Hydrogen in metals

Interstitial alloys that can store hydrogen at a greater density than either the liquid or solid element alone may have a role in future energy conversion and transmission schemes.

Donald G. Westlake, Cameron B. Satterthwaite and John H. Weaver

Research on interstitial alloys of hydrogen with metals began over a hundred years ago, but these systems had remained little more than idle curiosities until World War II. This outlook changed when hydrogen embrittlement became recognized as a serious problem in a large number of technologically important alloys and with the advent of nuclear-reactor technology, which stimulated interest in solid metal hydrides as moderators. Several studies of the thermodynamics of metal–hydrogen systems and of hydrogen diffusion in these systems followed. The discovery in 1972 that some metal hydrides exhibit superconductivity added further interest.

Today, many scientists, motivated by concern about the world's energy future, have developed schemes involving hydrogen and metal hydrides for the conservation, conversion and transmission of energy. Many believe that a "hydrogen economy" will have a prominent place in the energy picture of the future. Despite some lay resistance—sometimes referred to as the "Hindenburg syndrome"—research is going forward on numerous aspects of hydrogen technology. While the old bugaboo, embrittlement, is recognized as an essential consideration in nearly all aspects of this technology, there is probably no reason to consider it an insurmountable problem in any of them.

A promising line of technological investigation involves the storage of hydrogen in stable metal hydrides. Surprisingly, the density of hydrogen per unit volume is greater in these hydrides than in either liquid or solid hydrogen. Such compounds as $LaNi_5$ and FeTi are known to absorb up to one hydrogen atom per metal atom at room temperature and to release the hydrogen when the temperature is raised only a few degrees. The energy stored is in the form of the enthalpy for dissociation of the hydride. Obvious advantages for such storage systems over the conventional tanks of liquid hydrogen include safety in handling and the elimination of cryogenics. Energy-storage systems are basic to some of the novel schemes, such as solar, for energy generation.

Interest in metal–hydrogen systems has been aroused not only by these technically oriented stimuli, but also by recent developments in the basic physical properties of these systems. Some superconducting members of this class of materials have been found to exhibit features not found in other superconductors. Furthermore, the attack on the electronic and dynamic nature of these materials with the most advanced techniques—both experimental and theoretical—have recently produced a much clearer picture of their basic physical nature.

Hydrogen reactions

Hydrogen forms ionic hydrides by reaction with all of the alkali and alkaline-earth metals. It reacts exothermically to form metallic, semimetallic and semiconducting hydrides with the transition metals in Groups III, IV and V as well as with the rare-earth metals and the actinide metals; see the periodic table in figure 1. On the other hand, the transition metals in Groups VI, VII and VIII react endothermically and generally do not form stable hydrides. The most notable exception is palladium; the alloy PdH_x probably has been studied longer and more extensively than any other hydride.[1]

The reversible reaction of a metal with hydrogen gas is a stepwise process. A molecule of H_2 may become adsorbed on the metal surface and then dissociate into two adsorbed H atoms; alternatively, the molecule may first dissociate into two H atoms, which then become adsorbed. When adsorbed atoms diffuse into the metal lattice a solid solution is formed. Additional absorption of hydrogen can result in the formation of a compound; for example, a dihydride MH_2, where M represents a metal atom. The electronic character of the hydrogen solute is a question that has been discussed for more than twenty years, but recent experimental and theoretical advances have contributed greatly towards resolving this and other questions relating to the electronic structures of metal hydrides.

Many of the hydrides are very stable and can be prepared readily by reaction with hydrogen gas at pressures below atmospheric. Less stable ones, such as PdH_x at high hydrogen concentrations, are prepared electrolytically, by proton bombardment, or under very high pressures. B. Baranowski and his co-workers in Warsaw have developed a reaction chamber for pressures greater than 30 kbar. In this way they have been able to study solutions and compounds such as NiH that are unstable at lower pressure.

Crystal structures and morphology

Solid solutions of hydrogen in metals are not substitutional; they are interstitial. In general the metal hydrides can be viewed as body-centered cubic, face-centered cubic, hexagonal close-packed or face-centered tetrahedral sublattices of metal atoms, with hydrogen partially filling the octahedral or tetragonal in-

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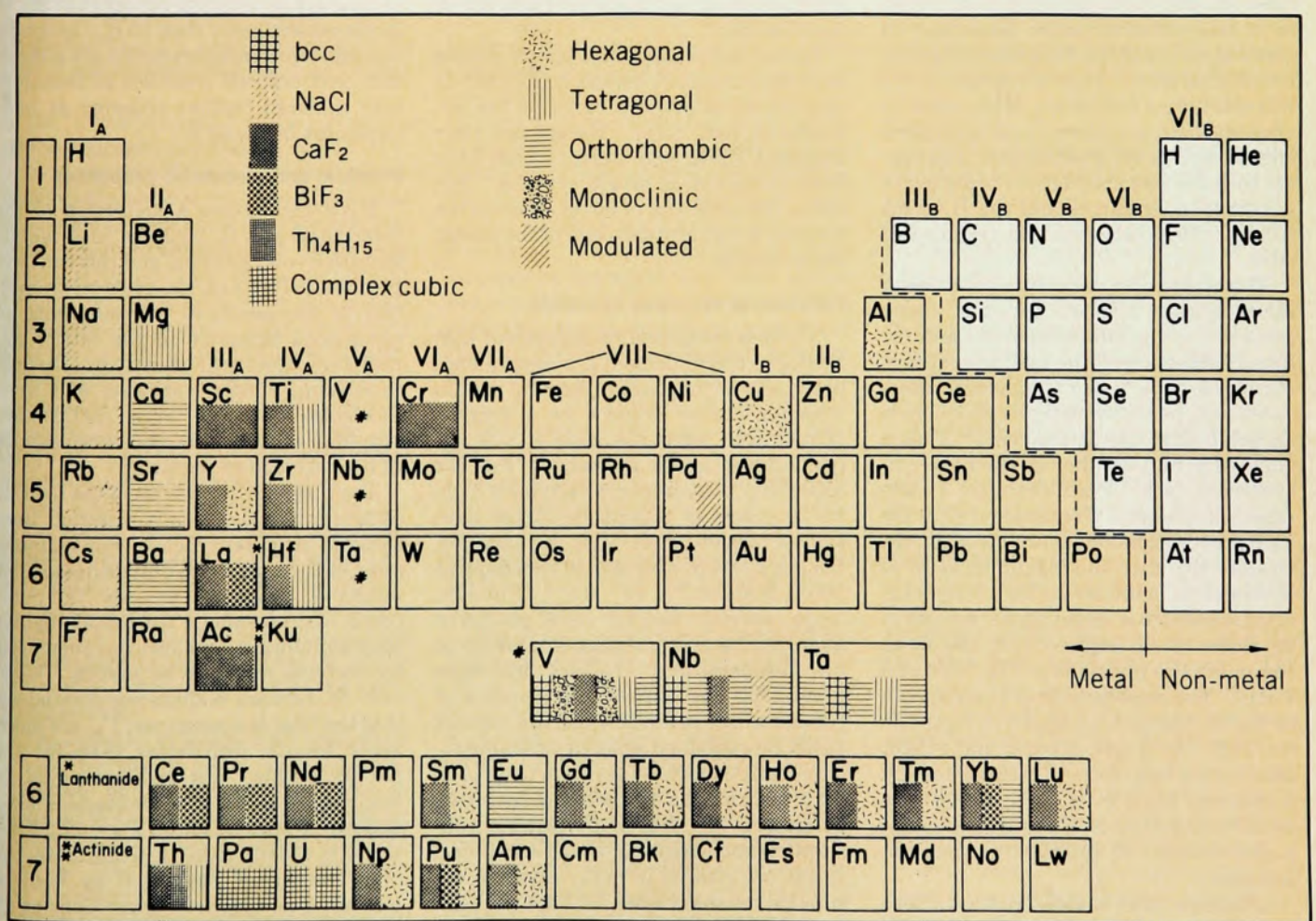
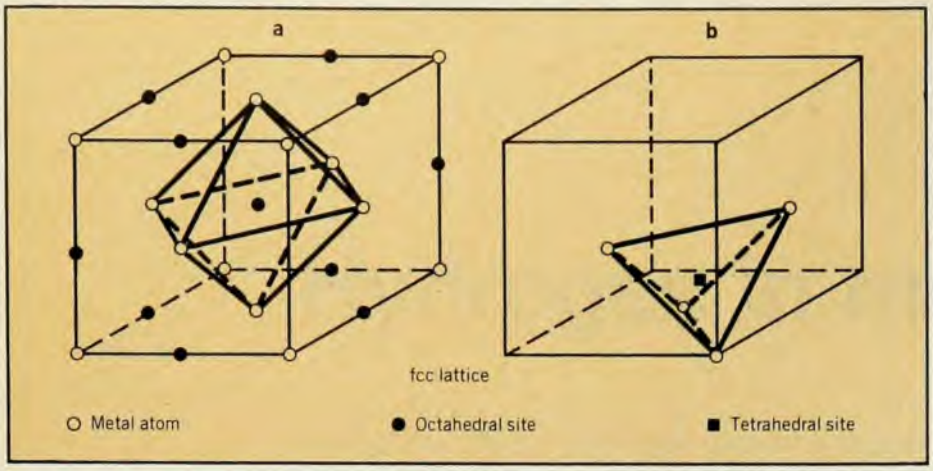
terstices. This is illustrated by the diagram on the left of figure 2, in which the open circles represent a face-centered cubic array of palladium atoms, and the solid circles represent all the octahedral sites. If all these sites were filled, the formula would be PdH and the crystal structure would be the same as that of NaCl.

The hydride of titanium, illustrated on the right of figure 2, also has the metal atoms on a face-centered cubic sublattice, but the H atoms occupy tetrahedral interstices. If these were completely filled, the formula would be TiH_2, but, just as in



Periodic table of the elements showing occurrence and structure of metal hydrides. Stoichiometries range from $MH_{0.5}$ (for M = V or Ta) to $MH_{3.75}$ (for Th). Many of the metals form more than one hydride, and many of these hydrides exhibit more than one crystal structure. For example, Tilman Schober, at KFA Jülich, has proposed the existence of nine hydride phases of Ta. (Figure courtesy of Mel Mueller). Figure 1



Models of hydride crystal structure based on a face-centered-cubic metal sublattice. In part **a**, (PdH_x), hydrogen atoms partially fill the octahedral holes shown by black dots. In part **b**, hydrogen atoms partially fill the tetrahedral holes shown by black squares. There would be eight such sites in the unit cell shown here; so the maximum value for x is 2. Figure 2

PdH_x and many other metallic hydrides, some of the interstitial sites are normally empty. The titanium-hydride phase exists over a range of composition, with the fraction of interstitial sites occupied depending both on the partial pressure of hydrogen in the gas phase and on the temperature. The rare earths form similar dihydrides, with the hexagonal close-packed metal lattice transforming to a face-centered cubic sublattice of metal atoms, and the H atoms occupying tetrahedral sites. Most of the rare earths will also form a trihydride, MH_3, some by allowing hydrogen atoms to fill octahedral sites as well as tetrahedral sites, and others with the metal sublattice reverting to a hexagonal structure and the H atoms filling both octahedral and tetrahedral sites.

The body-centered cubic sublattice of metal atoms appears to offer many possibilities for stoichiometries and ordered sublattices of the hydrogen atoms. Figure 3a depicts the tetrahedral interstices and, as shown in figure 3b, there is an octahedral site at the center of each cube edge and another at the center of each cube face. Thus, there are 12 tetrahedral sites and 6 octahedral sites for each unit cell containing two metal atoms. Despite this fact, the maximum ratio of hydrogen to metal atoms for a body-centered sublattice of metal atoms appears to be three (as in alpha-UH_3); the more common ratio is one (as in VH, NbH and TaH). The arrangement of H atoms can be highly ordered, as shown in figure 3a for TaH. In Ta_2H, a particular subset constituting half of the 12 hydrogen atoms is missing, while in V_2H (figure 3b) the same H sublattice is shifted so that octahedral instead of tetrahedral sites are occupied.

Although these models are shown here as body-centered cubic sublattices of metal atoms, they actually undergo distortions during hydride formation that cause them to be orthorhombic and therefore optically anisotropic. Thus, by using polarized light to examine this hydride microscopically, we can see the "domains" that comprise the particle, as shown on the cover of this issue of PHYSICS TODAY. Tilman Schober and Linke have shown that parallel, lamellar domains are "twins." The three observable color shades are manifestations of the different crystallographic orientations of the domains.

Distortion of the metal lattice during hydride formation makes it difficult or impossible to prepare many of the hydrides in bulk form. Exceptions have included PdH_x and CeH_x, which have been prepared as single crystals. For these, the sublattice of metal atoms in the hydride is just an expansion of the parent metal lattice.

Diffusion of hydrogen in metals

There is fairly general agreement that hydrogen embrittlement is a consequence of the agglomeration of H atoms at certain inhomogeneities within a metal sample. If hydrogen were not mobile, this agglomeration would not occur. But the diffusivity of hydrogen is extremely high, 15–20 orders of magnitude higher than that of oxygen or nitrogen; for example, the jump rate of hydrogen in vanadium at 300 K is about 2×10^{12} sec^{-1}. Furthermore, several theories have predicted hydrogen tunnelling—quantum effects at low temperatures. Indeed, hydrogen motion has been reported in tantalum at temperatures as low as 10 K; this can not easily be explained without tunnelling.

Numerous techniques have been used for measuring the diffusivity of hydrogen in metals. Studies of permeation, absorption and evolution, which are subject to surface effects, in many cases do not provide reliable values for bulk diffusivity. Because hydrogen in solid solution causes an expansion of the lattice, changes in concentrations can be monitored by measurements of electrical resistivity, of x-ray lattice parameters, of movement of the center of gravity or of relaxation of lattice distortion (the Gorsky effect). All these methods have been used to obtain H diffusivities. In the case of tritium we can use tracer techniques. At least three other techniques have been used to measure H diffusion in equilibrium situations, where the distribution of H is uniform: nuclear magnetic resonance, quasi-elastic neutron scattering and Mössbauer resonance.

Hydrogen, deuterium and tritium offer the largest relative mass differences for studies of isotope effects. According to classical rate theory, the ratio of diffusivities $D_1/D_2 = (m_1/m_2)^{-1/2}$, but such a relationship is not observed for metal–hydrogen systems. Palladium provides an outstanding example. Because the activation enthalpy for diffusion of hydrogen in Pd is greater than that for diffusion of deuterium, at temperatures below 375 K deuterium diffuses faster than hydrogen!

Another consequence of the high mobility of hydrogen is that ordering transitions can occur even at temperatures below ambient. Such transitions have been reported in the hydrides of V, Nb, Ta and Zr. Very recently, neutron diffraction has indicated that a complex type of long-range ordering occurs in PdH_x at temperatures lower than 75 K. Magnetic susceptibility measurements are suggestive that ordered hydrides of tantalum may undergo further ordering at temperatures below 65 K.

Physical and electronic properties

Hydrogen causes a distortion of the interstitial site it occupies in a metal–hydrogen solid solution, and this can have profound effects on the physical properties of the solution. Observations of anomalous behavior in the lattice parameters, electrical resistivity, thermal expansion, elastic constants and thermoelectric power of "pure" metals have now been explained by low concentrations of hydrogen as an impurity.[2]

The magnetic properties of the hydride phases can be drastically different from those of the parent metal. For example, most of the rare-earth dihydrides exhibit magnetic ordering at low temperatures—ferromagnetic for metals lighter than gadolinium and anti-ferromagnetic for terbium and heavier metals. However, W. Edward Wallace has pointed out that the Néel temperatures, T_N, are much lower for the dihydrides than for the parent metals. For terbium metal he reported $T_N = 235$ K, while Hagai Shaked and his co-workers found $T_N = 17.2$ K for terbium dideuteride. Furthermore, the nine trihydrides examined by Wallace exhibited no magnetic transitions at all down to 4 K. Like many other hydrides, these rare-earth dihydrides have electrical resistivities similar in magnitude to those of their base metals. Trihydrides of

many of the same metals, however, are semiconductors.

The physical appearance of the Group-IIIA and lanthanide dihydrides is quite different from that of the metals themselves: The dihydrides are dark, with colors ranging from grey to blue. From optical measurements we can see that the reflectance of visible light ($2 \lesssim h\nu \lesssim 3$ eV or $4000 \lesssim \lambda \lesssim 7000$ Å) for the dihydrides is from about 5 to 25% while most metals reflect about 50–70% in the visible. The low reflectance of these dihydrides can be explained in terms of a low-energy, infrared plasmon (a collective resonance) of the free carriers of the system.[3] Figure 4 shows the reflectance spectrum of LuH_2 in comparison to lutetium metal.

Electronic structure

Recent calculations have examined the effects of hydrogen on the electronic energy states of numerous metals. Before those calculations were performed, there were many heated discussions about the character of hydrogen in a metal lattice, and three divergent schools of thought emerged. These sought to treat metal-hydride systems according to

- the "anion model" which assumed charge transfer from the metal to the hydrogen site;
- the "screened-proton model," which suggested that the electron deserted its proton and occupied metallic band states, and
- the "covalent model," which viewed the metal-hydrogen bond as covalent.[1]

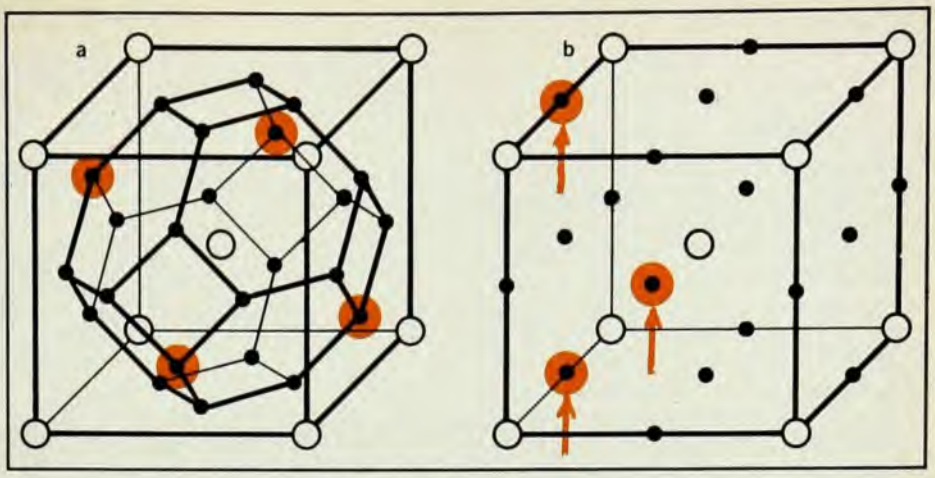
In the early 1970's Alfred Switendick convincingly showed that hydrides should be treated through modern calculational band-structure techniques.[4] Since then several groups[5] have made significant strides toward quantifying the metal–hydrogen interactions. We can expect that the understanding of these complicated systems will continue to improve in the next few years, particularly because experimentalists are now probing the electronic band structures through optical and photoelectron spectroscopies.

The electronic structure of metal hydrides can be treated through a discussion of the density of states of the mono-, di- and higher hydrides. While details are, of course, ignored in this approach, it is possible to emphasize the various effects that accompany the "switching on" of the interstitial hydrogen potential in a host-metal lattice.

The densities of states of a hypothetical d-band transition metal, monohydride, dihydride and trihydride are shown in figure 5. Although they are shown rather schematically, with detailed features omitted, they should serve to illustrate the discussion.

In part a of figure 5 we show the density of states of the metal with a parabolic sp band and relatively narrow, partially occupied d bands. The density of states of the corresponding metal monohydride is shown in part b. Several important points can be made from the figure, supported by numerous calculations for monohydrides (notably PdH) and a host of experimental data, including optical data for V, Nb and Ta monohydrides. A well defined bonding band forms below the base of the d bands, resulting from a hybridization of the hydrogen s and the metal sp states. Intuitively, it can be argued that the metal states that have significant wavefunction amplitudes at the hydrogen sites (the s states) will "see" the hydrogen potential and will hybridize. This holds for both occupied and unoccupied states of the appropriate crystal symmetry. Those states that are more localized on the metal sites (the d states) will be much less affected; this is shown by sketching the d bands as nearly unchanged in figure 5b. They are, however, somewhat lower, to account for the increased overall stability of the hydride. At the same time the Fermi level E_F must shift upward to account for the added electrons coming from the hydrogen, unless new states appear below E_F. In the case of PdH (or PdD), this shift is seen very clearly, because the Fermi level moves out of the d-band manifold and into the region of the sp bands.

The density of states of a metal dihydride such as YH_2 is shown in part c of figure 5. Comparison with those of the metal and the monohydride shows that profound changes have occurred. Switendick first discussed these changes and showed that they are due principally to the presence of two hydrogen atoms in the unit cell. Because there are two, the bonding and antibonding combinations of the hydrogen 1s Bloch orbitals can be formed. Some states are lowered by as much as 15 eV, from well above to well below the Fermi level. The result is that a complete band (two states per band) forms below E_F to accommodate the electrons contributed by the hydrogen.



Interstitial sites occupied by hydrogen in the body-centered sublattices of metal atoms. In part **a** all tetrahedral interstices are shown as black dots. Not shown are the "octahedral holes" at the center of each cube edge and at the center of each cube face, as in part **b.** In TaH, H atoms occupy the sublattice shown in color. In Ta_2H, the two hydrogen atoms on the right are missing. In part **b,** V_2H has the same sublattice as Ta_2H but it is translated with respect to the metal sublattice (as shown by the arrows) so that the occupied sites are octahedral. Figure 3

Photoelectron and optical techniques have only recently been applied to hydrides, with results that have supported Switendick's general model for dihydrides. In particular, they have been valuable in locating the bonding band, assessing its angular-momentum character (it is strongly hybridized), measuring the shift in E_F with composition and probing the occupied conduction bands.[3,6]

A critical factor in the formation of a dihydride is the spatial separation of the two hydrogen atoms, which is defined by the atomic spacing of the host lattice. Switendick has argued, and John Weaver (one of the authors) and his associates have verified with photoelectron spectroscopy measurements, that if the hydrogen sites are too closely spaced, the bonding–antibonding separation would be too great for the dihydride to form.

The lanthanides can in most instances form trihydrides by the filling of both tetrahedral and octahedral interstices of the metal lattice. As could be expected, the additional hydrogen promotes further hybridization and modification of the electronic band structure of the solid. This is shown in part d of figure 5; the bonding band is wider and its center lies farther below the Fermi energy. The narrow conduction band is sketched as a weak, vestigial foot at E_F, as has been observed[6] in Th_4H_{15}. In the case of CeH_3, it may be that E_F falls in the gap above the bonding band to give rise to the observed concentration-dependent transition of metal to semiconductor.

The degree of charge transfer has been argued at great length within the framework of the older models mentioned above. As yet there is no consensus, but the results of recent self-consistent band-structure calculations for PdH and

YH_2 have supported the notion that there is a transfer of charge to the proton site in these hydrides.

Superconductivity in metal hydrides

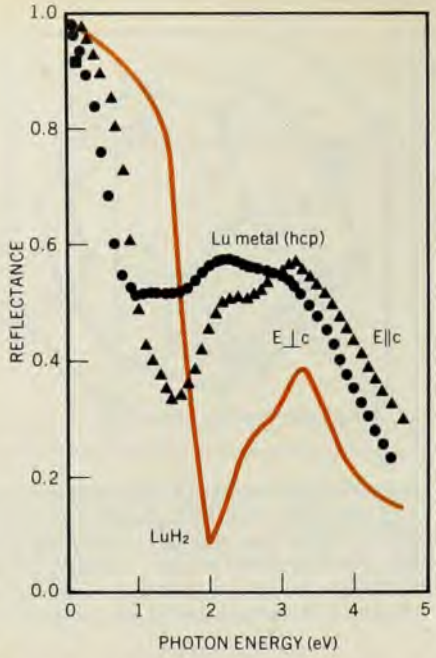
The discovery of superconductivity in Th_4H_{15} (by Cameron Satterthwaite and Ival Toepke in 1970) and in PdH_x (by T. Skoskiewicz in 1972) contradicted the conventional wisdom that hydrides are non-superconductors and that the addition of hydrogen degrades superconductivity. These revelations contributed to the already growing interest in metal hydrides. The further discovery by Bernd Stritzker and Werner Buckel in 1972 that the system of palladium hydride and deuteride exhibits an inverse isotope effect generated additional interest and controversy.[7]

Of the *binary* hydrides only PdH and Th_4H_{15} are known to exhibit superconductivity. Each displays a transition temperature considerably higher than that of the pure metal, so it is apparent that the presence of hydrogen contributes significantly to superconductivity of these materials.

A number of survey studies of *ternary* metal-hydride systems have yielded examples of elevation of the superconducting transition temperature T_c associated with the addition of H. Most interesting among these are PdM_yH_x (where M is Cu, Ag or Au), in which T_c's as high as 16 K have been recorded in metastable hydrides prepared by the ion implantation of hydrogen. Other superconducting ternaries include $NbRu_yH_x$, ZrV_2H_x and HfV_2H_x, as well as thorium-alloy hydrides resembling Th_4H_{15}. Although the ternary compounds have interesting features of their own and may provide insight into the role of hydrogen in superconductivity, we shall limit our discussion here to the thorium and palladium hydrides Th_4H_{15} and PdH_x.

The Bardeen–Cooper–Schrieffer theory and more recent extensions of it appear to provide the framework for a theoretical description of superconductivity in metal–hydrogen systems. According to these theories, the basic mechanism responsible for the superconducting state is an attractive interaction between electrons of equal and opposite momentum and spin (Cooper pairs), caused by a mutual interaction with the lattice vibrations (phonons)—more specifically, an exchange of virtual phonons between electrons. In the original BCS weak-coupling theory, the interaction was assumed to be relatively insensitive to the details of the phonon spectrum, an assumption that was surprisingly successful for a large number of superconductors.

More recent theories, however, have included a frequency-dependent interaction which, summed over the phonon and electron states, yields an interaction parameter λ from which one can calculate the superconducting transition temperature.



Optical reflectance spectra of single-crystal, hcp, lutetium metal and fcc LuH_2 as measured by Weaver and his coworkers. The metal is optically anisotropic (hcp structure), exhibits the onset of interband absorption below about 0.1 eV, and has reflectances in the visible spectrum typical of metals. LuH_2 has no interband absorption below about 1.7 eV, the sharp decrease in the reflectance at 1.5 eV corresponds to a plasmon edge. Figure 4

Thorium hydrides

Thorium forms two hydrides of known composition and crystal structure:

- the dihydride, ThH_2, which is not superconducting and
- the higher hydride, Th_4H_{15}, which has a transition temperature of about 9 K. (Thorium itself is superconducting, with $T_c = 1.37$ K.)

In the dihydride, thorium forms a face-centered tetragonal lattice with hydrogen occupying the tetrahedral interstices; in Th_4H_{15} the crystal structure is complex, displaying an intricate body-centered structure with four formula units per unit cell: $Th_{16}H_{60}$, as shown in figure 6. Besides having a remarkably high transition temperature, Th_4H_{15} has the distinction of having the highest known equilibrium hydrogen-to-metal ratio.

The preparation of nearly stoichiometric bulk samples of Th_4H_{15} presents a real materials-related challenge. Bulk material of stoichiometric composition and of nearly theoretical density can be prepared by reaction at about 900 deg C and approximately 1 kbar of hydrogen; reproducibility is far from ideal, but experiments show that:

- there is little variation of T_c with hydrogen concentration in the Th_4H_{15} single phase with the H/Th ratio between about 3.20 and 3.75;
- within experimental uncertainty, there appears to be no appreciable H–D isotope effect;
- there is a relatively large positive effect of hydrostatic pressure on T_c (the change in T_c with pressure is about 40 mK/kbar), and
- specific-heat measurements indicate that superconductivity in Th_4H_{15} does not deviate appreciably from the predictions of BCS weak-coupling theory.

Our understanding of the superconducting mechanism in Th_4H_{15} is still very tentative—in part because of the complexity of the Th_4H_{15} structure. The relative invariance of T_c with hydrogen concentration or isotope exchange suggests that the hydrogen local-mode contribution to the superconducting interaction may be small. The electronic role in the superconducting interaction is difficult to assess quantitatively, in the absence of detailed band-structure calculations for Th_4H_{15}. Because the crystal structure is so complex, and 5f bands and relativistic effects need to be included, it is not likely that such calculations will be attempted. Nevertheless, it is clear from figure 5 and from photoelectron-spectroscopy studies[6] that the electronic structure of superconducting Th_4H_{15} is very different from that of nonsuperconducting ThH_2. These differences must be considered in any theoretical modeling.

Palladium hydrides

The wide range of physical and chemical properties of PdH (and PdD) has intrigued scientists for the last 100 years and well over a thousand papers have been published on this system. It is therefore surprising that the superconducting character of PdH went unobserved until 1972.

Two interesting features of superconductivity in PdH_x are the very sharp dependence of the transition temperature on the H/Pd ratio and the large inverse isotope effect (according to the BCS theory and most experimental evidence, T_c should *decrease* with increasing isotopic mass although, as figure 7 shows, T_c for PdD_x is *higher* than that for PdH_x). Transition temperatures as high as 16 K in metastable Pd–noble metal–H compounds present an additional interesting dimension to the PdH system.

After many attempts to develop a theoretical understanding of superconductivity in the PdH_x system, it is generally agreed that the hydrogen (or deuterium) plays an essential role in quenching the palladium's paramagnetism. From tunneling measurements we also know that a significant fraction of the pairing interaction responsible for superconductivity arises from an interaction between the electrons and the high-frequency hydrogen vibrations, as suggested by Bishwa Ganguly. There is, however, little agreement about the importance of this

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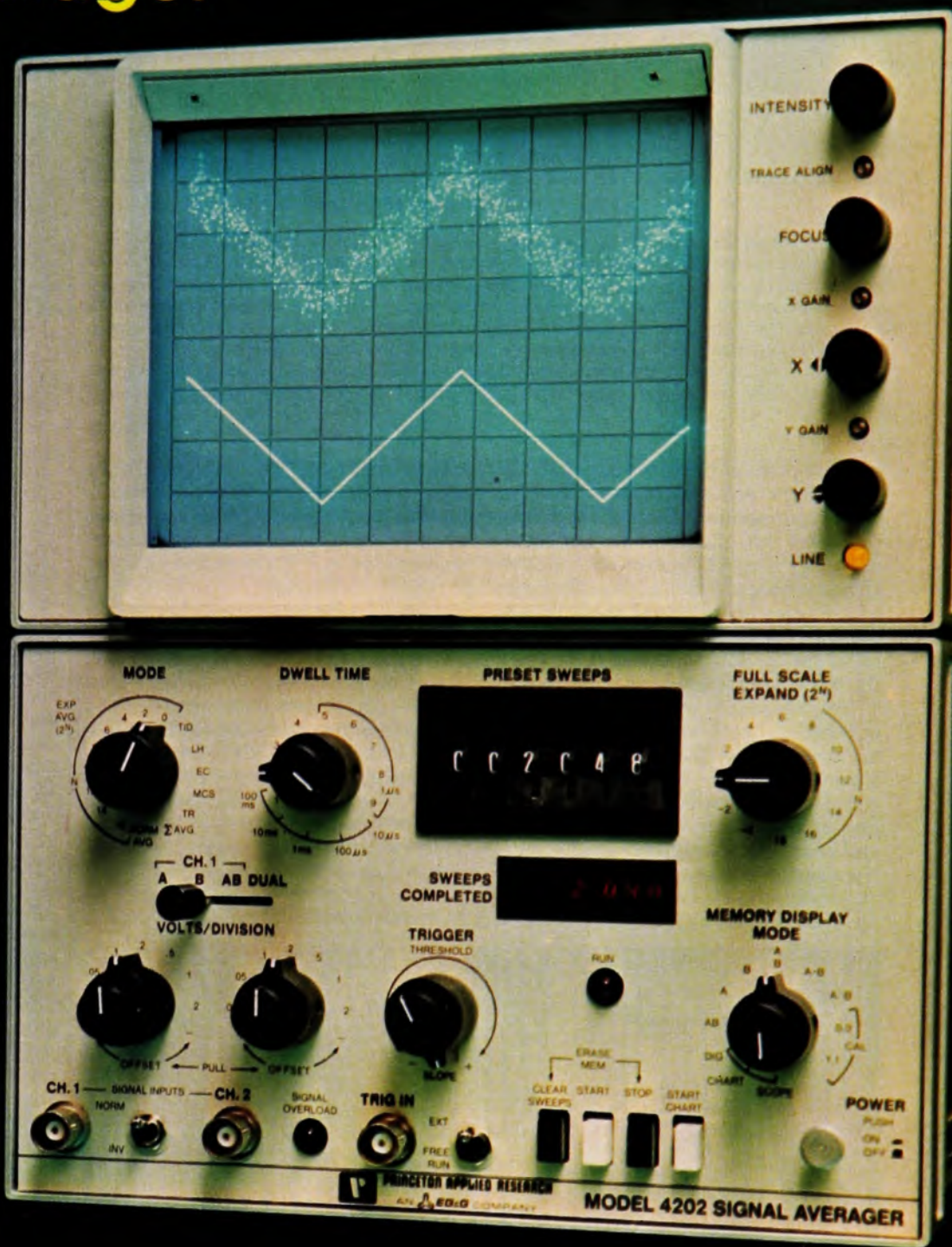

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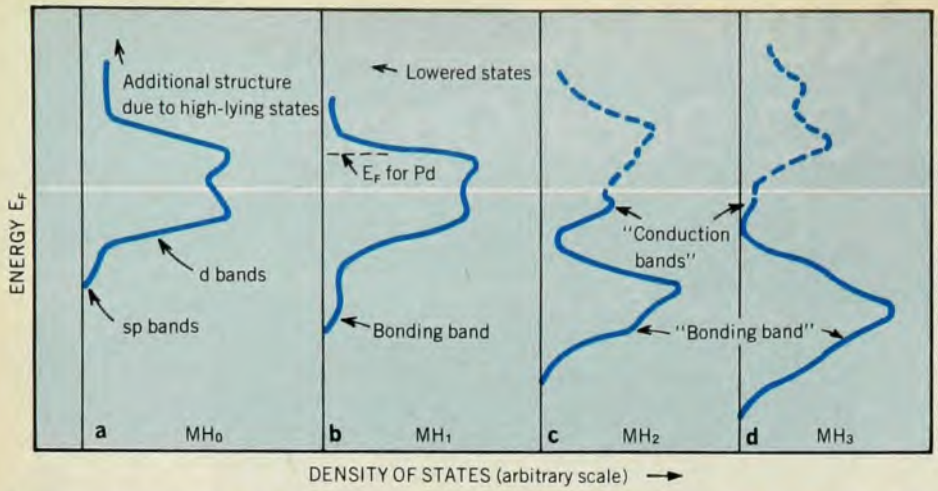


Density of states for a metal (MH_0), a monohydride (MH_1), a dihydride (MH_2) and a higher hydride (MH_{3+}) shown schematically (adapted from reference 4). In part **a**, partially occupied metal d bands are shown to be superimposed on the parabolic sp bands. The d bands in the monohydride are similar to those of the metal because the curves are schematic. The bonding band containing states of hybridized M–H character is shown at the base of the d bands. The Fermi level of Pd lies near to the top of the d bands and is shifted into the sp region when H is added to the metal. The occupied density-of-states in parts **c** and **d** are based on photoelectron spectroscopy results for ThH_2 and Th_4H_{15} (by Weaver et al.); the curves for the empty states are highly schematic. Figure 5

effect relative to the contribution of the (palladium) acoustic modes. So far, tunneling experiments have not been able to resolve this question. Recent calculations by Dimitri Papaconstantopoulos and his colleagues[5] indicate that the major contribution stems from these optical phonons, and this interaction may account for the steep increase in T_c when the H/Pd ratio approaches unity.

One reasonably successful theoretical approach is based on William L. McMillan's extension of BCS to strong-coupling superconductors. For materials that contain atoms of widely differing masses, one can separate the contributions of light and heavy atoms and assign a value for λ, the electron–phonon interaction parameter, to each. The contribution from the heavier atom (Pd) reflects the acoustic phonon mode, and that from the lighter atom (H or D) reflects the optic mode. Thus, for atom X in compound $X_a Y_b$

$$\lambda_X = \frac{n(o)_X \langle I_X^2 \rangle}{M_X \langle \omega_X^2 \rangle}$$

where the square of the electron–phonon matrix element averaged over the Fermi surface, $\langle I_X^2 \rangle$, the atomic mass M_X, and the phonon frequency ω_X are those appropriate to atom X. $n(o)_X$ is the density of electron states in the vicinity of the X atom at the Fermi energy. Then the value of λ used for T_c is $\lambda_X + \lambda_Y$.

The transition temperature for the superconductor is then obtained from McMillan's formula:

$$T_c = \frac{\theta_D}{1.45} \exp\left\{-\frac{1.04\,(1+\lambda)}{\lambda - \mu^*\,(1+0.62\lambda)}\right\}$$

where θ_D is the Debye temperature; μ^*, a measure of the electron–electron Coulomb interaction, is estimated or determined from experiment.

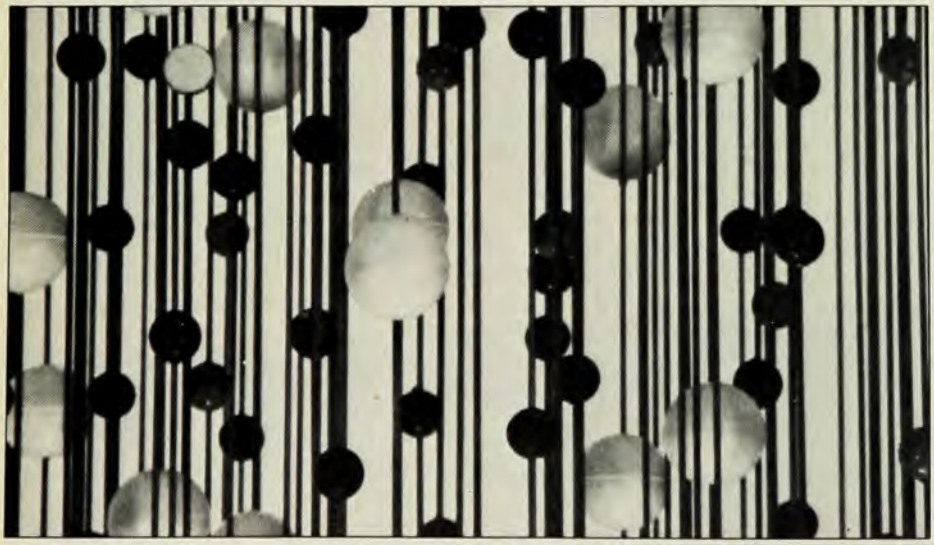
Switendick was the first to calculate microscopic properties or electronic structure for the PdH system.[4] As we mentioned earlier, there have been several recent refinements of those calculations, and the quantitative understanding of the one-electron states in stoichiometric PdH is now quite good.

Papaconstantopoulos and his colleagues[5] recently reported self-consistent band calculations for PdH. Using those calculations, they derived a value for $n(o)$, the density of electron states in the vicinity of the hydrogen atom as defined above, through the electron–phonon interaction equation. They then showed that $n(o)$ and λ increase significantly with the H/Pd ratio, as is observed experimentally and, further, that T_c has the observed H/Pd dependence.

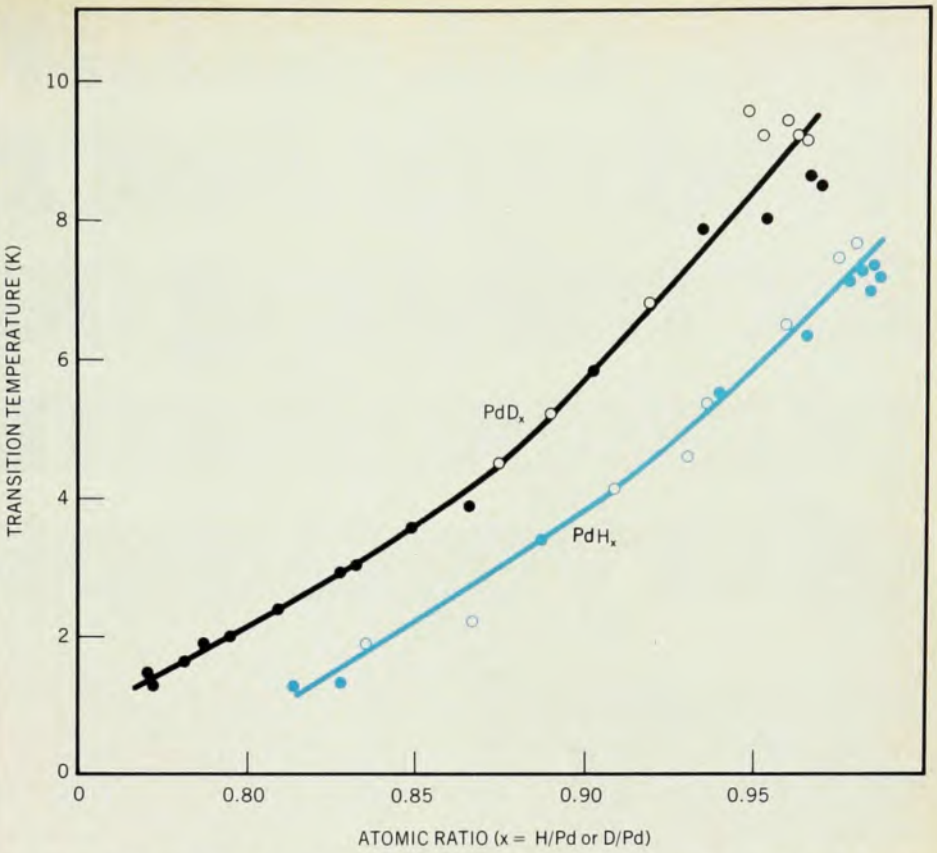
The most unusual feature of superconductivity in PdH_x and PdD_x, the inverse isotope effect, is still in want of a satisfactory explanation. A number of attempts have been made to explain it as the result of a difference in the phonon spectra of PdH_x and PdD_x resulting from the mass difference and a difference in the Pd–H and Pd–D force constants. This approach is discussed by Nathan Jacobi and Laurent Caron[8] and they list most of the references to earlier work in their paper. Papaconstantopoulos's group,[5] for example, finds agreement with experiment by considering the effect on the optic modes of a force constant that is 20% larger for Pd–H than for Pd–D. Experimental evidence for such a difference comes from tunneling and from analysis of inelastic neutron-scattering data. The agreement may be fortuitous, however, because their calculation ignores any difference in electronic structure that might result from the difference in mass and the resulting difference in zero-point motion of H and D, and it also ignores any effect on the acoustic modes due to these differences.

Robert Miller and Satterthwaite[9] proposed a qualitative model for the isotope effect based on a postulated difference in PdH_x and PdD_x electronic structure. They suggest that a difference could result from the proton spending a larger fraction of its time in close proximity to the surrounding palladium atoms than the deuteron does, because the proton zero-point amplitude is about 15% larger than that of the deuteron and the lattice constants are very nearly the same.

Recent evidence for electronic differences from specific-heat measurements and nuclear magnetic resonance tends to support this electronic hypothesis. Very



Model of part of the unit cell of Th_4H_{15}. The crystal structure, whose unit cell contains four formula units, was first proposed by W. H. Zachariasen in 1953 on the basis of x-ray diffraction measurements that yield only the symmetry and spacing of the thorium atoms. Recent neutron diffraction measurements by Mel Mueller and his coworkers confirmed this structure. Figure 6



Variation of temperature T_c with hydrogen concentration for PdH_x (in color) and PdD_x (in black) showing the large inverse isotope effect. The figure includes data by Robert J. Miller and Satterthwaite (open circles) and by James Schirber and Clyde Northrup (filled circles). Figure 7

probably both electron and phonon differences could be involved in the complete explanation.

The quantitative evaluation of the zero-point motion and its impact on the one-electron band structure remains a challenge. The "frozen nucleus" or "rigid-ion" assumption, which is important in all one-electron band calculations, should be examined carefully.

For various reasons, some classes of materials have been studied very thoroughly while others have not. The hydrogen-in-metals system constitutes a large and diverse class, which, until recently, has largely been ignored both by experimental and by theoretical physicists. Recent studies have not only pointed the way toward possible large-scale technological applications, but have also revealed physical, chemical and metallurgical properties in unexpectedly rich variety. As well as the properties discussed in this article, these include the lattice-gas phenomena (including the many recently discovered lattice-solid ordered phases), the quantum-solid aspects of these materials (including the effects of zero-point motion, tunneling, and unpredictable isotope effects) and the surface physics involving the $H_2 \rightarrow 2H$ dissociation. Exploration of these phenomena and properties and others yet unsuspected will undoubtedly produce more interesting physics and more useful applications.

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