

High-temperature metamagnetism of the hydride $Y_2Co_7H_6$

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Pseudomonocrystalline samples of the hydride $Y_2Co_7H_6$ were obtained for the first time ever. It was observed that the hydride is a highly anisotropic metamagnet with relatively weak critical field of the first-order metamagnetic transition (H_{cr}) = 20–15 kOe in the temperature interval 4.2–300 K, but with a high Néel temperature (470 K). The metamagnetic transition in the hydride is accompanied by considerable magnetostriction lattice deformations even at room temperature ($\lambda_s = -0.35 \times 10^{-3}$). A model is proposed to explain the causes of the onset of metamagnetism in the hydride $Y_2Co_7H_6$.

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1. INTRODUCTION

It is known¹ that one of the remarkable properties of intermetallic compounds of rare-earth metals (R) and of yttrium with transition 3d metals (T) is their ability to absorb large amounts of hydrogen gas to form hydrogen-containing compounds – hydrides – that are stable in a wide temperature interval. The crystalline structure and the magnetic properties of the hydrides can differ substantially from the properties of the initial compounds.^{2,3} Until recently their magnetic properties were investigated using isotropic powdered samples, since hydrides were obtained in the form of finely dispersed powders produced as a result of spontaneous crumbling of the alloy ingots following the introduction of the hydrogen. This made it quite difficult to obtain unambiguous results and to interpret them.

In this paper we present, for the first time, results of an investigation of the magnetic properties of the hydride $Y_2Co_7H_6$ carried out on bulky pseudomonocrystalline samples with texture axis of the type $\langle 0001 \rangle$.

2. EXPERIMENTAL TECHNIQUE

Coarse-grain ingots of single-phase alloy Y_2Co_7 were saturated with hydrogen at a hydrogen pressure 10 atm at room temperature for one hour. The amount of absorbed hydrogen was determined from the mass increase of the hydrogen-saturated compound. The samples for the investigations were prepared from large single-crystal grains of the alloy, which were not subjected to spontaneous crumbling, and constituted plates of area 2×2 mm and thickness 0.5 mm. An x-ray diffraction examination of these samples has shown that they have a good crystallographic texture of type $[0001]$ perpendicular to the plane of the plate: the maximum angle of the deviation of the c axis of the individual grains from the texture axis of the sample did not exceed 6° . Thus, these samples can be regarded as pseudomonocrystals of the hydride $Y_2Co_7H_6$.

The compounds Y_2Co_7 and $Y_2Co_7H_6$ are isostructural and have a rhombohedral crystal lattice of the Gd_2Co_7 type. The addition of hydrogen causes a strong change in its parameters.³ Whereas at room temperature Y_2Co_7 has $a = 4.99$ and $c = 36.23$ Å, $Y_2Co_7H_2$ has $a = 5.16$ and

$c = 38.18$ Å. The volume of the unit cell increases in this case by 12.6%.

The magnetization was measured by an induction method in pulsed magnetic fields up to 100 kOe in the temperature interval 4.2–360 K, and on a vibration magnetometer in static fields up to 24 kOe in the temperature range 4.2–700 K. The error in the measurement of the magnetization was 5% in pulsed fields and 3% in static fields. The magnetostriction was measured with a strain-gauge pickup of the type FKPL-0.8 with its active region glued to the surface of the plate with BF-2 adhesive. The measurement error was approximately 10%.

3. PRINCIPAL RESULTS

Figure 1 shows the magnetization curves $\mu_m(H)$ of the single crystals of Y_2Co_7 and $Y_2Co_7H_6$ measured at $T = 4.2$ K in pulsed magnetic fields along and across the axis $c \parallel [0001]$. The magnetization curves of Y_2Co_7 are typical of uniaxial ferromagnets. When it is magnetized along the c axis (the easy magnetization axis of Y_2Co_7) saturation is reached in weak fields equal approximately to the demagnetizing field of the sample (curve 1). The value of the molecular magnetic moment in the saturation state is $\mu_m = 9.6\mu_B$. The magnetization curve perpendicular to the c axis characterizes the magnetic crystallographic anisotropy of the Y_2Co_7 compound (curve 1'). The anisotropy field is $H_a = 105$ kOe at $T = 4.2$ K.

When the hydride $Y_2Co_7H_6$ was magnetized along the c axis in a certain field $H = H_1$, an abrupt increase of the magnetic moment, with saturation in a field $H = H_2$ was observed (curve 2). The molecular magnetic moment is in this case $\mu_m = 6.5\mu_B$. Magnetic hysteresis is observed when the field is decreased. The $\mu_m(H)$ curve in the basal plane of the hydride is a straight line whose extrapolation to the value of the magnetic moment μ_m induced along the c axis yields a field 300 kOe (curve 2').

The temperature dependences of the molecular magnetic moment of the hydride along the c axis in fields 50 kOe and 6 kOe are shown in Fig. 2 (curves 2 and 3). The figure shows also for comparison the $\mu_m(T)$ plot of the initial compound Y_2Co_7 in $H = 6$ kOe (curve 1). It can be seen that the $\mu_m(T)$

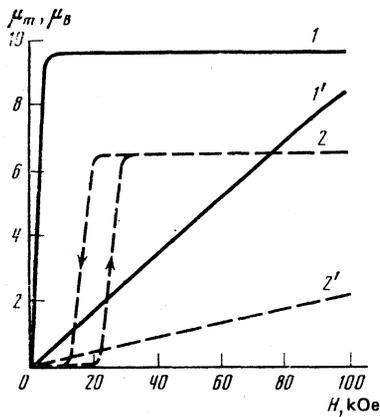


FIG. 1. Magnetization curves along different crystallographic directions of the single crystal Y_2Co_7 ($1-H \parallel c$, $1'-H \perp c$) and of the pseudomonocrystal $Y_2Co_7H_6$ ($2-H \parallel c$, $2'-H \perp c$) at $T = 4.2$ K.

plot of Y_2Co_7 has the usual Weiss form up to the magnetic-ordering temperature $T_c = 639$ K. The $\mu_m(T)$ plot of the hydride in a field 6 kOe has an antiferromagnetic character. The Néel temperature T_N of the hydride is approximately 470 K; it is impossible to determine it exactly because of the escape of hydrogen in the vicinity of this temperature section $a-b$ in Fig. 2). The equality of $\mu_m(T)$ for the desorbed sample and for the single-crystal Y_2Co_7 at $H = 6$ kOe is, first, evidence of reversibility of the processes that take place upon absorption and desorption of the hydrogen, and, second, confirmation of the single-crystal character of the particular hydride sample.

The temperature dependences of the critical field H_1 and H_2 are shown in Fig. 3, which is the phase $H-T$ diagram of the magnetic state of the hydride.

The transition from the antiferromagnetic (AF) state into the ferromagnetic (F) state in the $Y_2Co_7H_6$ hydride is accompanied by large magnetostriction distortions of crystal lattice. The dependence of the longitudinal magnetostriction $\lambda_{\parallel}(H)$ in the case of magnetization along the c axis duplicates qualitatively the $\mu_m(H)$ dependence: when H is increased from 0 to H_1 at room temperature, $\lambda_{\parallel}(H)$ increases

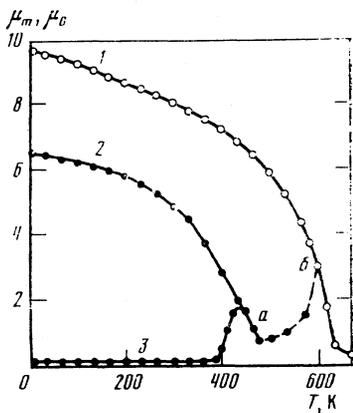


FIG. 2. Temperature dependences of the molecular magnetic moment of Y_2Co and of $Y_2Co_7H_6$ plotted along the c axis: 1- Y_2Co_7 , $H = 6$ kOe; 2- $Y_2Co_7H_6$, $H = 50$ kOe; 3- $Y_2Co_7H_6$, $H = 6$ kOe.

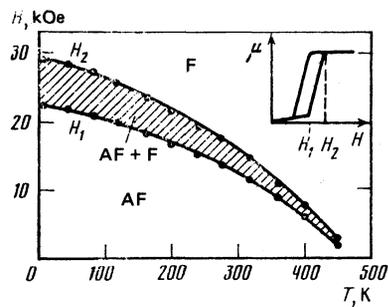


FIG. 3. Magnetic $H-T$ phase diagram of $Y_2Co_7H_6$ along the c axis.

linearly from 0 to $\lambda_{\parallel}(H_1) = -7 \times 10^{-6}$, and then, in the region $H_1 < H < H_2$, it increases sharply and reaches very high values ($\lambda_{\parallel S} = -0.35 \times 10^{-3}$) upon saturation in the region $H \gtrsim H_2$. The transverse magnetostriction λ_{\perp} increases linearly with the field without exhibiting any anomalies whatever in the region of the transition, and is small in magnitude (λ_{\perp} at $H \gtrsim H_1$ is equal to -13×10^{-6}).

4. DISCUSSION OF RESULTS

It is known⁴ that the initial compound Y_2Co_7 has a crystal lattice of the Gd_2Co_7 type (space group $R\bar{3}m$) and contains five nonequivalent cobalt positions. Since the yttrium is not magnetic in this compound ($L = S = 0$), the magnetic moment and the Curie temperature of the compound are determined by the magnetic moment of the cobalt and by the Co-Co exchange interaction. The compound Y_2Co_7 is a ferromagnet with collinearly ordered magnetic moments of the cobalt sublattices. Therefore, the average magnetic moment per cobalt ion at $T = 4.2$ K is $\mu_{Co} = \mu_m / 7 = 9.6 / 7 = 1.37 \mu_B$.

Absorption of hydrogen leads to formation of the hydride $Y_2Co_7H_6$ with the same type of crystal lattice as before. The lattice parameters a and c of the hydride increase by approximately 3 and 5% compared with the initial compound, causing an increase in the distance between the magnetoactive atoms of the cobalt. Consequently, and also because of the change of the electron density in the hydride $Y_2Co_7H_6$, the ferromagnetic order vanishes and the average value of μ_{Co} drops to $0.93 \mu_B$. From the $\mu_m(T)$ curve measured in a weak magnetic field $H = 6$ kOe it can be concluded that an antiferromagnetic ordering was produced in the hydride. The coexistence of a relatively weak negative Co-Co exchange interaction and of a high magnetic-anisotropy energy is the cause of the singularities of the magnetic properties of the hydride. When a magnetic field is applied along the c axis, there is no flopping of the magnetic sublattices. The antiferromagnetism vector, in contrast to most antiferromagnets, does not become perpendicular to the field. At $H > H_1 = H_{cr}$ the compound goes over directly from the AF into the F state. It is known that such transitions are called metamagnetic.^{5,6}

Since the critical field H_{cr} of the metamagnetic transition is approximately equal to the effective field H_{ex} ,⁶ of the intersublattice exchange interaction we have for the hydride $Y_2Co_7H_6$ $H_{ex} \approx H_1 = 20$ kOe. At the same time, the effective

tive field of the exchange intrasublattice interaction H_{ex}^0 can be estimated from the relation $H_{\text{ex}}^0 + k_B T_N / \mu_{\text{Co}}$. It amounts to approximately 7500 kOe for $\text{Y}_2\text{Co}_7\text{H}_6$. Thus, $H_{\text{ex}} \ll H_{\text{ex}}^0$ in this hydride. From the magnetization curve in the basal plane we find that the saturation field $H^{\text{sp}} = H_{\text{ex}} + H_a$, determined by extrapolation of the initial section of the magnetization curve to the value of the field-induced saturation magnetic moment along the c axis, is equal to approximately 300 kOe. (Here H_a is the effective magnetic-anisotropy field.) Consequently, in the hydride $\text{Y}_2\text{Co}_7\text{H}_6$ we have $H_{\text{ex}} \ll H_a$, i.e., we are indeed dealing with a metamagnet, in which a phase transition takes place from the AF to the F phase when a field is applied along the c axis. The slope of the magnetization curve of the hydride in the interval between the values of the external field H_1 and H_2 is practically equal to $1/N$, where N is the demagnetizing factor of the sample. Consequently, AF and F phases coexist in this field interval and the metamagnetic first-order transition in the hydride $\text{Y}_2\text{Co}_7\text{H}_6$ proceeds via the appearance of nuclei of the F phase in the AF matrix and their growth on account of the displacement of the interphase metamagnetic walls, as predicted theoretically in Ref. 7. The metamagnetic hysteresis is probably due to the difficulty of formation and growth of the nuclei of the new phase.

One of the features of the synthesized metamagnet $\text{Y}_2\text{Co}_7\text{H}_6$ is its high Néel temperature alongside the weak negative intersublattice exchange interaction. This is due apparently to the nonequilibrium distribution of the hydrogen atoms within the limits of the crystal lattice of the hydride. Indeed, the crystal lattice of Y_2Co_7 can be approximately regarded as consisting of alternating blocks that are close in structure to the compounds YCo_2 and YCo_3 . Yet it is known that YCo_2 , under the conditions used in the present paper to obtain the hydride $\text{Y}_2\text{Co}_7\text{H}_6$, absorbs approximately 1.3 hydrogen atoms per atom of the compound YCo_2 (YCo_2H_4 , Ref. 1), while YCo_3 absorbs only 0.05 ($\text{YCo}_3\text{HH}_{0.5}$, Ref. 8). Therefore the crystal structure of $\text{Y}_2\text{Co}_7\text{H}_6$ may turn out to be layered, similar to FeCl_2 (Ref. 9), and the Co-Co distances for the different Co-Co pairs

differ greatly in magnitude. The latter is probably the cause of the strong inhomogeneity of the Co-Co exchange interactions within and between the magnetic sublattices produced when the compound Y_2Co_7 is hydrogenized.

5. CONCLUSION

We obtained pseudomonocrystalline samples of the hydride $\text{Y}_2\text{Co}_7\text{H}_6$. This hydride is a metamagnet with high Néel temperature and with weak energy of intersublattice exchange. The metamagnetic first-order phase transition takes place in it probably via the onset and growth of nuclei of a ferromagnetic phase induced by the field, and is accompanied by large magnetostriction deformations of the crystal lattice even at room temperature. Since the first-order metamagnetic phase transition takes place in samples with small demagnetizing factor almost jumpwise, materials of this type can have very high values of $d\lambda/dH$ and are of definite interest for practical applications in magnetostriction converters.

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