Light-Induced Metal-Insulator Transition in a Switchable Mirror

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Rare earth hydride films can be converted reversibly from metallic mirrors to insulating windows simply by changing the surrounding hydrogen gas pressure at room temperature. At low temperatures, *in situ* doping is not possible in this way as hydrogen cannot diffuse. However, our finding of persistent photoconductivity under ultraviolet illumination offers an attractive possibility to tune yttrium hydride through the $T = 0$ metal-insulator transition. Conductivity and Hall measurements are used to determine critical exponents. The unusually large value for the product of the static and dynamical critical exponents appears to signify the important role played by electron-electron interactions.

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Trivalent rare earth hydrides stabilized in thin film form demonstrate spectacular optical and electronic properties [1–8]. Dihydrides such as YH_2 and LaH_2 are good metals; the trihydrides are large gap semiconductors. A thin film of YH_x or LaH_x can be transformed rapidly from metal to insulator, from shiny mirror to transparent window, simply by changing the surrounding hydrogen gas pressure or an electrolytic cell potential.

The continuous and reversible nature of the transformation, as well as the fine-tuning of materials properties afforded by the periodic table, provide a compelling basis for technological development. These same characteristics make switchable mirrors also attractive for scientific scrutiny. The fundamental nature of the metal-insulator transition with hydrogen concentration x is not well understood, although it underlies the attention-getting optical and electronic changes. Pronounced electron-electron interactions have been posited to lead to the opening of the large optical gap [9,10]. If experimentally confirmed as the causative agent [11,12], metal hydride films would be placed in the broad class of highly correlated materials that include transition metal oxides, cuprate superconductors, and colossal magnetoresistance perovskites. Unlike nearly all Mott-Hubbard systems, however, the metal-insulator transition in YH_x and LaH_x is continuous, unaccompanied by a structural phase transition, and could provide a rare window on critical behavior in the strong electron interactions limit.

We systematically investigate the magnetotransport properties of YH_x for temperatures T between 0.35 and 293 K in magnetic fields H up to 14 T for chosen values of x. Metal-insulator transitions are properly defined only at $T = 0$, where the electrical conductivity is finite in the metal and zero in the insulator. Hydrogen diffusion is ineffective as a means to drive the transition at low T, but we find that charge carriers created by UV irradiation at $T < 1$ K persist for days at temperatures as high as 200 K. This persistent photoconductivity enables us to finely tune the conductivity σ and the Hall coefficient R_H through the quantum critical point. The metal-insulator transition takes place in the hcp γ phase of YH_x and shows no inclination towards a structural instability. We find for the metal qualitative agreement with the finite-size scaling picture of quantum phase transitions, but with an anomalously large product of the static and dynamical critical exponents, $z\nu = 6.0 \pm 0.5$. An unusually large value of $z\nu$ (4.6 ± 0.4) also has been observed in $Ni(S, Se)_2$ [13], the only other Mott-Hubbard system so characterized, and appears to be a signature of a metal-insulator transition in the highly correlated limit.

We run the gamut from metallic to insulating YH_x samples by loading a 550 nm thick Y film, covered by 5 nm Pd, up to a hydrogen pressure $p(H_2) = 50$ bars at room temperature. Our samples are sufficiently thick to be in the three-dimensional limit. The yttrium hydride film is mounted in a specially designed loading cell [14] with electrical and optical access that fits into the bore of the 14 T superconducting magnet of our ^{3}He system. A calibrated carbon resistor is mounted on the Cu cell, in good thermal contact with the sample. Light from an ultraviolet stroboscope (spectral range ~220–700 nm, maximum repetition rate 10 Hz) is guided to the cell by way of an UV silica fiber and illuminates the whole sample, which is disk-shaped with a diameter of 7 mm. The sample is thermally anchored via its sapphire substrate, which is attached to the cell with a thin layer of GE7031 varnish, and by way of four 25 μm diameter Au wires that are connected at the perimeter of the disk by ultrasonic wedge bonding. The over-determined set of van der Pauw configurations yields consistent values of the longitudinal and Hall conductivities, indicating the good homogeneity of the sample in the ab plane. Homogeneity along the c axis is ensured by loading hydrogen at room temperature for at least one day [6], after which we typically find $d\ln\sigma/d\ln t < 0.01$, where t is time. The measurements are frequency independent for $f < 1$ kHz and Ohmic for all x and T for voltage drops across the sample below 0.1 mV (power levels below 10 nW). We emphasize that the 5 nm Pd cover, necessary for hydrogen diffusion into the sample, does not inhibit electrical measurements.

Atomic force microscopy shows that such a thin layer of Pd leads to the formation of 10 nm wide disconnected islands instead of a closed cap layer, while Rutherford backscattering confirms that upon exposure to the air an approximately 5 nm thick insulating, but optically transparent, Y_2O_3 layer forms between the Y and Pd. Thus, the Pd islands do not cause short-circuiting of the YH_x, in agreement with our observation of a systematic change with x of $\sigma(T \to 0)$.

We start with the metallic virgin Y film and successively load it to $p(H_2) = 0.2$ μbar, 1 μbar, and 50 bars at room temperature. Both the polycrystallinity of the film and the hydrogen vacancies serve as sources of disorder. Subsequent to every transformation of the sample, $\sigma(T)$ is measured for $0.35 < T < 300$ K and the Hall voltage $V_H(H)$ is determined at $T = 0.35$ and 4.2 K. We show in Fig. 1 the influence of the UV illumination on the low temperature conductivity, $\sigma(T = 0.35\ \mathrm{K})$, at $p(H_2) = 50$ bars. When the lamp is turned on, the radiation heats the sample and σ rises sharply. The temperature reaches a constant value at $T = 0.4$ K, and the slow increase in the conductivity (filled circles) under constant illumination reflects an increase in carrier concentration. When the lamp is switched off, the sample cools down to 0.35 K, and the residual increase in $\sigma(T = 0.35\ \mathrm{K})$ is conclusive proof of persistent photoconductivity. Upon the completion of the illumination cycles, we find no measurable relaxation in $\sigma(T = 0.35\ \mathrm{K})$ for at least the order of days. In Fig. 1, photodoping changed the charge carrier density $n(T = 0.35\ \mathrm{K})$ from 5.0×10^{18} to 7.5×10^{18} cm^{-3}, assuming a one band model for the Hall conductivity. The effect of UV illumination is weaker at higher T and vanishes above a temperature $T_p(x)$ that decreases with decreasing x. We find $T_p \sim 1$ to 10 K for our light source for $p(H_2) \sim 10$ μbars to 50 bars. Relaxation of σ and n remains absent as long as $T < T_{h1}(x)$, but they are restored to their initial values once T exceeds $T_{h2}(x)$. The threshold temperatures $T_{h1}(x)$ and $T_{h2}(x)$ are much higher than $T_p(x)$ and coincide with the temperatures between which hysteresis in $\sigma(T)$ is observed due to hydrogen vacancy ordering [15], typically of order 200 and 270 K, respectively. Therefore, we keep T below 50 K after illumination.

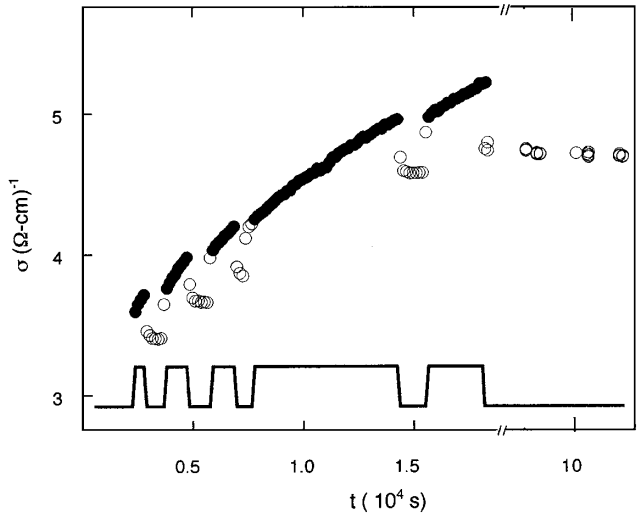

FIG. 1. Persistent photoconductivity in YH_x at $T = 0.35$ K after illumination by an ultraviolet stroboscope at time t. As the radiation is switched on and off (solid line), the sample warms to 0.4 K, but returns to a higher, stable value of the conductivity σ upon cooling to base (open circles).

Once the sample has become insulating at $p(H_2) = 50$ bars, we use consecutive combinations of H_2 unloading and persistent photoconductivity to drive the sample metallic. The former method is applied to vary n by large amounts while the latter is used to fine tune n close to the quantum critical point. The microscopic mechanism of the unusual persistent photoconductivity that we have discovered is not known, but must contain the following elements. First, the UV illumination cannot create carriers by simple activation across the Coulomb gap in the insulator. Charge carriers—measured directly by the Hall effect—can be generated only at very low T, but survive almost to room temperature. Hence, there must be some subtle rearrangement of the hydrogen bonding, perhaps akin to hydrogenated amorphous silicon. Second, these carriers fill in the gap until it goes to zero at n_c, where any strong temperature dependence of V_H disappears. This does not mean that UV illumination cannot continue to have some effect in the metal. Hydrogen bonding configurations can continue to respond to the UV, but no new gap is opened: neither $n(T)$ nor $\rho(T)$ demonstrate thermally activated behavior in the metal.

We plot in Fig. 2 the resulting $\sigma(T)$ curves on a log-log scale. In this overview of the complete data set, it is clear that the uppermost three curves with $n > 10^{22}$ cm^{-3} are metallic, while the bottom three with $n < 10^{19}$ cm^{-3} and definite negative curvature are insulating. This is borne out by the temperature dependence of the Hall voltage. We compare in Fig. 3 $V_H(H)$ at $T = 0.35$ and 4.2 K for YH_x samples with $n(T = 0.35\ \mathrm{K}) = 8.9 \times 10^{18}$ and 3.4×10^{22} cm^{-3}, respectively. The one order of magnitude change in temperature makes little difference to the Hall response in the metal, but it leads to increasing carrier freeze-out with decreasing temperature in the insulator.

The nine middle curves in Fig. 2 with $10\ (\Omega\,\mathrm{cm})^{-1} < \sigma(T = 0.35\ \mathrm{K}) < 70\ (\Omega\,\mathrm{cm})^{-1}$, where the Mott conductivity $\sigma_M \sim 30\ (\Omega\,\mathrm{cm})^{-1}$, deserve closer examination. Extrapolation to zero temperature, where the conductivity will assume a finite value solely in the metal, requires a linear as opposed to a logarithmic temperature scale. We find that σ varies linearly with $T^{1/6}$ over more than two decades in T in the immediate vicinity of the metal-insulator transition (Fig. 4), with an extrapolated value for the critical density n_c between 1.18 and 1.45×10^{19} cm^{-3}. We expect power law behavior in temperature for the conductivity, but $\frac{1}{6}$ is an anomalously small

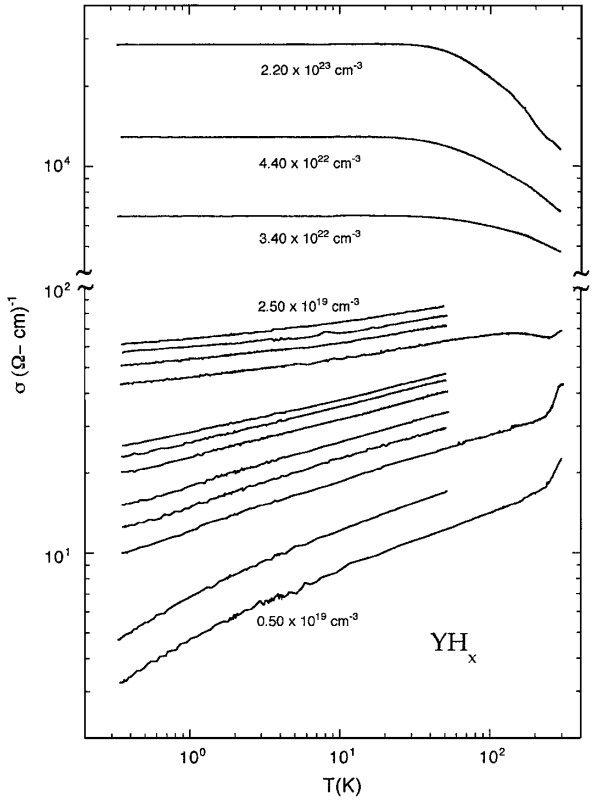

FIG. 2. Conductivity σ as a function of temperature T for a YH_x film at a series of charge carrier densities $n(T = 0.35\ \mathrm{K})$. The metal-insulator transition is tuned by a combination of hydrogen gas loading (curves up to 300 K) and UV illumination (curves up to 50 K). Unlabeled curves have $n = (0.75, 0.89, 1.07, 1.18, 1.45, 1.51, 1.64, 1.88, 2.12, \text{and } 2.32) \times 10^{19}\ \mathrm{cm}^{-3}$.

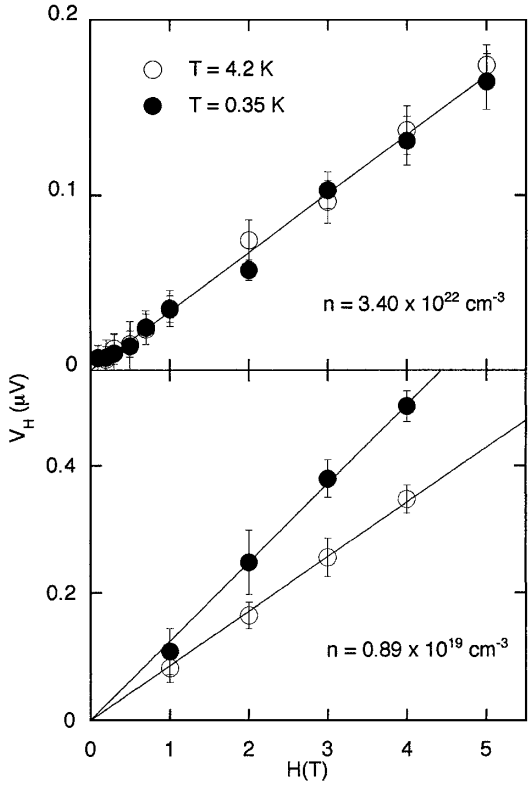

FIG. 3. Hall voltage V_{H} vs magnetic field H for metallic (top) and insulating (bottom) compositions. The carrier density is temperature independent in the metal.

exponent [13,16] that we ascribe to the influence of the quantum critical point. Attempts to fit the data to more conventional exponents over any decent range in T lead to noticeable curvature in $\sigma(T)$. The hydrogen content x can be determined for curves running up to 300 K by comparison of the $\sigma(T = 293\ \mathrm{K})$ values with those from electrolysis experiments [5]. We find $x = 2.93$, 2.90, 2.83, 0.2, 0.08, and 1.9 (bottom to top), giving $2.83 < x_c < 2.90$, where x_c is the critical hydrogen content. Therefore, the metal-insulator transition is not accompanied by a structural phase transition since it takes place within the purely hcp γ phase of YH_x which exists for $x > 2.7$.

Using the extrapolated values of $\sigma(T = 0)$ from Fig. 4, we find a critical form for the static conductivity, $\sigma(0) = \sigma_o(n/n_c - 1)^{\mu}$, with best fit values $\sigma_o = 63 \pm 5\ (\Omega\,\mathrm{cm})^{-1} \sim 2\sigma_M$, $n_c = 1.39 \pm 0.03 \times 10^{19}\ \mathrm{cm}^{-3}$ and conductivity exponent $\mu = 1.0 \pm 0.1$ (Fig. 5, inset). Dynamical scaling posits that in the critical region the dependence of the conductivity on n and T can be generalized to a single function. A quantum phase transition involves both a correlation length ξ and a correlation time ξ_τ that diverge, $\xi \sim (K - K_c)^{-\nu}$ and $\xi_\tau \sim (K - K_c)^{-z\nu}$, when some control parameter K other than temperature approaches its critical value K_c. The static and dynamical response are inextricably bound together, a linkage reflected by the convolution of the usual correlation length exponent ν with a new dynamical

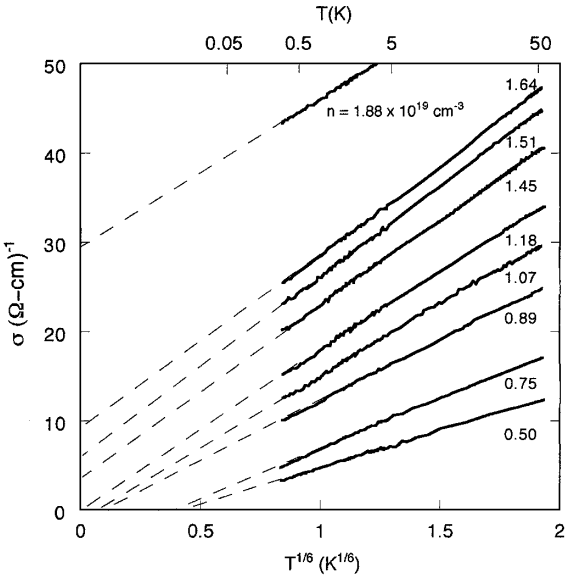

FIG. 4. The conductivity σ varies as the $\frac{1}{6}$ power of temperature T near the quantum critical point at n_c. Dashed lines are extrapolations to $T = 0$, giving $1.18 < n_c < 1.45 \times 10^{19}\ \mathrm{cm}^{-3}$.

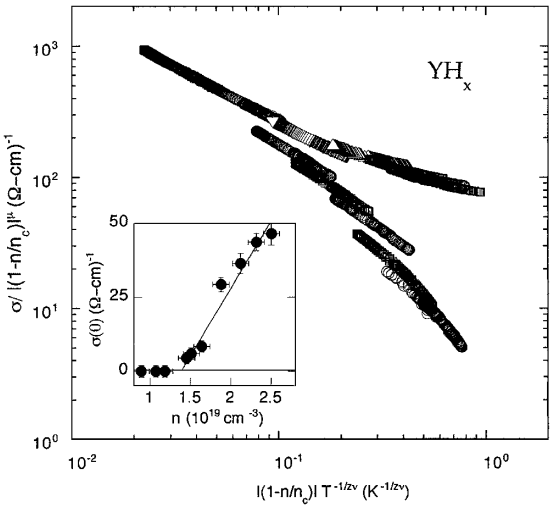

FIG. 5. Dynamical scaling curve for the seven metallic and five insulating data sets closest to the $T = 0$ metal-insulator transition with $\mu = 1$, $n_c = 1.39 \times 10^{19}$ cm^{-3}, and $z\nu = 6$ (consistent with Fig. 4). The peculiarly large $z\nu$ may be a signature of strong electron correlations. Inset: the zero temperature conductivity $\sigma(0) \propto (n/n_c - 1)^\mu$ yields a conventional conductivity exponent $\mu = 1$.

critical exponent z [17]. At the quantum critical point $\sigma(T) \propto T^{\mu/z\nu}$, which yields $z\nu = 6$ in combination with the previously found conductivity exponent $\mu = 1$.

Wegner scaling [18] gives $z = 3$ for noninteracting electrons in a random potential at a $T = 0$ metal-insulator transition. More generally, and in particular for cases where electron-electron interactions enter the physics [19],

$$\sigma(n, T) = b^{-\mu/z\nu} f\{(n - n_c)b^{1/\nu}, Tb^z\}, \qquad (1)$$

where f is a scaling function, b is an arbitrary scale parameter, and we are using carrier density n as our drive parameter K. By Eq. (1), $\sigma/|n - n_c|^\mu$ should only be a function of $|n - n_c|T^{-1/z\nu}$.

We attempt to collapse our conductivity data for all $n < 2.50 \times 10^{19}$ cm^{-3} on such a scaling curve in Fig. 5. We fix $\mu = 1$ and $n_c = 1.39 \times 10^{19}$ cm^{-3}, as determined independently from the inset, and vary $z\nu$. The data in the metal collapse reasonably well for $z\nu = 6.0 \pm 0.5$, but no $z\nu$ (or any self-consistent combinations of μ, n_c, and $z\nu$) truly overlay the insulating curves. Dividing $\sigma(n, T)$ by the interpolated critical curve $\sigma_c(T, n = n_c) = 18.8\ (\Omega\,\mathrm{cm})^{-1}/\mathrm{K}^{1/6}\ T^{1/6}$ works similarly well in the metal and similarly poorly in the insulator [20]. If hyperscaling holds, i.e., $\mu = \nu$, then $z = 6$ for YH_x. This value is much higher than $z = 2$ derived from dynamical scaling analyses of the amorphous alloy NbSi [21] and the doped semiconductor Si:P [22], both of which lie closer to the strong disorder limit.

An unexpectedly large value of $z\nu(4.6 \pm 0.4)$ also is found in the Mott-Hubbard transition metal compound $NiS_{2-x}Se_x$ [13], and appears to mark continuous metal-insulator transitions in the highly correlated limit. A comparably large magnitude $z\nu = 6.0 \pm 0.5$ for YH_x then seems to indicate the important role played by electron-electron interactions physics in metal hydride films. This unusual characteristic manifests itself both in the peculiar low temperature form of $\sigma(T)$ near n_c (Fig. 4) and in the quantum critical conductivity scaling (Fig. 5). The apparent large effective dimensionality, $d + z \approx 9$, of YH_x is at a minimum indicative of additional exponents at the quantum critical point [13,23] and may account for scaling's limited quantitative success in this metal-insulator transition universality class.

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