Arguments for dideuterium near monovacancies in PdD

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Abstract. Molecular D_2 does not form in bulk PdD because the electron density sufficiently high so that antibonding orbitals are occupied. The electron density can be lower in the vicinity of a vacancy. We examine the possibility that sigma-bonded dideuterium can occur at the lowered electron density near a monovacancy in PdD.

1. Introduction

Excess heat has been observed in many Fleischmann-Pons experiments over the years, generally supporting the claims made by Fleischmann and Pons in 1989 [1,2]. The many negative results found in the early experiments of 1989 can be attributed in part to a lack of understanding of basic requirements that were clarified later on [3-5]. A remarkable feature of the effect is that a prodigious amount of energy is produced; much greater than can be attributed to chemical reactions (for which physical evidence is absent). The conjecture that the energy is due to a new nuclear process has historically been met with much skepticism, due to the absence of commensurate energetic particles which would be expected if nuclear reactions were responsible [6]. In a nuclear reaction, the energy produced is expressed as energetic particles as a consequence of local energy and momentum conservation. Excess energy produced in the Fleischmann-Pons experiment without commensurate energetic particles challenges long established ideas about how nuclei react, suggesting that there is a new kind of physical process in which nuclei interact in some new way in which the energy is expressed through other degrees of freedom.

We have described in earlier publications a new mechanism which is capable of coherent energy exchange between two-level systems and an oscillator under conditions where the transition energy of the two-level system is a great many times the characteristic energy of the oscillator [7,8]. This mechanism seems to be capable of converting an MeV-level nuclear energy quantum into a very large number of meV-level phonons under conditions relevant to the Fleischmann-Pons experiment. We have proposed a two-step reaction mechanism that involves first the transfer of excitation from the hindered $D_2/^4He$ system to unhindered two-level systems which then convert the nuclear energy quantum to phonons using this new energy conversion mechanism. Under conditions where the excitation transfer step is the "bottleneck" which determines the overall rate for the two-step reaction, the reaction rate can be estimated from the associated excitation transfer matrix element. We have recently computed the nuclear part of this matrix element using a brute force numerical calculation, and we find that it is sufficiently large to account for the rate of excess heat production if the screening energy [9] is about 150 eV.

For the process consistent with our model to occur, molecular D_2 must be present in the lattice. In this respect, our model differs from other models which are currently more popular [10,11]. In our view, many practical aspects of the Fleischmann-Pons experiment and related experiments can be understood in terms of maximizing molecular D_2 inside the lattice. In this proceedings paper, we will focus on the issue of D_2 in PdD, which will focus our attention on issues related to the local electron density and vacancies.

2. Preferred electron density

Our arguments in this paper are based on the notion (from embedded atom theory [12-14]) that there exists a preferred electron density that deuterium or dideuterium wants to see, that is similar in molecular or solid state environments. If so, then we might use PdH as a reference for deuterium in Pd, and PdH_2 as

a reference for dideuterium in Pd.

In the case of PdH, we make use of the results of Balasubramanian et al [15] who give an atomic separation of 1.53 Angstroms. For PdH_2, we use the results of Balasubramanian et al [16], who give an a separation between the Pd atom and the center of the H_2 molecule to be 1.67 Angstroms. In this case, the two hydrogen atoms bond as a molecule with a separation of 0.81 Angstroms. To estimate the Pd electron density at 1.67 Angstroms for PdH_2, we performed a Dirac-Fock calculation for atomic Pd in the ground state $(4d)^{10}$ configuration (which was found by Balasubramanian et al to be the dominant Pd configuration), and found the Pd electron density to be 0.0332 electrons/Angstrom^3 (see Figure 1). A similar computation for the Pd $(4d)^{9.35}(5s)^{0.65}$ configuration leads to an electron density at 1.53 Angstroms of 0.0686 electrons/Angstrom^3.
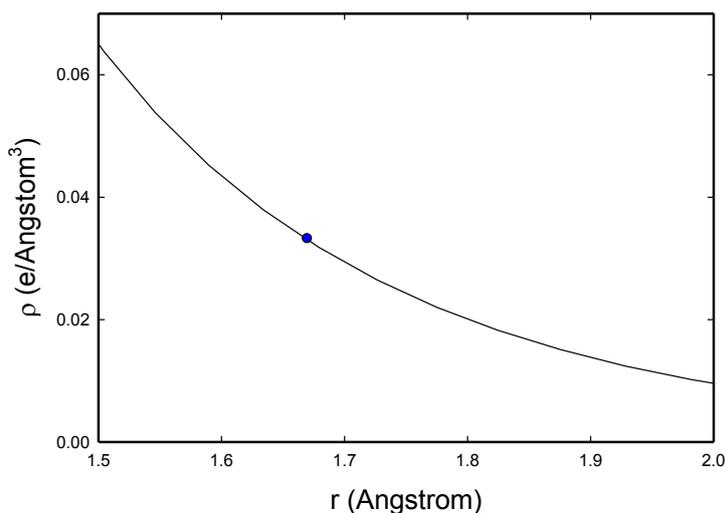
Fig. 1. – Electron density from a Dirac-Fock calculation of Pd $(4d)^{10}$ configuration in the vicinity of 1.67 Angstroms relevant to the PdH_2 molecule.
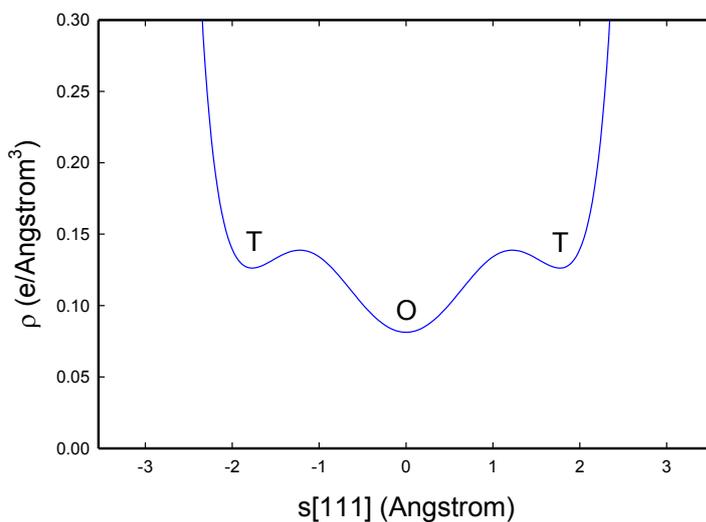
Fig. 2. – Model electron density due to Pd in the vicinity of an octahedral site in PdH.

3. Pd electron density in PdH

If we consider the electron density due to only the Pd atoms in PdH from a simple superposition of the atomic orbitals, we obtain the result for a scan centered at an octahedral site along the [111] direction shown in Figure 2. We see that the electron density is lowest at the octahedral site in this model, with a density of 0.081 electrons/Angstrom^3. The electron density in this model is significantly higher at the tetrahedral sites, indicating that one would expect hydrogen in PdH to occupy the octahedral sites since the Pd electron density at these sites is closer to the Pd electron density in molecular PdH.

A computation of H_2 in electron gas at an electron density of 9.3×10^{-3} electrons/a_0^3 was published by Christensen et al [17]. This electron density corresponds to 0.0628 electrons/Angstrom^3, and is reasonably close to the octahedral site electron density in PdH from above (0.081 electrons/Angstrom^3). The equilibrium distance between the two hydrogen atoms in this case is about 1.9 a_0, which is 1.005 Angstroms. This perhaps provides the closest connection to the discussion above. The electron density once again is higher than in the case of σ-bonded PdH_2, and the H_2 molecule responds by increasing its separation because of the occupation of antibonding states.

4. Electron density near a monovacancy in PdH

We next consider the electron density due Pd atoms near a monovacancy in PdH. In Figure 3 we show the Pd electron density from a simple superposition of Pd atomic orbitals, where the vacancy is indicated at -3.54 Angstroms, and where the along the [111] direction the electron density is equal to the preferred electron density of molecular H_2.
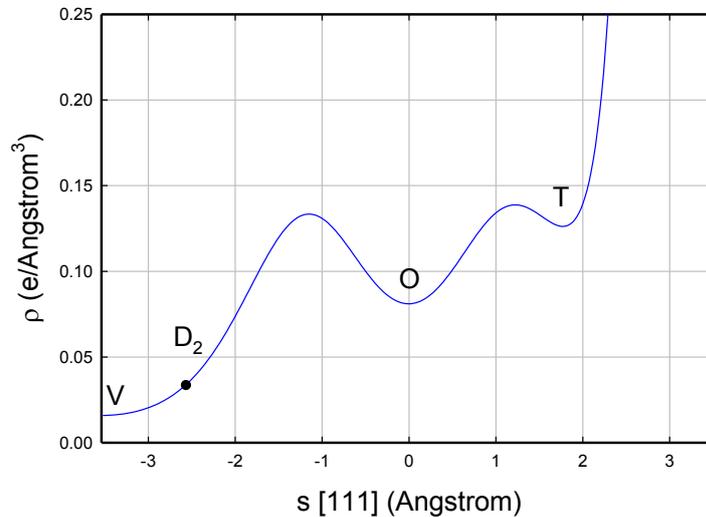
Fig. 3. – Model electron density due to Pd near a monovacancy in PdH.

We note that this model gives an electron density at the octahedral site location near the vacancy to be very close to the optimum for single H as judged by the PdH molecule. The calculation of Velikova et al [18] is consistent with a displacement of 0.26 Angstroms for single H occupation from the octahedral site location.

5. Statistical mechanics

To estimate the probability that a D_2 molecule is present in a monovacancy, we require a statistical model. Binding energies for single hydrogen atoms in octahedral sites have been estimated by several authors, including Nordlander et al [14] and Velikova et al [18]. The binding energies of Velikova et al are relative to hydrogen in solution at low concentration, which suggests that we need consistent models for deuterium in the bulk and trapped in vacancies. We begin with the bulk model, where the chemical potential can be related to the loading above the beta phase boundary through

$$\mu(x) - E_D(0) \;=\; k_B T \ln \frac{x}{1-x} + \Delta E + (x - 0.60)\frac{d\mu}{dx} \tag{1}$$

Here $E_D(0)$ is the deuterium binding energy in dilute PdD_x; the variable x is the D/Pd ratio; and ΔE is the binding energy at D/Pd = 0.60 minus the binding energy at D/Pd=0. We have used ΔE = -135 meV [19], and

$$\frac{d\mu}{dx} \;=\; 514 \; \frac{meV}{D} \tag{2}$$

This is consistent with the measurements of Chun and Ra [20].
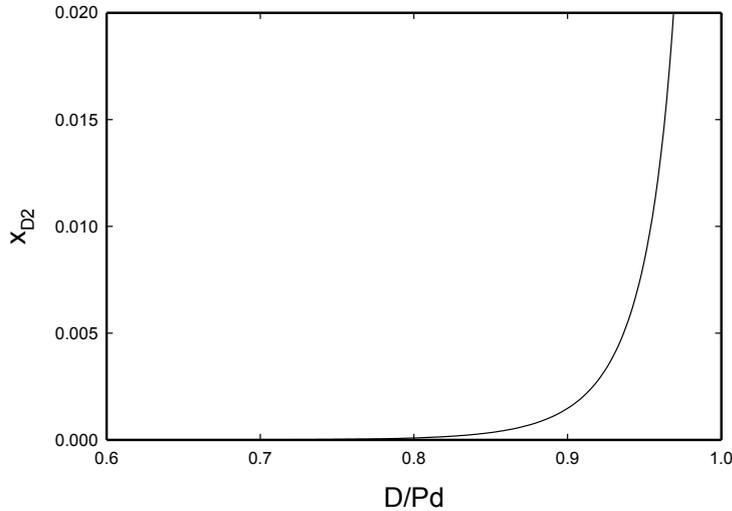
Fig. 4. – Model calclation of occupation of D_2 near monovacancies.

For the occupation of the octahedral sites in the vicinity of a vacancy, we can use a model based on

$$p_m \;=\; \frac{g_m e^{-(E_m - \mu m)/k_B T}}{\sum\limits_n g_n e^{-(E_n - \mu n)/k_B T}} \tag{3}$$

For the degeneracy g_m, we have included the spin and statistical factors; for the energies E_m, we have used the results of Velikova et al [18]. From the computations in [18], we know that a dideuterium molecule is unstable in the presence of unoccupied octahedral sites in the vicinity of a monovacancy. So we have added the possibility of D_2 occupation only when there are 7 deuterons in the vicinity of the monovacancy. This is consistent with the computations of Liu et al for hydrogen in W [21]. In the

calculation of Velikova et al, the energy of the D_2 molecule is about 1 eV above deuterium atom occupation of the octahedral sites. Unfortunately, we do not as yet have a good number for the D_2 energy relative to bulk deuterium for $5D+D_2$ occupation around a monovacancy. In the computation shown in Figure 4, we have assumed that the additional D has to go up by 200 meV from $E_D(0)$ to make a D_2 molecule.

The amount of D_2 in this model increases with loading above a threshold near 0.85. We recall that the excess heat increases with loading above a threshold in much the same way. This is consistent with models that we have put forth which start with D_2 in the lattice as a prerequisite for the reactions which result in excess power and ^{4}He.

6. Conclusions

Excess heat in the Fleischmann-Pons experiment has been seen in a large number of experiments. At present there is no consensus among those in the field as to what physical mechanism is responsible. Our attention over the past decade has been focused on new reaction mechanisms which are driven by D_2 to ^{4}He transitions, with the energy converted into phonon excitation. For this reaction mechanism to work, we require D_2 to be present in the lattice, which is not an easy thing to happen if the lattice is PdD. Molecular D_2 cannot form in bulk PdD because the electron density is too high. According to the arguments here, D_2 can form near vacancies, and we have focused on the occurrence of D_2 near a monovacancy. Since the electron density due to Pd is reduced near the site of a missing Pd atom, the electron density in our simple models drops to levels at which D_2 normally binds to Pd.

We have been of the opinion for many years now that important aspects of the Fleischmann-Pons experiment can be understood simply if we are trying to maximize D_2 occupation. Since D_2 doesn't form in bulk PdD, and since there are very few vacancies initially in Pd, the cathodes start out with essentially no ability to host molecular D_2. So, according to the discussion above, we need to create vacancies. Vacancies are stabilized when Pd is highly loaded with deuterium [22-23]. Previously we estimated that a D/Pd loading of about 0.95 was required in order for the vacancies to become favored thermodynamically. However, since the diffusion coefficient for vacancies is so small near room temperature, vacancies have great difficulty diffusing in from nearby surfaces. Instead, it seems more probable that inadvertent codeposition of Pd on highly loaded Pd is responsible. This is consistent with observations of impurities below the outer surface of cathodes, and it is consistent with the very long time that cathodes need to remain loaded prior to observations of excess power. Codeposition has been verified as being able to produce superabundant vacancies [24]. The short onset time of excess power in the Szpak experiment is consistent with this point of view. Vacancies in this scenario would be created near the outer surface, so that only the near-surface region would be active. This is consistent with the observation of produce ^{4}He in the gas phase, which could not diffuse if created in the interior.

Once vacancies have been produced, then they need to be filled with molecular D_2. According to the model described above, this requires high loading above D/Pd of about 0.85. The correlation between loading and excess power has been observed in experiments [3], and the results are consistent if one assumes that the level of excess power production is correlated with D_2 occupancy. It remains to compute the D_2 binding energy in a monovacancy with 7 deuterium atoms present.

7. References

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