J. Magn. Soc. Japan 23, 445-447 (1999)

Effect of Hydrogen Absorption on the Magnetic Properties of Itinerant-Electron Metamagnetic Compounds Y(Co_{1-x}Al_x)₂

N.V. Mushnikov^{1,2}, Tsuneaki Goto¹, V.S. Gaviko², A.V. Ilyushenko² and N.K. Zajkov²

¹Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan ²Institute of Metal Physics, S. Kovalevskaya 18, 620219 Ekaterinburg, Russia

(Received May 1, 1998;

Accepted August 26, 1998)

The high-field magnetizations of $Y(Co_{1-x}AI_x)_2H_y$ have been measured for $0 \le x \le 0.075$ and $0 \le y \le 3.44$ in pulsed high magnetic fields up to 42 T. The itinerant metamagnetic transition is broadened, but clearly observed in $Y(Co_{0.925}AI_{0.075})_2H_y$ with $y \le 0.72$. The value of the critical field B_c of the transition decreases nearly linearly with increasing hydrogen content in the region $y \le 0.28$, which is consistent with the decrease of the transition field due to Al substitution for Co in the parent compound. A weak spontaneous moment appears in all the hydrides, which originates from a partial structural disordering of the lattice induced by hydrogen absorption.

Key words: intermetallic compounds, metamagnetism, magnetic properties, hydrogenation

1. Introduction

Laves phase compounds YCo_2 and $LuCo_2$ are typical of strongly exchange-enhanced Pauli paramagnets and exhibit itinerant electron metamagnetism at critical fields 69 T and 74 T, respectively. ¹⁾ This transition is considered to originate from the shape of DOS around the Fermi level. ²⁾ The substitution of Al for Co in YCo_2 leads to a volume increase, which increases the DOS at the Fermi level, enhances paramagnetism and reduces the critical field of the metamagnetic transition. ³⁾

Intermetallic Laves phase compounds absorb a large amount of hydrogen and their lattices expand up to about $\Delta a/a = 7$ %, depending on the hydrogen content. ⁴⁾ The hydride YCo₂H_x was reported to retain a Pauli paramagnet. ⁵⁾ Later, YCo₂H_{3.5} was found to reveal ferromagnetic behavior at 4.2 K with relatively small spontaneous moment of ~ 0.25 $\mu_{\rm B}/{\rm Co}$. ⁶⁾ This was interpreted as a consequence of the volume expansion and the electron transfer from the d-electron states to the hydrogen induced states. However, all the available data were obtained only for the maximum hydrogen content. There is no information about the effect of hydrogen on the metamagnetic transition, the critical field of which will be very sensitive to the hydrogen content. ¹⁾

In order to clarify the origin of the effects of hydrogen absorption on the magnetic properties of the metamagnetic Laves phase compound in this study, we have measured the high-field magnetization curves of hydrides $Y(Co_{1-x}Al_x)_2H_y$ for x=0, 0.06 and 0.075; $y \le 3.44$ together with amorphized $YCo_2H_{3.06}$.

2. Experimental Details

Samples of $Y(Co_{1-x}Al_x)_2$ were prepared in a semilevitation crucible by an induction melting under argon atmosphere, followed by annealing at 900°C for a week. Powder X-ray diffraction confirms the sample to be single phase with the cubic Laves phase structure.

Hydrogenation of the samples was carried out with high-purity hydrogen gas. The hydrogen concentration was controlled by varying the hydrogen pressure and temperature.

High magnetic fields up to 42 T were produced using a wire-wound pulse magnet with a duration time of about 20 ms. The magnetization was measured by an induction method with a set of compensated pickup coils. The temperature dependence of the magnetization was measured using a vibrating sample magnetometer in a magnetic field 0.6 T.

3. Results and discussion

Figure 1 shows the high-field magnetization curves of $Y(Co_{0.925}Al_{0.075})_2H_y$ with different hydrogen content y. The parent compound exhibits a sharp metamagnetic transition at 30 T. In the hydrides with low hydrogen content, the metamagnetic transition broadens, but can be observed clearly for the hydrogen concentration up to y=0.72. The value of the field-induced magnetic moment decreases gradually with increasing y. All the hydrides have a weak spontaneous moment, consistent with the previous study ⁶. The spontaneous moment changes



Fig. 1. Magnetization curves of Y(Co_{0.925}Al_{0.075})₂H_v.



Fig. 2. Magnetization curves of Y(Co_{0.94}Al_{0.06})₂H_y.

with y passing through a maximum at y=0.28.

Similar hydrogen effects were observed on the highfield magnetization curves of $Y(Co_{0.94}Al_{0.06})_2$ (Fig. 2), and YCo_2 . However, the applied magnetic fields up to 42 T were not enough to see the metamagnetic transition in the hydride of YCo_2H_y .

Figure 3 shows the value of B_c as a function of the lattice parameter both for the hydrides $Y(Co_{0.925}Al_{0.075})_2H_y$ (open circles) and for the two different hydrogen-free compounds with Al concentrations $Y(Co_{0.94}Al_{0.06})_2$ and $Y(Co_{0.925}Al_{0.075})_2$ (closed squares). The lattice parameters determined for the two hydrogen-free samples are in good agreement with the data $^{7)}$, whereas their values of B_c are consistent with the data ³⁾. It can be seen that the change of B_c due to hydrogen absorption in the region y < 0.28 is consistent with the difference of B_c in the hydrogen-free samples. In the case of $Y(Co_{1-x}Al_x)_2$, the volume expansion is considered to contribute to the decrease of $B_c^{(8)}$. The change in the Al content from 0.06 to 0.075 leads to the volume increase $\Delta V/V=2.5\times 10^{-3}$. If we take the compressibility of the hydrogen-free samples to be $K=dlnV/dP=1\times10^{-3} kbar^{-1}$, the observed volume



Fig. 3. Critical field B_c as a function of the lattice parameter *a* for $Y(Co_{0.925}Al_{0.075})_2H_y$, *y*>0 (open circles); $Y(Co_{0.925}Al_{0.075})_2$ and $Y(Co_{0.094}Al_{0.06})_2$ (closed square).

increase corresponds to a negative pressure of -2.5 kbar. If we assume that the change of B_c comes only from the volume expansion, we can estimate the pressure effect of B_c to be $dB_c/dP \sim 4$ T/kbar. However, the magnetization measurements of a related compound Lu(Co_{0.88}Ga_{0.12})₂ under high pressure give considerably lower value dB₀/dP=1.0 T kbar⁻¹⁻¹). Such a large discrepancy should be attributed to the decrease of the electron density in the 3d-band, giving the shift of the Fermi level to the lower energy side. The decrease of the electron density is due to the substitution of Al atoms with unfilled 3d states for Co. Since relatively small amount of absorbed hydrogen produces the change of B_c like the substituted Al, we can conclude that the absorbed hydrogen behaves as an electron acceptor. This behavior is similar to that of hydrogen in Fe-containing intermetallics⁴⁾

Duc et al. ¹⁰⁾ found that the Curie temperature of the $R(Co_{1-x}Al_x)_2$ systems with different R becomes maximum at a critical lattice parameter $a_c=7.27$ Å, where the intraatomic exchange interaction in the Co atoms is considered to have a maximum value. The lattice parameter, at which the value of B_c in the hydride system $Y(Co_{0.925}Al_{0.075})_2H_y$ becomes minimum, is surprisingly close to this value.

The hydrides of $Y(Co_{0.925}Al_{0.075})_2H_y$ with y>1.12 have no metamagnetic transition in high magnetic fields up to 42 T. In this concentration region, the effect of the s-d hybridization between the hydrogen-induced states and the 3d states will become large, which destroy a sharp DOS peak below the Fermi level responsible for the metamagnetic transition in this compound ²⁾. Band structure calculations of the hydrides are necessary to understand the mechanism of the suppression of itinerant electron metamagnetism at high hydrogen concentrations.

The temperature dependence of the magnetization measured in a magnetic field of 0.6 T is shown in Fig.4. The magnetization decreases monotonically with increasing temperature up to 400-500 K. At higher temperatures, the increase of the magnetization was



Fig.4. Temperature dependences of the magnetization of compounds with small amounts of hydrogen and amorphized $YCo_2H_{3.06}$ in a magnetic field 0.6 T.

J. Magn. Soc. Japan, Vol. 23, No. 1-2, 1999

observed accompanied by the irreversibility in the temperature dependence of the magnetization. This suggests the existence of a structural transformation.

Since we have observed the spontaneous moment together with the metamagnetic transition, the moment does not originate from the intrinsic magnetic properties. All the studied hydrides are single phase with the MgCu₂-type structure. However, X-ray diffraction patterns of the hydrides are broadened in comparison with the parent compounds. Hydrogen treatment at elevated temperature and pressure is known to lead sometimes to complete disappearance of X-ray diffraction patterns (hydrogen-induced amorphization). We obtained hydrogen-amorphized YCo₂H_{3.06} by hydrogen treatment at 510 K and 10 bar. This amorphized compound is a ferromagnet with a spontaneous moment of 1.1 $\mu_{\rm B}/{\rm Co}$ and the Curie temperature is higher than 500 K, as shown in Fig.4. This behavior is very similar to that of amorphous hydrogen-free YCo₂, which is known to be a ferromagnet with a spontaneous moment of ~ 1.0 $\mu_{\rm B}/{\rm Co}^{11}$. We consider that the appearance of the weak spontaneous moment in $Y(Co_{1-x}Al_x)_2H_y$ is attributed to partial structural disordering produced by hydrogen absorption. As a measure of such disordering, the broadening of X-ray diffraction patterns can be considered. As seen from Fig.5, there exists a strong correlation between the spontaneous magnetization and the halfwidth of the most intensive [3,1,1] X-ray diffraction line. We can speculate that such disordering produce ultrafine Co clusters ¹²⁾. Although these clusters are too small to be detect by means of X-ray diffraction techniques, they will exhibit the temperature dependence of the magnetic moment shown in Fig.3, which is quite different from that of metallic cobalt.

4. Conclusion

The magnetization curves of $Y(Co_{1-x}Al_x)_2H_y$ hydrides were measured in pulsed high magnetic fields up to 42 T



Fig.5. Spontaneous magnetization as a function of halfwidth of the [311] X-ray diffraction lines for hydrides with small hydrogen contents.

together with hydrogen-free compounds and hydrogenamorphized $YCo_2H_{3.06}$. The main results obtained are summarized as follows:

1) The itinerant metamagnetic transition is broadened by hydrogen absorption, but can be observed clearly in $Y(Co_{0.925}Al_{0.075})_2H_v$ with $y \le 0.72$.

2) Hydrogen absorbtion reduces the critical field of the transition B_c in $Y(Co_{0.925}Al_{0.075})_2H_y$. The critical field decreases nearly linearly with increasing the lattice parameter *a* in the low concentration region *y*<0.28. The decrease of B_c is consistent with that due to Al substitution for Co in the parent compound.

3) The metamagnetic transition disappears in the high concentration region y>1.12. This may occur due to the effect of the s-d hybridization between the hydrogen-induced states and the 3d states.

4) A weak spontaneous moment appears in all the hydrides and its value correlates with the broadening of X-ray diffraction lines. The appearance of the moment is attributed to a partial structural disordering of the crystal lattice induced by hydrogen absorption.

5) The hydrogen-amorphized $YCo_2H_{3.06}$ was found to be a strong ferromagnet. The magnetic properties are very similar to those of amorphous YCo_2 .

Acknowledgement

The stay of N.V.M. in ISSP was supported by the Ministry of Education, Science and Culture of Japan.

References

- T. Goto, H. Aruga Katori, T. Sakakibara, H. Mitamura, K. Fukamichi, and K. Murata: J. Appl. Phys., 76, 6682 (1994) and references therein.
- 2) M. Aoki and H. Yamada: Physica B, 177, 259 (1992).
- T. Sakakibara, T. Goto, K. Yoshimura, K. Murata, and K. Fukamichi: J. Magn. Magn. Mat., 90-91, 131 (1990).
- 4) W.E. Wallace: in *Hydrogen in Metals*, edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978), Vol.1, p.169.
- 5) K.H.J. Buschow and A.M. Van Der Kraan: J. Less-Common Met., 91, 203 (1983).
- K. Fujiwara, K. Ichinose, H. Nagai, and A. Tsujimura: J. Magn. Magn. Mat., 90-91, 561 (1990).
- 7) K. Yoshimura and Y Nakamura: Solid State Commun., 56, 767 (1985).
- J.G.M. Armitage, R.G. Graham, P.C. Riedi, and J.S. Abell: J. Phys.: Condens. Matter, 2, 8779 (1990).
- M. Brouha, K.H.J. Buschow, and A.R. Miedema: *IEEE Trans. Magn.* MAG-10, 182 (1974).
- 10) N.H. Duc, T.D. Hien, P.E. Brommer, and J.J.M. Franse: J. Magn. Magn. Mat., 104-107, 1252 (1992).
- 11) K. Fukamichi, T. Goto, Y. Satoh, T. Sakakibara, S. Todo, U. Mizutani, and Y. Hoshino: *IEEE Trans. Magn.* MAG-22, 555 (1986).
- 12) L.J. de Jongh, J. Bartolome, F.J.A.M. Greidanus, H.J.M. de Groot, H. Stipdonk, and K.H.J. Buschow: J. Magn. Magn. Mat. 25, 207 (1981).