I CHAPTER : SHORT HISTORY OF HYDROGEN

I.1 DISCOVERY OF HYDROGEN

Stimulated by the results of Cavendish the Swedish Carl Wilhelm Scheele and the English Joseph Priestley reported independently from each other in 1774 the existence of a new component of air that they described as „fire air" (hydrogen). In 1781 Cavendish burnt his „burning air" (oxygen) with this new „fire air" and obtained nothing but water.

On June 5, 1783 the Montgolfier brothers made their first successful flight with a balloon. Alexandre Cesar Charles, a French scientist not knowing that the Montgolfier brothers had used hot air for their balloon, made a flight on August 28 of the same year with a balloon filled with hydrogen. The 25 m^3 of hydrogen necessary to fill his balloon were obtained by pouring sulphuric acid onto iron chips in a barril placed below the balloon.
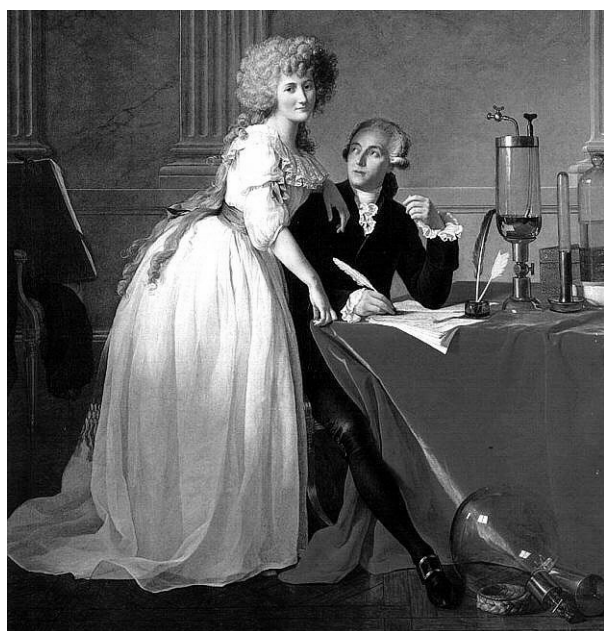

Fig. I.1: Antoine Laurent Lavoisier (1743 - 1794) with his wife and collaborator Marie Anne, Painting of Louis David (Detail).
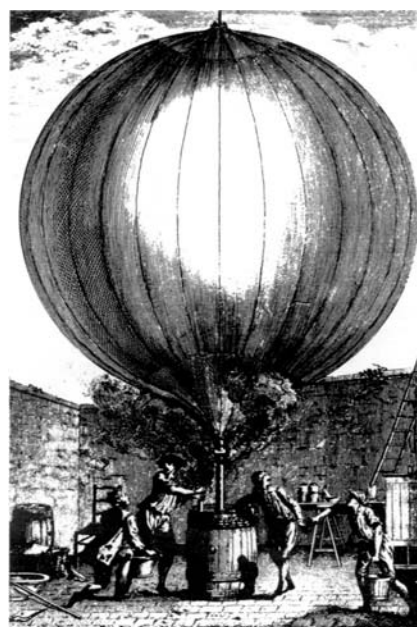

Fig. I.2: Alexandre Cesar Charles with his hydrogen filled balloon in 1783

After the Germans Kirchhoff und Bunsen had demonstrated in 1861 the presence of hydrogen in the spectra of the Sun it became evident that hydrogen was the most abundant element in the Solar System. Hydrogen is the lightest element of the Periodic System, but about 90 % of all atoms are hydrogen atoms. Together they account for about 75 % of the total mass of the Universe. Hydrogen produced on Earth is able to escape the gravitational field. This explains the very low concentration of hydrogen gas in our atmosphere.

After approximately 1800 the only significant application of hydrogen gas was for lighting and heating. A change came in the middle of the 20th century when natural gas was massively used for heating.

In 1839 Sir William Grove constructed the first fuel cell. Although simple in principle the fuel cell remained for a century a curiosity since it turned out to be rather difficult to make a workable device out of it. In addition the discovery in 1866 of the dynamo provided a most attractive way to transform mechanical energy into a new energy carrier: electricity. As a consequence electrical batteries lost their position as energy provider and were relegated to special applications, for example for mobile energy storage applications. The fuel cell of Grove did not even survive since another device made its apparition: the internal combustion engine.
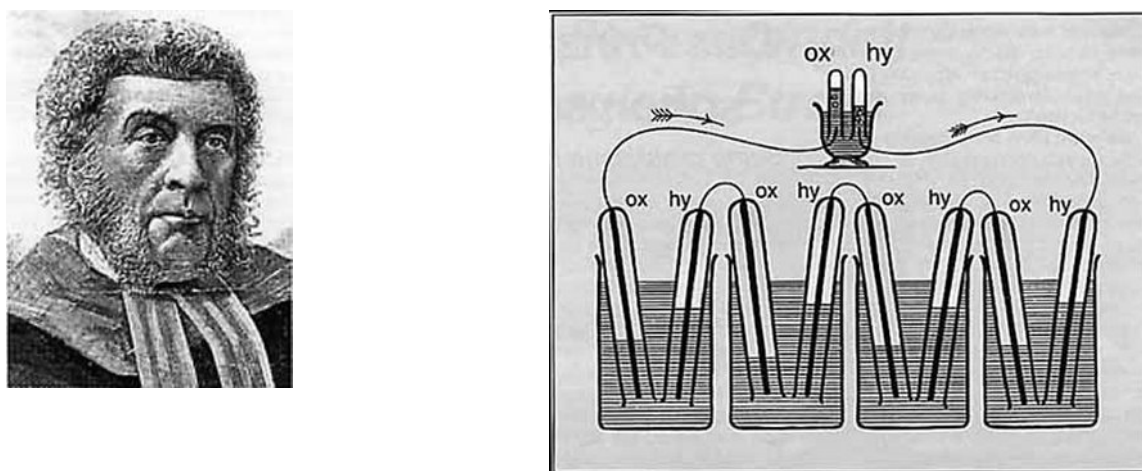

Fig. I.3: Sir William Robert Grove (1811 - 1896) (left panel) constructed already in 1839 a fuel cell consisting of four elements placed in series: Each element contains two glass tubes with a platinum electrode in sulphuric acid The upper part of the glass tubes contains either oxygen (ox) or hydrogen (hy). The electric current generated by the four elements is used for the electrolysis of water in the top part of the drawing[1]

In 1909 Fritz Haber, a German chemist discovered a procedure to synthesise Ammonia (NH_3) directly from the element H and N. Haber received the Nobel prize for this discovery in 1918. Shortly later Carl Bosch, managed to adapt Haber's procedure to produce vast amount of ammonia. This provided Germany with a valuable source of material for explosives and fertilisers.
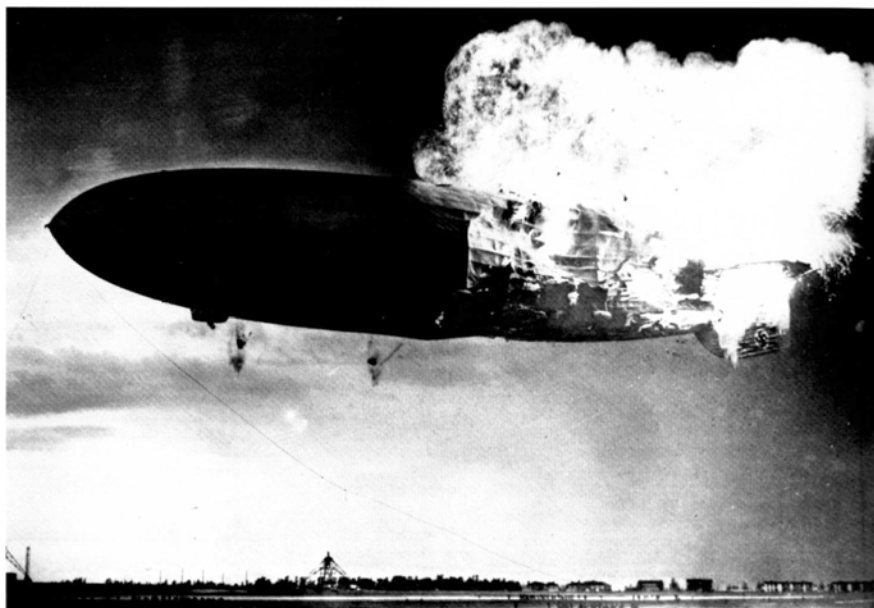
Fig.I.4: During docking in Lakehurst, New Jersey, U.S.A., the "Hindenburg" burned down completely on May 6, 1937.

After World War I the consumption of ammonia increased drastically so that larger and larger quantities of hydrogen were needed. Furthermore, hydrogen was increasingly used in the food industry

I.2   USE OF HYDROGEN

Nowadays the world consumption of hydrogen in the chemical industry is approx. 350 Mrd. m^3 per year. As a m^3 of hydrogen gas (under standard conditions) weights approx. 90 g the amount of hydrogen used in chemistry is more than 30 Mio tons. About half of it is used for the synthesis of 85 000 t ammonia (2000 m^3 hydrogen gas and 667 m^3 nitrogen gas are necessary for 1 ton of ammonia). 80% of NH_3 is used for fertilisers and the remaining part for the synthesis of plastic materials.

More than a quarter of the world production of hydrogen is used in oil refineries primarily to separate sulphur, nitrogen and metallic impurities, as well as for the transformation of hydrocarbons. Significant quantities of hydrogen are also in chemistry for the synthesis of intermediate products such as amines and hydrogen-superoxides. The hardening of comestible fats, whose conservation is improved by addition of hydrogen, requires high quality hydrogen. Further important applications, although modest in total consumed amount, are for example, the use of hydrogen in electronics to avoid oxidation of semiconductors, for the cooling of large power generators, and in engineering for the welding and cutting of metals as its combustion with oxygen occurs around 3000 ^{o}C.

One further very important application of hydrogen is, although not realised by many, in metal-hydride batteries based on $LaNi_5H_x$, which already now have conquered an important part of the multi-billion rechargeable battery market. Their superior stored energy/ weight ratio makes them especially attractive for mobile telephones.
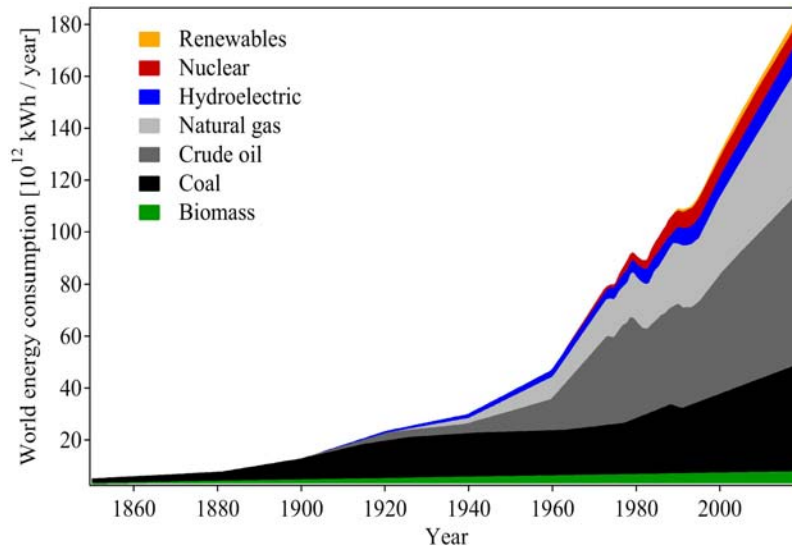
Fig. I.5 : World energy consumption since 1850.

Very recently, hydrogen is attracting considerable interest as a potential energy carrier. This triggered by the observation that mankind's energy consumption is growing with ever-increasing pace and will continue to do so for the foreseeable future. Energy scenarios invariably predict a large (1.5 to 3-fold) increase in primary energy requirements by 2050, an increase that chiefly reflects the growing energy demand from the developing world (see Fig. I.5). Fossil fuels contribute the lion's share to energy production.

Over the last decades large additions have been made to the world's proven and attainable reserves of fossil fuels, particularly to those of natural gas, and these amounts could in principle fuel the world for many centuries to come. However (although it still is not an unambiguously proven fact) there is an increasing number of strong indications that carbon dioxide emissions lead to global warming, and this trend is matched by societal concerns on this issue. Mankind's carbon dioxide emission is illustrated from a historical perspective in Fig. I.6.

There are in principle three different approaches to alleviating the problems associated with the energy hunger of humanity, namely:

1. preventing the cause of global warming to escape into the atmosphere (i.e. CO_2 sequestration), known as the 'clean fossil hydrogen' option;
2. a drastic efficiency increase in energy usage;
3. a transition from fossil fuels to sustainable, carbon dioxide neutral ones.

The " clean fossil hydrogen" option can be realised only by separating, removing and storing of the carbon or CO_2 extracted from the reformed primary fuel. The secondary H_2 energy carrier can then be used in highly efficient conversion units; hydrogen obtained in this way can be seen as a bridge to the last, sustainable option (point 3).

The second alternative, namely, increasing energy efficiency, has been facilitated enormously by new technology developed over the last few decades. Examples include better construction materials and insulating foams for houses; multipane windows, high efficiency heating systems,
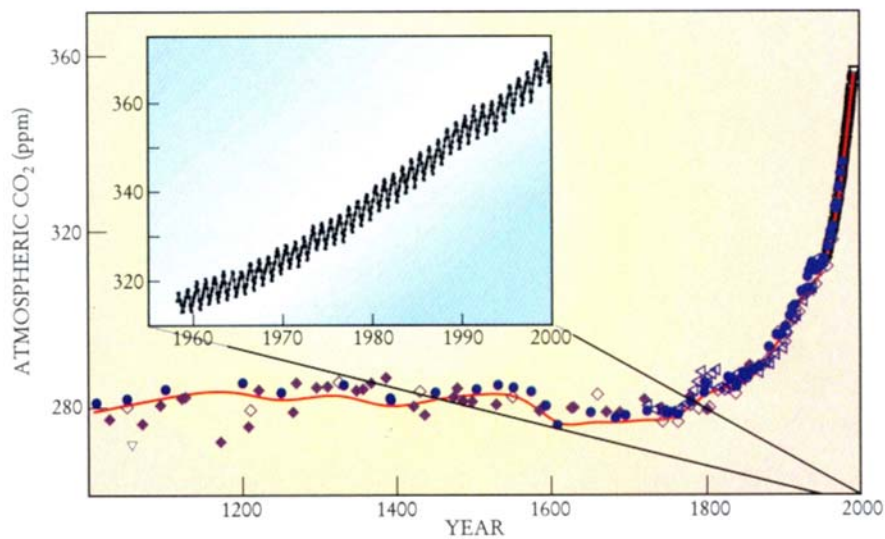
Fig. I.6: Mankind's emission of CO_2 since the year 1000. Atmospheric carbon dioxide levels have increased by more than 30% since the industrial revolution started in the mid-18th century. Until 1800, atmospheric CO_2 had remained at about 280 parts per million (ppm) for several millennia. Data before 1958 stem from measurements of air bubbles trapped in ice cores recovered from several sites in Antarctica. The CO_2 data displayed in the inset were measured on air samples taken by Charles D. Keeling and collaborators at Mauna Loa, Hawaii. The seasonal variations evident there reflect the seasonal breathing of the terrestrial biosphere in the Northern Hemisphere: CO_2 is removed by strong vegetal growth in spring and summer and returned by respiration and remineralization in the fall and winter (from Physics Today[2] August 2002)

combined heat and power stations, more efficient engines, motor oils with better lubricity and lower viscosity, better fuels, more aerodynamic shapes of automobiles, larger aeroplanes, better turbines etc. However, part of all the progress made has not been translated into a reduction of energy usage but rather into an increase of consumer comfort. In some instances an increase of efficiency has even led to a dramatic increase of energy consumption. Air transport may serve as an example.

The last option, namely, the transition from the present fossil fuel era into a renewable and sustainable future energy world, is the ultimate one. The central idea is that all the energy is produced by "clean" means such as wind turbines, photovoltaics, geothermal power stations, etc. Within any future sustainable energy scenario storage of energy is a key ingredient. The inherently intermittent nature of renewable energy sources renders buffering and storage of energy indispensable. At present energy buffering is mainly provided by fossil fuel-generated electricity. This is not possible when intermittent sources represent more than 30% of the total energy sources. It is therefore necessary to look for other energy carriers. Hydrogen is in this context one of the most attractive candidates since it can be integrated in a clean hydrogen-water-hydrogen closed material loop and offers interesting storage and distribution possibilities. Through electrolysis and fuel cells it can also be linked to the other clean energy carrier: electricity.
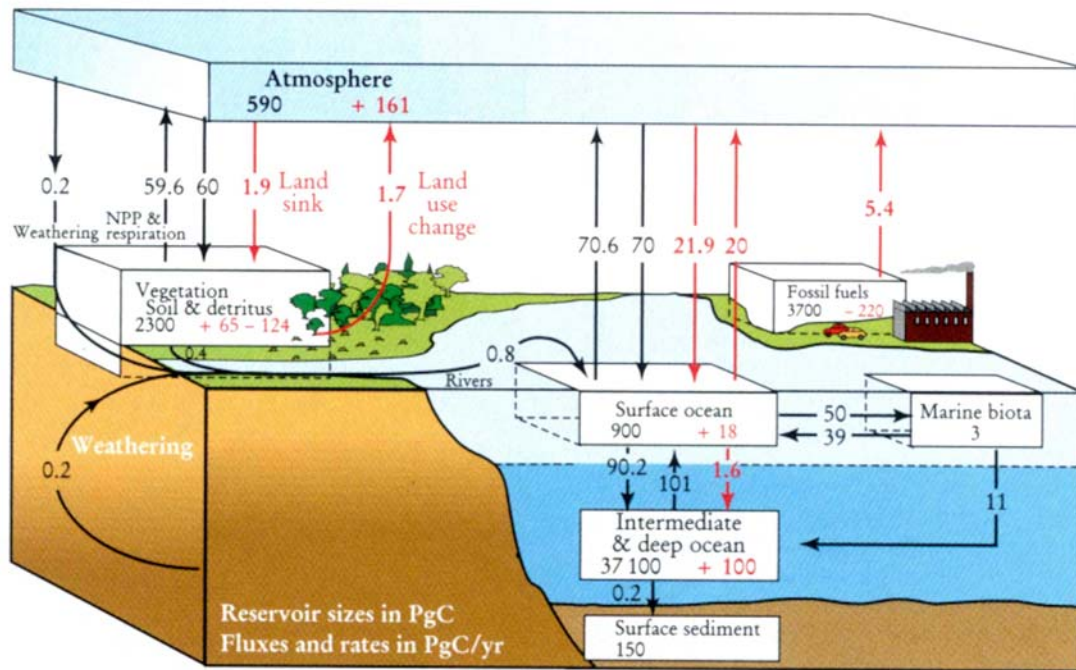
Fig. I.7: Fluxes of the global carbon cycle (in units of 10^{12} kg/year) between the atmosphere land and oceans averaged over the year 1980. The fluxes generated by mankind are in red, while the natural fluxes are in black. The net flux between reservoirs is balanced for the natural processes but not for the one created by mankind. Within the boxes, black numbers give the sizes (in units of 10^{12} kg) of the reservoirs around 1800 and red numbers indicate the changes that have occurred until 1980. For the "land" box the first red number is speculative; the second one is related to deforestation (from ref.2)

The storage of hydrogen is at the origin of the interest in the interaction of hydrogen with materials. In this lecture we consider the interaction of hydrogen with metals, with special emphasis on the condensed matter physics aspects.

I.3   HYDROGEN IN METALS

Soon after the discovery of the metal Palladium in 1803 by W.H. Wollaston it was observed that this metal could absorb large amounts of hydrogen. This was the starting point of a long interest of scientists (both fundamentally and technologically oriented) in the interaction of hydrogen with metals, which in many respects is still alive because of the richness of fascinating phenomena exhibited by metal-hydrogen systems in general. Typical remarkable properties are:

The possibility of dissolving large quantities of hydrogen (up to H/M ~3) in transition metals and intermetallic compounds. In many hydrides, the density of hydrogen is higher than that of solid hydrogen (see Table I.1).

Table I.1: Comparison of the hydrogen contents in various metal-hydrides [a,b]. ρ is the density of the host material, N_H the number of hydrogen atoms per unit volume, wt% the weight percentage of hydrogen, and ρ_H the mass density of hydrogen in the material under consideration.

Substance	ρ [kg m^{-3}]	N_H [10^{28} m^{-3}]	wt%	ρ_H [kg m^{-3}]
H_2O	1000	6.7	11.0	111
H_2SO_4	1841	2.2	2.0	36
liq CH_4	425	6.3	25.0	105
liq H_2	71	4.2	100.0	71
TiH_2	3800	9.2	4.0	153
ZrH_2	5610	7.3	2.1	122
YH_2	3958	5.7	2.2	95
LaH_2	5120	4.4	1.4	73
LaH_3	5350	6.5	2.1	108
$LaNi_5H_6$	6225	5.3	1.4	88
$TiFeH_{1.95}$	5470	6.2	1.9	101
$Mg_{0.97}Ni_{0.03}H_{1.85}$	1800	7.9	7.3	132
NbH_2	8400	10.9	2.2	181
VH_2	6100	14.4	4.0	240
PdH	12000	6.8	0.9	113
$NaAlH_4$	1270	5.7	7.4	94

a) From Van Mal[3],
b) Wiswall and Reilly[4]

b) A very high diffusion coefficient D of hydrogen in metals compared to that of other interstitials such as O, N, C, B (see Fig. I.8). Possibility of quantum diffusion at low temperatures.

c) The concentrations of hydrogen is in general continuously variable. Above the critical point this is possible without crossing phase boundaries in metal-hydride systems such as Pd, Nb, Ta, V (in general for T>T$_{critical\ point}$). Possibility of studying dilute as well as concentrated alloys (metal-hydride alloys are highly non-stoichiometric).

d) Isotopes effects in most physical quantities (H : D : T with mass ratios of 1 : 2 : 3 are ideally suited to study isotope effects in diffusion, superconducting T$_c$, etc.).

e) Superconductivity in PdH$_x$, Pd$_{1-y}$Ag$_y$H$_x$ with T$_c$'s as high as 16 K in materials which do not show any tendency to become superconducting (Pd is a strongly enhanced paramagnet).

f) Metal-hydride alloys can be prepared easily by electrolytic charging or by hydrogen gas loading. This makes the hydrides a sort of easy prototype of the vast class of the years ago, he first chanced to intermingle small carbon atoms with large iron atoms, and
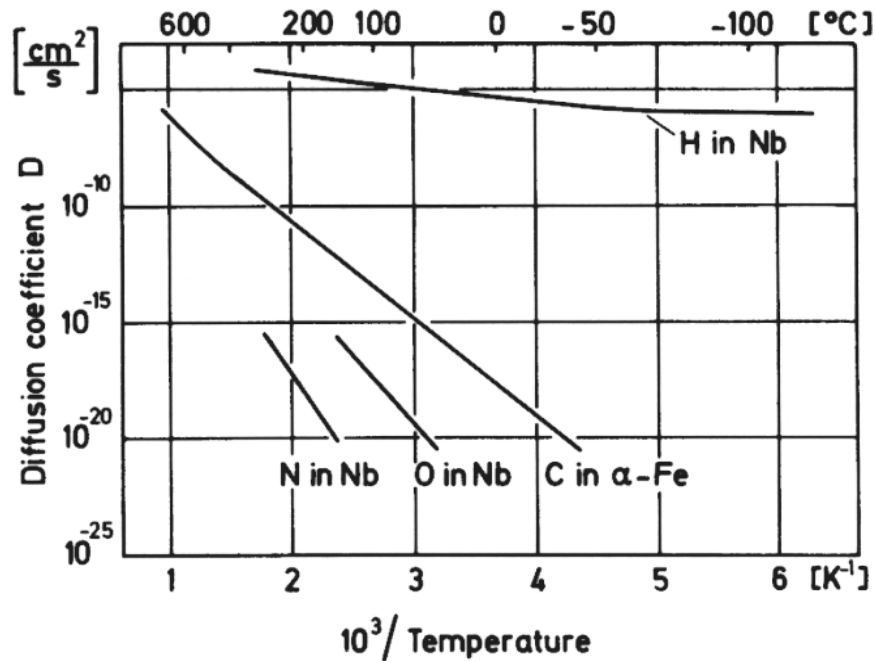
Fig. I.8: Diffusion coefficients of H (Schaumann et al.[5]), N and O (Powers and Doyle[6]) in Nb and C in α-Fe (Lord and Beshers[7]) after Völkl and Alefeld[8].

interstitial alloys which have played their role in man's history ever since, about 4000 thus to forge both swords and ploughshare (and so his destiny).

g) Potential applications of hydrogen as an energy carrier are direct consequences of points a), b) and f) and also of the fact that hydrogen stored in the form of metal hydrides is safe (Lundin and Sullivan[9]) and that the combustion of H in air produces only negligible quantities of pollutants. This will be discussed in the last chapter of this course.

A totally unexpected development was initiated in 1995 by the discovery in our laboratory [10] of spectacular changes in the optical and electrical properties in metal-hydride films of yttrium and lanthanum near their metal-insulator transition. The dihydrides are excellent metals and shiny while the trihydrides are large gap semiconductors and transparent in the visible part of the optical spectrum (see cover of this lecture notes). As the transition from a shiny to a transparent state is reversible and simply induced at room temperature by changing the surrounding hydrogen gas pressure or electrolytic cell potential, these hydrides can be used as **switchable mirrors**. In the meantime exploratory research has revealed that not only YH_x and LaH_x, but all the trivalent rare-earth hydrides and even some of their alloys exhibit switchable optical and electrical properties. In the transparent state they have characteristic colours: for example, YH_3 is yellowish, LaH_3 red, while some alloys are almost colourless. This enhances their technological potential tremendously.

The great richness of new phenomena in the electrical and optical properties of these materials makes them also very attractive for fundamental condensed matter physics. Soon after the discovery that metal-hydride films of yttrium, lanthanum and rare-earth metals could be reversibly and continuously switched between a shiny metal and a transparent large gap semiconductor, it was realised that their properties could probably not be understood in terms of one-electron theories. Similarly to high-T_c superconductors two lines of thoughts have been proposed: a Peierls-like models, strongly correlated electron models similar to those proposed for high temperature superconductors and so-called GW-band structure models. Several projects have been started in our group to investigate experimentally in detail typical switchable metal-hydride films to identify the nature of their metal-insulator transition. The final aim is to find out which theoretical model is most appropriate and to use this knowledge for the optimisation of switchable mirrors. We are presently working on metal-hydride smart coatings for applications in solar collectors, in smart windows and in fibre optic hydrogen sensors.

I.4   AIM OF THIS LECTURE

The aim of this lecture is to give an introduction to some of the basic problems of metal-hydride systems without trying to be comprehensive. We shall first start by giving a "macroscopic" description of the properties of metal-hydrides and discuss their phase diagrams, pressure composition isotherms, critical point behaviour and their relation to the lattice-gas and Ising models. This will bring us to the crucial question of the nature of the interaction of two hydrogen "atoms" or "ions" in a metal and a brief description of the elastic interaction model of Wagner and Horner will be given. We shall then discuss the nature of H in metals and the electronic structure of metal-hydrides. The emphasis will be on developing an intuitive understanding of covalent and ionic binding in transition metal-hydrides and so-called complex hydrides (e.g. Mg_2NiH_4, Mg_2CoH_5 and Mg_2FeH_6 or $NaAlH_4$). We turn then our attention to the dynamical properties of metal-hydride systems such as diffusion, Gorsky effect, and electromigration. The lecture ends with a discussion of the role of hydrogen in a future sustainable energy scenario and of the safety problems involved in handling hydrogen.

I.5   REFERENCES

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