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Magnetic properties of intermetallic compound hydrides and deuterides

F. Ishikawa^a, I. Yamamoto^a, M. Yamaguchi^{a,*}, Y. Shimazu^a, T. Goto^b, H. Mitamura^b^aDepartment of Physics, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan^bInstitute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106-0032, Japan

Abstract

The magnetic properties of LaCo_5 hydrides and deuterides were investigated by (1) in situ magnetization at 77 K in 20 T which related magnetization with hydrogen/deuterium composition, and (2) high field magnetization at 4.2 K up to 44 T for well-characterized samples. The β -phase $\text{LaCo}_5\text{H(D)}_{3.4}$ is recognized as a saturated ferromagnet, like the metal phase LaCo_5 . The γ -phase $\text{LaCo}_5\text{H(D)}_{4.3}$ undergoes a metamagnetic transition from a low moment state to a high moment state at a critical field of 35 T (hydride) or 38 T (deuteride). These magnetic properties are discussed in relation to the electronic structure. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The absorption of hydrogen by intermetallic compounds of rare earth elements R and Co results in drastic changes in their magnetic properties [1,2]. Recently, the physical origins of such changes have been elucidated from in situ magnetization measurements, high or ultra-high magnetic field experiments and usage of single crystal hydrides, as satisfactorily shown for YCo_3H_x [3]. The compound LaCo_5 , known as a typical hydrogen-absorbing alloy, forms two types of hydride, the β -phase $\text{LaCo}_5\text{H}_{3.4}$ and the γ -phase $\text{LaCo}_5\text{H}_{4.3}$, under ordinary conditions [4]. The magnetization of LaCo_5H_x , obtained by low magnetic field experiments, decreases with increasing x , but ferromagnetism is maintained up to the γ -phase [5,6]. This magnetic behavior causes magnetic field effects on the equilibrium pressure and the equilibrium electrode potential [7].

The magnetic properties of the metal phase LaCo_5 and the β -phase $\text{LaCo}_5\text{H}_{3.4}$ were precisely investigated for single crystals [8]. Both phases are ferromagnets with the easy direction of the c -axis and the Curie temperature is lowered from 870 to 470 ± 40 K as a result of hydrogenation. However, the γ -phase $\text{LaCo}_5\text{H}_{4.3}$ has not been examined precisely because of its chemical instability due to high equilibrium pressures. In addition, the deuterium pressure required to form the γ -phase is significantly higher than that of hydrogen: the plateau pressure for the

β - γ region is 0.4 and 0.2 MPa at 296 K for the deuterium and hydrogen system, respectively. In this paper we report the magnetization of $\text{LaCo}_5\text{H(D)}_x$ by an in situ method and high magnetic field experiment. We then discuss the hydrogen(deuterium)-induced changes in the magnetic properties and the electronic structure in connection with related RCo_5 compounds and hydrides.

2. Experiments

The LaCo_5 sample was prepared by arc-melting the constituent metals (99.9% purity La and 99.99% purity Co) under pure argon atmosphere. The ingot was then annealed at 1220 K for 24 h for homogenization. Powder X-ray diffraction showed the sample was single phase with the CaCu_5 -type structure.

Firstly, the magnetization of $\text{LaCo}_5\text{H(D)}_x$ was observed at 77 K by the in situ method reported previously [9] in order to determine the relationship between the magnetization and the hydrogen/deuterium composition. The sample holder was connected to PCT equipment with which the hydrogen composition was controlled. We applied pulsed magnetic fields with a rising time of 3 ms up to 20 T, which is larger than the anisotropy field of LaCo_5H_x . Every magnetization curve indicated saturation below 20 T. We plotted the magnetization at 20 T as a function of hydrogen/deuterium composition (Fig. 1). As the composition increases, the magnetization gradually decreases between the metal phase and the β -phase, but abruptly between the β -phase and the γ -phase. This

*Corresponding author. Tel.: +81-45-339-4149; fax: +81-45-338-1157.

E-mail address: yamaguch@dnj.ynu.ac.jp (M. Yamaguchi)

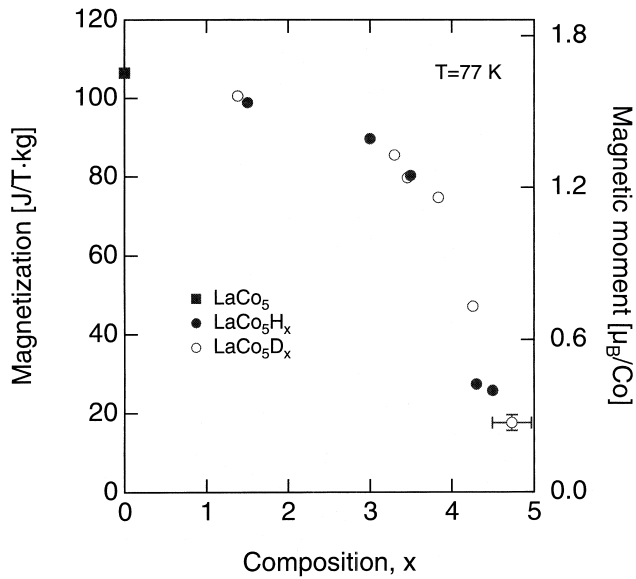


Fig. 1. Magnetization vs. hydrogen/deuterium composition at 77 K for LaCo_5H_x and LaCo_5D_x .

behavior agrees with a previous result obtained in low magnetic fields [6]. No clear differences in the magnetization were observed between the hydrogen and deuterium systems within the experimental accuracy.

Secondly, the high field magnetization was measured at 4.2 K for $\text{LaCo}_5\text{H}(\text{D})_x$. These samples were prepared in glass capsules by the following process. We introduced the samples into cylindrical glass capsules (15 mm long \times 2 mm inner diameter) with glass wool and a glass rod in order to prevent the movement of the sample by strong pulsed fields. After the samples reacted with hydrogen or deuterium at room temperature, the glass capsules were sealed. The hydrogen/deuterium composition was checked by measuring the magnetization at 77 K and comparing with the result in Fig. 1. The magnetization was measured by an induction method in pulsed fields up to 44 T with a rising time of 5 ms. In both the first and the second experiment, the accuracy of the hydrogen composition was $\pm 5\%$ and that of the magnetization was $\pm 2\%$.

Fig. 2 illustrates the high field magnetization curves at 4.2 K for LaCo_5H_x and LaCo_5D_x . For the metal and β -phases, the high curvature in lower fields was due to magnetic anisotropy [8]. It is notable that the magnetization of the β -phase is completely saturated in fields higher than 20 T. There are no intrinsic differences in the magnetic properties between the β -hydride and deuteride, although their magnetization curves deviate slightly from each other, which is likely caused by a small difference in hydrogen/deuterium composition. The magnetic moment was derived by extrapolating the magnetization from higher fields to zero field, as shown in Table 1.

The γ -hydride and deuteride have a much smaller magnetization than the metal and β -phases. Both the γ -hydride and deuteride show metamagnetic transitions at

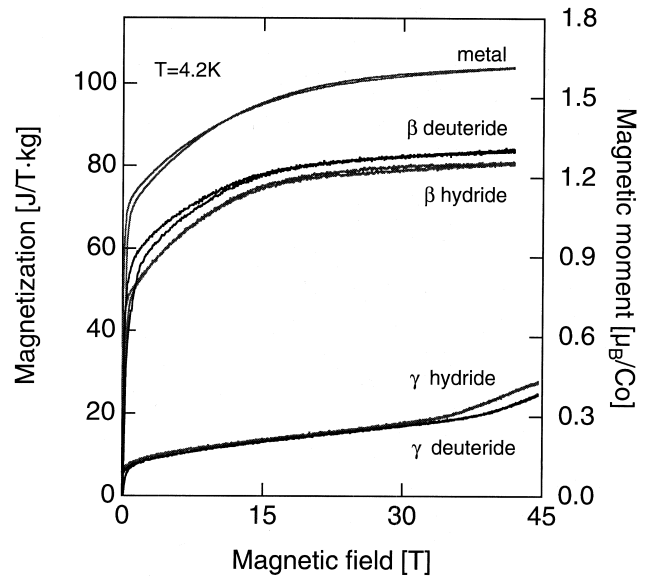


Fig. 2. High field magnetization curves at 4.2 K for LaCo_5H_x and LaCo_5D_x .

critical fields: $B_c = 35$ T for the hydride and $B_c = 38$ T for the deuteride, where the critical field is defined as the onset point. The same results for the critical fields were obtained when other samples were tested, as shown in Fig. 3. Accordingly, the difference between the critical fields must be a real isotope effect, and not due to the discrepancy in the composition. It is noteworthy that all hydrides show equal magnetization at the critical field. It is very rare that an isotope effect appears in the magnetic properties. To our knowledge one other example is that the Curie temperature is 174 K for UH_3 and 172 K for UD_3 [10].

3. Discussion

The compound LaCo_5 is a saturated ferromagnet like other RCO_5 compounds, in which the Co moment is $1.5 \mu_B$ or larger [11]. In a saturated ferromagnet, the majority spin band is fully occupied by electrons, that is, the Fermi level is located at the top of the majority spin band, and only the minority spin band has empty states [3]. Judging from the fact that the magnetization of the β -phase is completely saturated above 20 T, this phase is recognized as a saturated ferromagnet like LaCo_5 . The magnetic moment is reduced from $1.53 \mu_B/\text{Co}$ in the metal phase to $1.21 \mu_B/\text{Co}$ in the β -phase. This decrease in the moment is caused by the increase in electron population of the 3d band, assuming that the density-of-states (DOS) curve is rigid for the 3d band. That is, some electrons originating from hydrogen atoms fill the empty states above the Fermi level in the minority spin band: the $0.32 \mu_B/\text{Co}$ decrease in the magnetic moment from LaCo_5 to $\text{LaCo}_5\text{H}_{3,4}$ means that 47% of the electrons from hydrogen atoms occupy the minority states accompanied by a rise of the Fermi level in

Table 1
Magnetic data for LaCo_5 and its hydrides and deuterides

Compound	M (4.2 K) ($\text{J T}^{-1} \text{kg}^{-1}$)	μ (μ_{B}/Co)	T_{c} (K)	B_{c} (T)	Magnetic state ^a
LaCo_5	98.3	1.53	870		SF
$\text{LaCo}_5\text{H}_{3.4}$	77.9	1.21	470 ± 40		SF
$\text{LaCo}_5\text{D}_{3.4}$	78.8	1.22			SF
$\text{LaCo}_5\text{H}_{4.3}$	9.9	0.15		35	WF or ferri
$\text{LaCo}_5\text{D}_{4.3}$	9.4	0.14		38	WF or ferri

^a SF, saturated ferromagnet; WF, weak ferromagnet; ferri, ferrimagnet.

the DOS curve. The remaining 53% of electrons must be contained in the metal–hydrogen bonding band which is located in the energy region lower than the 3d band. This kind of model successfully explained the magnetic properties for the YCo_3H_x system in which 10 and 90% of the electrons from hydrogen atoms enter into the 3d band and the bonding band, respectively, while the upper part of the 3d band is rigid against hydrogenation [3].

Hence, we apply the present model to related RCo_5 compounds and their β -phase hydrides RCo_5H . The decrease in Co moment is reported to be $1.55 \rightarrow 1.25 \mu_{\text{B}}$ for $\text{YCo}_5 \rightarrow \text{YCo}_5\text{H}_{2.8}$ and $1.74 \rightarrow 1.49 \mu_{\text{B}}$ for $\text{GdCo}_5 \rightarrow \text{GdCo}_5\text{H}_{2.8}$ [12]. Accordingly, 54% (the Y system) or 47% (the Gd system) of electrons from hydrogen atoms occupy the upper part of the 3d band, raising the Fermi level. In the hydrides RCo_5H_x ($\text{R}=\text{La}, \text{Gd}, \text{Y}$), on average about half of the electrons from hydrogen atoms occupy the 3d states above the Fermi level of the metal phase. Such a rise of the Fermi level in the 3d band occurs in the case from LaNi_5 to LaNi_5H_7 , as indicated by the band calculation [13]. Fig. 4 shows the dependence of the

Co moment on the electron population in the 3d band assuming the upper part of the 3d band is rigid against hydrogenation. In the same figure we plot the Ni concentration dependence of the 3d moment for the $\text{Y}(\text{Co},\text{Ni})_5$ system obtained experimentally and theoretically [14]: as the electron population increases, the 3d moment decreases linearly; nevertheless, the saturated ferromagnetic state is maintained up to 60% Ni. It is understood that the metal and β -phases are saturated ferromagnets.

There are two possible mechanisms for the metamagnetic transition observed in the γ -phase: one is itinerant electron metamagnetism from a weak ferromagnetic state to a stronger ferromagnetic state due to field-forced separation between the spin subbands. The other is spin flip from a ferrimagnetic state to a ferromagnetic state due to field-forced spin rearrangement. The occurrence of metamagnetism, regardless of its mechanism, indicates that the γ -phase is not a saturated ferromagnet. We presume that electrons from hydrogen atoms occupy the 3d states in the γ -phase at the same rate as in the β -phase. But breakdown of the strong ferromagnetic state occurs in the γ -phase; as a consequence, a weak ferromagnetic state

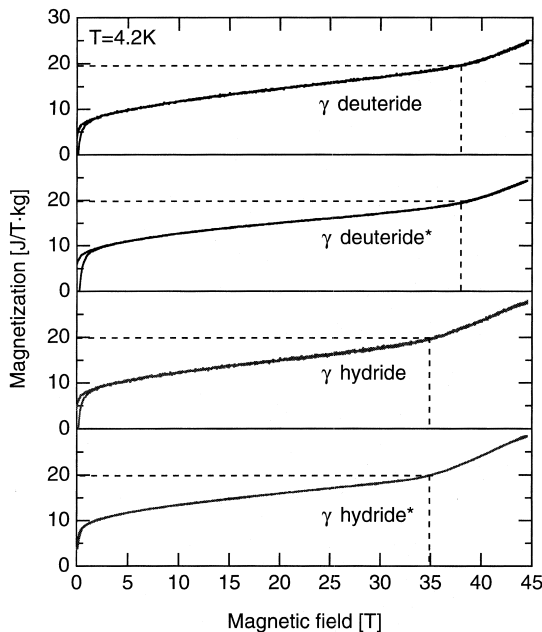


Fig. 3. Metamagnetic transitions in γ -phase $\text{LaCo}_5\text{H}(\text{D})_x$ at 4.2 K. *A different LaCo_5 sample.

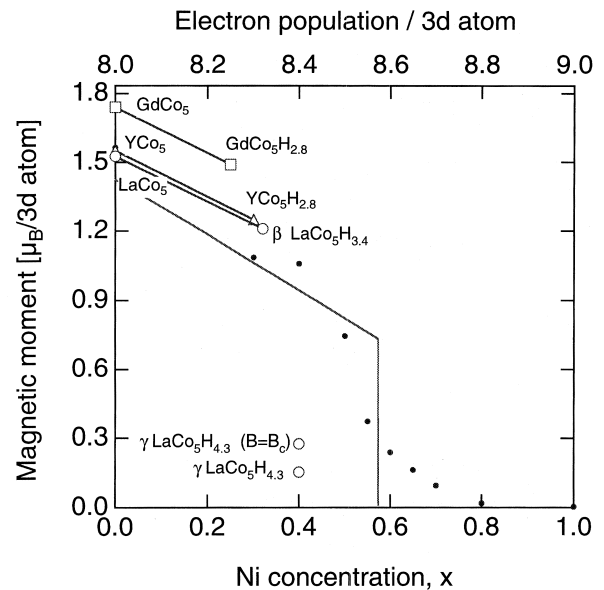


Fig. 4. Electron population dependence of the 3d moment in RCo_5H_x and $\text{Y}(\text{Co},\text{Ni})_5$. The solid line indicates theoretical data and the small circles are experimental data for $\text{Y}(\text{Co},\text{Ni})_5$ [14].

appears. The value of the spontaneous moment for the γ -phase is comparable to that of the weak ferromagnetic state in $Y(\text{Co,Ni})_5$, as illustrated in Fig. 4. It is considered that this weak ferromagnetic state transits to a stronger ferromagnetic state due to the itinerant electron metamagnetism. Moreover, the γ -phase shows a considerable increase in magnetization with magnetic fields before the metamagnetic transition. Similar behavior is also indicated by typical itinerant electron metamagnetism in $Y\text{Co}_2$ and $Y\text{Co}_3$ [15,16].

The isotope effect on the metamagnetism is difficult to explain. The critical field for itinerant electron metamagnetism depends on the detailed structure of the DOS. Probably, the local environment of the cobalt atoms is different between the γ -hydride and deuteride, which is speculated to have some relationship with the isotope effect on the equilibrium pressure.

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