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Magnetic properties of YCo_2 hydrides

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Abstract

The magnetic and structural influences of hydrogen absorption were studied on the itinerant electron metamagnet YCo_2. The system YCo_2H_x forms two crystalline hydrides of the α phase ($0<x<0.3$) and the β phase ($1.5<x\leq3.5$). The hydride samples also include small amounts of the non-intrinsic ferromagnetic component due to the partial structural disordering upon hydrogen absorption. The high field susceptibility indicated that the α phase is an itinerant electron metamagnet in which the critical field is possibly lower than that of YCo_2. The β phase has no metamagnetic transition. The hydrogen-induced changes in the magnetic properties are discussed on the basis of the itinerant electron magnetism.

Keywords: Magnetic property; Itinerant electron metamagnetism; Metal hydride; High magnetic field; YCo_2

1. Introduction

The C15-type Laves phase compound YCo_2 is a typical itinerant electron metamagnet which shows a transition from a paramagnet to a ferromagnet at the critical field of $B_c=69$ T at 4.2 K [1]. Systematic experimental and theoretical investigations have made clear that this metamagnetism originates in the position of the Fermi energy in the peculiar band structure of YCo_2, so that the critical fields strongly depends on the lattice volume [2–4].

Meanwhile, the compound YCo_2 can absorb hydrogen up to the composition of $YCo_2H_{3.5}$, resulting in a large lattice expansion of $\Delta V/V\approx23\%$. Approximately, hydrogen absorption corresponds to a large negative chemical pressure to the compound. So far, several authors studied the hydrogen-induced effects on the magnetic properties of YCo_2 and related compounds [5–8]. In particular, Mushnikov et al. examined the hydrides based on the pseudobinary compound $Y(Co_{1-y}Al_y)_2$ because the critical field is much lower than YCo_2, for instance $B_c=30$ T for $y=0.075$ [7,8]. As a result of hydrogen absorption, the critical field was found to decrease linearly with increasing hydrogen composition in the region $x<0.28$.

In this paper, we study the magnetic influences of hydrogen absorption in the pure compound YCo_2. After the formation of hydride phases is investigated by X-ray diffraction, the magnetic properties of YCo_2H_x are observed in high fields up to 47 T followed by discussion.

2. Experiments

2.1. Hydride phases

The compound YCo_2 was prepared by arc melting yttrium (99.9% purity) and cobalt (99.99% purity) with annealing at 1223 K for 48 h. Powder X-ray diffraction showed that the C15-type Laves phase structure was formed without any impurity phases.

The hydrides were obtained from the gentle reaction with hydrogen gas (seven nine purity) at room temperature because a violent reaction at elevated temperatures possibly brought about large structural disordering [5]. The error of the hydrogen composition x was ±3%. Powder X-ray diffraction indicates that the system YCo_2H_x forms two kinds of hydrides, which are termed the α and β phases. The diffraction lines of each phase can be indexed by the C15-type Laves phase structure with clearly different lattice constants as illustrated in Fig. 1. The fraction of the β phase in the sample, which was determined from the relative line intensity of the β to the α phases, varied with x as plotted in the same figure. The single-phase hydride is

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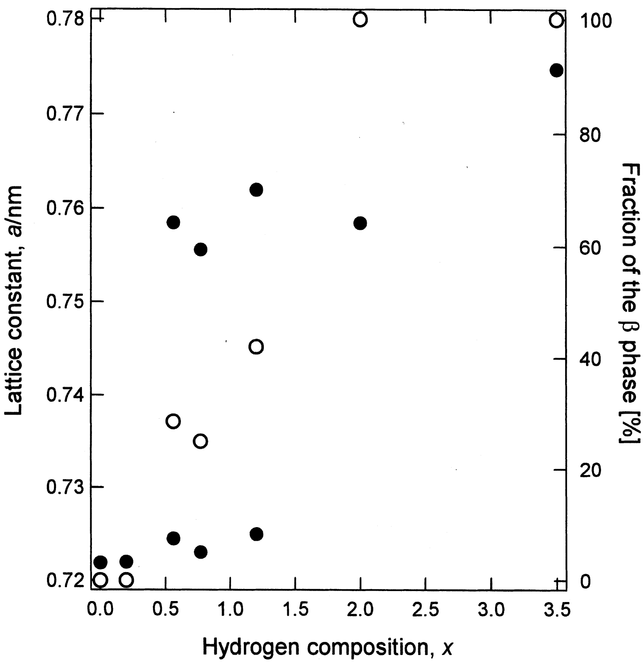

Fig. 1. Lattice constants (closed circles) and the fraction of β phase (open circles) for YCo_2H_x.

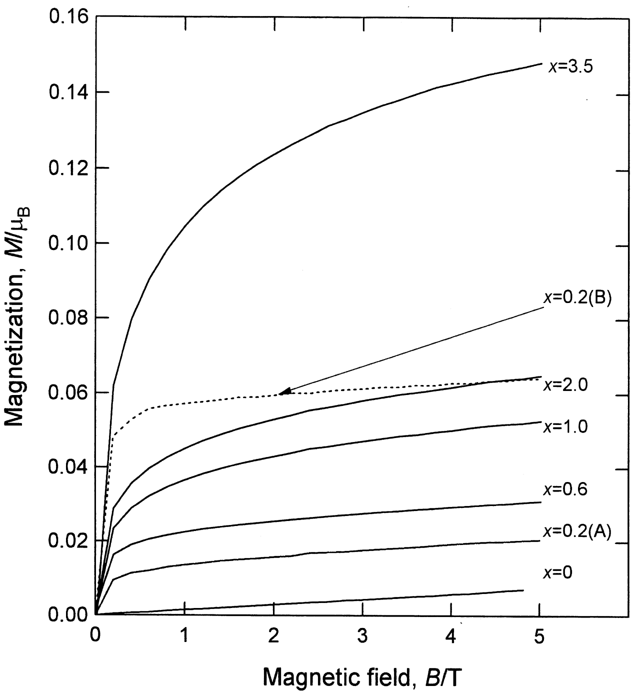

Fig. 2. Magnetization curves at 5 K up to 5 T for YCo_2H_x. The magnetization is expressed per Co atom.

estimated to range from $x=0$ to 0.3 for the α phase and from $x=1.5$ to 3.5 for the β phase. Accordingly, the two-phase region exists in the nominal composition between $x=0.3$ and 1.5. These α and β phases are presumed to correspond to the regions of a solid solution and a hydride phase in the pressure composition isotherm, respectively. It is noted that the system YCo_2H_x has no hydride in the range of lattice constant between 0.725 and 0.755 nm. The X-ray diffraction patterns were analyzed by the Rietveld method with the aid of the RIETAN program [9]. Then, the α phase was confirmed to have the ideal position parameters of $x=y=z=0$ for 8a Y and $x=y=z=5/8$ for 16d Co in the space group $Fd3m$. But the atomic positions were not determined in the β phase.

2.2. Magnetic properties

Magnetization was measured in static fields up to 5 T by a SQUID magnetometer in the temperature range between 5 and 300 K. Fig. 2 presents the magnetization curves at 5 K. The matrix compound YCo_2 is discernible to be paramagnetic. In all hydride samples, in contrast, a small spontaneous magnetization appears and it seems to increase with increasing hydrogen composition. We did not believe this tendency as the intrinsic property of the hydride phases. Thus, we prepared two samples A and B for the α phase $YCo_2H_{0.2}$ by different processes. Sample A crushed to submillimeter size was reacted with hydrogen at room temperature as gently as possible, on the other hand, sample B pulverized to several tens of μm size was rapidly reacted at about 400 K. As a result, the spontaneous magnetization of sample B is much larger than that of sample A. Nevertheless, the slopes of both magnetization curves agree with each other. Therefore, the spontaneous magnetization is ascribed to the structural disordering which was formed during the hydrogen-absorbing process. It is difficult to observe its existence by usual X-ray diffraction. But the structural disordering is presumed to form a precipitated phase, at least for the α phase samples. The similar phenomenon was found when hydrogen was absorbed in YCo_2 and $Y(Co_{1-y}Al_y)_2$ [5–8]. Thus, the intrinsic magnetic property of the α phase must be Pauli paramagnetic like YCo_2. In the β phase with $x=2.0$ and 3.5, a small moment is induced by magnetic fields and it tends to saturate in higher fields.

The temperature dependence of magnetization in a constant field of 1 T is shown in Fig. 3. The magnetization, or the susceptibility, of YCo_2 has the broad maximum around 260 K as recognized as the typical behavior of the itinerant electron metamagnetism. For the hydride samples, the magnetization is partially due to the non-intrinsic ferromagnetic component which decreases gradually with increasing temperature [8]. The magnetization of the α phase $YCo_2H_{0.2}$ is little reduced up to 300 K. Accordingly, it is speculated that the susceptibility of $YCo_2H_{0.2}$ shows a broad maximum if the non-intrinsic moment does not exist. In contrast, the magnetization of the β phase $YCo_2H_{3.5}$ is abruptly reduced below 40 K, which is likely an intrinsic property of this phase.

High field magnetization was measured in pulsed high fields up to 47 T at 4.2 K by an induction method in which

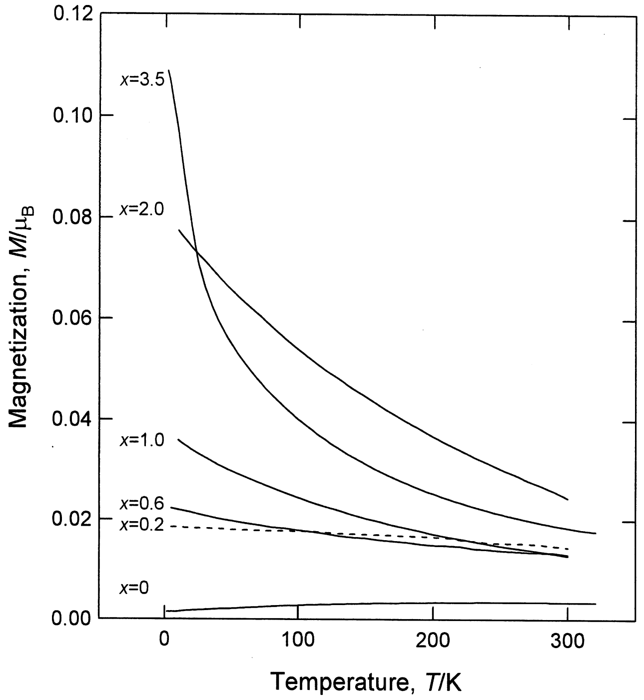

Fig. 3. Temperature dependence of magnetization in 1 T for YCo_2H_x. The magnetization is expressed per Co atom.

the duration of the pulsed fields was 20 ms. Fig. 4 illustrates the high field magnetization curves of YCo_2H_x for different x values. As the hydrogen composition increases, the magnetization curves change gradually from concave to convex shapes. The α phase hydride ($x=0.2$) has a concave magnetization curve. Such a concave curve is precursory for the itinerant electron metamagnetic transition, which is typically shown by YCo_2 and YCo_3 [1,10]. Contrary to this, the hydrides ($x=2.0$ and 3.5) have the convex magnetization curve, indicating that the magnetization tends to saturate in higher fields. The intermediate hydrides ($0.4 \leq x \leq 1.2$) have the magnetization curve mixed with convex and concave shapes because of the α+β two-phase region.

Fig. 5 plots the hydrogen composition dependence of the high field susceptibility χ_{hf} in the fields above 40 T derived from Fig. 4. The value of χ_{hf} shows a maximum at $x=0.2$, then decreased abruptly until $x=1.0$. Here, YCo_2 itself is an exchange-enhanced Pauli paramagnet with large χ_{hf}. It must be remembered that the hydride with $x=0.2$ is of the single α phase and the hydrides with $0.3<x<1.5$ are of the α+β phases. Accordingly, the χ_{hf} of the single α phase ($0<x<0.3$) is larger than that of YCo_2 and that the observed value of χ_{hf} is decreased in the α+β two phase region because of smaller values of χ_{hf} in the β phase. The critical field B_c for the itinerant electron metamagnetism is known to have a close relation to the magnitude of high field susceptibility [4]. As a consequence, the value of B_c in the α phase must be lower than that of YCo_2, 69 T. But, actually, it is higher than the maximum applied field of 47 T.

For only the $YCo_2H_{3.5}$ sample, the dM/dt signal in ultra-high fields was measured by an induction method with a destructive one-turn coil to check the existence of a

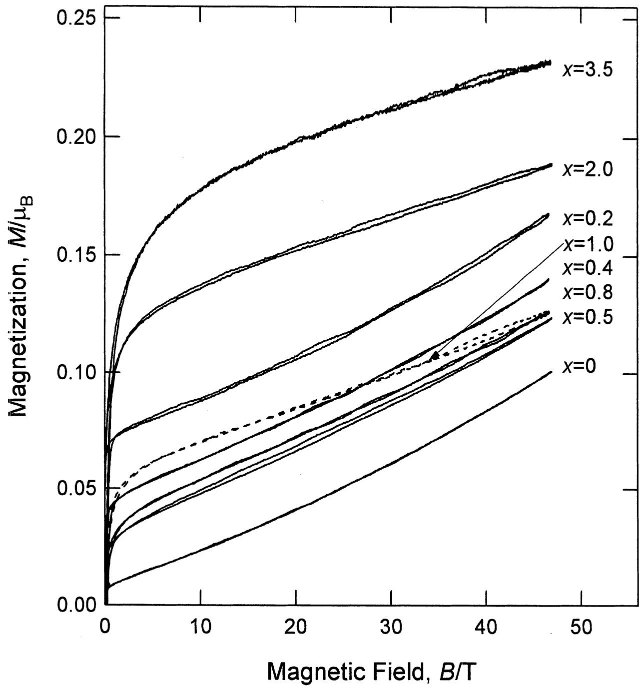

Fig. 4. High field magnetization curves at 4.2 K up to 47 T for YCo_2H_x. The magnetization is expressed per Co atom.

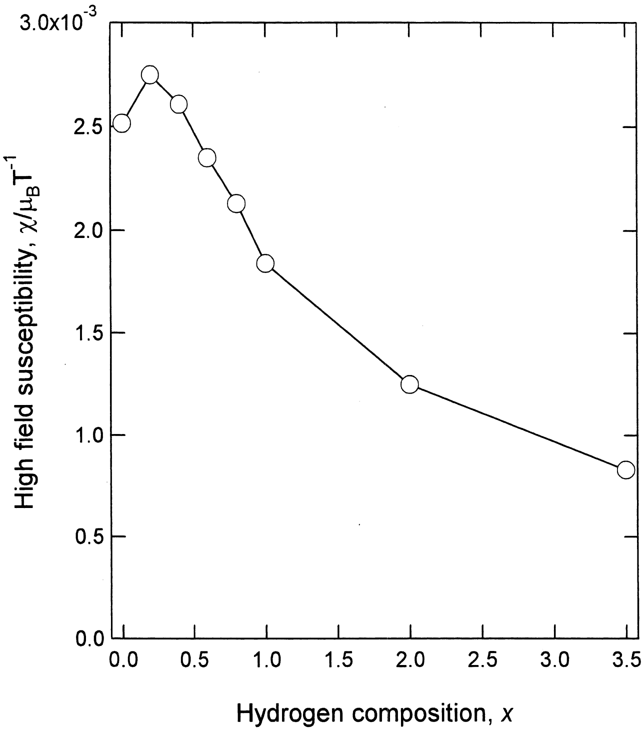

Fig. 5. High field susceptibility ($B>40$ T) at 4.2 K for YCo_2H_x. The susceptibility is expressed per Co atom.

magnetic transition. The duration of the field was 6 μs [10]. As a consequence, the β phase $YCo_2H_{3.5}$ showed no magnetic transitions up to 100 T at 10 K. Thus, the β phase is not an itinerant electron metamagnet at all. But, in the hydrogen-rich samples, it is difficult to separate the magnetization of the β phase and the structural disordering because this disordering is increased with increasing hydrogen composition.

3. Discussion

The lattice volume, or the lattice constant, is the predominant factor to determine the magnetic properties of the YCo_2-related compounds. In $Y(Co_{1-y}Al_y)_2$, the critical field B_c is decreased with increasing lattice constant due to Al substitution: $B_c = 66$ T for $y = 0.096$ ($a = 0.722$ nm) and $B_c = 0$ T for $y = 0.15$ ($a = 0.732$ nm) [4]. Comparing with this fact, the α phase is a metamagnet, but its lattice constant ($a = 0.7219$ nm for $YCo_2H_{0.2}$) is still too small to induce the metamagentic transition below 47 T. If the lattice constant dependence of B_c is common between the Al-substituted and the H-absorbed compounds, the lowering in B_c of $YCo_2H_{0.2}$ is estimated to be about 0.5 T. This lowering is ascribed to the increase in the density of state (DOS) at the Fermi energy due to the narrowing of the bandwidth which is caused by the lattice expansion.

On the other hand, the β phase $YCo_2H_{3.5}$ is not an itinerant electron metamagnet although the lattice constant $a = 0.7585$ nm for $YCo_2H_{2.0}$ is large enough to induce ferromagnetism in the case of $Y(Co_yAl_{1-y})_2$. As pointed out by Dac et al. [11] and Mushnikov et al. [8], the intra-atomic exchange interaction becomes maximum at the critical lattice constant of $a = 0.727$ nm in RCo_2-related compounds where R is a rare earth element. The lattice constant of the β phase far exceeds this critical value. In addition, the electronic structure must be much modified in such a hydrogen-rich hydride: a metal–hydrogen bonding band is necessarily formed below the d-band and the DOS curve is largely modified near the Fermi energy as usual ternary hydrides [12]. These cause the β phase to have no metamagnetic transition. The β phase seems to be a ferromagnet because of the convex magnetization curve and the abrupt decrease in magnetization with temperature. But its saturation magnetization of about 0.25 μ_B corresponds to that in the paramagnetic state of YCo_2 just before the transition to the ferromagnetic state [1]. We need further magnetic and structural investigations to make clear the magnetic properties of the β phase.

In conclusion, the α phase YCo_2H_x ($0 < x < 0.3$) is an exchange-enhanced Pauli paramagnet in the ground state like the matrix compound YCo_2. This phase possibly undertakes the itinerant electron metamagnetic transition whose critical field is lower than that of YCo_2. On the other hand, the β phase YCo_2H_x ($1.5 < x \leq 3.5$) is not an itinerant electron metamagnet. This difference in magnetism is related to the modification of electronic structure due to hydride formation.

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