Antiferromagnetism of the cobalt sublattice in YCo_3H_x hydrides

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A study was made of magnetic properties, specific heat, and Mössbauer spectra of $YCo_3H_{\approx 4}$ hydrides. It was established that at low temperatures the ground magnetic state of these hydrides was antiferromagnetic and not paramagnetic as assumed earlier. The application of a magnetic field induced a metamagnetic phase transition from the antiferromagnetic to the ferromagnetic state. Saturation of YCo_3 with hydrogen reduced the density of conduction electrons and increased the Debye temperature.

1. INTRODUCTION

It is known[1-3] that absorption of hydrogen by intermetallic compounds of rare-earth metals (R) with 3d transition metals (T) can alter radically the physical properties of these compounds. Among the R-Co intermetallics the compounds YCo_3 and Y_2Co_7 have similar crystal structures, absorb hydrogen at low pressures and temperatures, and form hydrides which are stable at room temperature and atmospheric pressure.[4] The ferromagnetic ordering of YCo_3 and Y_2Co_7 changes to a more complex behavior: the spontaneous magnetization disappears for certain concentrations of hydrogen in the hydrides and the magnetization curves behave metamagnetically. Opposite points of view have been used to interpret the magnetic behavior of these hydrides. It is concluded in Refs. 5 and 6 that in the absence of a magnetic field the Co subsystem is in the paramagnetic state (Y does not have a magnetic moment), whereas the application of a magnetic field induces a metamagnetic transition of the electron subsystem from the paramagnetic to the ferromagnetic state (P → F transition). On the other hand, it is assumed in Refs. 7–9 that the cobalt subsystem is ordered antiferromagnetically and a metamagnetic transition takes place from the antiferromagnetic to the ferromagnetic state (AF → F transition).

We identified the ground magnetic state of the hydrides YCo_3H_x and $Y_2Co_7H_x$ by investigating hydrides with the maximum hydrogen concentration YCo_3H_x $(x \approx 4)$ by Mössbauer spectroscopy measurements of the specific heat and magnetic properties. We established that the low-temperature ground magnetic state of these hydrides is antiferromagnetic and not paramagnetic. We selected the compound YCo_3 by choosing between YCo_3 and Y_2Co_7 because the former was characterized by lower magnetic ordering temperatures and a higher stability of the hydrides, so that the hydrides could be investigated in the magnetically ordered and paramagnetic ranges of temperatures; the $Y_2Co_7H_x$ hydrides were known to be unstable in the paramagnetic range.

2. EXPERIMENTAL METHOD

The compound YCo_3 was prepared by arc melting in a helium atmosphere (the materials used were Y and Co, both of 99.9% purity). The Mössbauer spectra were recorded using YCo_3 to which 3 at.% of the ^{57}Fe isotope was added: $Y(Co_{0.96}{}^{57}Fe_{0.04})_3$. After annealing at 1000 °C for 70 h the results of x-ray structure metallographic analysis indicated that the content of other phases in the samples did not exceed 3%.

We hydrogenated the samples with gaseous deuterium or hydrogen at room temperature under a pressure of 10^6 Pa using a method described earlier.[9] The concentration of the deuterium or hydrogen in our hydrides corresponded to the formulas $YCo_3D_{3.8}$ and $Y(Co_{0.96}{}^{57}Fe_{0.04})H_{4.19}$ and the samples contained the maximum amounts of deuterium and hydrogen that could be achieved for hydrides stable at room temperature and atmospheric pressure. The lattice parameters (rhombohedral crystal lattice of the $PuNi_3$ type, space group $R\bar{3}m$) of the original compounds and their hydrides are listed in Table I. The magnetic properties were investigated using compacted isotropic powder samples and a vibration magnetometer in static fields up to 20 kOe at temperatures in the range 4.2–700 K or an induction method in pulsed magnetic fields up to 200 kOe at 4.2–300 K. The error in the determination of the magnetic moment was 3 and 5%,

TABLE I. Lattice parameters, magnetic ordering temperatures, and magnetic moments of intermetallics YCo_3 and $Y(Co_{0.96}{}^{57}Fe_{0.04})_3$ and their hydrides.

Compound	Lattice parameter		$T_C(T_N)$, K	μ_S, μ_B, $T=4.2$ K
	a, nm	c, nm		
YCo_3	5.00	24.36	310	1.8
$Y(Co_{0.96}{}^{57}Fe_{0.04})_3$	5.00	24.36	390	–
$YCo_3D_{3.8}$	5.26	26.61	215	–
$Y(Co_{0.96}{}^{57}Fe_{0.04})_3H_{4.1}$	5.27	26.57	226	1.95 *

*Magnetic moment measured in a field $H = 200$ kOe.

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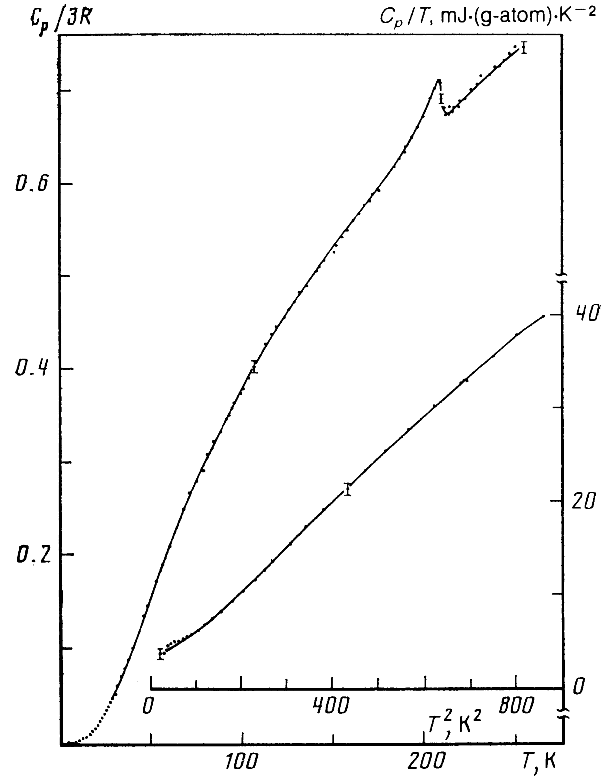

FIG. 1. Temperature dependences of the specific heat C_p of the hydride $YCo_3D_{3.8}$. The inset shows the dependence of C_p/T on T^2 at low temperatures.

respectively. The Mössbauer investigations were carried out, using a YaGRS-4 spectrometer with a source of ^{57}Co embedded in chromium, under constant acceleration conditions at 4.2 and 300 K. The specific heat was measured by a quasiadiabatic method in a calorimeter filled with helium under a pressure of ≈ 150 Pa; the error in these measurements was ≈ 1–2% up to 7 K and $\approx 0.5\%$ at $T > 7$ K.

3. SPECIFIC HEAT

Figure 1 shows the temperature dependence of the specific heat C_p of $YCo_3D_{3.8}$. In contrast to the original compounds, the specific heat of R-T hydrides was investigated for the first time. At low temperatures ($T < 14$ K) the specific heat of the original compound and hydride was found to obey

$$C_p = \gamma T + \beta T^3 \qquad (1)$$

with the coefficients γ and β listed in Table II. In the above expression the first term represents the contribution of excited electron states and, according to the band theory of metals, this electron coefficient γ is proportional to the density of the electron states at the Fermi level $n(E_F)$ [we are ignoring the magnetic contribution to C_p, which is fully justified because the magnetic ordering temperatures are much higher than the range in which the coefficients in Eq. (1) were determined]. Consequently, as we can see from Table II, the hydride $YCo_3D_{3.8}$ exhibits a reduction in $n(E_F)$ by a factor exceeding 2. The reduction of the density of the electron states at the Fermi level, which in the case of YCo_3 is located near a peak of $n(E)$ (Ref. 11), is most probably due to a change in the curve representing the density of states of the original intermetallic as a result of hydrogenation. It should be pointed out that the observed reduction in $n(E_F)$, i.e., the density of the conduction electrons, would be difficult to deduce from an investigation of the electrical resistivity of YCo_3H_x hydrides because saturation of R-T intermetallics with hydrogen is accompanied by spontaneous breaking up into powders as a result of strong internal stresses induced by hydrogenation.

TABLE II. Parameters β and γ and Debye temperatures of intermetallic YCo_3 and its hydride $YCo_3D_{3.8}$.

Compound	β, mJ·mol^{-1}·K^{-4}	γ, mJ·mol^{-1}·K^{-2}	T_D, K
YCo_3	0.34	59.0	285
$YCo_3D_{3.8}$	0.21	22.6	418

The second term in Eq. (1) is associated with thermal vibrations of the crystal lattice. If we know the coefficient β, we can use the relationship

$$T_D^3 = 12\pi RN/5\beta,$$

where R is the gas constant and N is the number of atoms per formula unit, to find the Debye temperature T_D listed in Table II. The increase of T_D for the hydride compared with the original compound may be attributed to an increase in the elastic constants because of formation of an ordered hydrogen superstructure, which imparts an additional "rigidity" to a crystal. Such an increase in the elastic constants had been observed earlier during hydrogenation of Y_2Co_7: it was deduced from the temperature dependences of the magnetostriction.[9]

An increase in temperature revealed a specific heat peak (Fig. 1) in the dependence $C_p(T)$ at $T \approx 210$ K. According to the theory of phase transitions, this behavior is associated with a second-order phase transition occurring in the hydride. We shall show below that this transition is from the antiferromagnetic to the paramagnetic state.

4. MAGNETIC PROPERTIES

The original compound YCo_3 is a collinear ferromagnet with the easy magnetization axis parallel to the c axis and a molecular magnetic moment of $\mu_s = 1.8\mu_B$ in the single-crystal state at $T = 4.2$ K (Ref. 12). The increase in the Curie temperature by 26% when only 4% of the Co atoms are replaced with Fe (Table I) is not unexpected, because the dependence of T_c on the iron concentration in $Y(Co_{1-x}Fe_x)_3$ compounds is strongly nonmonotonic.[13]

Hydrogenation alters considerably the magnetic properties of the intermetallic YCo_3. Figure 2 shows the tempera-

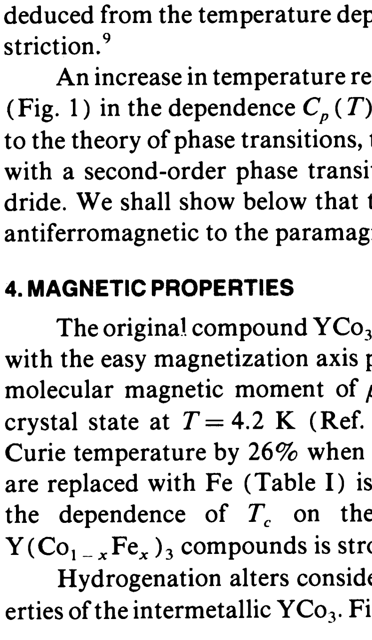

FIG. 2. Temperature dependences of the molecular magnetic moment of the hydride $YCo_3D_{3.8}$ in magnetic fields $H = 2$ kOe (1), 10 kOe (2), and 20 kOe (3).

ture dependences of the molecular magnetic moment obtained in various magnetic fields for the hydride $YCo_3D_{3.8}$. We can see that the spontaneous magnetization disappears practically completely and the dependence $\mu_m(T)$ exhibits a magnetization peak (at $T \approx 215$ K) typical of antiferromagnets and coinciding on the temperature scale with the specific heat peak in the $C_p(T)$ dependence. The magnetization curves of such hydrides exhibited metamagnetic behavior. Magnetization in a certain range of magnetic fields H_1–H_2 (≈ 130 kOe) increased strongly the magnetization, but the $\mu_m(H)$ curves did not reach saturation in high fields and this was clearly due to the fact that measurements were made on isotropic samples. The $\mu_m(H)$ curves of $YCo_3H_{3.8}$ were given in Ref. 5 and in the case of $YCo_3D_{3.8}$ it was found that our results agreed well with those in Ref. 5.

The magnetic behavior of the hydride $Y(Co_{0.96}{}^{57}Fe_{0.04})_3H_{4.1}$ was in qualitative agreement with the behavior of the hydride $YCo_3D_{3.8}$ and the magnetization peak of the dependence $\mu_m(T)$ shifted toward higher temperatures (Table I) and the metamagnetic transition field decreased. We plotted in Fig. 3 the $\mu_m(H)$ curves obtained at different temperatures for the hydride $Y(Co_{0.96}{}^{57}Fe_{0.04})_3H_{4.1}$.

The magnetic and calorimetric investigations of the YCo_3H_x hydride with high hydrogen concentrations demonstrated quite clearly that at low temperatures these hydrides were antiferromagnets with $T_N \approx 220$ K and the application of a magnetic field induced a metamagnetic AF → F phase transition. Lowering of the magnetic ordering temperature caused by saturation of the intermetallic YCo_3 with hydrogen was due to a reduction in the density of the conduction electrons, as demonstrated by an investigation of the specific heat, and also due to an increase in the interatomic distances. The magnetic moment of the hydrides was practically the same as that of the original compound.

The final answer as to whether the hydride $YCo_3H_{\approx 4}$ is a low-temperature paramagnet or antiferromagnet can be obtained however only as a result of neutron diffraction or Mössbauer investigations. The susceptibility and specific heat peaks at $T \approx 220$ K can be attributed to disordering of hydrogen on increase in temperature of the hydride, so that without a study of the magnetic structure of the hydrides a reliable conclusion could not be reached.

5. MÖSSBAUER INVESTIGATIONS

The original compound YCo_3 has three inequivalent positions of Co: 18*h*, 6*c*, and 3*b*; the relative populations of these positions are 6:2:1. Figure 4a shows the Mössbauer spectrum obtained at 4.2 K for the original ferromagnetic compound $Y(Co_{0.96}{}^{57}Fe_{0.04})_3$: it consists of three sextets with the approximate intensity ratio 6:2:1. The average effective field $H_{\rm eff}$ at the ^{57}Fe nuclei is 168 kOe (the actual values at the 18*h*, 6*c*, and 3*b* positions are 185, 151, and 134 kOe).

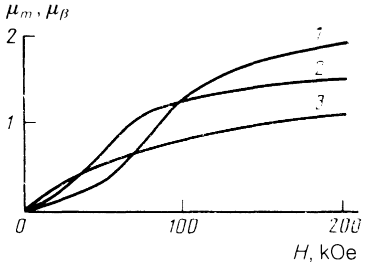

FIG. 3. Magnetization curves of the hydride $Y(Co_{0.96}{}^{57}Fe_{0.04})_3H_{4.1}$ at $T = 4.2$ K (1), 200 K (2), and 240 K (3).

The Mössbauer spectrum of the hydride $Y(Co_{0.96}{}^{57}Fe_{0.04})_3H_{4.1}$ at $T = 4.2$ K, shown in Fig. 4b, also consists of three sextets with the approximate intensity ratio 6:2:1. Consequently, the main conclusion that follows from a comparison of the spectra in Figs. 4a and 4b is that the Co sublattice of the hydride is magnetically ordered at low temperatures and the magnetic and calorimetric investigations indicate that the ordering of the Co subsystem is antiferromagnetic below $T_N = 226$ K. A confirmation of the magnetically ordered state of the Co ions at $T < T_N$ was provided by the Mössbauer spectrum of the hydride $Y(Co_{0.96}{}^{57}Fe_{0.04})_3H_{4.1}$ recorded at temperatures $T > T_N$ (Fig. 4c, $T = 300$ K) and representing a superposition of three paramagnetic doublets.

The following conclusions can be drawn from the Mössbauer spectra. Firstly, the intensities of all three subspectra do not correspond exactly to the ratio 6:2:1 (the best agreement between the experimental and computer-calculated spectra is obtained approximately for 6:2.8:2.3) so that iron replaces cobalt nonuniformly at the three positions. This behavior had been observed earlier in neutron diffraction investigations of pseudobinary compounds $Th(Co_{1-x}Fe_x)_5$ (Ref. 14). It should be pointed out that the classical RCo_3 cell contains fragments of the crystal lattice of RCo_5 (Ref. 15), so that the nonequiprobable replacement of Co with Fe in YCo_3 is quite likely.

Secondly, the average effective field at the ^{57}Fe nuclei in the hydride $Y(Co_{0.96}{}^{57}Fe_{0.04})_3H_{4.1}$ is $H_{\rm eff} = 213$ kOe (the actual fields at the 18*h*, 6*c*, and 3*b* positions are 258, 205, and 125 kOe), i.e., it increases by 26% compared with $H_{\rm eff}$ of the original compound. The effective field at the ^{57}Fe nuclei in the intermetallic $Y(Co_{0.96}{}^{57}Fe_{0.04})_3$ can be represented in the form[16]

$$H_{\rm eff} = a\mu_{\rm Fe} + b\langle\mu_i\rangle, \tag{2}$$

where *a* and *b* are constants and $\langle\mu_i\rangle$ is the average magnetic moment of the atoms located at the sites where the nearest neighbors are the atoms of ^{57}Fe. Since there are 24 Co atoms per atom of ^{57}Fe in $Y(Co_{0.96}{}^{57}Fe_{0.04})$, it follows that the immediate environment of the ^{57}Fe atom consists of the Co atoms and, therefore, we have to substitute $\langle\mu_i\rangle = \mu_{\rm Co}$ into Eq. (2). Hydrogen saturation of YCo_3 hardly affects the magnetic moment of the Co ions, as confirmed by the magnetic measurements. Therefore, an increase of $H_{\rm eff}$ in the hydride compared with the original compound is due to an increase in $\mu_{\rm Fe}$. An increase in the magnetic moment of the iron ions due to hydrogen saturation of R-Fe intermetallics is their characteristic property.[1] In the case of the hydride YFe_3H_5 the value of $\mu_{\rm Fe}$ increases by 14% (from 1.67 to $1.90\mu_B$) compared with the original compound.[1]

We shall conclude by noting that the antiferromagnetic ordering of the magnetic moments in the cobalt sublattice in $YCo_3H_{\approx 4}$ hydrides (and also in samples with lower hydrogen concentrations) can be extended also to $Y_2Co_7H_x$ hydrides, because they share the same crystal structure and

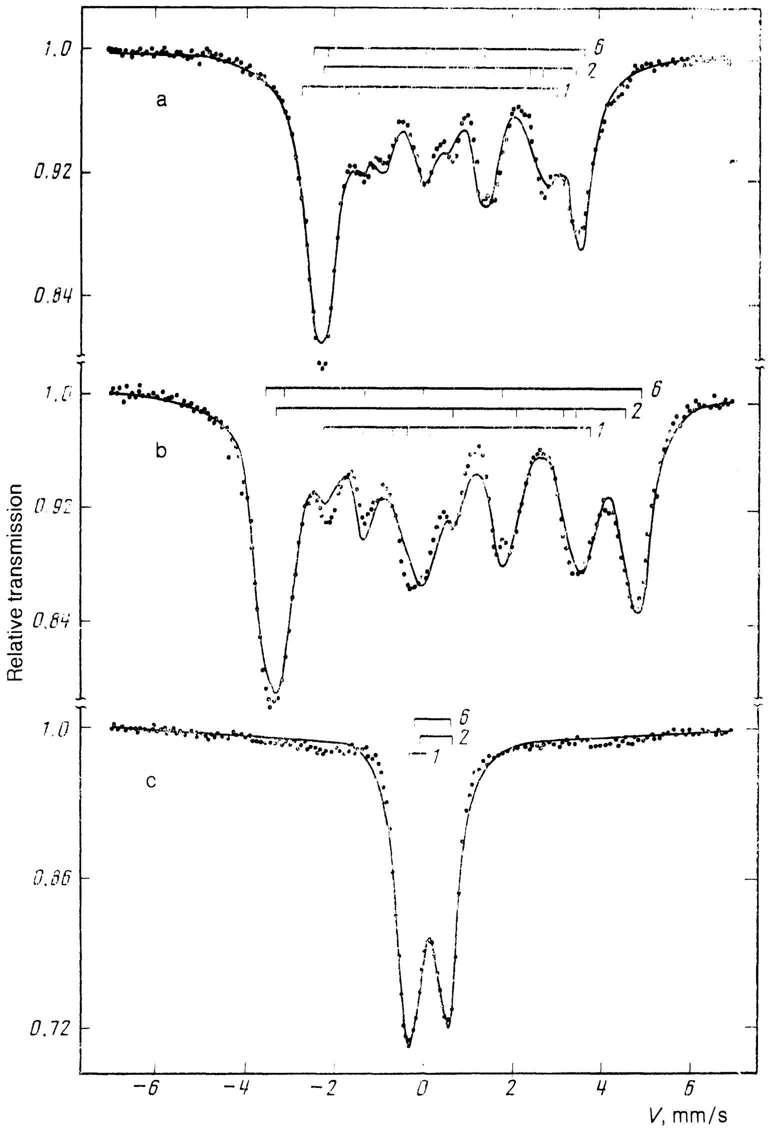

FIG. 4. Mössbauer spectra of the original compound $Y(Co_{0.96}{}^{57}Fe_{0.04})_3$ at $T = 4.2$ K (a) and of its hydride $Y(Co_{0.96}{}^{57}Fe_{0.04})_3H_{4.1}$ at $T = 4.2$ K (b) and 300 K (c). The points are the experimental values and the continuous curves are calculated on the basis of a computer analysis of the spectra.

complex magnetic properties of the original compounds and hydrides with YCo_3H_x.

6. CONCLUSIONS

1. Hydrogenation of YCo_3 intermetallics produces stable hydrides of the composition $YCo_3H_{\approx 4}$ and changes the ferromagnetic ordering of the magnetic moments in the Co sublattice to antiferromagnetic. Magnetization of these hydrides induces a metamagnetic AF → F phase transition. The magnetic moment of the cobalt ions in these hydrides is practically the same as that of the original compound.

2. Saturation of YCo_3 with hydrogen reduces the density of the conduction electrons which, together with an increase in the atomic distances, is the reason for the reduction in the magnetic ordering temperature of the $YCo_3H_{\approx 4}$ hydrides (by ≈35%).

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