Molecular D_2 Near Vacancies in PdD and Related Problems

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Abstract

Excess heat is observed correlated with ^{4}He in PdD excess heat experiments, consistent with proposed $D_2/^4$He reaction mechanisms. The electron density is too high in PdD for molecular D_2 to form, so we consider the problem of D_2 formation in a monovacancy, and related problems involving other metal deuterides and hydrides.
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1. Introduction

At present there is no general agreement among those working on cold fusion as to what physical mechanism is responsible for excess heat [1], or for other anomalies. In our work, we have tended to separate the associated theory issues into those requiring new physical mechanisms, and those which involve conventional aspects of physics, materials science, or chemistry [2]. For example, it is possible in our view to understand many important aspects of cold fusion experiments by focusing on the conventional issues.

From experiment we know that ^{4}He is produced in amounts commensurate with the excess energy produced [3]. In these experiments the ^{4}He is measured in the gas phase, which implies that the active sites must be close to a surface since helium diffusion is slow in PdD near room temperature. Once helium is trapped in defects, it is hard to remove it near room temperature since the binding energy can be an electron volt or more. Consequently the determination of the ratio of energy produced to ^{4}He observed is not a simple experiment since it becomes problematic to get all of the ^{4}He out [4]. It is now 2012, and it remains the case that only two measurements exist in which a significant effort was made to scrub all of the helium out of the cathode in such a measurement. The results from both of these experiments are consistent with a ratio of 24 MeV. This ratio is significant since it is the mass difference between two deuterons and a ^{4}He nucleus. In this case this experimental evidence is consistent with proposed physical mechanisms involving two deuterons as reactants, and ^{4}He as a product.

As we have remarked upon previously, the absence of energetic particles in amounts commensurate with the energy produced [5] means that no reasonable conventional Rutherford picture nuclear reaction can be consistent. There is no

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Rutherford-type mechanism possible in which a 24 MeV reaction energy can be shared among a modest number of final state particles in a manner consistent with experiment. As a product particle, the ^{4}He nucleus must be born with an energy less than 10–20 keV to produces few enough secondary neutrons to be consistent with measurements. If we were to propose that a 24 MeV quanta were somehow shared among nearby deuterons, we would have to find a way that the reaction energy be divided up and given to at least 25,000 of them so that the resulting neutron emission from subsequent dd-fusion reactions could be low enough to be consistent with experiment.

Given this situation, we might reasonably assert that some kind of new mechanism is responsible; one that involves two deuterons locally, produces ^{4}He, and communicates the reaction energy to low energy condensed matter degrees off freedom. Theoretical models that we have pursued work in this way; however details associated with the reaction mechanisms are discussed elsewhere [6], and are generally not needed in connection with the discussion to follow. We already have enough in such an ansatz to provide a foundation for addressing conventional physics, materials science, and chemistry issues associated with the experiments.

2. Background Electron Density

There is a school of thought that says that the local background electron density is an important parameter in understanding hydrogen as an interstitial in metals [7]. In essence, hydrogen is looking for a specific background electron density; at the optimum electron density the energy is minimized, so that at either lower or higher electron densities the energy increases. Of course, the mathematical formulation of the associated model includes two-body potentials along with the embedding energy. Nevertheless, we can make substantial progress in understanding many basic issues in metal hydrides simply by focusing single-mindedly on the background electron density.

We have described a version of this argument previously in the case of hydrogen and deuterium in Pd [8] (for the arguments that follow, hydrogen will be largely interchangeable with deuterium). We focused first on the diatomic molecule PdH where the interatomic separation at minimum energy is 1.53 Å; the corresponding background electron density in a single configuration relativistic Dirac Fock calculation is 0.069 electrons/Å^3. According to the line of argument that we are following, we now know the background electron density preferred by hydrogen. It may be useful to see how this value compares with the density-dependent embedding energy from embedded atom theory, which is shown in Fig. 1. We see that the minimum embedding energy occurs at an electron density of 0.069 electrons/Å^3, which is consistent with our estimated of the background electron density in the PdH molecule. This is encouraging.

The background electron density along the [111] direction in PdD as calculated using a simple superposition of atomic Pd electron density profiles is shown in Fig. 2. One sees that the lowest electron density occurs at the O-site, and that local minima occur at the T-sites. The electron density at the O-site in this model is 0.079 electrons/Å^3, which is a bit higher than the optimum electron density (a bit higher than 0.070 given in [9], and a bit lower than the DFT result of Orondo, which is near 0.095 electrons/Å^3 [10]). Based on the arguments above, we would expect hydrogen occupation of the O-sites in preference to T-sites (this argument is well known), since the electron density is too high at the T-sites. The corresponding difference in the embedding energy is 164 meV (and about 322 meV for the DFT densities, which suggests that the O–T excitation energy if measured from experiment will tell us something about the electron density at the O-site).

Nickel is known to have a lower solubility for hydrogen and deuterium. Based on the discussion above, we might conjecture that the electron density is higher, which is checked through an analogous superposition calculation for the background electron density in Ni shown in Fig. 3. We see that the background electron density is higher in this model, with the minimum (0.132 electrons/Å^3) found at the O-site. Once again we would expect that O-site occupation would be preferred over T-site occupation because the electron density is even higher at the T-site. It is probable that one could use the difference in solubility between Ni and Pd to estimate the increase in the O-site electron density in Ni.
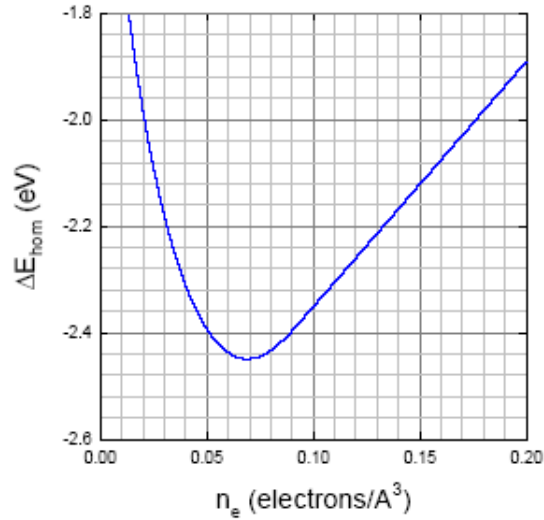
Figure 1. Embedding energy for hydrogen as a function of the background electron density from [7].

Alternatively, one could likely develop a systematic determination of O-site electron densities from experimental He solubility data.

A similar calculation for H in Au is shown in Fig. 4. In this case we might imagine that the solubility might be higher since the electron density seems to be lower. However, a check with the literature shows that the solubility is much lower, suggesting that this superposition model probably underestimates the electron density at the O-site.
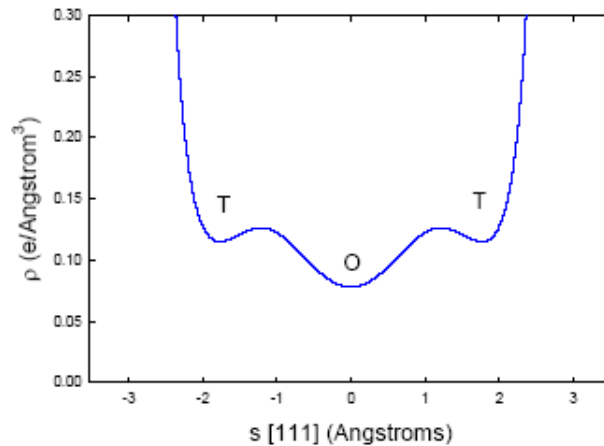

Figure 2. Background electron density along the [111] for PdD (with $a = 4.081$ Å).

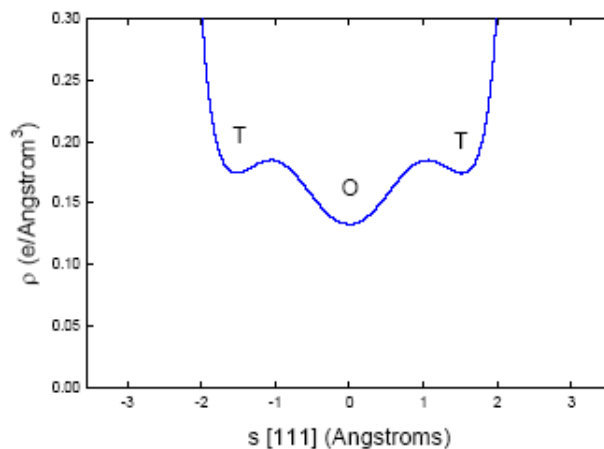**Figure 3.** Background electron density along the [111] for Ni (with $a = 3.52$ Å).

It seems reasonably clear that we are seeing a commonality in the background electron density along the [111] direction in these simple fcc metals. The shape is nearly the same in all cases, and the only major difference is in what the minimum electron density at the O-site is. Based on the embedding energy of Fig. 1, we note that a modest increase in the minimum electron density above the optimum can produce a large reduction in the hydrogen solubility.

3. Molecular H$_2$ with Background Electrons

It would be useful to consider the extension of these ideas to the case of molecular H$_2$ embedded in an environment with some background electron density. Unfortunately the situation in this case is a little more complicated. For example, a
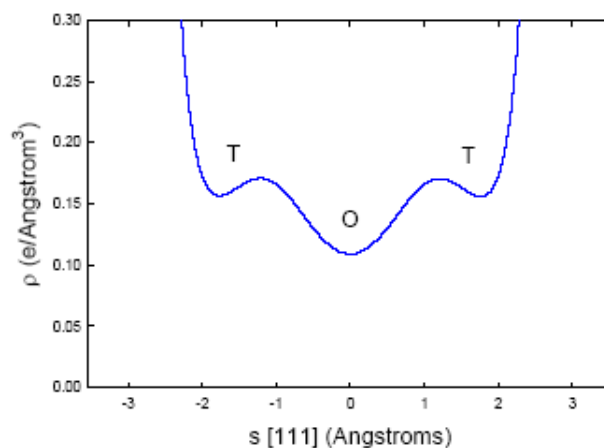

Figure 4. Background electron density along the [111] for Au (with $a = 4.0788$ Å)).
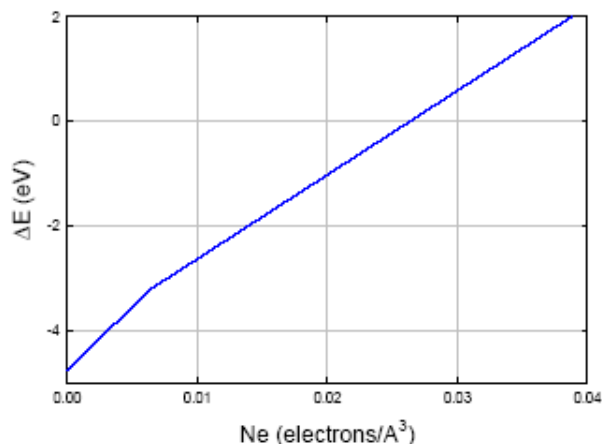
Figure 5. Embedding energy for H_2 with vacuum separation [12].

hydrogen atom experiences a significant attractive energy due to the background electron density alone, while there is no such effect for the H_2 molecule. Instead, the H_2 molecule is much more polarizable [11], so that there is a long-range attractive dipole–dipole interaction which dominates the potential when the molecule is separated from the atom.

The dipole–dipole interaction changes how we think about the H_2 molecule problem qualitatively then. It is no longer the case that the molecule is looking for the optimum electron density. Instead, we should begin with the long-range dipole–dipole interaction. Consider in the discussion that follows the case of a triatomic molecule formed by an atom with molecular H_2. When this interaction is weak, as in the case of rare gas-diatomic hydrogen molecules, then the molecule approaches the atom seeing an increasingly attractive potential up to the point where the electron density becomes sufficiently high that a substantial increase in the embedding energy occurs.
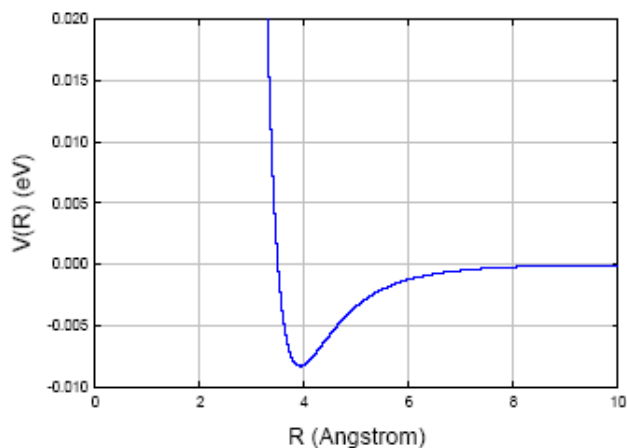

Figure 6. Lennard–Jones model potential for Xe–H_2 as a function of the Xe–H_2 separation.
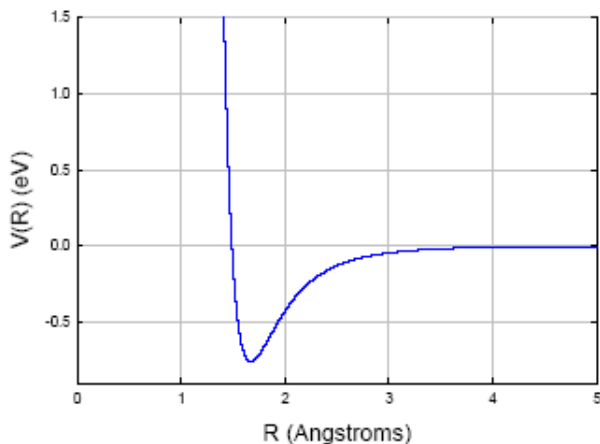
Figure 7.   Lennard–Jones model potential for Pd–H_2 as a function of the Pd–H_2 separation.

For example, in the case of Xe–H_2, the potential minimum occurs at a separation of 3.9214 Å. We compute the background electron density of Xe at this radius to be 2.1×10^{-5} electrons/Å^3, corresponding to an embedding energy of about 8.1 meV. The binding energy is 8.3 meV. Note that models that take into account dipole–dipole coupling have long been used to model the spectra of molecular hydrogen rare gas molecules [13].

In the case of Pd–H_2 the potential minimum occurs at 1.67 Å, at which point we estimate the background electron density is 0.033 electrons/Å^3. The associated embedding energy is about 1.4 eV for a 0.74 Å H–H separation (and perhaps 1.1 eV for a 1.48 Å separation); and the binding energy is about 0.76 eV [14]. In this case, the Pd–H_2 configuration is a more strongly bound than the bent H–Pd–H configuration by about 0.19 eV [15]. The minimum energy found in a Quantum Espresso calculation of PdH_2 corresponds to a binding energy of about 1.6 eV [16]. We have wondered for some time why the binding should be so strong in this DFT model; in light of the discussion above we suspect that the Pd polarizability is overestimated in the DFT calculation.

Finally, in the case of NiH_2 the binding of molecular H_2 is more than 2 eV at the local minimum corresponding to Ni–H_2 according to Niu et al. [17]. In this case, the stronger dipole–dipole attraction pulls the molecule to higher electron density where the bent H–Ni–H configuration is favored; in this case the binding energy is near 2.7 eV. Consequently NiH_2 is unstable against decay to the lower bent H–Ni–H configuration.

We know that the H–H separation increases as the electron density increases. A calculation of the potential for H_2 in jellium at an electron density of 0.0628 electrons/Å^3 is given in Christensen et al. [18], where the potential minimum is about 1 Å; this density is just below the threshold (near 0.10 electrons/Å^3 in Dechiaro's calculation) where no potential minimum occurs in this density regime [19]. We note that the H–H separation in atom–H_2 molecules tends to be larger than what might be expected in a jellium calculation due to the dipole–dipole interaction which can produce additional stretching of the H–H bond.

4. D_2 in Vacancies

The electron density is too high in bulk Pd for molecular D_2 to form; hence it seems reasonable to consider the lower electron density available in vacancies [8]. Our focus has been on the monovacancy, since it is in a sense the simplest theoretical problem, and since there seems to be indirect evidence from high–current co-deposition experiments that
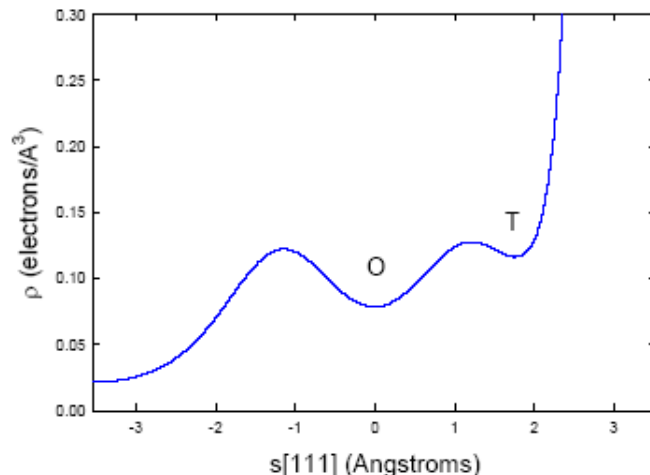
Figure 8. Background electron density along the [111] for PdD (with $a = 4.081$ Å) in the vicinity of a monovacancy.

conditions under which they are expected correspond to conditions under which excess heat is observed [20,21]. A lower electron density occurs in more complicated vacancy structures, such as divacancies and microvoids; such structures are less interesting to us, since larger amounts of volume are present where the electron density is "too low," such that we would expect internal D_2 gas formation which seems to us uninteresting.

Let us begin by considering the electron density in the vicinity of a Pd vacancy in PdD. The simple superposition estimate based on Dirac–Fock Pd electron densities is shown in Fig. 8. The minimum electron density at the vacancy site has now dropped to 0.022 electrons/Å^3, which is below the background electron density for H_2 formation in PdH$_2$ (this density would be relevant in the case of a molecule in the vacancy closest to one Pd atom, as long as the polarizability of the atom in the solid is similar to the polarizability of the isolated atom). This compares with 0.020 in [9], 0.015 electrons/Å^3 in Dechiaro's DFT calculation [16].

Based on the discussion above, whether molecular H_2 or D_2 will behave similarly in a monovacancy then depends critically on whether the Pd atomic polarizability is impacted because of bonding to other atoms. To investigate, we consider first the calculation of Nakatsuji and Hada [22], where the binding of an H_2 molecule on molecular Pd$_2$ was analyzed. The binding in the case of an H_2 molecule aligned and centered with a Pd$_2$ molecule leads to a binding energy of 0.63 eV, which is a bit less than the 0.76 eV energy of Ref. [14] for PdH$_2$; this might indicate a minor reduction in the Pd polarizability due to bonding.

To pursue this, we consider the calculations of Wilke and Scheffler [23] for H_2 above a Pd [100] surface. The potential isocontours are seen to correspond to a binding energy no more than about 0.35 eV under conditions where the H–H separation is less than 1 Å. Such a result seems consistent with a further reduction in the Pd atomic polarizabililty due to additional bonding. There are many related computations in the literature of H_2 over a clean Pd surface in different orientations, and in general the binding energy is only a few tenths of an eV under conditions where the separation is less than 1 Å.

Based on this there seems to be no reason not to expect D_2 formation in principle in the vicinity of a monovacancy. The question of the associated binding energy is more interesting; for example, we might expect the binding energy to be similar to that of H_2 on a clean Pd surface. In the literature there is theoretical and experimental support for a molecular H_2 adsorbed state on Pd [210] with a binding energy of 0.27 eV [24,25].

To pursue this we have carried out some exploratory calculations based on an embedded molecule model based on

$$E_{\text{tot}} = \sum_{j<k} \phi_{jk}\left(r\right) + \Delta E_{\text{hom}}\left(\rho\right).$$

The interaction between the Pd atom and the molecule is dominated by dipole–dipole interactions at large distance, with a reduction in strength at smaller distances; this motivated us to adopt

$$\varphi_{jk} = -\frac{C}{\left(r^2 + r_0^2\right)^3}.$$

One can develop a reasonable fit to molecule, cluster, and surface Pd–H_2 calculations with such an empirical interaction potential. Inside the metal we expect a screening of the long range interaction for distant atoms due to the conduction electrons (the associated Thomas–Fermi screening length is less than 1 Å).

If we neglect screening, the resulting models show a strong binding of the H_2 or D_2 molecule due to attractive Van der Waals contributions from many nearby Pd atoms. With screening the minimum energy occurs for the molecule at the center of the vacancy, and the molecule energy is above the vacuum level. Since part of the attractive interaction is bonding rather than dipole–dipole interaction, we tried working with models where exponential screening was deferred. Perhaps it is useful to consider one such calculation (see Fig. 9). In this case we have selected the parameters C and r_0 close to the PdH atom values, with screening deferred to about $4r_0$, and no correction for the reduction in embedding energy at increased H–H separation. This model was selected since it gives a minimum energy in the vicinity of what would be required to connect with the excess power as a function of loading curves from experiment. In this kind of a model, the total energy can be lowered when the molecule goes away from the center of the monovacancy since there are more Pd atoms that are closer in this direction. The O-site is located at 2.04 Å in the [100] direction, and we see that the minimum effective potential occurs for a displacement on the other side, closer to the Pd atom at the center of the next cell. The electron density in this model is very high at the O-site, around 0.066 electrons/Å, so that the H–H separation will be more than 1 Å in the absence of a cage effect. Note that something of a cage effect is expected in this configuration due to the five Pd atoms that surround the molecule. The potential in this calculation is defined relative to the vacuum molecule. According to the calculations of Orondo, the bulk O-site potential per hydrogen atom is about –250 meV at a loading near 0.85 [10]. If the excess power versus loading curves are a result of D_2 occupation of a monovacancy in this sense, then the molecule potential needs to be somewhere near 300 meV [8]; in Fig. 9 it goes down to –370 meV which is a little too deep. Note that under discussion here is D_2 binding that is a little stronger than for adsorbed H_2 on Pd[210] discussed above.

Dechiaro has carried out Quantum Espresso calculations for this configuration [16], and obtains a minimum potential near 1.45 Å away from the vacancy center, of close to –1 eV relative to the energy at the vacancy center. Since these DFT calculations overestimate the well depth in the PdH molecule, we might expect a similar overestimate for the attraction in the monovacancy calculation; hence, a corrected version of the calculation might give a reduction in energy near 400 meV. If so, then there would begin to be a connection between the models and the excess power versus loading curves from experiment.

We have noted previously that the molecule is unstable if nearby O-sites are unoccupied in the monovacancy [8]. We recently noticed a discussion of this effect in the early paper of Rosato and Cleri [9].

In a recent paper by He et al. [26], there is a discussion of H_2 in a monovacancy in Pd at different loadings. The 5+2 occupation of the monovacancy was not considered in this work, but one can find a discussion of 6+2 occupation. While the H–H separation is small for this configuration, the molecule is well separated from the Pd atoms. We consider this to be significant in connection with screening effects. The overlap probability between two deuterons is impacted strongly by screening, as has been often noted in the literature. One would expect screening due to conduction electrons, but the Thomas-Fermi screening length for an electron in the center of a monovacancy is near 0.7 Å, which is too small to
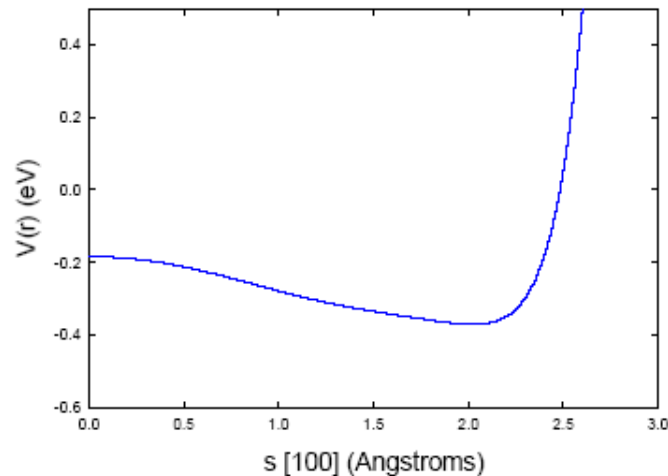
Figure 9. Model H_2 or D_2 potential in as a function of distance in the [100] direction of a monovacancy with seven interstitials.

make much of a difference. A molecule at higher electron density would be expected to see increased screening, but the Thomas–Fermi length scales very slowly with density.

In our view the key issue is the proximity with a higher-Z metal atom. In our models for the reaction mechanism, the maximum reaction rate is proportional to the phonon exchange matrix element for the $D_2/^4$He transition, which is proportional to $\exp(-G)$, where G is the associated Gamow factor. Hence, any increase in screening impacts the reaction rate exponentially. Consequently, the minor increase in screening near the O-site due to the higher electron density will already lead to a significant enhancement in the coherent reaction rate over the screening at the vacancy center. If the deuterons tunnel together at even higher electron density closer to the Pd atoms then one would expect even more screening. There may be the possibility of even more enhancement due to orbital hybridization with an inner shell if the one sigma orbital is close to a metal atom when the deuterons get close to each other. In the exploratory calculations we have done so far looking for such hybridization we have found only minor effects.

If so, then the goal would be to arrange for a D_2 molecule to be close to nearby metal atoms, and not keep them distant near the center of a monovacancy. A similar comment could be made in response to the recent proposals by Storms for hydrogen and deuterium in voids; from our perspective where the electron density is low the problem looks very much like vacuum physics.

Note that we would expect similar effects associated with monovancies in other metal deuterides and hydrides. Dechiaro has carried out calculations of molecule formation in monovacancies in many metal hydrides. In the case of Ni and Au, the DFT calculations show effects similar to those in Pd, and H_2 or D_2 molecule formation is predicted very much like in the case of Pd.

5. Thoughts on the Piantelli Protocol for NiH

There has been much recent interest in excess heat in NiH experiments with gas phase hydrogen loading [27]. At present there is no agreement as to what mechanism is responsible for the excess heat observed. We have proposed that excess heat in this system is based on HD/^{3}He transitions, as an analog of the $D_2/^4$He transitions for PdD systems [2,6]. While the latter has some support in ^{4}He observations connected with the energy produced, there is as yet no experimental

clarification as to whether such a correlation exists (or does not exist) between ^{3}He and energy in the NiH system.

In the event that HD/^{3}He transitions are involved, then we face the problem of HD formation (similar to the problem of D_2 formation in PdD). The electron density in Ni is higher at the O-sites than in Pd, so it is much more difficult to load. On the other hand, the interstitial density doesn't need to be as high for the stabilization of the vacancies. The question is how might we arrange for HD in Ni, given that a protocol has been put forth by the Piantelli group [27].

In this protocol, the Ni is loaded with hydrogen and then deloaded repeatedly, with an increase in hydrogen uptake each cycle. Given that the solubility of hydrogen in bulk Ni is so low (parts in 10^{-4}) [28], what is responsible for increasing hydrogen uptake at the percent level? We have conjectured that vacancies are being produced during this cycling, and that the observed uptake is due to a loading in the vacancies. Note that since there is low electron density available within the monovacancy, hydrogen can find its optimum electron density with a corresponding solubility per vacancy O-site higher than that of Pd. One might ask how the local hydrogen density gets sufficiently high to stabilize vacancies in Ni since the solubility is so low. Apparently segregation occurs in the miscibility gap in NiH$_x$, where either there is no H, or regions with NiH$_{0.7}$ occur [29]. Consequently the hydrogen density gets to be sufficiently high locally so that vacancies can be stabilized [20]. In contrast to the PdD experiments done near room temperature, at the elevated temperature of the Piantelli experiments, some limited vacancy diffusion can occur.

6. Discussion

The deuterium molecule requires low electron density to form, which motivates our interest in vacancies in PdD and other metal hydrides and deuterides. We have argued previously that inadvertent codeposition can create monovacancies if the loading is sufficiently high (above 0.95 near room temperature in PdD). The D_2 molecule in the vacancy is unstable if there are unoccupied O-sites present, so we require a substantial loading (above 0.85 if the binding energy is close to the observed H_2 surface state in PdH) to stabilize the molecule. The situation in Au seems similar qualitatively; but Ni seems to show a higher polarizability, so that the HD may be a bit less stable in a Ni vacancy. It remains the case that we need experimental evidence to clarify whether sigma-bonded dideuterium molecules actually form along the lines discussed. Magic angle NMR at least has the potential to resolve the issue. Within the picture outlined here there should be many more candidates than just Pd or Ni for showing excess heat. Ni alloys with good hydrogen solubility (such as demonstrated by Celani at this conference) have the potential to be important in the future. We have made use of a simple empirical model to try to understand the calculations of Dechiaro, which we think gives too strong of a binding energy for dideuterium near the O-site of a monovacancy with the other O-sites occupied. Progress on the development of a potential model derived from DFT calculations will allow for realistic tunneling calculations in the future.

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