Magnetic properties of the YCo_3–H system

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Abstract

The YCo_3–H system is an interesting system, which shows a dramatic influence of hydrogen absorption on its magnetic properties. The β-hydride phase has been divided into β_1 and β_2 phases originally due to their different magnetic properties. Our measurement of the absorption isotherm at room temperature, however, shows clearly that the β phase is actually separated into two phases. Thus a new hydride phase has been identified. Magnetisation measurements have also been made using a VSM. The results show that the β_1 phase is most likely to be paramagnetic. We also observe that the β_2 phase seems to have two Curie temperatures. Because there are three types of Co atoms in the YCo_3 structure, we would infer that the magnetic ordering of the different Co atoms takes place at different temperatures in this phase.
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1. Introduction

A number of investigations have been performed on the magnetic properties of Y–Co intermetallic compounds [1–3], and on the influence of hydrogen content on these properties, especially for the systems of Y_2Co_7 and YCo_3 [4–9]. YCo_3 has the rhombohedral R-3m crystal structure, usually presented in hexagonal coordinates, and conveniently described in terms of the alternate stacking of cells of the $CaCu_5$ type and cells of the $MgZn_2$ type structure [3,10]. In addition to the α (solid solution) phase, there are two established hydride phases in the YCo_3–H system, β and γ, although the β phase has been shown to contain two distinct magnetic regions. Even the magnetic properties of YCo_3 itself are still controversial. Magnetic measurements showed that it was ferrimagnetic [1,2], but a polarised neutron diffraction study suggested that it was ferromagnetic with small anti-parallel magnetic moments on the Y atoms [3]. The β hydride phase was originally divided into β_1 and β_2 phases on the basis of their different magnetic properties. The β_1 phase, YCo_3H_x for $1.0<x<1.5$, is paramagnetic [6] (or antiferromagnetic [8] with a Néel temperature of 273 K, according to a later paper by the same author); on the other hand, the β_2 phase, with $1.5<x<2.0$, is ferromagnetic, having a Curie temperature of 237 K. The γ phase, $3.5<x<4.0$, is antiferromagnetic with a Néel temperature of 200 K [7,8]. Within the overall β phase, the question arises as to whether the magnetisation changes continuously with x, within a given phase or only changes discontinuously at the phase boundary. Another question is whether the β1 phase is actually paramagnetic or antiferromagnetic. We aimed to answer both these questions.

2. Experimental

The polycrystalline alloy, YCo_3, was prepared by arc melting Y (99.9% purity) and Co (+99.9% purity) metal pieces in an argon atmosphere, followed by annealing at 1050 °C in an argon atmosphere for 7 days, and then crushed into powders of dimension smaller than 45 μm. X-ray analysis showed that the sample powder contains extraneous phases of YCo_5, Y_2Co_7 and YCo_2 amounting to about 5% by mass. The pressure–composition isotherms of the YCo_3–H system were measured using a volumetric system. The magnetisation measurements were made on a vibrating sample magnetometer (VSM), at Manchester University, UK, with the magnetic field in the 0–12 T

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range. The sample powders were mixed with glue and solidified, and were then held in place by PTFE tape.

3. Results and discussion

Fig. 1 shows the pressure–composition isotherms of the YCo_3–H system at various temperatures. The isotherms at 152, 122 and 92 °C were taken during desorption, whilst those at 62 and 28 °C were measured during absorption. The isotherm at 152 °C shows two plateau corresponding to the solid solution α-phase and two hydride phases, β and γ. When the temperature is reduced to 62 °C and then to 28 °C, the isotherm clearly shows that the β phase is separated into two separate phases, β_1 and β_2. This convincingly explains why concentrations in the β_1 and β_2 ranges show different magnetic properties. Kierstead's measurements of the desorption isotherms of YCo_3 hydrides showed some indications of the third plateau, but this was not mentioned in the text [11]. Referring to the absorption isotherm measured at 28 °C, the phase fields of the YCo_3H_x system exist between: $x=0$–0.03, α phase; $x=0.03$–1.2, $\alpha+\beta_1$ phases; $x=1.2$–1.35, β_1 phase; $x=1.35$–1.8, $\beta_1+\beta_2$ phases; $x=1.8$–2.0, β_2 phase; $x=2.0$–3.8, $\beta_2+\gamma$ phases; $x=3.8$–5.0, γ phase.

The XRD pattern of $YCo_3H_{1.6}$ taken at room temperature is shown in Fig. 2. There are two peaks at 34 degree, which can be indexed to 1 0 −8 diffraction line of the β_1 phase and of the β_2 phase, respectively. Therefore $YCo_3H_{1.6}$ is a mixture of the β_1 phase and the β_2 phase, and this is consistent with the pressure–composition isotherm. The lattice parameters and Co–Co distances of the four single phases of YCo_3–H system are shown in Table 1. This implies that β_1 and β_2 phases have the same crystalline structure, with slightly different lattice parameters.

Fig. 3 shows the magnetisation of YCo_3H_x at 4 K. YCo_3 ($x=0$) itself shows a ferromagnetic response, which satu-
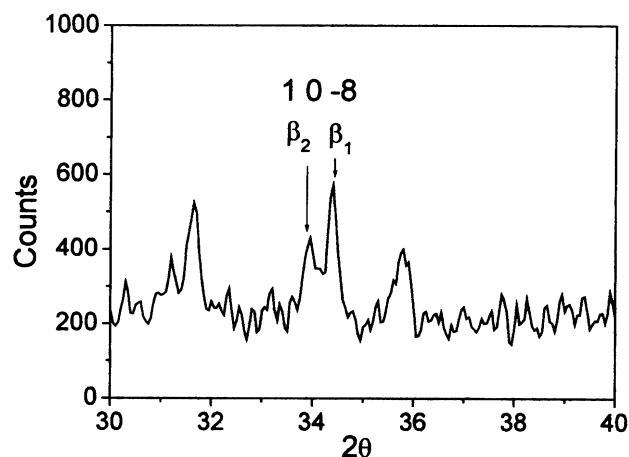

Fig. 2. XRD pattern of $YCo_3H_{1.6}$.

Table 1
Lattice parameters

	$a = b$ (Å)	c (Å)	Distance (Å)	
			Co_1–Co_3	Co_2–Co_3
YCo_3	5.0170	24.371	2.52	2.46
$YCo_3H_{1.3}$, β_1	5.0164	25.919	2.76	2.44
$YCo_3H_{1.9}$, β_2	5.0017	26.980	2.87	2.44
$YCo_3H_{4.6}$, γ	5.2730	26.844	2.81	2.49

rates rapidly at low field. Its saturated magnetic moment at 12 T is 0.69 μB/Co. The low spontaneous magnetisation of the β_1 and γ hydrides for $x=1.2$ and 4.6 is presumably caused by the ferromagnetic impurity content due to high Co concentration impurity phases. The magnetisation of the β_1 phase is much smaller than that of YCo_3, while the magnetisation of the β_2 phase is even higher than that of YCo_3 due apparently to a small additional magnetisation present at 4 K; and finally the magnetisation of the γ phase ($x=4.6$) is very small again. The magnetisation curves of the β_1 and the γ hydrides are nearly the same, which
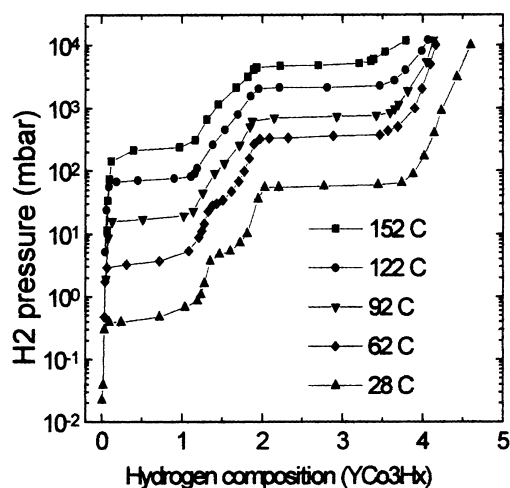

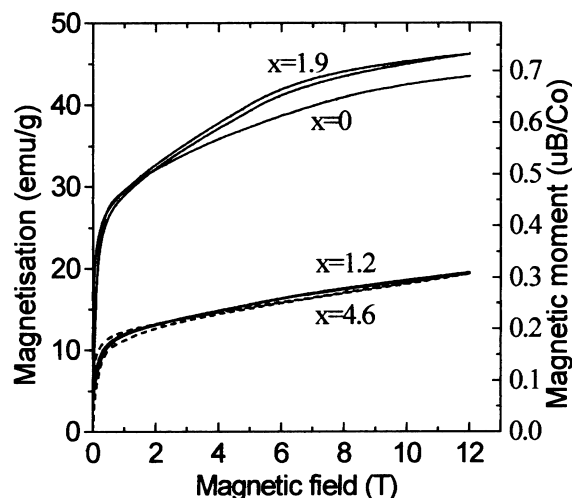Fig. 1. Pressure–composition isotherms of YCo_3H_x.

Fig. 3. YCo_3H_x magnetisation at 4 K.

would suggest that these two phases have the same magnetic properties, hence supporting the assumption that the observed magnetism is due to impurities. This is inconsistent with the result of Bartashevich et al. [8], because their result showed that $YCo_3H_{4.0}$ has a higher magnetisation than $YCo_3H_{1.0}$. It is probably because that $YCo_3H_{4.0}$ falls into two phases region of the β_2 phase and γ phase at low temperature like 4 K, and the β_2 phase has a much higher magnetisation.

The results for the temperature dependence of the magnetisation for YCo_3H_x ($x=0$, 1.2, 1.9 and 4.6) are shown in Figs. 4 and 5. The variation in magnetisation of YCo_3 at 0.1 T shows a ferromagnetic characteristic, suggesting a Curie temperature around 250 K, but at 6 T the response is clearly ferrimagnetic, with the maximum magnetisation at 130 K. The β_1 hydride ($x=1.2$) shows paramagnetic characteristics at 0.1 T and 6 T. The β_2 hydride ($x=1.9$) shows ferromagnetic features at both 0.1 T and 6 T. The magnetisation at 0.1 T exhibits two sharp falls, one around 130 K, and the other around 230 K. The antiferromagnetic characteristic of the γ hydride can be clearly observed at 10 T, with a Néel temperature at 200 K, and is negligible at 0.1 T.

The ferrimagnetic behaviour of YCo_3 is consistent with previous measurements [1,2]. The anti-parallel magnetic ordering is negligible at low field (0.1 T) compared with the predominant ferromagnetic component, so it appears to be totally ferromagnetic; But at high field, at 6 T, the anti-parallel component is relatively large because the ferromagnetic component has saturated, so the ferrimagnetic feature can be observed. The data were taken at temperatures in equilibrium, so the two sharp falls of the
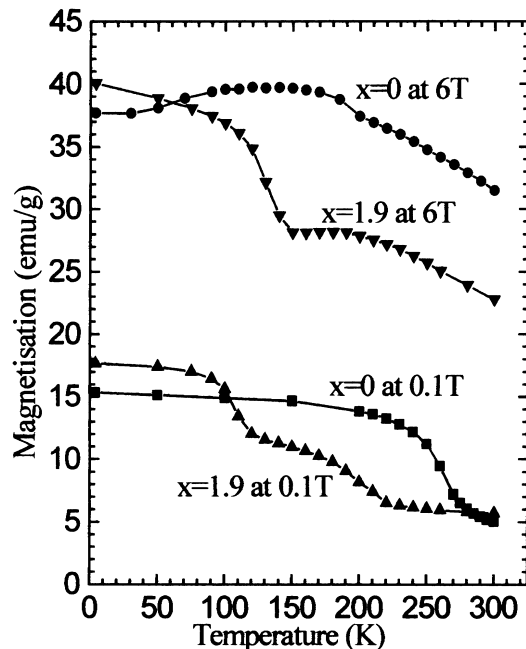

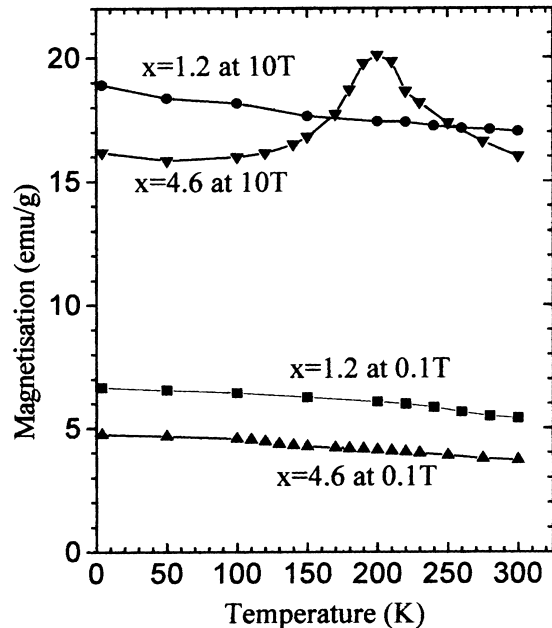Fig. 5. YCo_3H_x magnetisation vs. temperature for $x=1.2$ (β_1) and for $x=4.6$ (γ).

magnetisation of the β_2 hydride cannot be the effect of temperature rising or dropping. There are two probable reasons for this characteristic. The first is that the transition at 130 K could be a temperature induced metamagnetic transition, from a weak to an intermediate or saturated ferromagnetism. The second is that the β_2 hydride has two Curie temperatures. It is supposed that the three different types of Co atoms are divided into two groups, and their relative magnetic orderings take place one after the other as the temperature is lowered. Again the magnetisation of the β_2 hydride is higher than that of YCo_3 at low temperatures both at 0.1 T and 6 T, suggesting that the ground state here is ferromagnetic. Bartashevich et al. [7] showed that the γ hydride ($x=3.9$) is antiferromagnetic with magnetisation measurements of single crystal sample. The magnetisation of the β_1 hydride shows a similar shape to that of the γ hydride at 0.1 T, but is quite different at 10 T in Fig. 5. This implies that the β_1 hydride is purely paramagnetic and is different from the γ hydride.

4. Conclusions

A new hydride phase of YCo_3 has been found. It has been shown by accurately measuring the pressure–composition isotherms that there is a phase transformation within the previously observed β phase region. Thus the previous observation of the β_1 and β_2 magnetic behaviour can be attributed to the different structures of these phases. The magnetisation measurements show that YCo_3 is ferrimagnetic, the β_1 hydride is paramagnetic, the β_2 hydride is ferromagnetic, and the γ hydride is antiferro-

Fig. 4. YCo_3H_x magnetisation vs. temperature for $x=0$ (metallic) and for $x=1.9$ (β_2).

magnetic. Two probable reasons for the two sharp falls of the magnetisation of the β_2 hydride have been discussed. It has also been demonstrated that the β_1 hydride shows a different magnetic behaviour to the γ hydride. We intend to do neutron diffraction experiments on the magnetic structure of the YCo_3–H system in the near future, to relate the magnetisation behaviour to specific atom sites.

Acknowledgements

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