

Percolation and proximity effects in two-phase rare earth hydrides through electrical resistivity measurements

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 6267

(<http://iopscience.iop.org/0953-8984/3/33/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 11/05/2010 at 12:27

Please note that [terms and conditions apply](#).

Percolation and proximity effects in two-phase rare earth hydrides through electrical resistivity measurements

P Vajda, J P Burger and J N Daou

UA 803 du CNRS 'Hydrogène dans les Métaux', Bâtiment 350, Université Paris-Sud, F-91405 Orsay, France

Received 12 December 1990, in final form 19 April 1991

Abstract. We present electrical measurements for a mixture of two metallic phases: the pure rare earth (Gd, La) and the dihydride (GdH₂, LaH₂). The analysis for GdH_y, with $y = 2 - x$, shows that the GdH₂ phase has a continuous percolation path across the mixed medium even when its volume fraction is very small; this indicates that GdH₂ forms initially within the grain boundaries of the Gd metal. The proportionality between $d\rho/dT$, $(d\rho/dy)_T$ and $\rho^{3/2}$ confirms that the Gd and GdH₂ domains have very different shapes. We also observe an interaction between the ferromagnetic Gd domains and the excitation spectrum of the antiferromagnetic GdH₂ domains. This magnetic proximity effect is biggest for low y -values, so it can be related to magnetic percolation. In the case of LaH_y, we observe a superconducting percolation due to La up to $y \sim 1.6$. This high y -value clearly indicates that superconductivity is partially induced in the normally conducting LaH₂ phase by the corresponding superconducting proximity effect.

1. Introduction

The absorption of hydrogen by rare earths (R), i.e. the formation of the hydride RH_y, can give rise to a two-phase situation involving the pure R and the pure dihydride RH₂. It occurs if $y (= 2 - x) < 2$ and is related to the strong stability of the dihydride phase. However, for heavy trivalent R (Ho to Lu) as well as for Y and Sc, there exists a solid solution RH_y with $y \leq y_{\max}$ (which is, for example, $y_{\max} = 0.35$ at.% H/at.% R in the case of Sc) [1, 2]; these solid solutions are stable down to the lowest temperatures measured. This concentration limit y_{\max} decreases with decreasing Z within the lanthanide series (it is only 0.03 at.% H/at.% R for Ho [3]) and disappears completely for the lighter R (Dy to La). Thus, to avoid the presence of the solid solution phase, in this work we shall only consider two light R, namely Gd and La. In addition, it was interesting to study two systems with quite different low-temperature characteristics: the ferromagnetic–antiferromagnetic GdH_{2-x} and the superconducting–normally conducting LaH_{2-x}.

The corresponding R and RH₂ phases are both metallic, but with three conduction electrons per R atom for the R phase and with only one for the RH₂ phase [4]. This is why there is a relatively large difference between the two corresponding electrical resistivities $\rho(T)$. For instance, for non-magnetic lutetium, where

$$\rho(T) = \rho_r + \rho_{\text{ph}}(T) \quad (1)$$

(ρ_r is the residual resistivity, ρ_{ph} is the phonon resistivity), one obtains at room temperature $\rho_{Lu} \simeq 55 \mu\Omega \text{ cm}$ and $\rho_{LuH_2} \simeq 11 \mu\Omega \text{ cm}$, so that $\rho_R/\rho_{RH_2} = 5$ [5]. But for Gd and GdH_2 , there is a supplementary contribution to $\rho(T)$ [6], namely

$$\rho(T) = \rho_r + \rho_{ph}(T) + \rho_m(T). \quad (2)$$

$\rho_m(T)$ is the magnetic spin-disorder resistivity which tends to disappear below the magnetic transition temperature: Gd becomes ferromagnetic below $T_C = 293 \text{ K}$ while GdH_2 is antiferromagnetic (AF) below $T_N = 18.5 \text{ K}$ [7]. The absolute values of ρ_m (above T_C and T_N) are generally larger than $\rho_{ph}(T)$; for that reason, and also because $T_N \ll T_C$, the ratio ρ_{Gd}/ρ_{GdH_2} can be strongly T -dependent.

The conductivity σ of a binary mixture of high-conductivity (σ_{hc}) and low-conductivity (σ_{lc}) components can, in principle, be described by a semi-phenomenological percolation model [8, 9] given by the following formula

$$\frac{f(\sigma_{lc}^{1/t} - \sigma^{1/t})}{\sigma_{lc}^{1/t} + (f_c/1 - f_c)\sigma^{1/t}} + \frac{(1-f)(\sigma_{hc}^{1/t} - \sigma^{1/t})}{\sigma_{hc}^{1/t} + (f_c/1 - f_c)\sigma^{1/t}} = 0 \quad (3)$$

(where f is the volume fraction of the low-conductivity phase; note that $f = x/2$ if $\rho_R > \rho_{RH_2}$ and $f = y/2$ if $\rho < \rho_{RH_2}$). The resistivity $\rho = 1/\sigma$ depends on two morphology parameters: the first, f_c , corresponds to the critical volume fraction at which the high-conductivity phase begins to form a continuous percolating path across the binary phase system; the second, the exponent t , depends essentially on the shape of the low- and high-conductivity domains or grains [8], for which $t \approx 1$ if they have similar shapes.

One has thus two extreme situations: (i) the symmetric one where the binary system corresponds to a random mixture of spherical or ellipsoidal domains or grains: for this case, one expects the value of f_c close to $\frac{1}{2}$; (ii) the two asymmetric situations where the grains of one phase are coated by the second: in this case, one can have $f_c \simeq 1$ or $f_c \simeq 0$. The easiest percolation problems concern the case $\sigma_{hc}/\sigma_{lc} \gg 1$; if, for instance, $\sigma_{lc} = 0$ (an insulator) or $\sigma_{hc} = \infty$ (a superconductor), then equation (3) reduces to

$$\rho = \sigma_{hc}^{-1}/(1 - f/f_c)^t \quad \text{if } \sigma_{lc} = 0 \quad (4)$$

$$\rho = \sigma_{lc}^{-1}[1 - (1 - f)/(1 - f_c)]^t \quad \text{if } \sigma_{hc} = \infty. \quad (5)$$

The situation corresponding to equation (4) has been found in LuH_{2+x} [10], which is a mixture of metallic LuH_2 and insulating LuH_3 , with a very small value for f_c , indicating that LuH_3 tends to coat the metallic grains of LuH_2 . We want to mention here that, in the case of YH_{2-x} , there exists an electron-microscopic observation of a tendency for the dihydride YH_2 to precipitate, for small y ($= 2 - x$)-values, within the grain boundaries of the yttrium metal [11].

The original aspects of this work are:

(i) the difficulty of analysing the percolation problem for GdH_y , because of the relatively low ratio ρ_{Gd}/ρ_{GdH_2} : a situation yet to be studied;

(ii) the influence of the strong ferromagnetism of the Gd domains upon the weak antiferromagnetism of the GdH_2 domains, with a possible magnetic percolation problem; and

(iii) the superconducting percolation of the La phase within LaH_y which can in principle be much easier to deal with because $\rho = 0$ as long as $f < f_c$ (expression (5)).

2. Experimental procedure

The specimens were 20 mm × 1 mm × 0.2 mm strips cut from cold rolled 4N-grade Gd and La-foils obtained from the Ames Laboratory (Ames, Iowa, USA). They were contacted with four spot-welded platinum leads and loaded with hydrogen at 550 °C using a calibrated volume for the concentration determination, with a precision of ±1%. The resistivity measurements were made between 1.3 K and room temperature in a pumped liquid-helium cryostat, with a sample holder permitting measurement of up to seven different specimens at a time. The GdH_{2-x} samples were very stable through the entire measuring cycle, while the LaH_{2-x} specimens contaminated rapidly even during the short periods of handling in air, this contamination leading to oxide and hydroxide formation. In general, the LaH_{2-x} specimens were cooled rapidly across the FCC → DHCP transformation range of La in the interval 200 to 300 °C, which could explain the presence of H atoms in solution in the metallic phase [12] and the sometimes high residual resistivity values of some of the specimens. X-ray diffraction analysis of several of the hydrogenated samples has yielded spectra with narrow, well resolved lines on a low background, up to large angles, indicating a uniform crystallite distribution with sizes in the micrometre range and the absence of notable stress, which is not surprising in view of the high hydrogenation temperature.

3. Results and discussion

3.1. The Gd-GdH₂ system

In figure 1, we give the variation of $\rho(T)$ for the two pure phases of Gd and GdH₂. An interesting feature is the intersection of the two curves at two points: the first, at $T \simeq 80$ K, is related to the decrease in $\rho_m(T)$ for pure Gd while the corresponding term of GdH₂ remains constant as long as $T > T_N = 19$ K. The second intersection near $T \simeq 8$ K is related to the fact that $\rho_r(\text{Gd})$ is larger than $\rho_r(\text{GdH}_2)$. The reason for this, in addition to the point mentioned in the introduction, is probably the existence of ferromagnetic domains whose interfaces can give a supplementary contribution to $\rho_r(\text{Gd})$. In figure 2, for $T \geq 20$ K, we present the variation of $\rho(T)$ for the binary mixtures with $0.3 \leq y \leq 1.9$: all the corresponding curves have an intersection near 80 K, in agreement with figure 1. In figure 3, we give $\rho(y)$ at different temperatures; it is interesting to note that $d\rho/dy$ is not constant (except for $T \simeq 80$ K), a fact which indicates clearly that one cannot assume simply that the electrical current successively crosses the Gd and GdH₂ domains. The existence of such a curvature favours the previously mentioned percolation problem.

In figure 4, we indicate first that $\rho^{-3/2} d\rho/dT$ (at 200 K) has a linear variation with y , a fact which gives information on the values of f_c and t . The formula (3) can be written in the form:

$$\begin{aligned}
 2f_c\sigma^{1/t} &= A + \sqrt{A^2 + B^2} \\
 A &= \sigma_{hc}^{1/t}(f_c - f) + \sigma_{lc}^{1/t}(f + f_c - 1) \\
 B^2 &= 4f_c(1 - f_c)\sigma_{hc}^{1/t}\sigma_{lc}^{1/t}.
 \end{aligned}
 \tag{6}$$

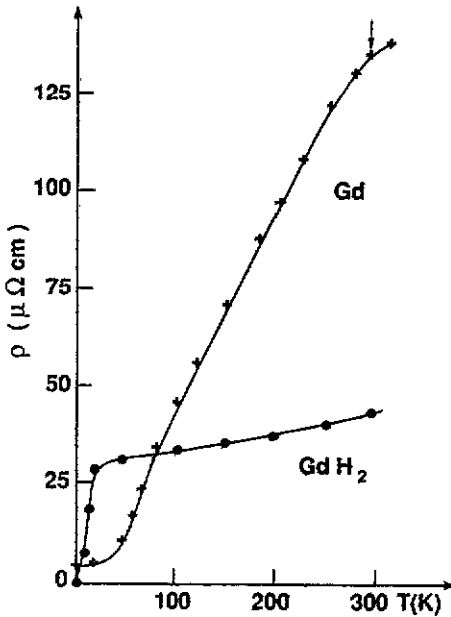


Figure 1. Temperature variation of the resistivity, $\rho(T)$, for pure Gd and pure GdH_2 .

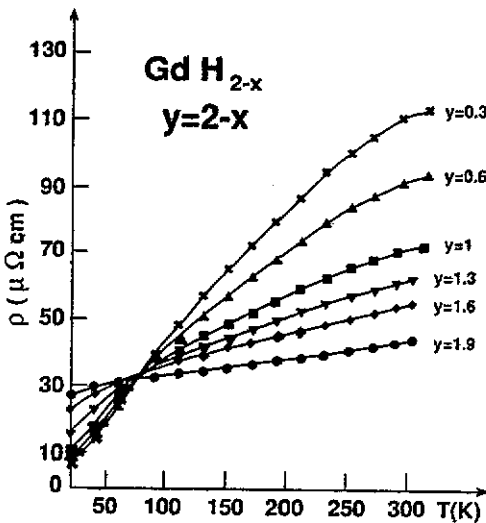


Figure 2. Temperature variation of the resistivity, $\rho(T)$, at $T > 20$ K, for the binary system GdH_y , with $0.3 \leq y \leq 1.9$.

The best agreement with the previously mentioned curve of figure 4 is obtained if one takes $B = 0$, i.e. $f_c = 1$, so that

$$\begin{aligned} d\sigma^{1/t}/dT &= (f_c - f)d\sigma_{hc}^{1/t}/dT + (f + f_c - 1)d\sigma_{lc}^{1/t} = \eta(f) \\ d\rho/dT &= -\eta(f)t\rho^{1+1/t}. \end{aligned} \quad (7)$$

This indicates clearly that $t \simeq 2$, a value very similar to that obtained for the mixture of the α - and β -phases of PdH_x [9] and for LuH_{2+x} [10]. The experimental value,

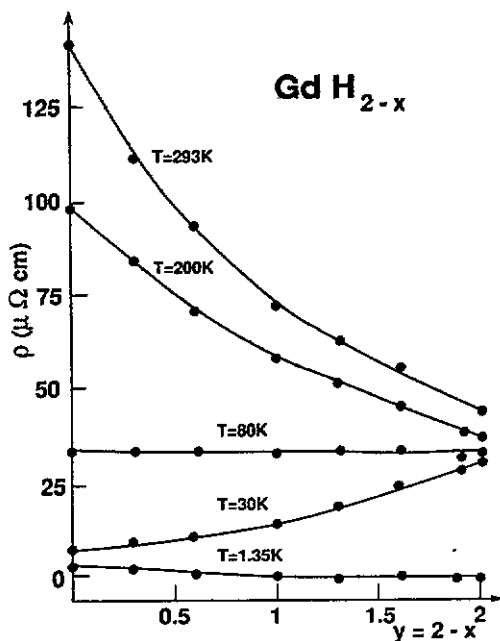


Figure 3. Variation of the resistivity, $\rho(y, T)$, at different constant temperatures, as a function of the hydrogen concentration $y = 2 - x$.

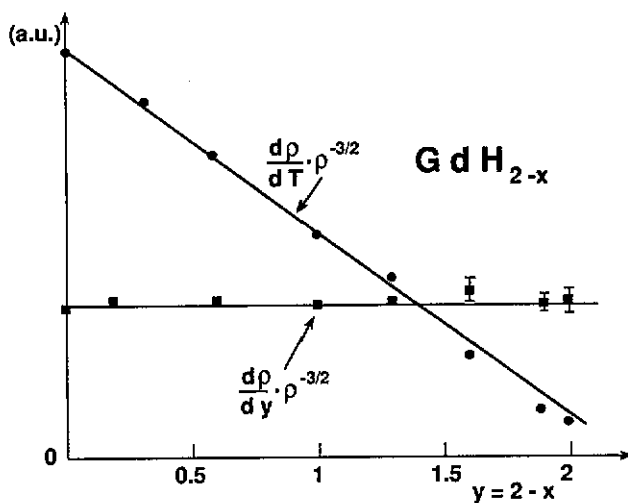


Figure 4. Variation of $\rho^{-3/2} d\rho/dT$ and of $\rho^{-3/2} (d\rho/dy)_T$ as a function of y , at $T = 200$ K.

$-0.151 (\Omega \text{ cm})^{-1/2} \text{ K}^{-1}$, for the slope of this curve, i.e. $\rho^{-3/2} (d/dy)_T (d\rho/dT)$, agrees exactly with the theoretical one, $-0.153 (\Omega \text{ cm})^{-1/2} \text{ K}^{-1}$, of formula (7), with $f_c = 1$, $t = 2$, $\rho_{\text{Gd}} = 98 \mu\Omega \text{ cm}$ and $\rho_{\text{GdH}_2} = 38 \mu\Omega \text{ cm}$. The second curve of figure 4 implies the fact that

$$\rho^{-3/2} |d\rho/dy|_T = C = \text{constant.}$$

The experimental value of C is equal to 116 ± 5 ($\Omega \text{ cm}$) $^{-1/2}$, while the theoretical one obtained from formula (6) (with $f_c = 1, t = 2$) is 122, i.e. there is again a relatively good agreement. The main result, namely $f_c = 1$, indicates that at low y -values GdH_2 tends to surround the Gd grains, with an immediate percolation along the grain boundaries. It is well known that the stability of hydrogen is always larger near defects like grain boundaries, dislocations or impurities than in a defect-free metal. With respect to the value of t , it indicates that the Gd and GdH_2 domains possess very different non-spherical shapes.

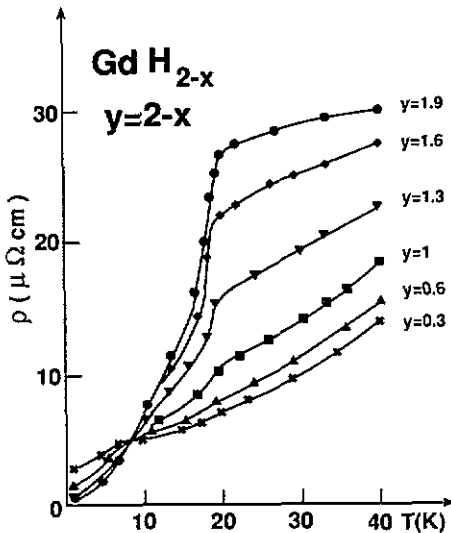


Figure 5. Temperature variation of the resistivity, $\rho(T)$, for the binary system GdH_y , with $0.3 \leq y \leq 1.9$, in the range $1.5 \leq T \leq 40$ K.

In figure 5, we show for $T \leq 40$ K, the variation of the magnetic term, $\rho_m(T)$, related to the antiferromagnetism of GdH_2 . A well defined anomaly occurs at $T = T_N = 18.5$ K which is observed for $y = 1.9, 1.6, 1.3$ and 1 ; the anomaly becomes smaller but continues to exist for $y = 0.6$ and 0.3 . In figure 6, we represent $d\rho/dT$ within the magnetic range $1.5 \leq T \leq 20$ K. For the pure dihydride ($y \geq 1.9$), one observes at low temperature ($T \leq 8$ K), an increase of $\rho_m(T) \propto T^n$, with n between 2 and 3, due to the scattering of the conduction electrons by the magnetic excitations or spin waves; for $T \geq 8$ K, $\rho_m(T)$ tends to become proportional to T up to about 13.5 K, probably because the whole spin-wave spectrum begins to be excited above 8 K (a similar situation occurs for the electron-phonon scattering for which $\rho_{ph} \propto T^n$, with $n = 3$ to 5 at low temperatures and $n \simeq 1$ at higher T). The second increase in $d\rho/dT$ approaching T_N is related to the decrease in the magnetic order parameter. The first anomaly tends, however, to change when y decreases:

(i) There is a variation in the shape of $d\rho/dT$, which begins to go through a maximum.

(ii) The temperature of this maximum, T_M , decreases with decreasing y , from $T_M \approx 6.6$ K for $y = 1.3$ to 4.2 K for $y = 0.6$.

All this shows that there is certainly an interaction between the ferromagnetic domains of Gd and the AF domains of GdH_2 , a phenomenon which can be ascribed to

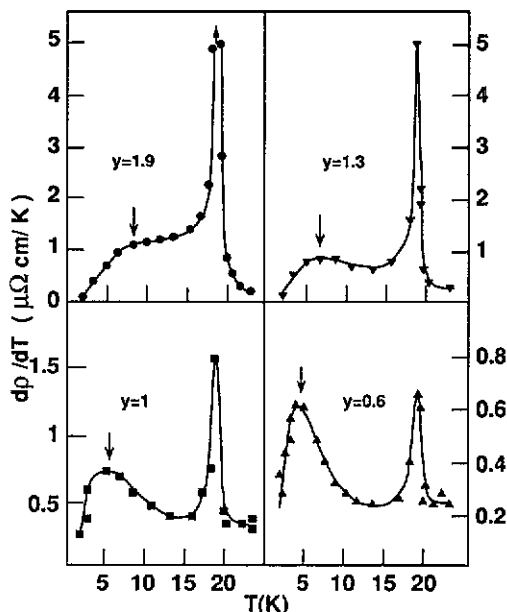


Figure 6. Temperature variation of the derivative, $d\rho/dT$, within the antiferromagnetic regime, for $0.6 \leq y \leq 1.9$. The two anomalies are related to the magnetic excitation spectrum and to the transition at the Néel temperature T_N .

a proximity effect due to the occurrence of molecular field interactions at the domain interfaces or to dipolar fields created by the ferromagnetic domains on the GdH_2 domains. *A priori*, one can consider that this interaction is not very strong because it affects only the AF spin-wave spectrum but not the AF transition temperature. It appears, nevertheless, that it has maximum efficiency for low y -values, which is understandable for two reasons: (i) for low y , the GdH_2 domains surround exactly the Gd grains; and (ii) they have a small thickness relative to that of the grain boundaries. For these geometrical reasons, it is evident that the excitation spectrum of the whole GdH_2 volume fraction can be affected by the Gd grains, i.e. the magnetism has a percolation behaviour similar to that of the resistivity.

3.2. The La-LaH₂ system

Compared with the case of GdH_{2-x} , the situation of the system LaH_{2-x} is more complicated for two main reasons:

(i) the metallic La-phase can be a mixture of two components—a cubic (FCC) and a hexagonal (DHCP) one; the conservation and the stability of the high-temperature (FCC) metallic phase at room temperature and below are due to the presence of defects (in this case, of H atoms in solid solution) and to a quench effect caused by rapid cooling from the hydrogenation temperatures of 500–600 °C [12];

(ii) pure La is much more sensitive than Gd to the absorption of oxygen, with eventual formation of an oxide; for that reason, it is not easy to avoid completely the presence of a small fraction of oxygen related to the preparation and the handling of the samples.

It has also been observed in YH_{2-x} that the presence of oxygen decreased the stability of the hydride [11]. For all these reasons, it is evident that the formation of

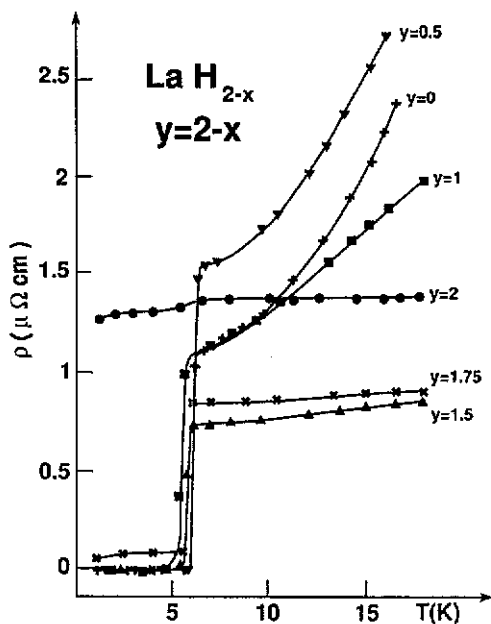


Figure 7. Variation of the intrinsic resistivity of LaH_y , $\rho_0(T) = \rho(T) - \rho_r$, with $0 \leq y \leq 2$.

LaH_2 in La may be different, i.e. less uniform than the formation of GdH_2 in Gd.

In figure 7, we present the resistivities $\rho(y, T)$ after subtraction of ρ_r . It is interesting to note that there is, at a given T , a strong initial drop of ρ with increasing y for $y \leq 1$; the corresponding $|\Delta\rho/\Delta y|_T$ is larger than $[\rho(y=0) - \rho(y=2)]/2$, which indicates that there is again a percolation problem, but of a different nature compared with that of GdH_y : $|\Delta\rho/\Delta y|_T$ is constant for $y \leq 1$ while there was always a curvature for GdH_y . This behaviour of LaH_y cannot be interpreted through formula (3), due probably to the previously mentioned more complex situation. For $y \geq 1$, the change of ρ with y is smaller than for GdH_y , i.e. again a different behaviour.

In figure 8, we show the total $\rho(T)$ for $T \leq 20$ K; one can see the complicated behaviour of the residual ρ_r , which increases first at low y ($y \leq 0.5$), decreases for $y \simeq 1$, and increases again for $y \geq 1.5$. As already mentioned, this is probably related to a non-controlled small absorption (a few at%) of hydrogen in the metallic phase of the specimens. An interesting feature concerns the occurrence of the superconducting transition: this occurs at $T_c \simeq 6$ K for cubic La while for hexagonal La it occurs at 5.1 K [13]; the cubic T_c is the one mostly observed. The superconducting percolation (with $\rho = 0$ for $T < T_c$) continues to exist up to $y = 1.5$ and disappears for $y = 1.75$, for which there remains below T_c a finite resistivity of the order of $0.1 \mu\Omega \text{ cm}$. By applying equation (5) one again obtains $t \simeq 2$ if $f_c = 0.81$ (corresponding to $y = 1.62$). This high value for f_c is surprising since, comparing it with GdH_y , one expects the continuous percolation for the La-phase to disappear as it does for Gd at low y -values. But this new percolation may have a different origin, not only related to geometrical domain percolation: superconductivity can be induced into a contacting normal metal by a superconducting order parameter through a proximity effect. It can even occur for small insulating (oxide) regions through the Josephson effect. A further support for this argument follows from the fact that, for $f > f_c$, the resistivity $\rho(T)$ decreases

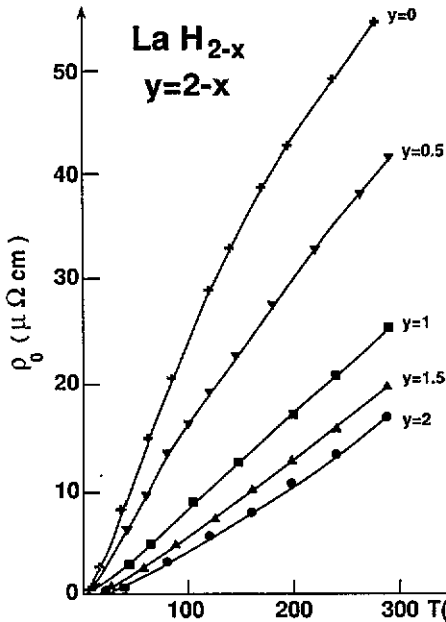


Figure 8. Temperature variation of the total resistivity, $\rho(T)$, for LaH_y , with $0 \leq y \leq 2$, in the range $1.5 \leq T \leq 18$ K. The superconducting transition occurs near $T_c = 6$ K.

slightly below T_c (figure 8), since by lowering T the proximity effect increases due to the increase in the superconducting order parameter. This decrease in ρ can also be related to an increase in the critical current within the proximity and the Josephson regions. It is to be noted that, even for $y = 2$ (figure 8), there remains a very small fraction of superconducting behaviour (drop below T_c) connected to the fact that the formation of LaH_2 is locally perturbed by the presence of the oxide and hydroxide.

References

- [1] Vajda P and Daou J N 1984 *J. Less-Common Met.* **101** 269
- [2] Daou J N and Vajda P 1988 *Ann. Chimie (France)* **13** 567
- [3] Daou J N, Vajda P and Burger J P 1987 *Solid State Commun.* **64** 937
- [4] Misemer D K and Harmon B W 1982 *Phys. Rev. B* **26** 5634
- [5] Daou J N, Lucasson A, Vajda P and Burger J P 1984 *J. Phys. F: Met. Phys.* **14** 2983
- [6] Burger J P, Daou J N, Vajda P and Lucasson A 1984 *J. Less-Common Met.* **103** 381
- [7] Vajda P, Daou J N and Burger J P 1991 *Proc. Int. Conf. on Metal-Hydrogen Systems (Banff, Canada, September 1990)* *J. Less-Common Met.* **172** 271
- [8] MacLachlan D S 1987 *J. Phys. C: Solid State Phys.* **20** 865
- [9] MacLachlan D S and Burger J P 1988 *Solid State Commun.* **65** 159
- [10] Daou J N, Vajda P, Burger J P and Shaltiel D 1988 *Europhys. Lett.* **6** 647; 1989 Erratum, *Europhys. Lett.* **8** 587
- [11] Chernikov A S, Savin V I, Fadeev V N, Landin N A and Izhvanov L A 1987 *J. Less-Common Met.* **130** 441
- [12] Daou J N and Viallard R 1965 *C. R. Acad. Sci. (Paris)* **261** 1845
- [13] Probst C and Wittig J 1978 *Handbook of the Physics and Chemistry of Rare Earths* vol 1, ed K A Gschneidner and L Eyring (Amsterdam: North Holland) p 749