnetic properties are very interesting. For several AB_2 Laves phases (A=rare earth, Y or Zr and B=transition element), the partial substitution in the B position, like in ZrB_2 alloys, may change the symmetry from C14 to C15 [1]. More complicated structural changes occur during hydrogen absorption in Laves phases. Besides the increase of lattice parameter the distortion of the crystalline lattice and phase transformation have been observed in many cases. Further interesting phenomena, including phase transformation, are expected to occur under high pressures. New data obtained in this way should enlarge our understanding of complicated behaviors of hydrogen in metallic lattices. However, surprisingly, studies of Laves phase hydrides using high pressures are very few.

Recently we succeeded [2–4] in the synthesis of novel hydrides with high H/Me ratios in such intermetallics as $ErFe_2$, YFe_2, YMn_2, $ZrFe_2$ and $ZrCo_2$. The systematic study of these intermetallics and their hydrides by using high hydrostatic pressure has been started. In this paper we report the equations of state (EOSs) for cubic $ErFe_2$, YFe_2 Laves phases and their orthorhombic hydrides $YFe_2H_{5.6}$ and $ErFe_2H_{5.6}$. Pressure-induced phase transformations have been found in both hydrides.

2. Experimental

Synthesis and characterization of YFe_2, $ErFe_2$ and hydrides $YFe_2H_{5.6}$ and $ErFe_2H_{5.6}$ were done as in Ref. [2]. Both hydrides contained the highest concentration of hydrogen available for these compounds. Powder samples were pressurized in a diamond anvil cell (DAC) with methanol and ethanol mixture as pressure transmitting medium. Experiments were carried out at 25 °C. The pressure was estimated by using a conventional ruby scale. Diffraction patterns were measured by an energy dispersive type X-ray diffraction system with a pure Ge detector. A tungsten tube operating at 47.5 kV and 27.5 mA was used as an X-ray source. The energy axis of energy spectrum and the fixed angle in diffraction were calibrated

---

*Corresponding author.

E-mail address: smf@ichf.edu.pl (S.M. Filipek).

[1] Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274-8510, Japan.

0925-8388/03/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0925-8388(03)00096-3

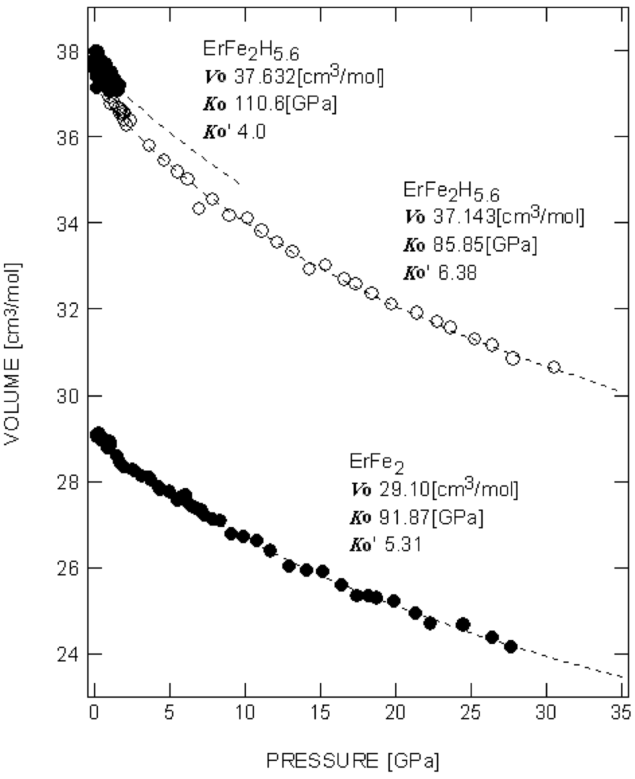

Fig. 1. Experimental and fitted equation of state of $ErFe_2$ and $ErFe_2H_{5.6}$.

by using fluorescence and diffraction lines from cubic InAs.

3. Results

3.1. $ErFe_2$ and YFe_2 intermetallic compounds

The initial C15 structures of these two intermetallics were stable at least up to 31 GPa. The volumes of both samples were determined by simplified profile fitting applicable for cubic phases. Their evolutions are presented in Figs. 1 and 4 and the EOS parameters are reported in Table 1.

3.2. $ErFe_2H_{5.6}$

The crystal structure of this hydride at ambient pressure is orthorhombic with space group *Imm*2 and the following lattice parameters: $a=0.5424$ nm, $b=0.5793$ nm, and $c=0.8009$ nm. The diffraction patterns of $ErFe_2H_{5.6}$ showed the orthorhombic *Imm*2 symmetry up to 1.69 GPa. A second phase crystallizing in the cubic C15 structure appears above 1.66 GPa. Above 1.69 GPa the diffraction pattern contained only the C15 phase. This transition was reversible since the orthorhombic phase was recovered when the pressure was reduced. The cell volume versus pressure of both phases is compared with that of $ErFe_2$ in Fig. 1. The EOS parameters obtained by a fit of the curves according to:

$$P=\frac{3}{2}\cdot K_0(x^{7/3}-x^{5/3})$$

$$\cdot\left[-\frac{3}{4}\cdot(4-K_0')\cdot(x^{2/3}-1)\right]\quad \text{with}\quad x=V_0/V$$

are given in Table 1. Concerning the low pressure orthorhombic phase the most compressible direction is along the *b*-axis while the *a* parameter is almost independent of pressure and *c* has an intermediate behavior. There is a small change in volume at the transition, $\Delta V=-0.6184$ cm^3/mol (-1.67%). The bulk moduli of the two phases at 1.7 GPa were 117 and 97 GPa for the low pressure orthorhombic phase and high pressure cubic phase, respectively.

3.3. $YFe_2H_{5.6}$

The crystal structure of $YFe_2H_{5.6}$ at ambient pressure is the same as that of $ErFe_2H_{5.6}$ with slightly larger lattice parameters: $a=0.5437$ nm, $b=0.5850$ nm, and $c=0.8083$ nm. Fig. 2 shows selected diffraction patterns registered in the low pressure region up to 2.58 GPa. Up to 1.5 GPa the patterns are indexed as the orthorhombic *Imm*2 structure with a monotonous decrease of the lattice parameters. The volume and lattice parameters of this phase were estimated by profile fitting by using *Imm*2 cell. Many peaks were overlaps of several diffraction lines. Among them, (112), (202), and (224) lines were almost independent peaks.

Table 1
Parameters of EOS for YFe_2, $ErFe_2$, $YFe_2H_{5.6}$ and $ErFe_2H_{5.6}$, where V_0, K_0 and K_0' correspond to the volume at $P=0$, the bulk modulus and its derivative, respectively

	Low pressure phase					High pressure phase				
	V_0 (cm^3/mol)	K_0 (GPa)	K_0'	*n*	Structure	V_0 (cm^3/mol)	K_0 (GPa)	K_0'	*n*	Structure
YFe_2	29.91	90.66	6.37	78	Cubic					
$YFe_2H_{5.6}$	39.63	99.89	4.0 fixed	52	Orth.	37.25	162.7	2.48	28	Orth.
$ErFe_2$	29.10	91.87	5.31	46	Cubic					
$ErFe_2H_{5.6}$	37.63	110.6	4.0 fixed	96	Orth.	37.14	85.85	6.38	24	Cubic

n is the total number of collected data, and Orth. means orthorhombic.

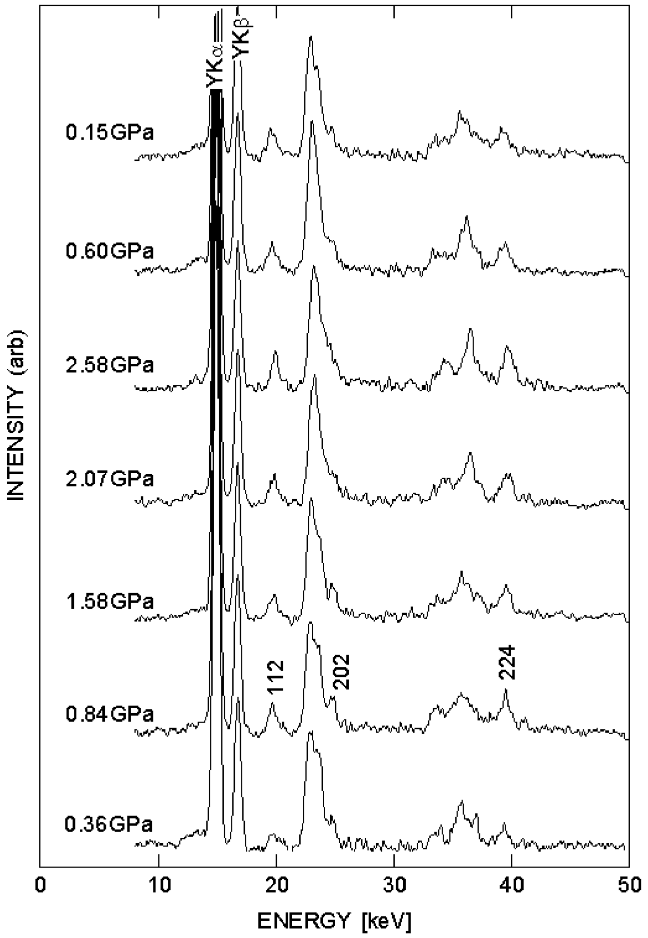

Fig. 2. Diffraction patterns of $YFe_2H_{5.6}$ observed at several pressures from 0.36 to 2.58 GPa and reduced to 0.15 GPa.

Clear observations of these peaks gave good results in profile fittings.

Above 1.5 GPa there was an anomaly in volume change and the line (202) became obscure at about 2GPa. Therefore it was supposed that initial orthorhombic *Imm*2 phase is stable up to 1.5 GPa. The pattern measured at 0.15 GPa after pressure reduction from 2.58 GPa did not differ from the initial pattern at $P=0$ indicating the reversibility of the transition. From 2 to 8 GPa the patterns show an intermediate phase or mixed phase.

Above 8 GPa up to 31.7 GPa the patterns can be refined with another orthorhombic cell in a *Pmm*2 space group. This cell as well as *Imm*2 cell can be derived from *Fd*3*m* cell of parent substance. Translation vectors were set as: $(1/2\boldsymbol{a}+1/2\boldsymbol{b},\ 1/2\boldsymbol{b}-1/2\boldsymbol{a},\ \boldsymbol{c})$ ($Z=4$, lattice parameters $1/\sqrt{2}a_0$, $1/\sqrt{2}a_0$, a_0) where $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ were the vectors in original cubic cell, a_0 was the size of them, and Z was number of formula in this cell. These are equal to those in low pressure *Imm*2 phase, but the body centered translations are lost at the transition.

The lattice parameters for both orthorhombic phases (orthorhombic a and b parameters are multiplied by $\sqrt{2}$ to compare with the cubic parameters) measured up to 31.7 GPa are presented in Fig. 3. Like $ErFe_2H_{5.6}$ the most compressible direction in *Imm*2 phase is along the b-axis. The cell volume and the resultant EOS curve are compared with those of YFe_2 in Fig. 4. The EOS parameters are given in Table 1.

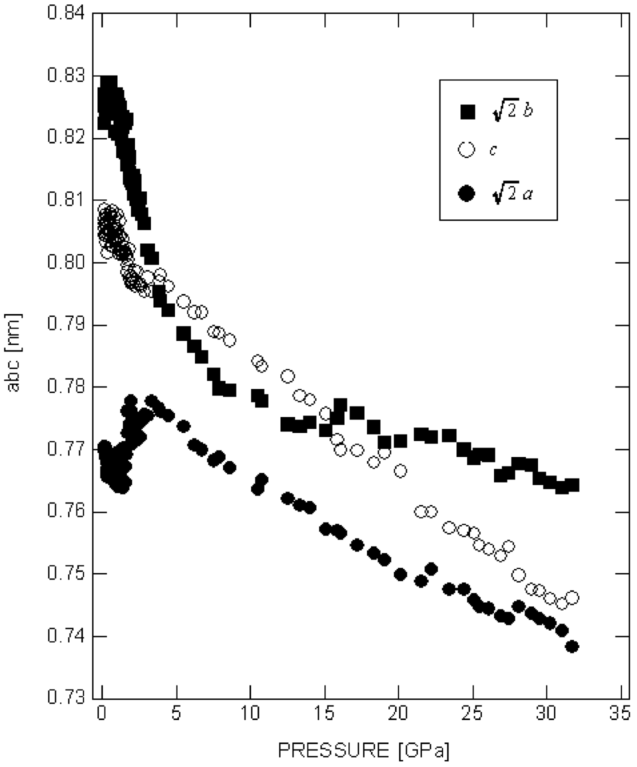

Fig. 3. Evolution of the lattice parameters of $YFe_2H_{5.6}$ in *Imm*2 and *Pmm*2 structure versus pressure.

4. Discussion and conclusion

The structural properties of YFe_2-H/D and $ErFe_2$-H/D systems are quite similar. YFe_2 and $ErFe_2$ crystallize in the same cubic C15 structure and their molar volumes are only slightly different (29.91 and 29.10 cm^3/mol, respectively). Moreover, the hydride or deuteride phases corresponding to the largest (H, D) content (about 5.6 H/f.u.), have the same orthorhombic structure. Therefore, it could be anticipated that changes in volume with compression would also be similar. In fact the measured bulk moduli for YFe_2 and $ErFe_2$ are 90.66 and 91.87 GPa, respectively. Their volumes decrease monotonously with pressure and the initial C15 structure remains unchanged up to the highest pressure available in our experiment (31 GPa). The crystal structure of $ErFe_2H_{5.6}$ and $YFe_2H_{5.6}$ at 0 GPa is orthorhombic *Imm*2. Although generally the bulk modulus tends to decrease upon hydrogen absorption in these systems, the bulk moduli of these two orthorhombic phases are larger than their parent intermetallics. This increase of the bulk

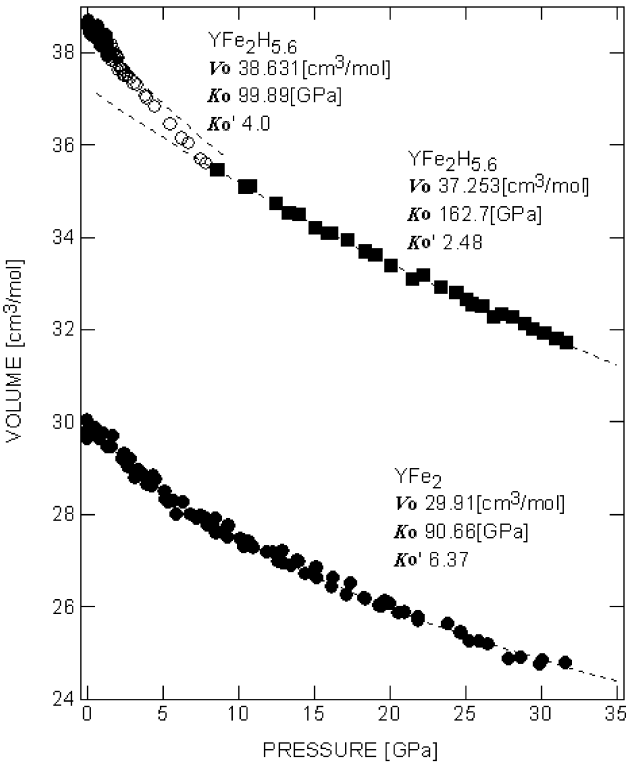

Fig. 4. Experimental and fitted equation of state of YFe_2 and $YFe_2H_{5.6}$.

modulus should be therefore rather related to the change of crystal symmetry.

The initial *Imm*2 phase of $ErFe_2H_{5.6}$ transforms reversibly into the cubic *Fd*3*m* phase near 1.7 GPa. This effect is not related to hydrogen desorption since the *Imm*2 phase appeared again when the pressure was released to the atmospheric value. Let us remark that addition of hydrogen to $ErFe_2H_4$ (cubic *Fd*3*m* symmetry [5]) results in forming orthorhombic *Imm*2 hydride $ErFe_2H_{5.6}$ with further increase of volume. Therefore the pressure-induced reversible *Imm*2⇒*Fd*3*m* transformation could be related to the stabilization of the cubic phase due to the shrinking of the interatomic distances. For $YFe_2H_{5.6}$ the situation is more complex since the orthorhombic *Imm*2 phase transformed reversibly at 1.5 GPa into an cubic intermediate phase and then in other orthorhombic phase above 8 GPa.

Both $ErFe_2$ and YFe_2 form different hydrides with various crystal structures. In these hydrides the lowering of the crystal symmetry with displacements of metallic atoms is related to the ordering of H or D atoms in preferential interstitial sites. The application of hydrostatic pressure might change the symmetry of the metallic lattice and in consequence the location of the sites occupied by H or D atoms. To understand more clearly the key parameters of these structural changes, the structural evolution versus applied pressure will be studied for the hydrides of $ErFe_2$ and YFe_2 with intermediate hydrogen content as well as for other Laves phases hydrides.

References

[1] D. Shaltiel, I. Jacob, D. Davidov, J. Less-Common Met. 53 (1977) 117.
[2] V. Paul-Boncour, S.M. Filipek, A. Percheron-Guégan, I. Marchuk, J. Pielaszek, J. Alloys Comp. 317–318 (2001) 83.
[3] S.M. Filipek, V. Paul-Boncour, A. Percheron-Guégan, I. Jacob, I. Marchuk, M. Dorogova, T. Hirata, Z. Kaszkur, J. Phys.: Condens. Matter. 14 (2002) 11261–11264.
[4] S.M. Filipek, I. Jacob, V. Paul-Boncour, A. Percheron-Guégan, I. Marchuk, D. Mogilyanski, J. Pielaszek, Polish J. Chem. 75 (2001) 1921.
[5] K. Shashikala, P. Raj, A. Sathyamoorthy, Mater. Res. Bull. 31 (1996) 957.