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The magnetic properties of ytterbium trihydride

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Ytterbium trihydrides ($2.02 < H/Yb < 2.96$) were synthesized at high hydrogen gas pressures by thermally decomposing aluminium hydride under high pressure. The magnetic susceptibility of ytterbium trihydrides was measured by the Faraday method at temperatures 78 to 300 K. The gram magnetic susceptibility of $YbH_{2.96}$ in the temperature range 78 to 295 K obeys the Curie–Weiss law with $P_{eff} = 4.37\,\mu_B$ and $T_\theta = -62.7$ K. The electrical resistance of ytterbium dihydrides were measured by the d.c. method at temperatures of 78 to 273 K. YbH showed a metallic resistivity in the temperature range 78 to 273 K, but $YbH_{1.2}$ and $YbH_{1.5}$ showed semiconducting characteristics at temperatures of 241 to 273 K and at 163 to 273 K, respectively. The band gap energy of $YbH_{1.2}$ which appeared to show semiconducting behaviour was 0.241 eV, and of $YbH_{1.5}$ was 0.294 eV.

1. Introduction

A new method for synthesizing massive hydrides under high pressures was developed and is reported elsewhere [1]. The synthesizing of ytterbium hydride with a high hydrogen content was easily realized. Usually, ytterbium hydrides were synthesized up to 60 atm hydrogen gas pressures with ytterbium metal between 200 and 300° C. Hardcastle and Flanagan [2] synthesized ytterbium hydrides ($H/Yb < 2.55$) and studied the magnetic properties and crystal structures. They reported that the crystal structure of ytterbium dihydrides was orthorhombic. $YbH_{2.55}$ was face centred cubic with BiF_3 structure and magnetic susceptibility was much higher than that of orthorhombic ytterbium hydrides.

Recently Źogal *et al.* [3] studied ytterbium hydrides ($H/Yb < 2.55$) by proton nuclear magnetic resonance (NMR) their results were in good agreement with those of Hardcastle and Flanagan [2].

The purpose of our study was to synthesize YbH_3 and to study its magnetic property. In addition, electrical properties of massive ytterbium dihydrides were investigated between 78 and 273 K by a d.c. method.

2. Experimental details

MgH_2 and ytterbium metal (99.9%) were provided by Ventron Co, USA. AlH_3 was supplied from Dow Chemical Corporation. The purities of AlH_3 and MgH_2 were estimated by X-ray diffraction analysis to be higher than 85%. The main residual materials of both hydrides were aluminium and magnesium, respectively. All preparations of the high pressure experiments were made under a dry helium atmosphere in a glove box. The hydride powders as a source of hydrogen, and ytterbium metal were pressed under a pressure of about 200 MPa into pellets of 4 mm diameter and 0.2 to 1.0 mm thick. Such pellets were set into the copper capsule as shown in Fig. 1. The capsule was 6 mm diameter × 7.1 mm high. Four boron nitride discs and two palladium discs were placed in the capsule as shown in Fig. 1. These discs were 4 mm diameter and 0.1 to 0.2 mm thick. Boron nitride discs were used to separate the sample and the hydrides which worked as solid hydrogen sources. Palladium discs acted as a filter for hydrogen atoms. Boron nitride discs and a boron nitride sleeve with o.d. 4.9 mm and i.d. 4.1 to 4.2 mm were used to isolate the solid hydrogen source from the copper capsule. The boron nitride discs, a sleeve and a copper capsule were baked under a vacuum of 10^{-4} torr at 600° C for 1 h. The assembled capsule was placed in the high pressure cell which mainly consisted of a pyrophyllite cube, a carbon heater and electrodes. The edge length of the pyrophyllite cube was 21 mm. The pyrophyllite cubes and the sleeves were dehydrated at 500° C for 1 h in air. A carbon heater was treated under about 10^{-2} torr at 1000° C for 2 h and a slide type cubic anvil device was used for high pressure treatment as shown in Fig. 2.

The temperature in the high pressure assembly was calibrated by the use of an alumel–chromel thermocouple. The temperature was controlled between room temperature and 300° C under pressure up to 5.0 GPa by an electric power control. The pressure calibration was carried out based on the NBS scale of 1971 [4]. The atomic ratio H/M of synthesized hydride and decomposed hydride were estimated by analysing the gases from thermally decomposed hydrides. The gas analysis was carried out using the Hitachi 163 gas chromatograph directly connected to a vacuum line. The pressure of the carrier gas was maintained at about 1 torr by connecting a rotary pump at the exit port of the gas chromatograph. The gas analysis system consisted of a vacuum furnace, a Tepler pump and a reduced pressure gas chromatograph. The accuracy of atomic ratio determination depended on the amount of gas generated in the vacuum furnace. When the gas volume was between 20 and 100 μmol, with an accuracy of ±0.05 of H/M. The magnetic

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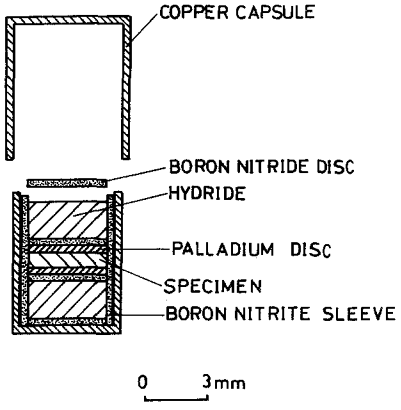

Figure 1 Diagram of a capsule for the synthesis of rare-earth hydride in the high pressure assembly. The hydride shown in the diagram is used as a solid hydrogen source.

susceptibility measurements of ytterbium hydride with high hydrogen contents were performed as a function of temperature between 77 and 300 K. The gram susceptibilities were measured by the Faraday method. The apparatus consisted of a semimicrobalance with a rotary pump and an electromagnet and a power supply capable of producing magnetic fields up to 1 T. The hydride specimen was tightly contained in a pyrex glass capsule which was 3.0 mm i.d. and 15 mm long.

After determining the sample weight, the capsule was placed upon the semimicrobalance. Dry helium gas allowed to enter the semimicrobalance system up to 20 torr after the pressure was sufficiently reduced by the rotary pump. $CuSO_4 \cdot 5H_2O$ was used as a magnetic standard. The electrical resistance of ytterbium hydrides were measured by a d.c. method between 78 and 273 K. A measurement system composed of a X–Y recorder, digital-voltmeter and an alumel–chromel thermocouple. The sample was placed between electrodes, which were pressed by a spring. Electrodes, thermocouple and a sample were contained in a pyrex tube filled with a dry helium gas shown in Fig. 3.

3. Results and discussion

Ytterbium hydride between $YbH_{1.92}$ and $YbH_{2.96}$ was synthesized under 4.0 GPa for 30 min at 250° C using AlH_3. The atomic ratio H/M of ytterbium hydride showed good correlation to the sample thickness of ytterbium metal. For example from a thickness of 0.2 to 0.3 mm ytterbium metal, $YbH_{2.96}$ was obtained. $YbH_{2.2}$ was prepared from 0.8 mm ytterbium metal.

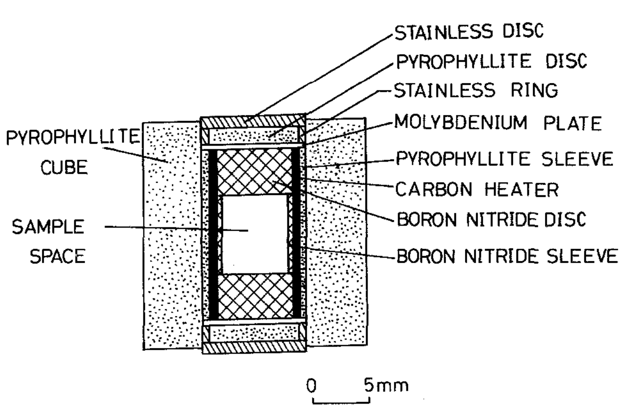

Figure 2 The cross-section of the high pressure assembly for the cubic anvil apparatus. The synthesizing capsule is placed in the sample space.

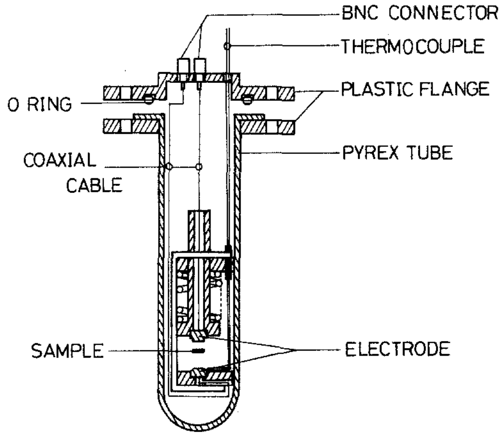

Figure 3 The cross-section of the measurement cell of the electrical resistance.

The temperature dependence of magnetic susceptibility of ytterbium hydride, χ against T and $1/\chi$ against T, are shown in Figs. 4 and 5, respectively. The paramagnetic Curie temperature and the numbers of effective Bohr magneton are summarized in Table I. The effective Bohr magneton of ytterbium hydrides increases with the atomic ratio H/Yb. The effective Bohr magneton of $YbH_{2.96}$ was in good agreement with the calculated value 4.54 for that of trivalent Yb ions. Also, magnetic susceptibility, χ, of $YbH_{2.96}$ was shown to be in good correspondence with that of Yb_2O_3 at room temperature. The measured value of Bohr magneton of $YbH_{2.2}$ was somewhat smaller than the calculated value, 2.45.

Warf and Hardcastle [5] indicated that the orthorhombic ytterbium dihydrides were paramagnetic. Furthermore, Wallace *et al.* [6] reported that YbH_2

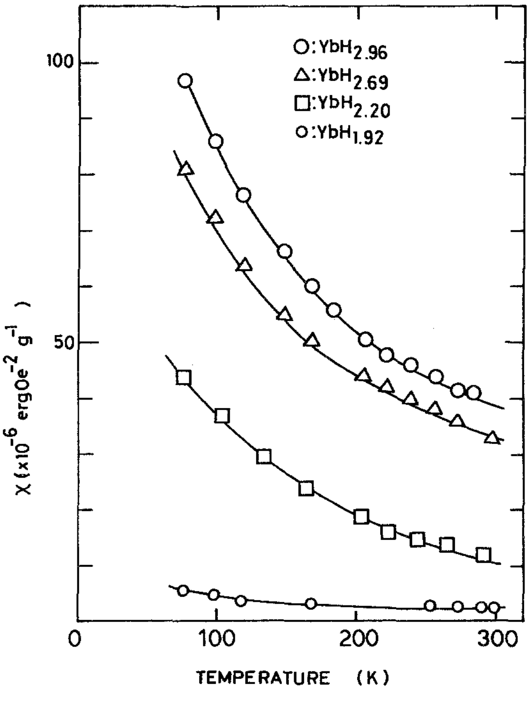

Figure 4 The relation between the magnetic susceptibilities (χ) of ytterbium hydrides synthesized under 4.0 GPa.

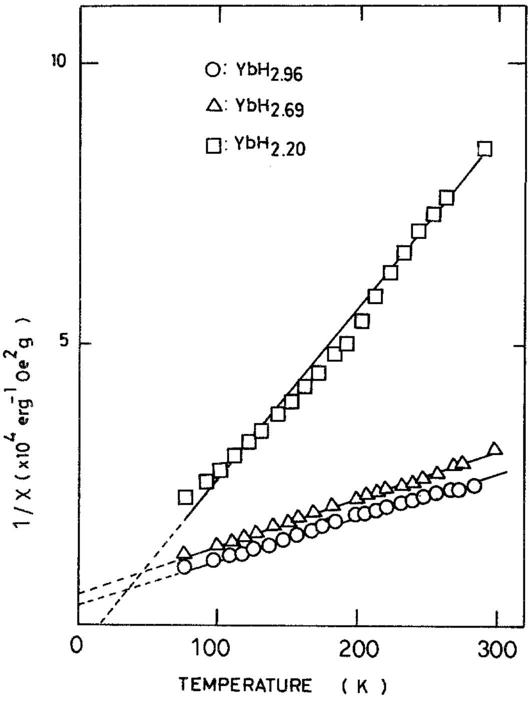

Figure 5 The relation between $1/\chi$ of ytterbium hydrides synthesized under 4.0 GPa.

was weakly paramagnetic or diamagnetic. In this synthesizing process, particularly in the preparation of hydride with a low hydrogen content, hydrogen concentration at both ends of the sample pallet was higher than in other parts. For this reason, $YbH_{2.2}$ was an admixture of trivalent and divalent ions. $YbH_{1.92}$ was weakly paramagnetic, which is in good agreement with Wallace *et al.* [6]. Fig. 6 shows magnetic susceptibility at room temperature; a reasonably smooth curve can be drawn through the plotted points. Although, the value of P_{eff} of $YbH_{2.96}$ was about 96% of the value of YbH_3, there were some problems in this study of ytterbium trihydrides. The purity of ytterbium trihydride was not as high as ytterbium metal, because in a high pressure experiment it is possible to contaminate a sample from surrounding materials under high pressure. However, there were no peaks of other materials in the X-ray diffraction pattern without ytterbium hydrides in our study. The other problem was that the quantity of sample synthesized was a very small amount, about several tens μmol. Furthermore, this hydride is unstable even in an inert atmosphere at nearly 0° C. For these reasons, we were not able to study the crystal structure of YbH_3 in detail by X-ray diffraction.

Fig. 7 shows a change of electrical resistance of YbH, $YbH_{1.2}$ and $YbH_{1.5}$ to $1/T$. The electrical resistance of YbH showed a metallic behaviour between 78 and 273 K. But that of $YbH_{1.2}$ and $YbH_{1.5}$ showed a semiconducting behaviour. On the assumption of a band model, the band gap energies for $YbH_{1.2}$ and $YbH_{1.5}$ were calculated to be 0.241 and 0.294 eV, respectively. $YbH_{1.2}$ and $YbH_{1.5}$ showed a change of band gap energy as shown in Fig. 7 at temperatures 241 and 163 K, respectively.

TABLE I The paramagnetic Curie temperature and the effective Bohr magneton for synthesized ytterbium hydrides

H/Yb	χ_g(RT) $\times 10^6$	C_m	P_{eff}	θ(K)
2.20	11.7	0.57	1.80	17.4
2.69	31.9	2.11	4.12	−73.4
2.96	39.5	2.37	4.37	−62.7

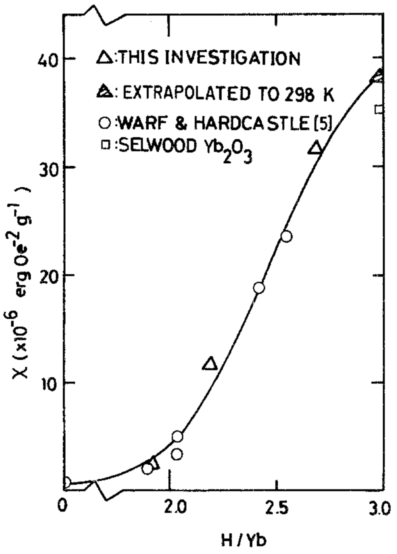

Figure 6 The magnetic susceptibility of ytterbium hydrides at room temperature.

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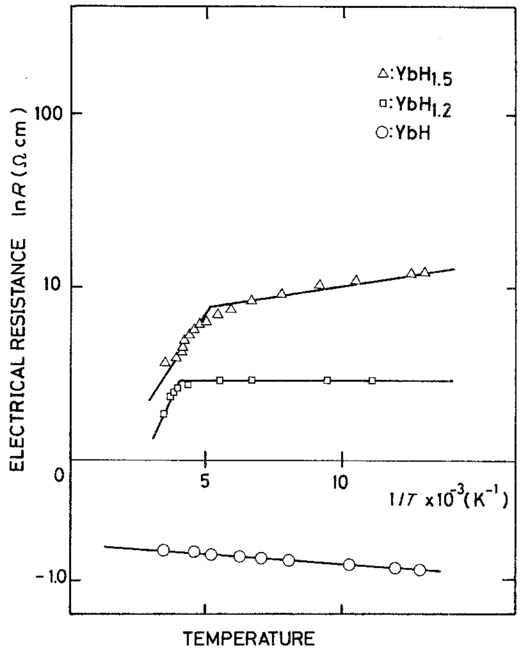

Figure 7 The relation between electrical resistance (ln R) and temperature ($1/T$).

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