

High pressure synthesis and magnetic properties of Dy₇Rh₃ and Tb₇Rh₃ hydrides

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Abstract

Intermetallic compounds Tb₇Rh₃ and Dy₇Rh₃, which crystallize in Th₇Fe₃ type hexagonal structure with the space group *P6₃mc* were hydrogenated under high hydrogen pressure in order to study influence of hydrogen on their structural and magnetic properties.

Hydrogen treatment of Tb₇Rh₃ and Dy₇Rh₃ even at moderate pressures resulted in formation of hydrides with *H/M* > 2. The hydrides retained symmetry of parent materials but large lattice expansion has been observed. After release of hydrogen pressure the hydrides were stable and could be kept for long time at normal conditions. Hydrogenation affects strongly magnetic properties of both Tb₇Rh₃ and Dy₇Rh₃. Treatment at 100 °C up to 10 kbar (H₂) did not cause their amorphisation or decomposition.

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1. Introduction

The rare earth intermetallic compounds R₇M₃ (R = rare earth metal, M = transition metal) crystallize in the Th₇Fe₃-type hexagonal structure with R atoms located in three non-equivalent sites. According to Olcese [1] who investigated magnetic properties of R₇M₃, R can form R₇M₃ intermetallics with several metals excluding Fe, Ru, Os and Co. Series of R₇M₃ intermetallics can be formed with M = Rh, and magnetic properties of these compounds above 77 K were reported in his paper. Moreover, it has been found that some of R₇M₃ compounds form stable hydrides with high hydrogen to metal ratio (La₇Ni₃ can form La₇Ni₃H_{19.3} at room temperature and only 50 bar) [2]. It was also revealed that the magnetic properties of those R₇M₃ hydrides were substantially different from their parent intermetallic compounds [3].

The properties of R₇Rh₃ intermetallics have been investigated intensively by Tsutaoka [4,5]. However, to our knowledge there are no reports concerning the properties of R₇Rh₃ based

hydrides. In order to examine the hydrogen influence on magnetic and electric properties of these alloys we started systematic studies on R₇Rh₃-H₂ systems from synthesis and low temperature measurements of Tb₇Rh₃H_x and Dy₇Rh₃H_x.

2. Experimental

Polycrystalline samples of Tb₇Rh₃ and Dy₇Rh₃ were prepared by arc melting rhodium (99.96% purity) with terbium (99.9% purity) and dysprosium (99.9% purity), respectively, in high purity argon atmosphere. The ingots were turned over and remelted several times in order to improve their homogeneity. Both rectangular and spherical samples were cut from the ingots. Tb₇Rh₃ and Dy₇Rh₃ alloys prepared in this way were then annealed in an evacuated quartz tube at 600 °C for 50 h and 400 °C for 24 h, respectively. Hydrogenations of Tb₇Rh₃ and Dy₇Rh₃ were carried out up to 10 kbar at 25 °C and 100 °C in the high pressure apparatus described elsewhere [6]. In these conditions hydrides Tb₇Rh₃H₂₈, Tb₇Rh₃H₂₉, Dy₇Rh₃H₂₈ and Dy₇Rh₃H₃₀ were obtained. However the formation of hydrides occurred at much moderate pressure conditions. Let us remark that results obtained for both hydrogen and deuterium were not different. The concentrations of hydrogen were determined by gas chromatography method with ±0.1 H/Me accuracy. Crystal structures of Tb₇Rh₃, Dy₇Rh₃ and their hydrides/deuterides were analyzed by using X-ray D8 Bruker diffractometer. Magnetizations and magnetic susceptibilities were measured using a vibrating sample magnetometer in magnetic fields up to 17 kOe. Magnetic susceptibilities of Tb₇Rh₃ hydride and Dy₇Rh₃ hydride were measured at 11 kOe and 10 kOe, respectively, in wide temperature range.

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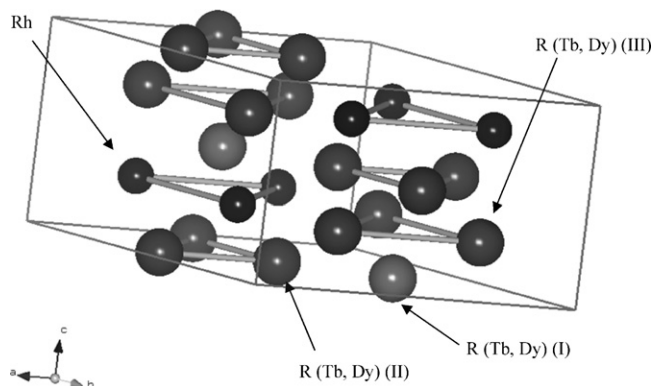


Fig. 1. Crystal structure of R_7Rh_3 intermetallics with Tb_7Fe_3 -type crystal structure ($P6_3mc$, hcp).

3. Results and discussions

The Tb_7Rh_3 , Dy_7Rh_3 and their hydrides/deuterides have Tb_7Fe_3 -type hexagonal structures (hcp) with $P6_3mc$ space group [1,7] in which the rare earth ions are situated in three non-equivalent crystallographic sites [8]. The positions of rare earth and rhodium atoms in crystal structure of Tb_7Rh_3 or Dy_7Rh_3 are shown in Fig. 1. The hydrogen/deuterium treatment of the Tb_7Rh_3 and Dy_7Rh_3 did not change the crystal structures but caused expansion of their crystal lattice manifested as a shift of peak positions towards lower angles as shown in Fig. 2. Tb_7Rh_3 and Dy_7Rh_3 absorbed large amount of hydrogen or deuterium even at low pressure of hydrogen/deuterium gas. After deuteration at 500 bar and 270 °C for 5 h the lattices of Tb_7Rh_3 and Dy_7Rh_3 expanded by 21.1% and 20.3%, respectively, forming deuterides stable at normal conditions.

Treatments conditions and properties of resulted compounds are collected in Table 1. In the pressures range investigated the lattice expansion did not depend on treatment conditions; at

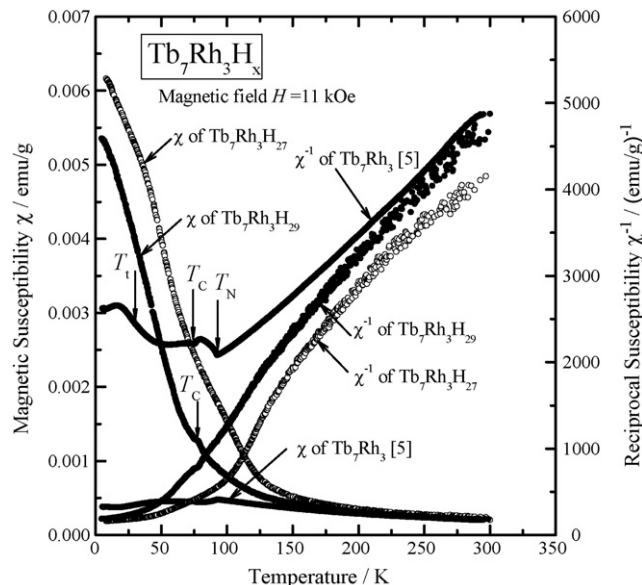


Fig. 3. Magnetic susceptibility χ and reciprocal susceptibility χ^{-1} of Tb_7Rh_3 [5], $Tb_7Rh_3H_{29}$ and $Tb_7Rh_3H_{27}$ as a function of temperature. T_C indicates the Curie temperature.

500 bar (H_2) and at 10 kbar (H_2) results were similar. This indicates that concentrations of hydrogen in synthesized hydrides do not depend much on hydrogen pressure used during hydrogenation/deuterization.

Comparison of magnetic susceptibilities measured at 11 kOe on Tb_7Rh_3 and Tb_7Rh_3 based hydrides is given in Fig. 3. At low temperature region the magnetic susceptibilities of hydrides are markedly higher than for the parent sample. The hydrogen-free Tb_7Rh_3 has shown re-entrant magnetic properties with antiferromagnetic, ferrimagnetic and another antiferromagnetic phase [4]. On the other hand, the Tb_7Rh_3 based hydrides exhibit

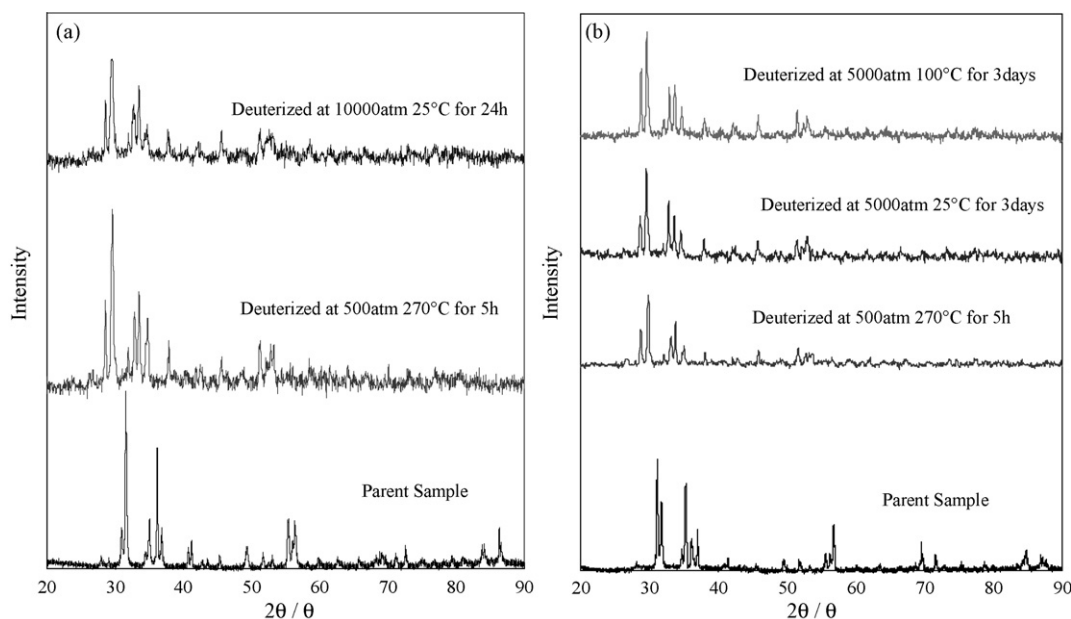


Fig. 2. XRD patterns of R_7Rh_3 and their deuterides: (a) Tb_7Rh_3 and (b) Dy_7Rh_3 .

Table 1
Data of Tb₇Rh₃ and Dy₇Rh₃ after different treatment by deuterium

Treatment conditions	Lattice parameter		Unit cell volume (Å ³)	Volume expansion (%)	D/metal ratio
	<i>a</i>	<i>c</i>			
Tb₇Rh₃					
Parent sample	9.767	6.14	507.3	0	0
500 bar (D ₂); 270 °C; 5 h	10.329	6.653	614.7	21.1	
10 kbar (D ₂); 25 °C; 1 day	10.338	6.65	615.5	21.3	27
Dy₇Rh₃					
Parent sample	9.749	6.107	502.7	0	0
500 bar (D ₂); 270 °C; 5 h	10.259	6.637	605	20.3	
5 kbar (D ₂); 25 °C; 3 days	10.369	6.627	617	22.7	
5 kbar (D ₂); 100 °C; 3 days	10.365	6.63	616.9	22.7	27

only ferromagnetic or ferrimagnetic ordering at low temperatures confirmed for Tb₇Rh₃H₂₇ where residual magnetizations with large hysteresis were observed at 4.2 K (Fig. 4). The ferromagnetic or ferrimagnetic ordering can be seen at 80 K while the Tb₇Rh₃ sample has the Curie temperature at 73 K [4]. The hydrides do not have meta-magnetic transitions in contrast to the parent sample in which such transition takes place at 35 K [4]. The residual magnetization of hydrides is relatively high and large hysteresis of magnetization curves is observed even at 75 K.

Fig. 5 shows magnetic susceptibilities of Dy₇Rh₃ and Dy₇Rh₃ based hydrides at magnetic field of 10 kOe. For the parent sample, Curie and Neel temperatures were found at 34 K and 56 K, respectively [5]. No such transitions were found for Dy₇Rh₃ hydrides due to the lack of discontinuities on their susceptibilities curves. The reciprocal magnetic susceptibilities of Dy₇Rh₃ hydride shows rather paramagnetic character at least between 30 K and 300 K. The change of magnetic properties upon hydrogenation can be related to both: increasing the distance between localized magnetic states and to changes in electronic structure due to hydrogen absorption (hydrogen atoms take positions in the interstitial lattice sites as protons while its electrons fill up the empty states moving Fermi level towards higher energy values). From Fig. 6, which shows magnetization curves of Dy₇Rh₃ at low temperature range, it is clear

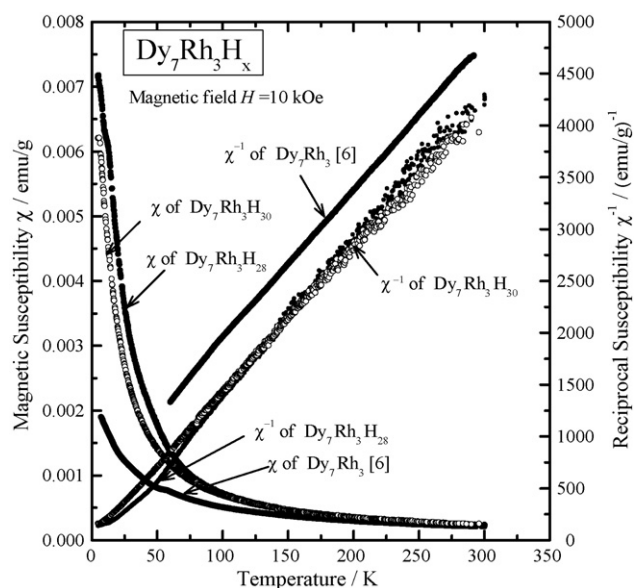


Fig. 5. Magnetic susceptibility χ and reciprocal susceptibility χ^{-1} of Dy₇Rh₃ [6], Dy₇Rh₃H₂₈ and Dy₇Rh₃H₃₀ as functions of temperature.

that residual magnetization appears near 30 K and increases with decreasing temperature. This suggests a magnetic transition into ferromagnetic or ferrimagnetic state which would exist below 30 K.

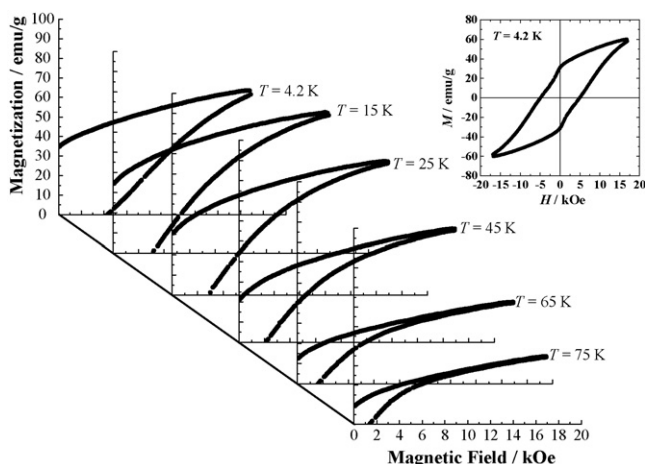


Fig. 4. Magnetization curves of Tb₇Rh₃H₂₇ at various temperatures.

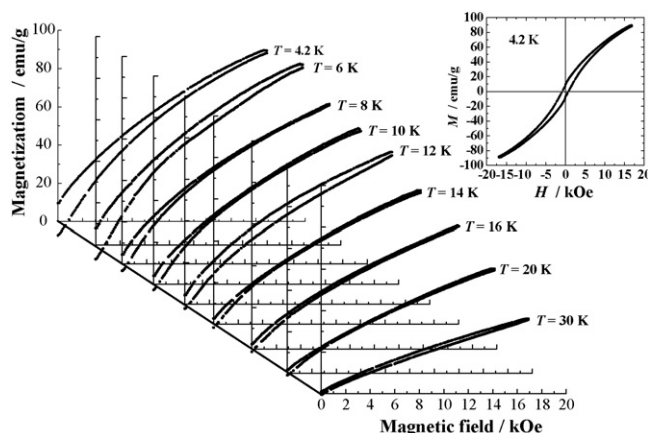


Fig. 6. Magnetization curves of Dy₇Rh₃H₃₀ at various temperatures.

4. Conclusion

Structural and magnetic properties of intermetallic compounds Tb_7Rh_3 and Dy_7Rh_3 treated with hydrogen/deuterium under pressure were studied. Both, Tb_7Rh_3 and Dy_7Rh_3 deuterides, maintained the same hexagonal structure as the parent samples, but a large volume expansion of unit cells was observed. Samples absorb hydrogen and form hydrides even at moderate hydrogen/deuterium pressure conditions. Magnetic properties of these hydrides were different from those of parent materials; magnetic anomalies were much weaker than in hydrogen-free alloys. This can be related to the change of interatomic distance and/or changes in the electronic structure of the alloy. For each hydride only one magnetic transition was observed leading to ferro- or ferri-magnetic ordering at 80 K (for Tb_7Rh_3 based hydride) or 30 K (for Dy_7Rh_3 based hydride). Magnetization curves of both, Tb_7Rh_3 and Dy_7Rh_3 hydrides showed a large residual magnetizations at low temperatures region. At 4.2 K both hydrides have ferromagnetic or ferrimagnetic ordered state.

The neutron diffraction and magnetic susceptibilities measurements at lower magnetic fields will be conducted in order to

determine the positions of hydrogen (deuterium) in crystalline lattice and for detailed description of the magnetic properties of hydrides. Other R_7M_3 -hydrogen systems are under investigations.

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