

Ana Maria Racu

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Micro-Raman spectroscopy study  
of ordering phenomena  
in  $\text{YH}_x$  thin films  
and in  $\text{CuTe}_2\text{O}_5$  single crystals

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Micro-Raman spectroscopy study  
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- J. Schoenes, A. Borgschulte, A.-M. Carsteanu, H. Kierey, M. Rode: *Structure and bonding in YH<sub>x</sub> as derived from elastic and inelastic light scattering*, J. Alloys Comp. **356-357**, 211-217 (2003)

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- A.-M. Carsteanu, M. Rode, D. Zur, A. Borgschulte, H. Schröter, und J. Schoenes: *Raman spectroscopy on  $\beta$ -YH<sub>2+ $\delta$</sub>  and  $\beta$ YD<sub>2+ $\delta$</sub>  thin films*, Verhandl. DPG (VI) **39**, 306 (2004)
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"Hydrogen: the simplest element,  
but still so versatile."

Joachim Schoenes, 2003  
(Physik am Samstagmorgen)

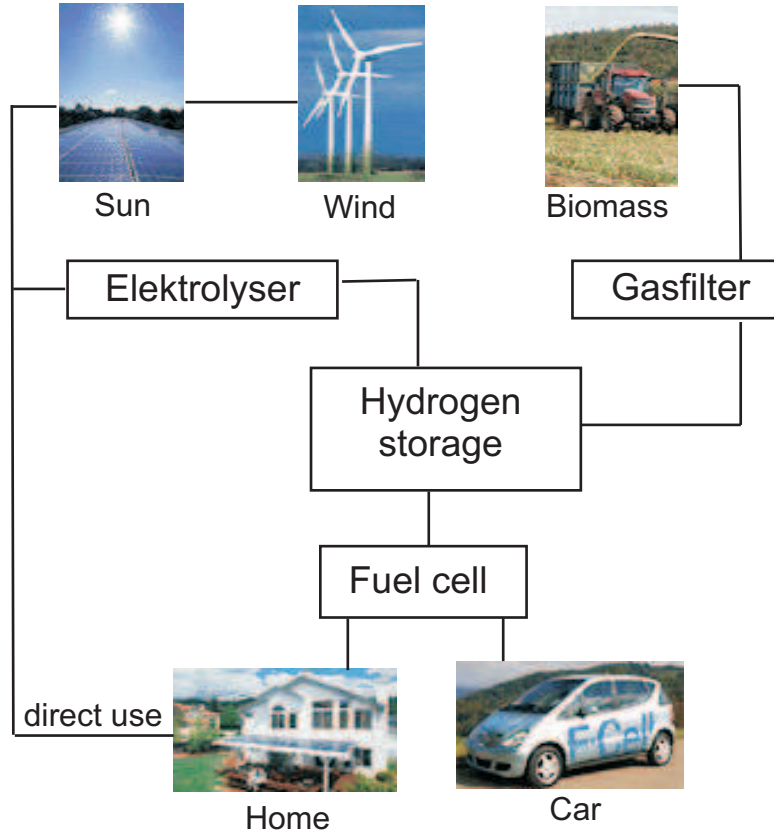
# Introduction

The physics of hydrogen in metals is exciting due to the manifold applications in technology and for basic research. Many metals absorb hydrogen when brought into a hydrogen gas atmosphere and desorb it when pumping away the hydrogen gas. The safe and compact storage of hydrogen in metals is a challenge because of the high volumetric density which can be obtained, even higher than in liquid hydrogen. The fuel cells use hydrogen as an energy carrier and produce electricity and heat whenever it is needed (Fig. 1). The metal hydrides found applications in rechargeable batteries. In these devices, hydrogen is introduced into the metal electrochemically during recharging and an electrical current flows during discharging. The rechargeable batteries are currently used in mobile applications, i. e. telephones, computers.

Hydrogen changes drastically the mechanical, electrical, magnetic and optical properties of the host metal. For example, Pd becomes superconducting and La loses its superconducting properties when loaded with hydrogen [1]. Eu and Nd change their magnetic properties from anti-ferromagnetic metals [2] to ferromagnetic semiconductors [3]. One of the most impressive transitions discovered in 1996 by Huiberts *et al.* [4] is the dramatic change in the optical properties of yttrium and lanthanum thin films near their metal-insulator transition: the dihydrides are metals while the trihydrides are insulators and transparent in the visible part of the optical spectrum. The transition from a metallic to a transparent state is reversible and occurs at room temperature simply by changing the surrounding hydrogen gas pressure or in an electrolytic cell. Soon it was shown that not only  $\text{YH}_x$  and  $\text{LaH}_x$ , but all the trivalent rare-earth hydrides and some of their alloys exhibit switchable optical properties. So far three generations of hydrogen based switchable mirrors have been discovered: (1) the rare-earth switchable mirrors, (2) the color neutral magnesium-rare-earth alloys, and (3) the magnesium-transition-metal switchable mirrors. Applications include energy-efficient windows, smart coatings in electrochromic devices, hydrogen indicators for catalytic and diffusion investigations, hydrogen sensors. A new and exciting application field is to use the switchable mirrors as hydrogen absorption detectors in a combinatorial search for new lightweight hydrogen storage materials [5]. By making thin films with controlled gradients in the local chemical composition of three or more constituents, it is possible to monitor optically the hydrogenation of typically  $10^4$  samples simultaneously. The goal is to find a hydrogen storage material with large hydrogen-mass and volume density and suitable absorption/desorption kinetics.

The discovery of the hydrogen based switchable mirrors challenged theoretical as well as experimental physicists to understand how the presence of hydrogen affects the electronic structure of the host metal and to investigate the origin of the metal-insulator transition in these materials. From the theoretical point of view, the problem of the phase transition is





**Figure 1:** Fuel cells give us a very efficient way to produce electric power and heat. In the whole circle of renewable energies they are the final element. The sun provides energy, solar cells or wind power catch it, hydrogen is the storage and the medium to transport the energy and the fuel cells generate the energy whenever and wherever it is needed.

cleared in two kinds of models: broken symmetry structures and strong correlations. The latest models suppose a negatively charged hydrogen with strong correlations between the two electrons.

For the understanding of the phase transition it is important to study the structural changes and lattice distortions induced by the hydrogen in the host metal. Moreover, the only samples which retain their structural integrity during the hydrogenation are the thin films. Unfortunately, hydrogen is not accessible for x-ray diffraction experiments. On the other hand, neutron diffraction was successfully applied only for powder samples, providing information about the phonon density of states.

This thesis presents the results of a Raman spectroscopy study on the structure and the lattice distortions of metal-hydride samples. Not only the first generation switchable mirrors, i. e. rare-earth hydrides, are accessible with this method. We also present the Raman measurements on samples of the second generation switchable mirror  $\text{Mg}_z\text{Y}_{1-z}$ , which we received from a collaboration with the group of Amsterdam. A complete analysis of the vibration modes and the conclusions about the structural distortions in these materials is given in Chapter 4.

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Chapter 5 presents Raman measurements on single crystalline  $\text{CuTe}_2\text{O}_5$  samples. Due to the low symmetry of the monoclinic structure, the calculations predict a large number of Raman modes with interesting polarization and angular intensity patterns. The number of phonons and their symmetry is calculated for the first time and compared to the Raman spectra. The observed Raman modes are identified and compared to the related compounds  $\text{CuO}$  and  $\text{TeO}_2$ . Substitutions of Zn and Ni on the Cu site preserve the crystal structure and induce changes in the magnetic properties. Moreover, a foreign phase was observed in the Raman mapping images of the sample substituted with Ni and it was identified to be  $\text{TeO}_2$ .



*"We have to love nature and appreciate her wonderful gifts, her marvelous ingenuity, her resourcefulness, her infinite variety. It is the same thing that has inspired me all my life."*

C. V. Raman, November 18, 1950

# 1

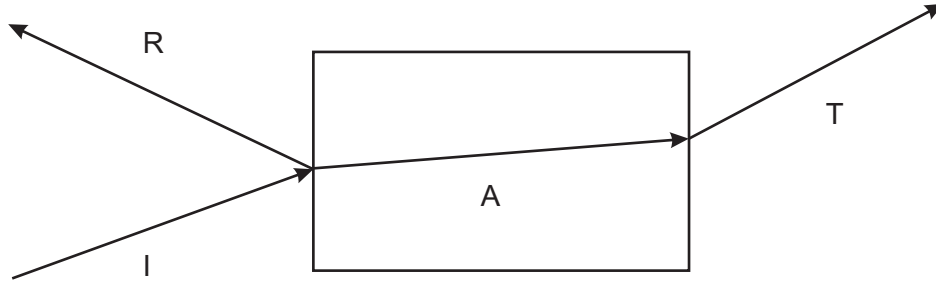
## The Raman effect

When electromagnetic radiation of energy  $h\nu$  irradiates a molecule, the energy may be transmitted, absorbed, or scattered. Optical spectroscopy provides numerous experimental tools to investigate optical, electronic and vibrational properties of solids. The individual techniques can be grouped into absorption, emission and scattering spectroscopies. In the Tyndall effect the radiation is scattered by particles (smoke or fog for example). In Rayleigh scattering the molecules scatter the light. Lord Rayleigh showed that the blue sky results because air molecules scatter sunlight. No change in wavelength of individual photons occurs in either Tyndall or Rayleigh scattering, i. e. they are called elastic scattering.

The effect of inelastic light scattering was discovered by Sir Chandrasekhara Venkata Raman in 1928 [6]. He was awarded the Nobel Prize in Physics 1930 "for his work on the scattering of light and for the discovery of the effect named after him". Independently, also Landsberg and Mandelstam [7] observed this effect. In the years before Raman made his discovery, inelastic scattering of light was proposed by several researchers, among them Brillouin [8], Smekal [9], and Mandelstam [10].

### 1.1 Inelastic light scattering

The interaction of light with a solid follows the standard laws of geometric optics and wave optics. Most experiments utilize a laser beam, which can be approximated by an electromagnetic plane wave. The processes that occur are depicted schematically in Fig. 1.1. Part of the intensity is reflected (R), whereas the remaining light enters the medium, being refracted. Inside the medium, the light is transmitted (T) and/or absorbed (A). These processes are ruled by the optical constants of the material such as the reflectivity, the refractive index or the absorption coefficient, all of which derive from the complex dielectric function. Part of the light propagating through the crystal



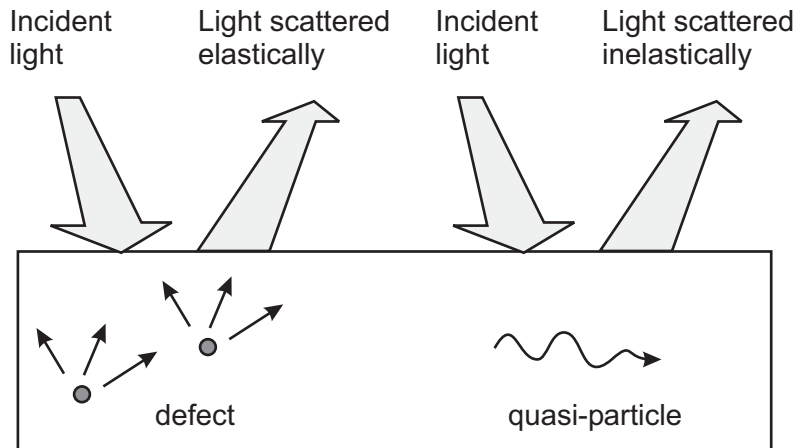
**Figure 1.1:** Interactions of light with a crystal. The arrows that are labelled I, R, A and T display schematically the incident light, the reflection, absorption and transmission of light intensity.

is scattered elastically (Rayleigh scattering). Only a tiny portion of the light intensity is scattered inelastically (Raman/Brillouin scattering).

Fig. 1.2 presents schematically the inelastic and elastic light scattering processes. While reflection and refraction are due to geometrical changes in the refractive index, scattering originates from inhomogeneities of the medium such as quasi-particles or defects. These inhomogeneities can be classified as being either time-dependent or time-independent, i. e. , either dynamic or static.

For purely geometrical or local inhomogeneities with no time dependence the scattering is elastic which means without a change of the light energy. The scattered intensity in the elastic processes is usually about 3 orders of magnitude smaller than the incident intensity.

Quasi-particles of the crystal can be viewed as dynamic scatterers which scatter light inelastically, accompanied by an energy transfer between light and the crystalline medium.



**Figure 1.2:** Elastic and inelastic light scattering on solids.