# Semiconductor-Metal-Semiconductor Transitions in the Superstoichiometric Dihydride $YH_{2.10}$

P. Vajda and J. N. Daou

*Hydrogène dans les Métaux, Bâtiment 350, Université Paris-Sud, F-91405 Orsay, France*

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A metal-semiconductor transition has been observed in the range 230–260 K for the first time in a slightly superstoichiometric rare-earth dihydride, $YH_{2.10}$ (as compared to the $x$-rich systems $CeH_{2+x}$ and $LaH_{2+x}$ with $0.7 \lesssim x \lesssim 0.9$), implying an order-disorder transformation in the octahedral sublattice of the excess hydrogen atoms as the driving mechanism. Furthermore, a resistivity minimum in the range 60–80 K was observed, indicating for the first time in such systems an additional metal-semiconductor transition towards lower temperatures.

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Unusual metal-semiconductor (M-S) transitions, in the sense that the low-temperature phase was metallic and the high-temperature phase semiconducting, were unambiguously observed for the first time in the rare-earth hydride system $CeH_{2+x}$, for $0.7 \leq x \leq 0.8$, by Libowitz, Pack, and Binnie.[1] The transition occurred between 200 and 240 K, depending on the excess hydrogen concentration $x$, and was already at that time related with a small tetragonal distortion of the originally fcc fluorite-type structure. Recently, these measurements on $CeH_{2+x}$ were repeated by Shinar *et al.* and extended to the system $LaH_{2+x}$ using a contact-free $Q$-meter technique.[2] In the latter case, similar M-S transitions were observed in the range $0.8 \leq x \leq 0.9$, with the peak temperatures $T_p$ for the resistivity situated in the interval 200–260 K. These authors analyzed the behavior at high temperatures in the framework of variable-range hopping and associated the transition with a superlattice of octahedral vacancies forming at temperatures below $T_p$ and breaking down above it.[3] The previously described measurements were all performed at temperatures higher than 120 K, because of obvious contact problems, the samples being very brittle and chemically reactive, and the $Q$-meter technique being difficult to adapt to a He cryostat. Thus up to now there existed no real low-temperature resistivity measurements in such systems.

We have been studying the electrical resistivity of nonstoichiometric rare-earth dihydrides for a series of metals and have established, as one important result among others, the close relation between the existence of an octahedral superlattice of the excess hydrogen atoms $x$ and the magnetism prevalent in many of these systems at low temperatures (for a review, see, e.g., Ref. 4). An incipient metal-semiconductor transition was noticed in $PrH_{2.76}$ at $T_p \approx 280$ K (Ref. 5) and in $NdH_{2.65}$ near 290 K;[6] attempts to heat the samples above room temperature led to their destruction. The data at low temperatures were dominated by magnetic and crystal-field effects.[7] Nonmagnetic $LuH_{2+x}$, on the other hand, formed a two-phase system, with precipitation of its insulating $\gamma$ phase, already for $x$ of the order of a few percent, leading to a percolating situation.[8]

The present Letter describes some results obtained from electrical resistivity measurements on the system $YH_{2+x}$, undertaken in the hope to gain new insights from this essentially simpler (nonmagnetic) and more stable compound. The specimens were prepared from 99.99 at.% pure yttrium foil obtained from the Ames Laboratory (Ames, Iowa) and contain the main (> 1 at.ppm) metallic impurities (in at.ppm) 20 Fe, 19 W, 5 Ni, 4 Cu, 3 Al, 3 Pb, < 2 Hf, and the other rare earths 11 La, 3.5 Pr, 3 Ce, 3 Gd, 2.8 Tb. They were cut into $20 \times 1 \times 0.25\text{-mm}^3$ strips and provided with four spot-welded platinum leads as contacts. The ensuing hydrogenation was performed in two steps: the first, at 550–600 °C, to give the "pure" dihydride, with ideally all tetrahedral sites occupied, in this case $YH_{1.97}$; the second, adding the excess hydrogen atoms $x$ on the octahedral sites, at 250–300 °C. For more details on the preparation and on the problems related to the exact $x$ determination, see, e.g., Ref. 9. The resistivity measurements were done by the classical four-point dc method in a pumped He cryostat, in the range $1.5 \leq T \leq 330$ K. The experiments were performed both on slowly cooled (cooling rate ~0.2 K/min) or relaxed ($R$) specimens and on those quenched ($Q$) from room temperature into liquid nitrogen (rate $\sim 10^3$ K/min), in order to block a possible hydrogen ordering on the octahedral sites. As shall be shown in the following, we have observed, for the first time, not only a metal-semiconductor transition, similar to the $x$-rich systems $CeH_{2+x}$ and $LaH_{2+x}$ (Refs. 1–3) in the range of 230–260 K, for a strikingly *low* $x$ value ($YH_{2.10}$), but, in addition, a completely unexpected semiconductor-metal transition below ~80 K.

Figure 1 shows the resistivity data of the relaxed ($R$) $YH_{2.10}$ sample taken with decreasing and increasing temperature, respectively, and on those of the quenched sample ($Q$) when heating from 4.2 K. The first observation concerns the appearance of a resistivity peak at $T_p = 235$ K upon cooling, which is shifted to $T_p = 256$ K

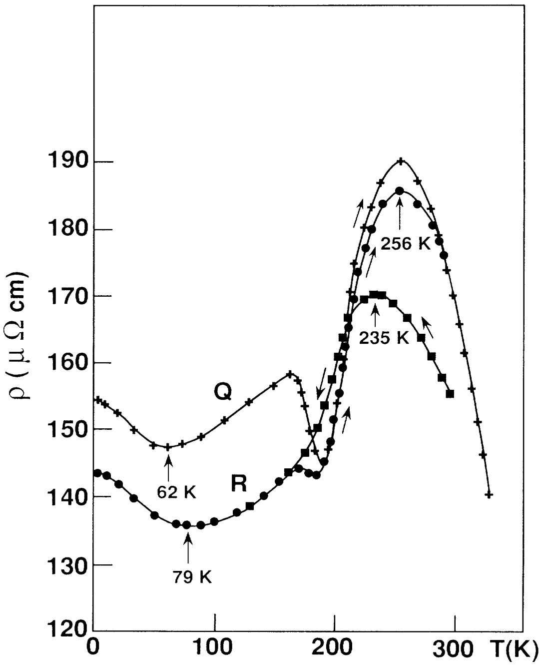

FIG. 1. Electrical resistivity of $YH_{2.10}$ as a function of temperature in the relaxed ($R$) and in the quenched ($Q$) state. Note the hysteresis in the relaxed sample in the cooling (■) and heating (●) cycles around 200 K and the different peak temperatures $T_p$. The low-$T$ minimum appears shifted in the quenched sample by 17 K.

following a hysteresis loop around 200 K upon heating. No electrical or structural measurements have been done, to our knowledge, on the superstoichiometric dihydride $YH_{2+x}$ below room temperature, but one can assume that, as in other analogous rare-earth dihydrides (see, e.g., Refs. 2 and 4 and references therein), the hysteresis near 200 K is due to an order-disorder process in the octahedral sublattice. X-ray diffraction spectra taken at room temperature and at liquid nitrogen showed no difference, in particular no line splitting on the face-centered-cubic metal lattice. (Small precursor anomalies in the range 150–180 K were observed on the simultaneously studied specimens with $x = 0.05$ and 0.08 and attributed to short-range ordering in the H sublattice; this will be the subject of a more exhaustive publication.) A simple test to confirm this idea is a quench across the anomaly region, shown by the curve labeled ($Q$) in Fig. 1. We note that the quench introduced a residual resistivity increase, $\Delta\rho_q$, of 12 $\mu\Omega$ cm, recovering in one simple stage centered at 180 K and joining the heating curve for higher $T$; the peak temperature $T_p$ is also the same as before the quench. Thus, it is reasonable to assume an $x$-hydrogen ordering between 220 and 200 K which can be blocked (at least in part) by a quench from the "disordered" range at room temperature. (A minor dip in the heating curve of the relaxed sample is probably due to the recovery of a small amount of disordered regions "quenched-in" during the first cooling procedure, the cooling rate of 0.2 K/min being apparently not low enough yet.) There remains the possibility of the precipitation of small concentrations of the trihydride phase when lowering the temperature and their evaporation again upon heating, giving rise to the resistivity anomaly. We can exclude this mechanism in our experiment after having measured the $\beta$-phase lattice parameter for $0 \leq x \lesssim 0.20$ between 80 and 300 K: The $\beta$-phase limit was always just above $x = 0.10$, both at room temperature and at liquid nitrogen.

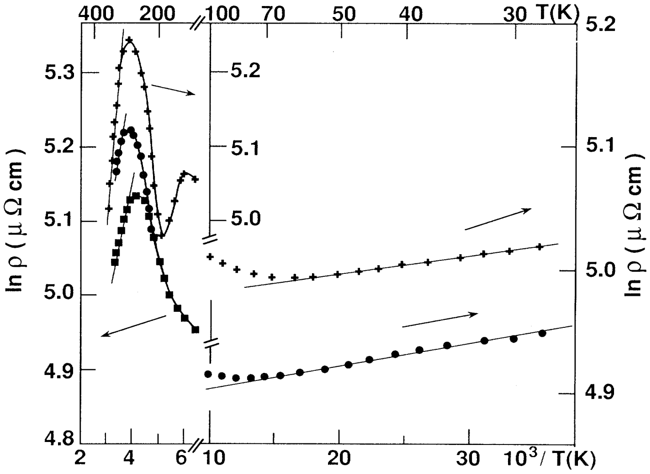

FIG. 2. ln$\rho$ as a function of $10^3/T$ in the high-$T$ (left-hand side) and in the low-$T$ (right-hand side) interval. Note the different ordinate scales. Symbols are the same as in Fig. 1.

The second striking observation is the minimum near 80 K followed by a renewed increase of resistivity down to liquid helium. Resistivity minima in metallic $RH_{2+x}$ systems were observed before, but they were usually flatter and occurred at lower temperatures; most important, however, is the fact that they were practically always seen on antiferromagnetically ordered systems,[4,10,11] indicating the onset of incommensurate order or of magnetic fluctuations. A Kondo minimum has also been measured in the heavy-fermion system $CeH_{2+x}$.[12] A very small minimum near 10 K in high-resistivity $LuH_{2.2}$ was the only other such manifestation in a nonmagnetic compound and was attributed to electron localization due to percolating scattering on the $\gamma$-phase regions.[8] All the arguments implying a magnetically induced origin can be omitted in the case of the Y ion. A Kondo effect due to magnetic impurities (Fe, Ni, Pr, Gd, Ce, Tb) is, in principle, possible, but the depth of the minimum seems too large for the quantities involved and should, in any case, be also observable for $YH_{2+x}$ of the same origin with other hydride concentrations $x$; yet no minimum whatsoever (to a measuring precision of several n$\Omega$ cm) could be measured in the simultaneously investigated $YH_{2+x}$ samples with $0 \leq x \leq 0.08$, none of them showing any M-S transformation at $T \gtrsim 200$ K, either.

We shall, therefore, try to interpret the observed resistivity behavior in $YH_{2.10}$ in terms of two M-S transitions and analyze the results accordingly. In Fig. 2, we plot the logarithm of $\rho$ as a function of the reciprocal temperature, to fit a relation of the form

$$\rho = \rho_0 \exp(E_a/kT) ,$$

where the activation energy $E_a$ is derived from the slope of the linear parts, as indicated. The high-$T$ part around $T_p$ (left-hand side of Fig. 2) reminds one very closely of the situation described for $LaH_{2+x}$ in Ref. 3. It goes so far that even the numerical value of

$$E_a(YH_{2.10}) = 15 \text{ meV} \quad (\rho_0 = 86\ \mu\Omega\,\text{cm})$$

for the relaxed sample is close to the 18 meV given in Ref. 3 for the lowest-resistivity $LaH_{2.80}$ specimen ($\rho_0 = 350\ \mu\Omega\,\text{cm}$). We are, thus, tempted to suggest the ordering transformation near 200 K as a possible driving mechanism towards carrier delocalization in a defect band around the Fermi level, creating the lower-$T$ metallic state. The fundamental difference between the earlier investigated $x$-rich systems[1-3] and our $YH_{2.10}$ lies in the fact that the superlattice in the *super*stoichiometric *di*hydrides is formed by the octahedral hydrogens themselves and not by their vacant sites such as in those *sub*-stoichiometric *tri*hydrides. Going further down in temperature (right-hand side of Fig. 2), these weakly metallic systems become semiconducting again,[13] the charge carriers being localized in very shallow levels separated by a narrow gap from the conduction band of

$$\Delta^R = 2E_a^R = 0.30 \text{ meV} \quad (\rho_0 = 132\ \mu\Omega\,\text{cm}) .$$

This situation is not very stable as it seems modified by the quenched-in defects: The gap becomes even narrower,

$$\Delta^Q = 2E_a^Q = 0.25 \text{ meV} \quad (\rho_0 = 144\ \mu\Omega\,\text{cm}) ,$$

leading also to an earlier S-M transition: $T_{\text{min}} = 62$ K as compared to the 79 K for the ($R$) case.

In conclusion, we have observed in $YH_{2.10}$ a very-narrow-gap semiconducting behavior below 60–80 K, turning metallic until a further M-S transition at 235–260 K yielding a semiconductor with an effective activation energy of $E_a = 15$ meV. The latter transition is driven by an order-disorder transformation of the octahedral H sublattice of the $x$ atoms, taking place around 200 K.

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