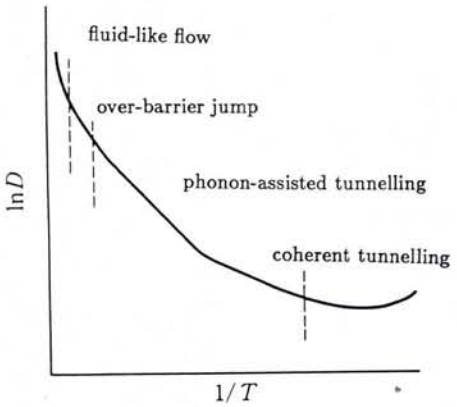

Fig. 3 — Schematic illustration of the variation of the hydrogen diffusion constant with temperature. Various regimes can be distinguished as discussed in the text. From Ref. 2.

atoms will move in Bloch states extending over many unit cells [4]. The diffusion rate will be given by the band-width of the hydrogen bands. The non-adiabatic coupling to the metal electron-hole pair excitations gives rise to a renormalization of the band-width calculated from the adiabatic potential energy surface [5]. This renormalization can be described as a consequence of the "Anderson orthogonality catastrophe", namely: the conduction electron eigenstate with the particle perturbed at one site has an infinitesimal overlap with the eigenstate with the particle in another site. Hopping therefore involves infinitesimal electron-hole pair excitations and is suppressed.

As the temperature is increased, phonon assisted tunnelling becomes possible [3]. The thermal motion of the lattice may produce a configuration where the tunnelling matrix element is larger than that of the undistorted lattice. At the same time, the tunnelling becomes incoherent owing to the fluctuations of the phonons. The same thing happens with fluctuations in the electron system at an even lower temperature, because the coupling to the electrons is stronger [6]. The result is that the life-time of the Bloch states decreases with increasing temperature. When the temperature becomes high enough for the coherence time τ to be shorter than the average time between jumps, the motion is completely diffusive with a diffusion constant [6]

$$D \cong W_{ren}^2 \tau a^2 \qquad (2)$$

where W_{ren} is the renormalized band width, and a is the lattice constant.

At even higher temperatures, the hydrogen atoms behave completely classically moving through the lattice by thermally activated over-barrier jumps. Hydrogen is so heavy and the barriers for diffusion so large that this is the dominant migration mechanism for most systems at most temperatures. When defects are present, the trapping and detrapping of hydrogen can dominate the diffusion properties [7]. Typical trapping energies are of the order 0.5 eV (compare the interstitial- and chemisorption energies in Fig. 2). Defects can therefore increase the apparent activation energy for diffusion considerably.

Crossover to the tunnelling regime has been observed at low temperatures in three cases [2]:

1) for hydrogen in bcc metals,
2) for chemisorbed hydrogen, and
3) for the very light isotope μ^+ in fcc metals.

The first two cases are characterized by a low (adiabatic) barrier for diffusion. As discussed above, the barrier is considerably smaller in the open bcc structure than in the more close-packed structures and, outside the surface, the barrier is very small for any structure, because the hydrogen atom can find the optimum density anywhere in the surface unit cell. The last case is characterized by the small mass of μ^+, making all quantum effects more pronounced. Quantum delocalization of hydrogen has been observed for hydrogen trapped in vacancies in Ni and Pd using channelling techniques at very low temperatures. By increasing the temperature, the occupation of excited states with a drastically different density distribution can be detected. The excitation energy involved is only of the order 3 meV [8].

At the highest temperatures, the motion of the hydrogen will be liquid-like.

Summary

The extensive experimental and theoretical studies of hydrogen inside and on metals have resulted in a convincing physical picture of the interaction. Binding sites, diffusion barriers, lattice relaxations, interactions with lattice defects, and trends in binding energies from one metal to another can be understood within a simple theoretical model.

In the process, a new description of bonding in a metallic medium has been developed, based on the concept of a unique function relating the energy of a given atom to the surrounding electron density. The theoretical framework, the effective medium theory [8], is capable of describing a vast number of systems and now forms the basis for classical simulations of temperature- and time-dependent properties. The hydrogen embrittlement process has, for instance, been simulated in this way [9].

Particular interest is focussed on the hydrogen — metal system because it provides a unique possibility for studying the quantum mechanics of a particle in contact with a heat bath. The theoretical and experimental development is fast. Quantum diffusion has now been established experimentally for a number of systems and theoretically, new insight has been gained into the coupling of the hydrogen motion to both phonons and electron-hole pair excitations. This opens the door to a new detailed understanding of hydrogen dynamics.

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Meetings

Up-date and Corrections

Address omitted in March

30 Aug. - 2 Sept. 1988 **Lisbon, Portugal**
9th European Sectional Conference on Atomic and Molecular Physics of Ionized Gases (9th ESCAMPIG)
C.M. Ferreira, Centro de Electrodinamica da UTL-INIC, Inst. Superior Técnico, P-1096 Lisboa Codex
A: 1.8.88 / PP: 31.5.88 / 150 / ESC 11000.– IOM before 31.7, 13000.– after; 13000.– mbrs. 4b) before 31.7, 15000.– after; 15000.–/17000.– others; 10000.– students; incl. proc.

New

5-9 Sept. 1988 Liège, Belgium
Workshop on the Future of Small-gap II-VI Semiconductors
R. Evrard, Institut de Physique, B-4000 Sart Tilman, Liège 1
NP / 40 / inv. / NATO / FB 10000.– all incl.

New

19-23 Sept. 1988 Rome, Italy
Restructuring of Physical Sciences in Europe and the USA, 1945-60
E. Di Silvestro, Dipto. di Fisica, Università di Roma 'La Sapienza', Ple. A. Moro, I-00185 Roma
A: 15.6.88 / PP / LIT 100000.– incl. proc.

Replaces School in Erice announced for 3-4 November 1988

2-6 Nov. 1988 Erice, Italy
Int. School of Materials Sci. and Technol. Workshop: Point, Extended and Surface Defects in Semiconductors
A. Cavallini, Dip. di Fisica, Via Irnerio 46, I-40124 Bologna
or G. Benedek, Dip. di Fisica, Via Celoria 16, I-20133 Milano