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Characteristics of Hydrogenation and Electronic Properties of Thin Film $Y-H_x$

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Abstract : Thin Film yttrium, 500 nm thick, was prepared by electron beam evaportion on sapphire substrate. Film was hydrogenated at room temperature upto 1 bar hydorgen pressure without any activation process. Electrical resistivity was measured by four-point DC method in the temperature range between room temperature and 30 K for various hydorgen concentration $x=0$ to 2.924 of YH_x sample. Temperature dependent resistance of $YH_{2.924}$ shows low temperature minmum at 105K ($36\mu\Omega$ cm deep), the metal-semiconductor transition at 260K, and a hysteresis, which are similar behavior to bulk $YH_x(x>2)$ experimental results.

1. Introduction

Metal-hydrogen system exhibit varoius interesting phenomenas which do not show up in host metal. Some part of those phenomena are understood, but there are still unknown details left. Recently, physicists predict superconductivity at about 230K in metal phase of atomic hydrogen.[1-5] Although it has been clear from the beginning, that very high pressures ($3x10^8$ bar) would be needed to create this phase. It was theoretically predicted that atomic hydrogen would be metastable at lower pressures, possibly down to zero pressure. But it was suggested that we would have superconducting under about $1x10^8$ bar pressure if small amount of yttrium, lanthanum, and possibly barrium is dissolved in sufficient quantities of

hydrogen (i.e. yttrium-hydrogen system).[6] It is well known that the early transition metals (e.g. Y and La) and some of the rare-earths can form trihydrides. These systems are also interesting since that the metal-to-semiconductor (M-S) transition is observed in some composition range near MeH_3(Me=3B-subgroup elements).[7]

Electrical property measurements under high pressure are usually done in high pressure diamond envil cell with sample shape as thin film because of limitation of the diamond envil cell size. So far there have been no experimental reports on this metallization of atomic hydrogen. For the introductory experiment, we tried to make thin film yttrium(Y) on sapphire substrate at room temperature , load hydrogen gas into Y film and measure temperatrue dependence of resistivity of $Y(H_x)$ system in the temperature range between room temperature and 30K under 1 bar pressure. The optical and acoustic electron-phonon coupling in YH_x system is examined by using Bloch-Gruneisen and Einstein formula of resistivity of metal-hydrogen system.

2. Experiments

Thin film Y samples were made with 99.9% purity Y(from Leico Industries, Inc) on sapphire substrate(10mm x 14mm,[1102]oriented surface). Y film was evaporated on substrate by electron beam under working pressure 8 x 10^{-8}torr(distance between E-beam source and substrate is about 40cm, substrate temperature is room temperature, and evaporation speed is 0.5nm/sec). The film is cutted into about 1mm x 10mm shape by tungsten carbite needle for the four-point DC resistivity measurement. Electrical leads were welded with 50 micrometer diameter Al wire by ultrasonic wedge bonder. The sample was mounted on sample holder for resistivity measurements in continuous flow cryostat without loading hydrogen (Fig. 1). Cooling rate and warming rate of the sample are about 12K/min. and 2K/min. respectively. Table 1 shows characteristics of several Y film samples. Average of resistivity ratio of the above samples was about 1.9, which is rather bigger than bulk. Difference may be due to the dimensions of thin film and/or impurities in film.

Table 1. Characteristics of thin film Y samples

Sample name	Y1.2	Y1.6	Y2.3	Y3.1	Y4.1	Y5
Film Thickness (nm)	500	500	500	500	500	500
Residual resistivity ($\mu\Omega$cm)	100	100	84	62	114	70
Resistivity ratio, ρ_{300K}/ρ_T	1.64	1.64	1.79	2.24	1.88	2.15

Hydrogen gas(99.999%pure) was introduced into the sample chamber at room temperature. Hydrogen pressure was increased step by step to reduce sudden change of the sample temperature due to hydrogen absorption. The resistivity of the sample was measured by four-point DC method during hydrogenation. When the resistivity of the sample(sample Y3.1) was changed to the desired value, the sample was cooled and warmed to measure the temperature dependence of resistivity. After this measurement hydrogen was loaded more into the sample and do the same experiments over. One of the samples(sample Y3.1) was examined the hydrogen absorption and desorption cycling effect.

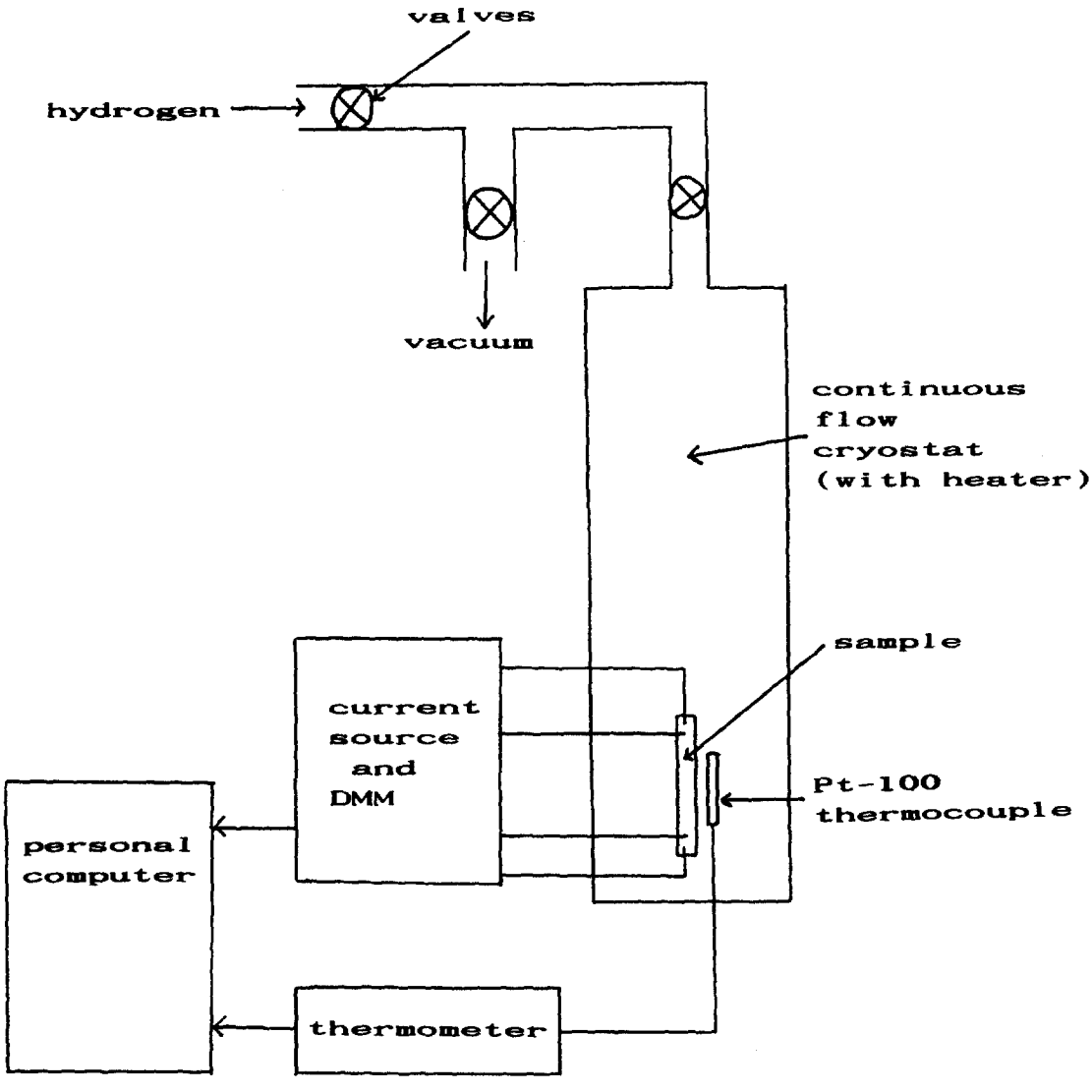

Figure 1. Schematic diagram of hydrogenation and electrical resistance measurement of thin film Y(Hx) system.

3. Results and Discussions

Hydrogenation

Figure 2 shows change of resistivity of Y2.3 sample during hydrogenation at room temperature. No activation process was needed for hydrogenation, in contrast to other metal–hydrogen system. In the beginning, the resistance increases gradually and reaches the peak($R/R_0=1.62$, R_0=resistance of Y) decreases down to minimum($R/R_0=0.2$). After this

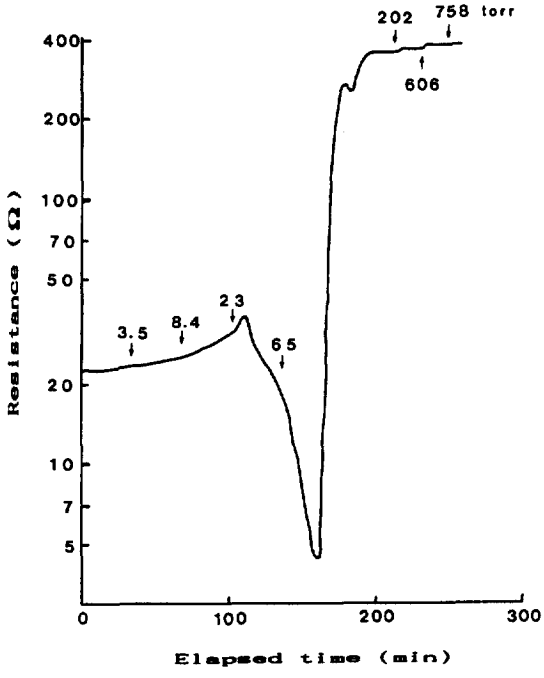

Figure 2. Resistance variation during hydrogen charging to 500 nm thick yttrium sample at room temperature(pressure in figure is equilibrium hydrogen pressure).

minimum, resistance increases enormously(R/R_0 =17.5). This rapid increasing of resistance indicates M-S transition, as other S-B subgroup metal-hydrogen system. Typical time duration for the equilibrium of hydrogen concentration was about 10min. at room temperature. Hydrogenation of Y foil(0.2 mm thick) was done at 550-600℃ for dihydride and at 250~300℃ for YH_{2+x}, x=0.10.[8]

It is known that M-S transition occurs at x = 2.8~3.0. Concentration of H in YH_x was not measured directly, but x would be greater than 2.8 because of M-S transition shown in our samples. In contrast to bulk, which is completely powdered at x=3, Y film was not powdered during the experiments.

Part of the hydrogen was evacuated when

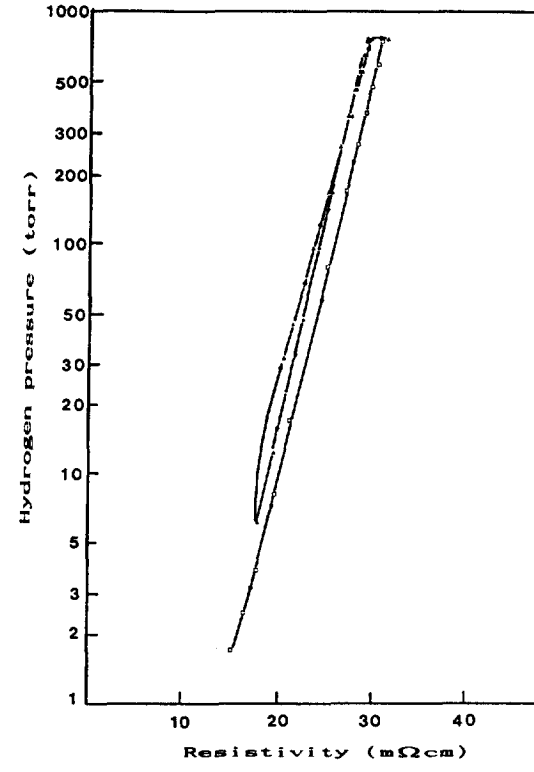

Figure 3. Resistivity variation during hydrogen absorption-desorption cycling at room temperature of 500 nm thick yttrium sample (Y3.1. sample). □ : 2nd desorption data, ▲ :3rd desorption data. △ :4th absorption data.

the sample chamber was pumped out. Resistance of YH_x reduced to the 61% of the maximum value when the sample(sample Y2.3)was in vacuum about 70 hours at room temperature.

Figure 3 shows the hydrogen absorption-desorption(A-D) process of sample Y3.1 Eventhough the number of cycles of A-D is small, resistances don't change much(about 10 %) in A-D cycles. One can see that it is possible to remove hydrogen from sample easily and also add hydrogen to sample

The electrical resistivity

The temperature-dependent part of the electrical resistivity, $\rho(T)$ can be expressed by Bloch-Gruneisen formula as follows,[9]

$$\rho(T) = c(T/\theta)^5 \int_0^{\theta/T} \frac{Z^5\, dZ}{(e^Z-1)(1-e^{-Z})} \quad (1)$$

were θ is Debye temperatrue, T is absolute temperature. Eq.(1) goes over at high enough temperature into the linear relation

$$\rho(T)=A^{ac}\, T, \quad (2)$$

where A^{ac} is constant.

For rare-earth hydride case, one can split the phonon spectrum into an acoustic part(low-frequency), with a cut-off given by the Debye temperature θ_D of the host metal(with θ_D ~100-300K), and a well separated optical part due to the H (or D)vibration, which can be expressed by a Einstein temperature(θ_E(H,D)~ 1000-1500K). One can rewrite Eq. (1) as follows.

$$\rho(T) = \rho^{ac}(T) + \rho^{op}(T) \quad (3)$$

At low temperature only acoustic phonons are excited. $\rho(T)$ would be $\rho^{ac}(T)$. It is possible to determine A^{ac} and θ_D from experimental data. At higher temperatures, acoustic and optical phonons are both excited. Thus it is possible to separate resistivity due to optical phonon excitation if $\rho^{ac}(T)$ is known.

Figure 4 shows temperature dependence of resistivity of thin film $Y(H_x)$ samples(sample Y 3.1). Experimental curves I, II, III and IV were obtained as follows; sample Y3.1 was loaded with hydrogen slowly like sample Y2.3 (refer

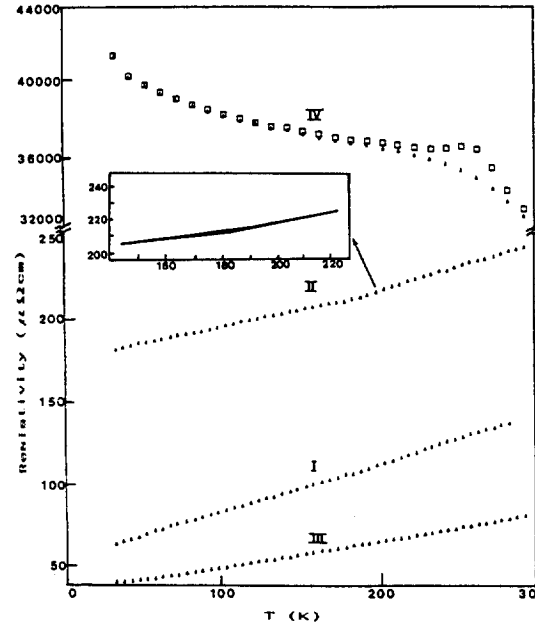

Figure 4. Electrical resistivity of 500 nm thick $Y(H_x)$ sample(Y 3.1 sample). Curve I, II, III and IV are explained in text.

Figure 2). Curve I; $\rho(T)$ before hydrogen loading, curve II; when resistance reached first peak during hydrogenation, hydrogenation was stopped and cool the sample and warm the sample for $\rho(T)$ measurement, curve III; after this measurement, we continue hydrogen loading. When resistance of the sample reached minimum point, stop loading, and redo $\rho(T)$ measurement, curve IV; after curve III measurements, continue hydrogen loading upto 1 bar pressure, wait until resistance doesn't change anymore. And start $\rho(T)$ measurement.

Hydrogen concentration was calculated by using quartz-crystal microbalance technique (QCM). Thin film Y sample(500 nm thick) was evaporated on 6 MHz AC-cut qurtz crystal with same evaporation condition as other samples. Hydrogen was loaded under same condi-

tion as other samples. Hydrogen concentration was calculated from this QCM measurement.[10] One can assume that at same hydrogen pressure, there will be same amount of thydrogen in QCM sample and sample on sapphire substrate.

Thus, curve II, III and IV corresponds to [H]/[Y]=0.05, 0.20 and 2.924 respectively. For curve I and II, one observes a very weak hystersis between 150K and 220K, and a kink at about 177K (shown in the inset of Fig. 4), which is pretty same as that the low temperature trasition exhibited in the solid solution phase of $YH_{0.15}$.[11]

One can note the change of residual resistivity of curves. The increase of curviture above 170K indicates the contribution of the optical phonons, due to conduction-electron scattering by the vibrations of the hydrogen.[8] Surprisingly, curve IV exhibits very different behavior than other curves. Curve IV shows; i) a hysteresis which shows up weakly from 70K and increase magnitude of hysteresis and maximize at 260 K, ii) the M-S transition appears near 260K. This might be due to order-disorder transformation of H in lattice.[5]

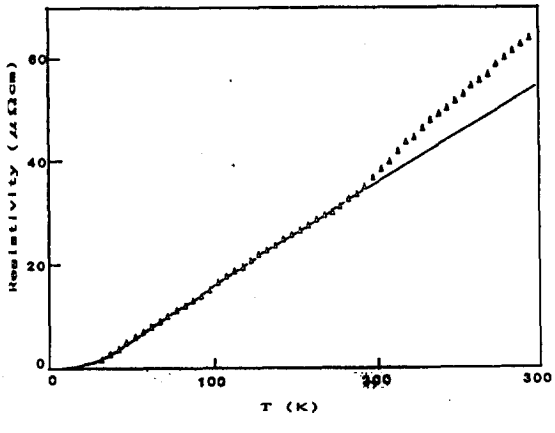

Figure 5. Temperature dependence of the resistivity of 500 nm thick YH_x sample (Y 3.1 sample). Background was subtracted from experimental data for comparision with calculated value(solid line is calculated value with c=131 $\mu\Omega$cm, θ=173.264, and backgroud=180$\mu\Omega$cm in Eq. (1))

Figure 5 shows typical curve fitting to the experimental data by using Eq. (1). Fitting program adjusts C, θ and background($\rho_{impurity}$)for best fitting in the temperature range 0 to 140K.[9] Table 2 shows fitting parameters of samples.

Table 2. Fitting parameters of thin film Y sample(Y 3.1)

curve name[a]	I	II	III
c ($\mu\Omega$ cm)	158	131	159
θ_D (K)	153	175	283
backgroud ($\mu\Omega$ cm)	61.7	18	41.4
A^{ac} ($\mu\Omega$ cm/K)	0.289	0.210	0.140
A^{op} ($\mu\Omega$ cm/K)	0.17	0.315	0.2[b]

a: details are explained in text

b: fit with shifting theoretical curve to 90K to positive direction in temperature axis in graph. It does not fit at all without temperature shifting.

The trend of the change of Debye temperature of our film samples is similar to the bulk sample ($\theta_D(Y)=210K$, $\theta_D(YH_2)=340K$[9]). but the magnitude is about 80% of the bulk. Deviation from calculated acoustic phonon resistance of curve I (not shown in here) indicates that very small amount of hydrogen is already absorbed during preparation of film in UHV chamber.

Optical phonon spectrum can be approximated by an Einstein delta funtion located at an energy[9]

$$\rho^{op}(T) = A^{op}\theta_E \quad (H)f(X_H), \quad (4)$$

where $f(X_H)=X_H/((e^{X_H}-1)(1-e^{-X_H}))$, $X_H=\theta_E$ (H)/T and $\theta_E(H)=1475K$. Optical resistivity can be obtained by using Eq.(3), e.g. $\rho^{op}(T)=\rho$ (T)$-\rho^{ac}$(T). ρ^{ac} (T)was calculated with fitting parameters which were determined by using low temperature range (T<140K) experimental data. In fact the difference $\rho(T)-\rho^{ac}(T)$ is sensitive to the choice of C and θ_D. But it was certain that there is definite deviation between experimental data and calculated acoustical resistance above 150K (Fig. 5). Figure 6 shows $\rho^{op}(T)$ versus calculated Einstein function of curve II, One can see deviation from 240 K, which indicates other kind of mechanism may be involved above 240K range. ρ^{op} form curve I also exhibits similar behavior as curve II. ρ^{op} from curve III does not fit to Eq (4). When calculated curve was shifted + 90K, experimental,

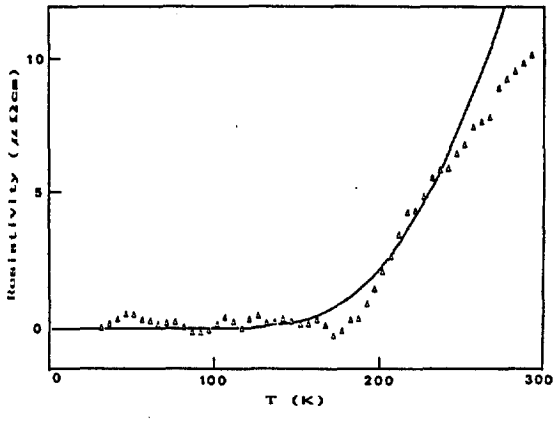

Figure 6. Temperature dependence of the optical resistivity of YH_x thin film (Y 3.1 sample). Solid line is calculated curve with A^{op}= 0.315 $\mu\Omega$ cm in Eq. (4). Experimental data (ρ^{op} (T)) are obtained by subtracting ρ^{ac}(T)data from ρ(T) (curve II in Fig. 3)

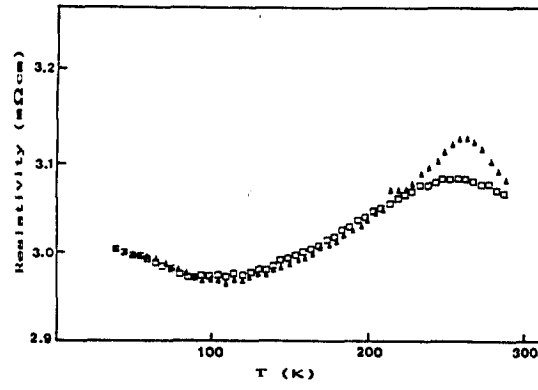

Figure 7. Electrical resistivity of 507 nm thick $YH_{2.9}$ specimen(Y5 sample). □ : data of cooling run and ▲ : data of warming run.

and calculated curves are well fitted each other (not shown in here). Figure 7 shows temperature dependence, of resistivity of sample Y5. This sample exhibits, i) at low temperature, there is minimum at 105K (36$\mu\Omega$cm deep), ii) the M—S transition at 260K, and iii) a hysteresis above 210 K. The above features were also observed in $YH_{2.095}$ bulk sample.[8]

An Arrhenius graph of the temperature dependence of YHx (Y5 sample) is shown in Fig. 8 to obtain an effective activation energy E_a.[8] Resistivity can be written as follows

$$\rho=\rho_0 \exp(Ea/kT)$$

Table 3 shows the comparison of several parameters of our data to Daou's work[8].

Table 3. Comparison of characteristics of our sample and bulk sample.

sample	low temperature minimum Tmin	low temperature minimum depth	M-S transition temperature	Ea (meV) LT[c]	Ea (meV) HT[c]
$YH_{2.9}$[a]	105K	36$\mu\Omega$cm	260K	0.163	4.96
$YH_{2.095}$[b]	40K	2.1$\mu\Omega$cm	284K	0.14	18

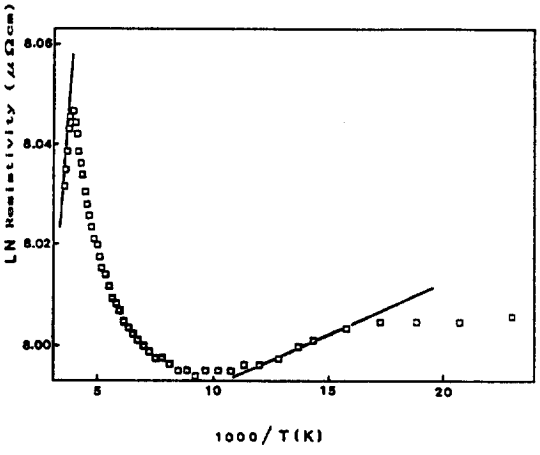

Figure 8. Arrhenius graph for 507 nm thick $YH_{2.9}$ specimen (Y 5 sample). Effective acrtivation energy was determined by the solid lines for low temperature side and high temperature side.

a: our work on 507 nm thick Y film which was loaded with 1 atm hydrogen gas.
b: warming data of quenched bulk sample.[8]
c: LT=activation energy of low temperature side.
HT=activation energy of high temperature side.

Figure 9 exhibits added resistivity due to hydrogen interstitials, $\rho_H=\rho(YH_X)-\rho(Y)$. Added resistivity has maximum at 260 K which can be attributed to the M-S transition temperature. There is also low temperature deep at 118K

4. Conclusion

This film Y specimens (500nm thick) were hydrogenated at room temperature without any activation processes. Maximum hydrogen con-

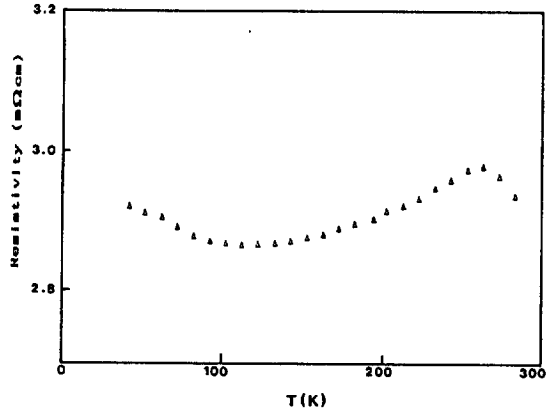

Figure 9. Added resistivity for hydrogen intersitials in 507 nm thick $YH_{2.9}$(Y5 sample).

centration was about 290 at. % with 1 bar hydrogen pressure. Temperatrue dependence of $YH_{2.9}$ exhibits low temperature minimum at 105K, metal -to- semiconductor transition at 260K, and a hysteresis was also observed, which are similar to experimental result of $YH_{2.095}$ foil specimen.[5] But there are several discrepancies in charateristics between film sample and bulk sample, but the origin of these is not clear yet. More systematic investigations, such as exact hydrogen concentration measurement of YH_x film sample (for temperature dependence of resistivity measurement), will be needed for better understanding of YH_x system.

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