MATERIALS SCIENCE

Y. Fukai

The Metal-Hydrogen System

Basic Bulk Properties

Second Edition

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Second, Revised and Updated Edition

With 287 Figures and 55 Tables

Springer

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Preface

Ten years after I wrote the first Edition of this book, the situation surrounding hydrogen is dramatically changed. A growing consensus on the possible role of hydrogen in future energy technology has incited worldwide efforts for the development of new hydrogen-storage materials and their application to rechargeable batteries and fuel cells.

Meanwhile, research in the basic properties of metal-hydrogen systems which this book addresses has also been advanced, more quietly but significantly. High-pressure experiments have unraveled new features of elemental hydrogen (a number of different quantum phases of solid H_2 and metallization of liquid H_2) as well as of many metal–hydrogen systems (superabundant vacancy formation, phase diagrams over wide p–x–T ranges). The quantum character (the quantum atomistics) of interstitial hydrogen atoms has come to be more thoroughly elucidated, and culminated in the complete description of quantum diffusion over the whole temperature range.

In order to incorporate these new developments in a consistent way, the previous Edition has been revised substantially, both in depth and breadth, especially in regard to high-pressure experiments and quantum-atomistic properties. Thus, many new critically evaluated data have been included, and some 300 references are added. Also, very recent topics, just looming out in this and closely related areas, are added as Appendices. It is my belief that this revised Edition should help envisage the cleanest picture of the metal–hydrogen system presently available, and arouse a renewed interest of the readers in this ever fascinating field.

The revision of this book has been supported by many colleagues and friends; K. Aoki for hydrogen-induced amorphization, D.K. Ross for neutron scattering, H. Wipf and R. Kadono for diffusion, P. Vajda for rare-earth hydrides and hydrogen–defect interactions, P. Herzig for the theory of rare-earth hydrides, and S. Tsuneyuki for the theory of elemental hydrogen, just to name a few. Above all, I have been greatly benefited by the kind assistance of P. Vajda, who has devoted the labors of reading all the chapters, one after another, and provided valuable comments and advice. I wish to express my sincere thanks to all these colleagues, with whose assistance this book has been brought to the present form.

Tokyo, September 2004 *Yuh Fukai*

Preface to the First Edition

I think it is expedient here to clearly specify the readership for whom this book is intended. Some readers might infer from the title that this is a data book convenient for occasional reference purposes. Most of the data on the bulk properties and a comprehensive list of publications are indeed compiled here, and will be found useful as they are. The primary purpose of the book is, however, rather to provide a coherent and consistent description of the basic bulk properties of the metal–hydrogen system, ranging from macroscopic properties such as solubilities and phase diagrams to microscopic properties such as atomistic states and diffusion. The emphasis has been placed on the physics of how these properties actually come about. This structure of the book is considered to be useful, and even necessary, not only for physicists but also for researchers interested in the materials-science aspects of the system. Who could have anticipated that the solubility of hydrogen in iron reaches a level as high as [H]/[Fe] $\approx$ 1 under a hydrogen pressure of 10 GPa; who could have anticipated that the diffusivity of hydrogen in metals increases at low temperatures; who could unravel the mechanism of "cold" fusion (if this indeed exists), without a basic understanding of the metal–hydrogen system? Obviously, these problems are not only of academic interest but also have profound technical implications.

To be more specific, this book covers the following topics: phase relations of the metal–hydrogen system over wide ranges of pressures (up to several hundred GPa), temperature (up to $\sim$2000 K), and composition (from pure metal to pure hydrogen); the site preference and quantum-mechanical states of interstitial hydrogen atoms; diffusion behaviors and mechanisms due to quantum-mechanical tunneling. A brief description is also given of the electronic structure that underlies these properties.

The manuscript was completed and sent to the publisher for review, but was later revised to a large extent to include the referee's comments and the developments made in this area since then. Some of them, for example, the metallization of elemental hydrogen, have been included in the text, but others are given in the Addenda at the end of Chap. 5.

Although our knowledge of the metal–hydrogen system is constantly increasing, this book should provide a sound basis for understanding future developments for many years to come and should serve as a lasting and useful

guide for scientists and engineers interested in the fundamentals and/or applications of the system.

I dedicate this book to those of my colleagues who have actively participated in this area of research. Also, I thank H. Sugimoto for his critical reading, Y. Saito for his assistance in the preparation of the manuscript and, finally, the Iketani Science and Technology Foundation for its financial support during some phases of the work.

Tokyo, March 1992 *Yuh Fukai*

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Contents

1 Hydrogen

There are three isotopes of hydrogen: protium, deuterium, and tritium. Some of the fundamental properties of these isotopes, including nuclear, atomic, and molecular ones, are listed in Table 1.1 [1.1–1.5] for convenience of later reference.

The elemental hydrogen exists in several different forms; as a monatomic gas at low densities, diatomic molecules under ordinary conditions, a metallic conductor at high pressures, and as an ionized plasma at very high temperatures. All these states are realized in different places in the Solar System, but on Earth, the elemental hydrogen usually exists only as molecules. In this chapter, we deal exclusively with the molecular form of elemental hydrogen.

1.1 Molecules

Molecular hydrogen is a very stable entity. Its electronic ground state, the singlet state $^1\Sigma_g^0$ has an energy lower than two atoms by $E_0 = 4.748\,\mathrm{eV}$ (the binding energy), and the equilibrium separation is very short, being $r_0 = 0.7416\,\text{Å}$. The electronic energy as a function of internuclear separation r (the adiabatic potential) and energy levels of the stretching vibration are shown in Fig. 1.1 [1.6].

For an H_2 molecule, the zero-point vibration energy is $E_v^0 = 0.372\,\mathrm{eV}$, and accordingly, the dissociation energy is

$$E_d = E_0 - E_v^0 = 4.476\,\mathrm{eV}\,. \tag{1.1}$$

The dissociation energy becomes isotope-dependent due to the isotope dependence of E_v^0. The energy of rotation along the two axes perpendicular to the molecular axis is smaller in comparison.

Due to large excitation energies of the stretching vibration, most of the molecules are in the ground state ($n_v = 0$) at ordinary temperatures ($T \leq 2000\,\mathrm{K}$), and its partition function can be approximately written as

$$Z_v = \sum_{n_v=0}^{\infty} \mathrm{e}^{-E_v^{n_v}/kT} \cong \mathrm{e}^{-E_v^0/kT} \tag{1.2}$$

The partition function for the rotational motion

Table 1.1. Some properties of hydrogen isotopes

	H	D	T
Nucleus			
Nuclear mass [M_p]	1.000	1.998	2.993
Nuclear spin	1/2	1	1/2
Nuclear moment [μ_B]	2.7928	0.8574	2.9788
Atom ($1s^1$)			
Ionization energy [eV]	13.5989	13.6025	13.6038
Molecule ($^1\sum_g^+$))			
Binding energy E_0[eV]	4.748	4.748	—
Dissociation energy E_d[eV]	4.478	4.556	4.59
Vibrational energy[a] E_v^0[eV]	0.5160	0.3712	0.3402
Rotational energy[a] B_r[eV]	7.32×10^{-3}	3.70×10^{-3}	—
Gas–liquid (normal)			
Critical point			
Temperature [K]	32.98	38.34	40.44
Pressure [MPa]	1.298	1.649	1.906
Boiling point at 0.1 MPa			
Temperature [K]	20.41	23.67	25.04
Latent heat [J mol^{-1}]	913	1235	1394
Gas–liquid–solid (normal)			
Triple point			
Temperature [K]	13.96	18.73	20.62
Pressure [kPa]	7.20	17.15	21.60

[a]Calculated from lowest excitation energies.

$$Z_r = \frac{1}{2} \sum_{J_r=0}^{\infty} (2J_r + 1) e^{-E_r^J/kT} \tag{1.3}$$

$$E_r^J = B_r J_r (J_r + 1) \quad J_r = 0, 1, 2, \ldots \tag{1.4}$$

can be approximately given by

$$Z_r \cong \frac{kT}{2B_r} = \frac{4\pi^2 I_r kT}{h^2} \tag{1.5}$$

where $I_r = {}^1/_2 M r_0^2$ is the moment of inertia of the molecule.

One important issue regarding the rotational motion is the existence of two distinct states, ortho(o)- and para(p)-states. The distinction comes from the requirement that the wave function of a molecule must be antisymmeteric

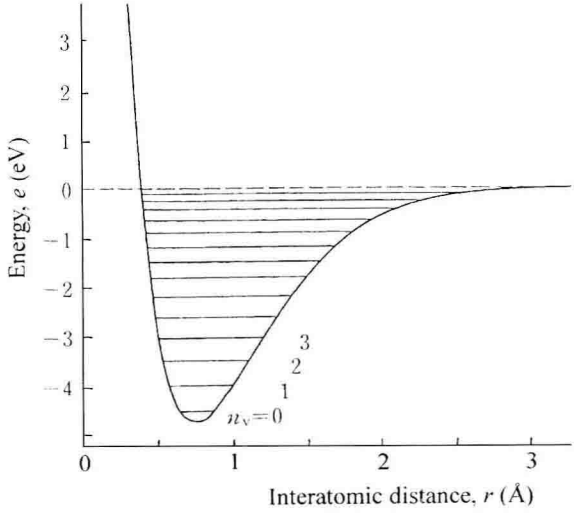

Fig. 1.1. Adiabatic potential and energy levels of the stretching vibration of H_2 molecule [1.6]

with respect to the interchange of the space coordinates of the two constituent fermions, and symmetric for interchange of bosons. Since the wave functions of the electronic ground state and vibrational states are symmetric with the interchange of the two nuclei, the symmetry requirement must be satisfied by the product of rotational and nuclear wave functions. In the case of protons and tritons (fermions) with nuclear spin $I = 1/2$, antisymmetric (odd J_r) and symmetric (even J_r) rotational states must be coupled with symmetric and antisymmetric nuclear states,respectively. These two groups of molecules are called o-H_2 (o-T_2) and p-H_2 (p-T_2), respectively. In the case of deuterons (bosons) with nuclear spin $I = 1$, on the other hand, they must be coupled with antisymmetric and symmetric rotational states, respectively. The energies and wave functions of rotational states of an H_2 molecule are shown in Fig. 1.2. Note, in particular, that hydrogen molecules do not always look like dumbbells; molecules in the $J_r = 0$ rotational state, the ground state of p-H_2 (p-T_2) and o-D_2, are spherically symmetric.

As there are $(2I+1)(I+1)$ symmetric and $(2I+1)I$ antisymmetric states for nuclear spin I, the population ratio of o-H_2 (o-T_2) and p-H_2 (p-T_2) in thermal equilibrium is give by

$$\frac{N_o}{N_p} = \frac{(I+1)\sum\limits_{J_r=\text{odd}} q_r^J}{I\sum\limits_{J_r=\text{even}} q_r^J}\,, \tag{1.6}$$

$$q_r^J = (2J_r+1)e^{-E_r^J/kT}\,. \tag{1.7}$$

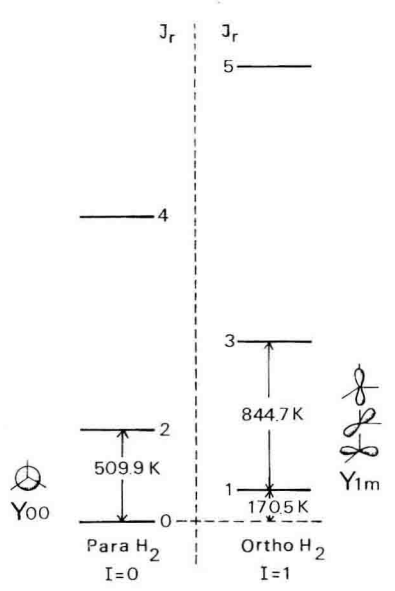

Fig. 1.2. Energy and wave functions of rotational states of para-H_2 and ortho-H_2 molecule. I, the total nuclear spin, is 0 or 1, J_r, the rotational quantum number is 0, 1, 2, ... [1.2]

As a function of temperature this ratio starts from zero at $T = 0$, and increases monotonically to $(I + 1)/I$ at high temperatures (already 2.990 at 300 K). In the case of D_2, the corresponding expression becomes

$$\frac{N_p}{N_o} = \frac{I \sum\limits_{J_r=\text{odd}} q_r^J}{(I+1) \sum\limits_{J_r=\text{even}} q_r^J} , \tag{1.8}$$

and approaches 0.5 at high temperatures (0.4999 at 200 K). Thus, at room temperature and above, H_2 (T_2) gas can be regarded as a 3:1 mixture of o-H_2 (o-T_2) and p-H_2 (p-T_2), and D_2 gas as a 2:1 mixture of o-D_2 and p-D_2. These mixtures are called normal hydrogens (n-H_2, D_2, or T_2).

Under ordinary circumstances, conversion between ortho and para states is so slow that the ortho–para ratio can be regarded to be constant during cooling to low temperatures. This slow ortho–para conversion acts as an internal heat source that causes evaporation of hydrogen at low temperatures. In order to attain the thermal-equilibrium population in the course of cooling, a gas mixture must be placed in contact with some catalyst, such as charcoal or nickel-silica.

In view of the apparent simplicity of the hydrogen molecule, it may come as a surprise to learn that the complete assignment of the energy-level structure was achieved rather recently – in 1970s. Since then, however, molecular