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Logarithmic Divergence of the Electrical Resistivity in the Metal Hydride $YH_{3-\delta}$

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As reported earlier, the metal hydride YH_x reveals spectacular switchable optical properties. In this Letter we report on another remarkable property of the hydrogen deficient $YH_{3-\delta}$ trihydride phase. A logarithmic temperature dependence of the electrical resistivity is observed within a large temperature range ($20 \leq T \leq 200$ K) for hydrogen deficiencies $0.01 < \delta < 0.15$. This dependence may be related to two dimensional weak localization or Kondo scattering of the conduction electrons. [S0031-9007(97)04448-7]

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The recent discovery of a metal-insulator transition in yttrium-, lanthanum-, and other rare earth (RE) hydride materials [1] with spectacular changes in their optical properties (YH_2 is shiny and metallic, while YH_3 is transparent and semiconducting) has revived the interest of theorists [2,3]. Until 1993 it was believed on the basis of early band structure calculations by Switendick [4] that YH_3 was a semiconductor with a gap $E_g \sim 1.5$ eV. More recent state-of-the-art self-consistent band structure calculations [5,6] failed, however, to reproduce a gap.

Two alternative models have very recently been put forward for the YH_3 trihydride phase. Kelly *et al.* [2] find a complicated hexagonal structure with a lower energy than the previously assumed HoD_3 structure and a direct energy gap of 0.8 eV. Since these calculations are based on the local density approximation which typically underestimates E_g by about 1 eV, the results of Kelly *et al.* can be considered as being consistent with our experimental findings ($E_g \simeq 1.8$ eV) [1,7]. Ng *et al.* [3] propose a model analogous to the Zhang-Rice singlet [8] for high-T_c superconductors: YH_3 is a Kondo-type insulator because of electron correlation effects. The hydrogen deficient trihydride $YH_{3-\delta}$ is expected to remain insulating as long as $\delta \leq \delta_c \simeq 0.2$ because the removal of a neutral hydrogen induces the presence of a localized electron with an effective Bohr radius comparable to the lattice spacing.

In order to shed some additional light on the electronic structure of $YH_{3-\delta}$ we investigated the temperature dependence of the electrical resistivity, the Hall coefficient, and the magnetoresistance as a function of the (octahedral site) vacancy concentration δ. These detailed transport measurements could be carried out for the first time because our $YH_{3-\delta}$ films, in contrast with bulk $YH_{3-\delta}$, remain structurally intact even after many hydrogen absorption and desorption cycles [9]. The transport measurements reveal a remarkable $\ln T$ dependence of the resistivity for $\delta < 0.15$ in $YH_{3-\delta}$. We have identified two possible sources of the $\ln T$ dependence: two-dimensional (2D) localization and Kondo scattering.

Yttrium films with a thickness d of 500 nm are prepared at room temperature by electron beam evaporation under high vacuum conditions (10^{-6} Pa). The films are covered *in situ* with a 5 nm thick protective palladium layer and subsequently loaded with hydrogen at room temperature. The characteristics of these films have been presented in detail in [9]. Measurements of the resistivity (four probe, dc) and the Hall effect (ac) are carried out in a cryomagnetic system between 4 and 300 K and in fields up to 7 T. Sample dimensions are of the order of 10×1 mm^2. The Hall voltages are measured with a vector lock-in analyzer operating at a frequency of 62 Hz. In the metallic phase the measuring currents are typically 1 mA, while for the insulating trihydride samples the currents are reduced down to the 10 μA range.

Figure 1 shows the resistivity ρ as a function of temperature of a $YH_{3-\delta}$ film for four different hydrogen

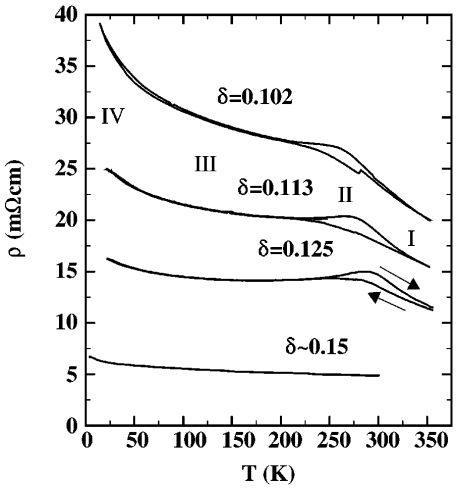

FIG. 1. Temperature dependence of the resistivity ρ in a 500 nm thick $YH_{3-\delta}$ film for four different values of the hydrogen deficiency δ. Four temperature regimes labeled I to IV can be distinguished (see text). The hysteresis in regime II is due to the order-disorder transition.

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concentrations, i.e., $\delta = 0.15$, 0.125, 0.113, and 0.102. Our experimental results indicate that the resistivity increases with decreasing hydrogen deficiency according to $\rho \propto \delta^{-1}$. The top three curves exhibit the same general temperature dependence with a high-temperature regime (I) above 300 K which is characterized by thermally activated transport and is followed upon cooling by an order-disorder transition (II) of the hydrogen vacancies (the hysteresis is due to this transition). At lower temperatures, in the ordered phase, a regime (III) emerges with a limited, negative $d\rho/dT$ which becomes more pronounced when increasing the hydrogen content. Finally, below 20 K a regime (IV) is found where the resistivity tends to diverge exponentially with decreasing temperature, typical for an insulator.

We will focus on regime III where only a limited increase of the resistivity is observed upon cooling. We note that for the experimental data in Fig. 1 with $\delta < 0.15$ the optical gap of about $\simeq$1.8 eV is clearly present and as $\delta \leq \delta_c \simeq 0.2$ thermally activated hopping transport should be observed [3]. However, we find that it is not possible to describe the experimental data of regime III in terms of the expected $\rho \propto \exp[(T_0/T)^\nu]$ temperature dependence with $\nu = 1/4$, $1/3$, or $1/2$. Surprisingly, we find [see Fig. 2(a)] that for 20 K $< T <$ 200 K the sample resistivity depends linearly on $\ln T$ for different hydrogen deficiencies $\delta < 0.15$. Figure 2(b) shows that this behavior is also obtained for ρ versus $\ln T$ with $\delta \simeq 0.01$. For this small δ the plot of σ versus $\ln T$ is clearly curved.

From a more detailed analysis of the resistivity data we find that the temperature dependence of the resistance per square $R^\square = \rho/d$ obeys for $0.01 \leq \delta \leq 0.15$ the empirical relations

$$\frac{dR^\square}{d\ln T} = -(0.32 - 2.1\delta)R^\square(20\ \mathrm{K}) \qquad (1)$$

and

$$R^\square(20\ \mathrm{K}) = \frac{788}{\delta}(0.32 - 2.1\delta). \qquad (2)$$

Equations (1) and (2) imply that for our films $-1/[R^\square(20\ \mathrm{K})]^2 \times dR^\square/d\ln T \simeq dG^\square/d\ln T \simeq \delta/788$, with $G^\square = 1/R^\square$ the conductance per square. This empirical dependence suggests an interpretation in terms of 2D weak electron localization [10]. We will argue below that it is reasonable to assume that our films are stratified into $N = (d/c)\delta$ conducting YH_2-like layers separated by insulating YH_3-like layers (with c comparable to the c-axis lattice spacing). Each conducting layer causes a correction of the conductance which is of the order of $[e^2/(2\pi^2\hbar)]\ln T$ implying that [11]

$$\frac{dG^\square}{d\ln T} \simeq \frac{e^2}{2\pi^2\hbar}\left(\frac{d}{c}\right)\delta \simeq \frac{\delta}{83} \qquad (3)$$

for $c = 0.666$ nm and $d = 500$ nm. As usual, e is the elementary charge and $\hbar = h/2\pi$ with h Planck's constant. As the exact value of the logarithmic slope in Eq. (3) will be strongly affected by spin scattering processes and disorder enhanced electron-electron interaction effects, the observed behavior in Fig. 2 is not inconsistent with 2D weak electron localization. Anyway, the functional dependence $G^\square = G^\square(T, \delta)$ is predicted correctly by the modeling of the $YH_{3-\delta}$ structure in terms of 2D disordered metal layers [Eq. (3)].

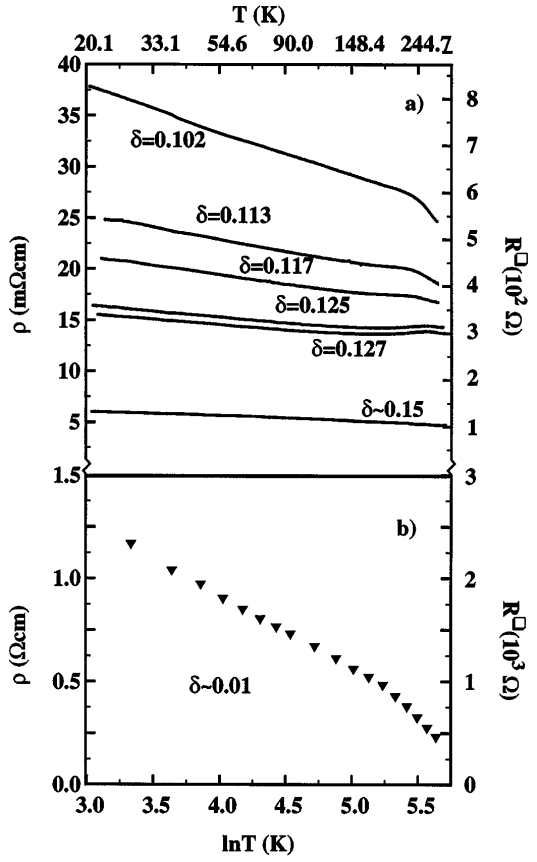

FIG. 2. Logarithmic temperature dependence of the electrical resistivity ρ and the resistance per square $R^\square$ which is observed in the $YH_{3-\delta}$ films in regime III (see Fig. 1). In (a) the increase of the logarithmic slope with decreasing hydrogen deficiency δ is illustrated. As shown in (b), the logarithmic temperature dependence clearly persists for a high resistivity film with an hydrogen deficiency as small as 0.01.

The idea of stratification is reasonable since superstructure formation has been observed in neutron diffraction measurements in superstoichiometric dihydrides REH_{2+z} with z close to 0.25 (e.g., $CeD_{2.26}$, $TbD_{2.245}$, $LaD_{2.25}$) [12] and predicted theoretically for YH_{2+z} by Sun *et al.* [13]. Moreover, Ratishvili and Vajda [14] predict a certain similarity between superstoichiometric dihydrides REH_{2+z} and substoichiometric trihydrides $REH_{3-\delta}$. This prediction which was derived for rare earth hydrides with the same crystal structure for REH_{2+z} and $REH_{3-\delta}$ seems to apply also for YH_x since the temperature dependence of the resistivity of $YH_{2.875}$ (see Fig. 1) is qualitatively similar to that of $YH_{2.10}$ measured by Daou *et al.* (see Fig. 3 in [15]).

The Hall coefficient R_H shown in Fig. 3 for four $YH_{3-\delta}$ samples with $\delta < 0.15$ also exhibits different regimes.

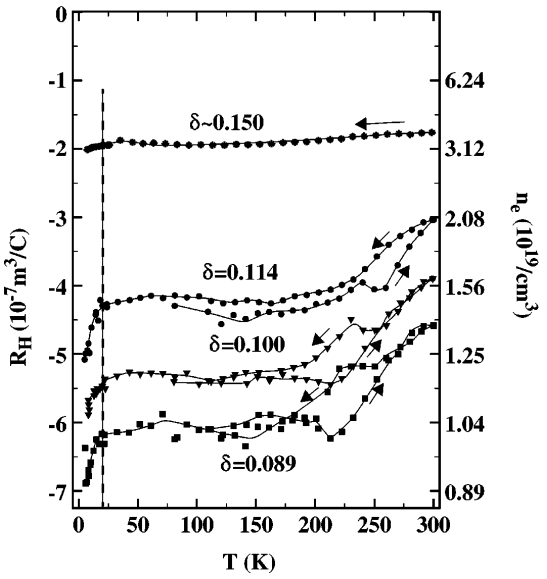

FIG. 3. Temperature dependence of the Hall constant R_H and of the corresponding electron density $n_e = -1/(R_H e)$ in a $YH_{3-\delta}$ films for four different values of the hydrogen deficiency δ. The hysteresis near 225 K is due to the order-disorder transition (see regime II in Fig. 1). Below 20 K (corresponding to regime IV in Fig. 1) the carrier density starts to decrease.

The sharp decrease below 20 K is consistent with a freeze-out of the charge carriers into localized states. In the regime where $R^{\square} \propto \ln T$ we find that R_H is independent of temperature. Our experiments therefore rule out the presence of predominant electron-electron interaction effects above 20 K, since these effects would lead to $dR_H/d\ln T = 2\, dR^{\square}/d\ln T$ [11].

The weak negative magnetoresistance varies approximately quadratically with applied field as shown in Fig. 4 for an $YH_{3-\delta}$ film with $\delta \simeq 0.01$. This agrees with the theoretical prediction for 2D localization with weak spin-orbit scattering when $B \ll \hbar/4eL_\varphi^2$, where the phase coherence length L_φ is limited by inelastic scattering as well as by spin-flip scattering at local magnetic moments. Since the quadratic behavior, i.e., $\Delta\rho(B)/\rho(0) \propto -B^2$ is observed up to 7 T, the interpretation in terms of 2D weak localization implies that L_φ becomes smaller than 5 nm. This rather small value for L_φ is not surprising in view of the low carrier concentration and the many structural defects which are expected to be present in the sample.

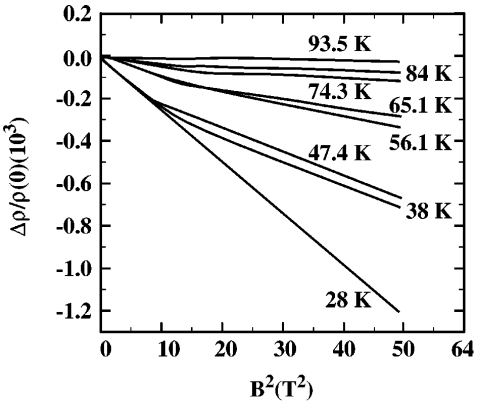

FIG. 4. Magnetic field dependence of the magnetoresistance for an $YH_{2.99}$ film [see Fig. 2(b)] at the indicated temperatures. Above 100 K the magnetoresistance vanishes within experimental errors. The magnetic field is applied perpendicular to the current and the plane of the film. Essentially the same results are obtained for a field perpendicular to the current but parallel to the plane of the film.

In the substoichiometric trihydride phase the film is predominantly c-axis oriented [9]. As we measure essentially the same magnetoresistance for B either perpendicular or parallel to the film plane, we have to assume that the superstructure in our samples consists of conducting sheets under an angle with the a, b plane similar to the (4,0,2) superstructure in superstoichiometric (fcc) dihydrides REH_{2+z}. We conclude that 2D localization offers an interesting and plausible framework to interpret our data, although it is experimentally found that ρ rather than σ varies as $\ln T$ for $20 < T < 200$ K. It is also important to note that below 20 K an important positive magnetoresistance is observed, which is probably related to the onset of a strong charge carrier localization at lower temperatures.

The logarithmic temperature dependence of the resistivity in our $YH_{3-\delta}$ films may also be related to Kondo scattering at local magnetic moments [16]. Since Ng *et al.* [3] find that $YH_{3-\delta}$ is a Kondo insulator, magnetic moments may be introduced by the H vacancies. The introduction of local magnetic moments by doping of a Kondo insulator has very recently been demonstrated experimentally for FeSi [17]. The observed negative quadratic (isotropic) magnetoresistance is also consistent with the presence of a Kondo effect.

Similar to the interpretation in terms of 2D weak localization, the interpretation in terms of Kondo scattering requires the presence of a metallic density of states $g(\varepsilon_F)$. For temperatures above the Kondo temperature, the Kondo effect induces an extra resistivity due to the spin scattering which depends logarithmically on temperature. For the free electron density n_e this results in a temperature dependence $d\rho(T)/d\ln T \propto N_i/g(E_F)/n_e \propto N_i/n_e^{4/3}$ with N_i the number of local magnetic moments. Within this line of reasoning Eqs. (1) and (2) imply then that

$$\frac{d\rho}{d\ln T} \propto \frac{N_i}{n_e^{4/3}} \propto \frac{1}{\delta}\,(0.32 - 2.1\delta)^2. \qquad (4)$$

Our interpretation in terms of a Kondo effect therefore requires that, when approaching the pure YH_3 phase, the ratio between the number of local magnetic moments and the density of free electrons rapidly increases with decreasing δ. At this point we note that theory as well as experiments on doped semiconductors are consistent with the appearance of local magnetic moments when approaching the metal-insulator transition, i.e., when reducing the doping

level [18]. Although it is obvious to relate both n_e and N_i directly to δ, we cannot exclude that other structural defects or impurities may contribute to both n_e and N_i.

Equations (1) and (2) imply that a negative temperature coefficient ($d\rho/dT < 0$) appears when $\delta < 0.15$. Surprisingly, a pronounced 3D metal-insulator transition is not observed for temperatures above 20 K even when decreasing δ down to 0.01. Instead a rather weak logarithmic increase of the resistivity is observed when lowering the temperature. A similar behavior in highly resistive materials and occurring over a wide temperature interval has recently been reported by Ando *et al.* [19] for a $La_{2-x}Sr_xCuO_4$ single crystal in the nonsuperconducting state. The similarity may possibly be only accidental; however, the idea put forward by Ng *et al.* [3] that the nonmetallic ground state of $YH_{3-\delta}$ is due to the formation of singlet states similar to the Zhang-Rice singlet [8] for high-T_c superconducting cuprates might be an indication that a similar mechanism is responsible for the observed $\rho \propto \ln T$ behavior.

In summary, the interpretation of the logarithmic temperature dependence in terms of 2D weak localization or in terms of Kondo scattering requires the persistence of metallic conduction for small hydrogen deficiencies δ. A plausible explanation for this metallic conduction [$g(\varepsilon_F) \neq 0$] relies on the formation of a stratified superstructure in our $YH_{3-\delta}$ material, where conducting sheets with a high hydrogen vacancy density provide metallic conduction even for very low overall vacancy densities. These metallic sheets are separated by insulating YH_3 sheets where the latter dominate the optical properties for $\delta < 0.15$. The metallic conduction process with a logarithmic temperature dependence of the resistivity is no longer effective at lower temperatures ($T < 20$ K) and is replaced with a hoppinglike conduction process. At the same time, the Hall constant signals the onset of a freeze-out of the charge carriers, while the magnetoresistance becomes strongly positive.

The switchable mirror materials are thus not only interesting because of their potential technological applications, but also offer interesting possibilities to study in detail different aspects of the transition towards insulating behavior by simply adjusting the surrounding hydrogen gas pressure or the voltage during electrolytic deposition [20].

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