

# The ABC's of the Hydrogen-Metal System

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## ABSTRACT

Some basic properties of the hydrogen-metal system are described with particular attention paid to the availability of close D-D pairs in metals. A brief description is also given of the behavior of energetic  $D^+$  ions during their passage through a metal lattice.

### 1. Introduction

There appears to be a general expectation that the occurrence of "cold fusion" phenomena, if any, is connected to some unusual and hitherto unknown behaviors of hydrogen in metals, especially in Pd. The purpose of this paper is to describe some basic properties of the hydrogen-metal system, the ABC's, the knowledge of which must be shared by everyone in this community. (For more details including most recent results, see Fukai 1993).

Roughly speaking, there are two ways for nuclear fusion to take place. The first, the ordinary way, is that the fusion occurs in the course of collision of two nuclei having energies high enough to overcome the mutual Coulomb repulsion. The second is that two nuclei are held at sufficiently short distances so that the nuclear fusion can be induced by the tunneling through the Coulomb barrier. As by definition the real "cold" fusion refers to the second (static) mechanism, most of the

discussions given below are on the equilibrium properties of the hydrogen-metal system, more specifically, the state of D-D pairs in metals. Only a brief description will be given of some properties that are relevant to dynamical processes.

A measure of the internuclear distance that produces observable fusion rates is given by the calculation of Koonin and Nauenberg (1989). They calculated fusion rates in diatomic hydrogen molecules of various isotopic composition, and their dependence on the internuclear distance by varying the hypothetical electron mass. Their results showed that the fusion rate depends nearly exponentially on the distance, and that for the d-d fusion rate to be  $10^{-20} \text{ s}^{-1}$ , the distance should be  $\sim 0.015 \text{ nm}$ . The question is whether there is any way to hold D-D pairs in metals at such a short distance. For comparison, at the distance of a  $\text{D}_2$  molecule ( $0.074 \text{ nm}$ ), the fusion rate amounts to only  $10^{-64} \text{ s}^{-1}$ , which is completely negligible.

## 2. Distance between hydrogen atoms in metals

Hydrogen atoms enter interstitial sites in metal lattices to form metallic alloys. The heat of solution  $h_s$  is different for different metal species, and for a given metal, varies with the hydrogen concentration as shown in Fig. 1 (Fukai 1993). In all the cases, the concentration dependence of  $h_s$  is similar. The

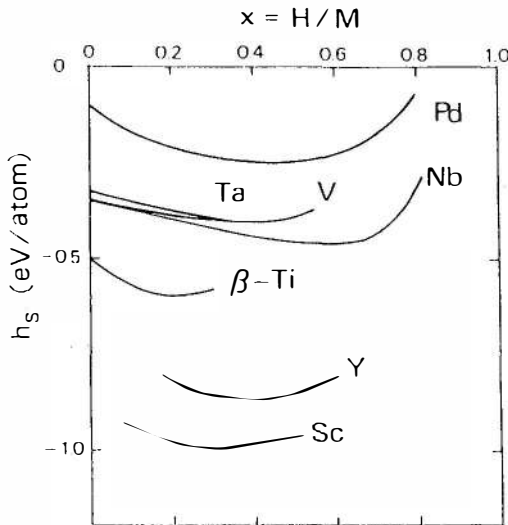


Fig. 1 The heat of solution of hydrogen in some metals as a function of hydrogen concentration. For data sources, see Fukai 1993.

overall lattice expansion caused by hydrogen atoms facilitates the dissolution of hydrogen at the beginning, but the short-range repulsion between hydrogen atoms gradually comes into play at higher concentrations.

In Pd, the heat of solution is  $h_s = -0.106$  eV at the infinite dilution, but it crosses zero at  $x = [\text{H}]/[\text{Pd}] \approx 0.84$ , and becomes positive thereafter (Flanagan and Lynch 1975). This implies that near the composition  $x \approx 0.84$ , there can be large concentration fluctuations in the hydriding process (e.g. by electrolysis), and at higher concentrations,  $\text{PdH}_x$  decomposes exothermically (by giving off heat). For D in Pd, the heat-of-solution curve is shifted by 0.026 eV upward (Wicke 1985), but the overall behavior is nearly the same.

There is an empirical rule that interstitial hydrogen atoms do not come closer than 0.21nm, another manifestation of the short-range mutual repulsion. In cases where the distance between neighboring interstitial sites is shorter than 0.21nm interstitial sites are only partially filled with hydrogens, either orderly or disorderly.

Maps showing the average D-density distribution can be Fourier-reconstructed from neutron diffraction data. Care must be taken in interpreting the density maps in disordered phases: whereas the maps indicate that hydrogens are distributed evenly over all the closely-spaced interstitial sites, the actual situation should be that they occupy only a small fraction of sites by trying to keep away from each other. In ordered phases, on the other hand, D-density maps provide useful information on the potential field for hydrogen atoms. Figure 2 shows D-density maps of  $\beta\text{-VD}_{0.51}$ , an ordered phase of the V-D system (Okada 1980). The distribution of D atoms is very strongly anisotropic, indicating that the potential is steeply increasing in the c-direction and is slowly-varying in the a-b direction. The amplitude of potential undulations can be estimated from the excitation energies to highly excited vibrational states (observed by inelastic neutron scattering) and the activation energies of diffusion at high temperatures where the migration proceeds essentially via jumps over saddle points (Fukai and Sugimoto 1992, Fukai 1993). Thus, a measure of potential undulations can be given as 0.5~1eV.

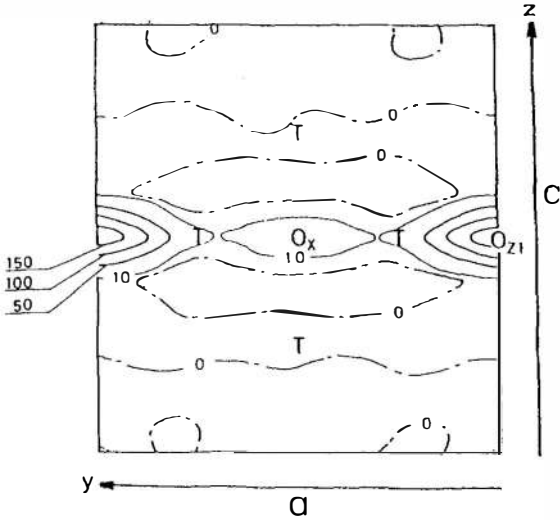
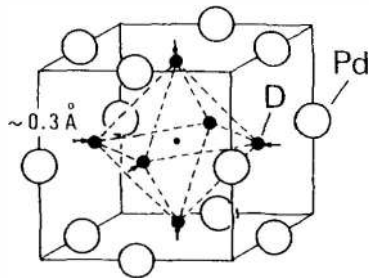


Fig. 2 D-density map in  $\beta$ -VD<sub>0.51</sub> (Okada 1980).

A possibility of hydrogen atoms coming a little closer arises when they are trapped by lattice defects, more specifically, by vacancies. Numerous experiments performed on the defect-trapping of hydrogen atoms have shown that in many metals a vacancy can trap as many as six hydrogen atoms with binding energies of the order of  $\sim 0.5$  eV (Myers et al. 1989). This does not imply that six hydrogen atoms are jammed in a very narrow space by replacing one metal atom. Rather, it is more appropriate to regard them as occupying six interstitial sites nearest to the vacancy. The actual configuration of D trapped by vacancies in Pd determined by the channeling method is depicted in Fig. 3 (Besenbacher et al. 1990). Hydrogen atoms are displaced slightly towards the

Fig. 3 Configuration of six D atoms trapped at a vacancy in Pd (Besenbacher et al. 1989).



center of a vacancy, and the mutual distance between them ( $\approx 0.185\text{nm}$ ) is certainly smaller than the normal distance in a stoichiometric PdD ( $\approx 0.28\text{nm}$ ). Recently, a number of calculations have been performed on the electronic structure and energies of hydrogen pairs in Pd (Wang et al. 1989, Sun and Tománek 1989, Lam and Yu 1989), and all the calculations agree in that the equilibrium pair distance becomes longer than the internuclear separation in a molecule.

### 3. Possibility of close D-D pairs in metals

It may be appropriate here to specify more clearly the requirement to be placed on the D-D distance. The ordinary procedure to calculate the fusion rate  $\Lambda$  is to evaluate the wave function of the relative motion of two D nuclei at the separation of  $\rho \sim 10^{-14}$  m, where nuclear interactions occur; viz.  $\Lambda = A |\Psi(\rho)|^2$ . This procedure is not applicable to a D-D pair in a metal because the potential field arising from interactions with metal atoms is fixed in position relative to the metal lattice, and therefore the separation of space variables into the center-of-mass and the relative coordinate cannot be made. However, the following considerations show that potential undulations in metals do not affect the problem seriously.

At small pair separations, the interaction potential can be written in any case as

$$V(r) \rightarrow e^2/r + V_0. \quad (1)$$

In a free space, the electronic energy is that of the He atom,  $V_0 = -51.8$  eV. The calculation of Koonin and Nauenberg (1989) which correctly incorporated this screening energy gave the D-D fusion rate ten orders of magnitude larger than the previous calculation which neglected this term ( $V_0 = 0$ ) (Van Siclen and Jones 1986). Judging from these results, the effect of potential undulations in metals, being only  $0.5 \sim 1$  eV, should not change the order of magnitude of the Koonin-Nauenberg's calculation. Thus, the requirement on the pair separation of  $\sim 0.015\text{nm}$  applies equally well to D-D pairs in metals.

The following discussions show that there is no way to sustain such close D-D pairs in any solids.

Let us consider the balance of forces exerted by the repulsion between two D atoms in a pair and the counteracting force arising from the distorted interatomic bonds of the surrounding lattice.

The repulsive force is estimated as  $f_p \approx e^2/r^2 \approx 1 \times 10^{-6} \text{ N}$  at  $r \approx 0.015 \text{ nm}$ , whereas the lattice force per bond can be estimated as  $f_b \approx (c_{11}/N_o) \cdot (\Delta l/l)$ , where  $N_o$  is the number of bonds per unit area. Substituting the values appropriate for Pd ( $c_{11} = 2.3 \times 10^{11} \text{ N/m}^2$ ,  $N_o = 6.6 \times 10^{18} \text{ m}^{-2}$ ) and for large strains of  $\Delta l/l \sim 1/3$ , the counteracting force is estimated to be  $f_b \approx 1 \times 10^{-8} \text{ N}$  at the largest. Thus, interatomic bonds in Pd are not strong enough to counteract the forces exerted by the close D-D pair. In fact, there is no solid on earth which is strong enough to sustain D-D pairs at such short distances. What actually happens is that the D-D pair relaxes to a distance where the force balance can be realized.

The same conclusion can be reached from energy considerations. The energy of a D-D pair in a metal can be approximated by the value in a free space;  $V(r) \approx 44.2 \text{ eV}$  at  $r \approx 0.015 \text{ nm}$ . The electronic energy corrections in a metal should be  $\sim 1 \text{ eV}$  at the largest. On the other hand, formation energies of lattice defects are much smaller;  $\sim 1.5 \text{ eV}$  for a vacancy and  $\sim 5 \text{ eV}$  for an interstitial atom in a metal of a melting point of  $T_m \approx 2000 \text{ K}$  (these values roughly scale with  $T_m$ ). This implies that a close D-D pair, if once created, should immediately transfer its energy to the surrounding lattice to attain some lower-energy configuration; even the creation of a number of lattice defects is energetically more favorable.

It may be added that the use of a screened Coulomb potential ( $e^2/r$ )  $e^{-\alpha r}$  for the first term of eq.(1) is erroneous. A literal application of a Thomas-Fermi formula which describes the screening by a dense electron gas gives a screening length of  $\alpha^{-1} = [4\pi e^2 N(E_F)]^{-1/2}$ , which becomes as small as  $\sim 0.02 \text{ nm}$  in Pd. This is a consequence of a peculiar situation in Pd that the Fermi energy  $E_F$  happens to fall on a very pronounced peak of the density of states  $N(E)$ . Calculations showed, however, that this peak arises from 4d electrons of Pd which are strongly localized on Pd atoms and therefore do not participate in the screening of nuclear charges in interstitial sites (Papaconstantopoulos et al. 1978). No such electrons are

available in metals that are effective in screening a singly-charged particle in such vicinities.

The screening would be more effective if there were negatively charged particles heavier than electrons. Indeed, when an electron in a D<sub>2</sub> molecule is replaced with a negative muon ( $\mu^-$ ) which is about 200 times heavier than an electron, the screening radius is reduced by this factor and the fusion probability is increased to  $10^9$  s<sup>-1</sup>. However, the use of the "effective mass" of conduction electrons in this context is a mistake. Conduction electrons behave as if they had a large mass when they travel over many atomic distances as waves. The concept of effective mass is simply inapplicable to the problem of static charge screening.

The upper bound for a d-d fusion rate in metals was calculated by Leggett and Baym (1989) by including possible many body effects, and was found to be very small ( $\sim 10^{-47}$  s<sup>-1</sup>), in agreement with the present discussions.

Thus, we cannot expect any measurable d-d fusion to occur in metals as long as we stay within the static regime.

Needless to say, the probability of realizing a close D-D pair configuration by thermal excitation is negligibly small, being  $e^{-44.2eV/kT} \approx 10^{-770}$  at room temperature.

#### 4. Effects of high pressure

Here I describe the pressure dependence of the distance between hydrogen atoms in elemental hydrogen and in hydrogen-metal systems.

Elemental hydrogen under normal pressure is an aggregate of stable covalent molecules weakly bound with each other by van der Waals interactions. Thus, the interatomic distance within a molecule ( $\approx 0.074$  nm) is much shorter than intermolecular distances, and a large compressibility of the elemental hydrogen results from the compression of the latter. In contrast, the pressure dependence of the former is very peculiar. The frequency of the stretching vibration, which reflects the bond strength in a molecule, increases with pressure up to  $\sim 40$  GPa but turns into a decrease thereafter. The decrease goes through a discontinuity at  $\sim 150$  GPa and continues on to  $\sim 250$  GPa where the sample becomes gradually more opaque (a phenomenon indicative of an electronic band

closure which leads eventually to a semi-conductive or semi-metallic state) (Hemley and Mao 1988, Mao and Hemley 1989). These observations imply that as more electrons tend to participate in the bonding between molecules at higher pressures, the bonding within the molecules becomes weaker and the interatomic distance correspondingly longer. Theoretical calculations predict that the metallization of hydrogen proceeds in two steps; a molecular crystal – an intermediate metallic structure with a remnant molecular bonding – monatomic metal (Brovman et al. 1972, Barbee et al. 1989). It is only after the monatomic metallic structure is realized that the minimum distance between hydrogen atoms decreases with pressure.

Fukai (1991) pointed out that the hydrogen volume in metallic environments, including interstitial hydrogen and elemental metallic hydrogen, follows a universal compression curve, which can be expressed to a good approximation by the Vinet-type formula,

$$p=3K_0(1-y)y^{-2}e^{-\eta(1-y)} \quad , \quad y=(V/V_0)^{1/3}$$

with the bulk modulus  $K_0=99.2$  GPa, the initial volume  $V_0=2.96 \times 10^{-3}$  nm<sup>3</sup> and  $\eta=4.47$ . Using this equation of state, we can estimate the pressure required to reduce the interatomic distance to  $\sim 0.015$  nm. The value comes out to be  $1.3 \times 10^6$  GPa ( $6.2 \times 10^5$  GPa for 0.02 nm), which is of the order of magnitude of the center pressure of the Jovian planets, Jupiter and Saturn. The occurrence of a piezonuclear fusion is only possible at these extremely high pressures hardly attainable in laboratory experiments.

## 5. Dynamical processes of D<sup>+</sup>'s in metals

Let us consider a nuclear fusion to be caused by the collision of incident energetic D<sup>+</sup>'s with D<sup>+</sup>'s in a metal lattice.

As the reaction cross section  $\sigma(E)$  increases steeply with the energy of an incoming D nucleus, the total probability of occurrence of such events depends solely on the availability of high-energy D nuclei. Cosmic rays and the acceleration of fracture-induced D<sup>+</sup>'s by transient electric fields built up across



the cracks (fracto-fusion) have been proposed as possible sources of such energetic particles.

In this section, I consider the fate of incident D<sup>+</sup>'s with energies of 1~500 keV after entering a metal lattice, whatever their source may be. At these energies, the incoming D<sup>+</sup>'s gradually lose their energies by interactions with conduction electrons, and finally come to rest by creating lattice defects when their energies decrease to ~10 eV. As the relation between the incident energy  $E_0$  and the total path length  $\lambda_0$  is approximately given by  $\lambda_0 \propto \sqrt{E_0}$  in this energy range, the energy of an incident D<sup>+</sup> decreases to  $E = E_0 (\lambda_0 - l)^2/\lambda_0^2$  after straggling over a distance  $l$  from the surface. For D<sup>+</sup> in Pd,  $\lambda_0 = 0.1\mu\text{m}$  for  $E_0 = 3$  keV. The rapid dissipation of incident energies restricts the possibility of nuclear fusion to within a thin surface layer.

In special cases when the direction of an incident beam lies within  $\sim 1^\circ$  of some principal crystal axes or planes, the penetration depth is increased by an order of magnitude (the ion channeling), and the nuclear fusion rate will be enhanced accordingly. The enhancement can be rather important because the beam of incident D<sup>+</sup>'s is concentrated near the center of channels where most of the interstitial D<sup>+</sup>'s (targets) are located.

Another effect of high-energy incident particles is to create a number of knocked-on D<sup>+</sup>'s which may induce additional fusion events. This effect is most important when incident particles are neutrons; the energy of neutrons can be transferred efficiently to hydrogens to create energetic D<sup>+</sup>'s.

In any case, it must be emphasized that the high-energy particles must be prepared outside solid samples. Particle energies are always dissipated in solids, especially the energies of charged particles in metals. The acceleration of any particles in metals up to the order of keV is simply impossible.

Finally, I wish to rectify the misconception that strong electric fields built up across the thin double layer near the electrode may induce some nuclear events. It is not the magnitude of field strengths but the energy acquired from the electric field that matters. The energy of D<sup>+</sup>'s acquired by acceleration across the double layer is  $\sim 0.1\text{eV}$  at the largest, which is completely negligible for nuclear events.

## 6. Conclusion

The properties described here are the very ABC's of the hydrogen-metal systems. In seeking for a mechanism of cold fusion phenomena, one should not ignore these ABC's but find some way to circumvent difficulties posed by them. The difficulties are great for the occurrence of nuclear fusion events, not to speak of the excess heat release. Even greater difficulties are expected for other fusion reactions involving pairs with higher-valence nuclei or three-body interactions. The hydrogen-metal systems, with all these ABC's are by no means friendly to cold nuclear fusion.

## 7. References

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