J. Condensed Matter Nucl. Sci. 13 (2014) 165–176

Research Article

Temperature Dependence of Excess Power in Two-laser Experiments

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Abstract

Data published previously on the two-laser experiment shows that the excess heat depends on temperature, and is mostly zero in the absence of a magnetic field. A new experiment shows higher excess power at higher temperature. We augment our previous empirical model with temperature dependence. A picture for the temperature dependence is described in terms of the elimination of ^{4}He which blocks active sites when the excess power is high.

Keywords: Active site blocking by helium, Letts 2-laser experiment, Temperature dependence of excess heat

1. Introduction

Excess power in the Fleischmann–Pons experiment [1,2] has been studied around the world following the initial announcement of the effect in 1989. Excess heat was observed to depend on the cathode loading [3], and also on the maximum loading during the cathode history [4]. Fleischmann and Pons described a positive feedback effect in which the excess power was increased at the end of a heater calibration pulse [5], suggesting that the effect was dependent on the cell temperature. Subsequently measurements from different groups showed that in some experiments the excess power increased with temperature [6–8].

As a separate discussion that has taken place over many years, people have been interested in how excess heat is triggered in these experiments. In early experiments, excess heat bursts seemed to occur randomly for the most part. Excess heat events at SRI seemed to be triggered by current ramps; subsequently more systematic studies yielded a linear dependence of excess power on current density above a threshold. Excess power was seen to be correlated with

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the surface deuterium current flux [9], and later on many experiments have sought to use this mechanism to stimulate excess power. Electrical current has by now been seen to stimulate excess power [10,11].

Letts and Cravens noticed that excess power could be stimulated using a weak laser incident on the cathode surface under conditions where the cathode was below threshold for excess power production [12]. Subsequent experimental work confirmed the existence of the effect. Some years later Letts and Cravens showed that excess power could be stimulated by two lasers [13]. A multi-year campaign to study the effect was carried out by Letts, which found a set of three "sweet spots" in frequency difference where excess power was maximized [14]. Two of these resonances were found to correspond to the Γ-point and L-point of the PdD optical phonon modes, which had been predicted to be favored since the compressional mode group velocity is zero. As yet it has not been clarified what the origin of the third peaks is. Conjectures have been made that it is due to H contamination (which would produce an impurity-related L-point close to the observed peak), or perhaps D in the codeposited Au layer. A detailed analysis of the data set was published [14,15].

2. Possible Temperature Dependence

Some of the two-laser experiments carried out as part of this study were done at different temperatures. If excess power in the two-laser experiment is sensitive to temperature, then perhaps we might improve the analysis of the data by taking this into account. For example, we remarked on a data point at 521 mW that was sufficiently high that it did not fit on the plot [14]; the corresponding experiment was done at a higher temperature than most of the others.

We begin by working with the data set discussed previously in [14], and we now fit to an excess power model of the form

$$P_{xs} = \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right)\sum_j A_j \frac{\gamma_j^2}{(f-f_j)^2+\gamma_j^2}.$$

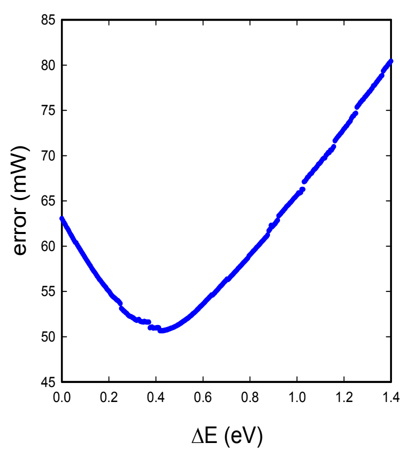

Figure 1. Error in the fit for excess power in mW as a function of ΔE in eV.

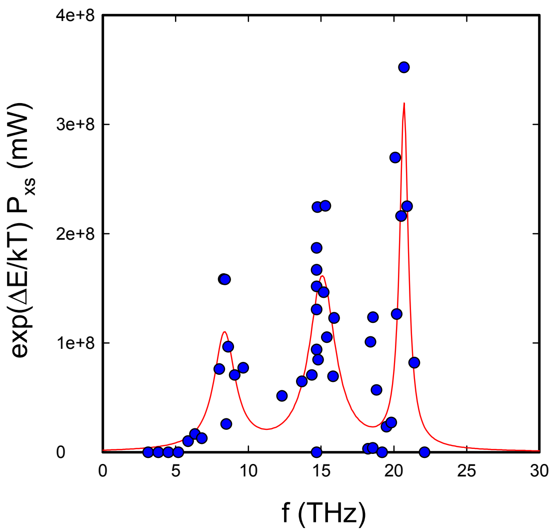

Figure 2. Scaled spectrum compared with empirical model for ΔE = 0.42 eV.

By least-squares fitting to the data we find that the error is reduced when ΔE is in the vicinity of 0.42 eV as shown in Fig. 1.

The scaled spectrum that results is shown in Fig. 2. Note that now all of the data points fit on the graph. A few of the data points have been corrected following a re-examination of the data set. The center frequencies in this model are 8.4, 15.1, and 20.7 THz, which are close to what we found earlier.

In his study of Fleischmann–Pons excess power as a function of temperature, Storms parameterized the results according to [7]

$$P_{xs} = P_0 \mathrm{e}^{-\Delta E/K_\mathrm{B}T}$$

consistent with $\Delta E = 670$ meV. Swartz reported a similar value consistent with 630 meV [8]. In earlier work ΔE was interpreted as the barrier energy for helium diffusion, in a picture where helium build up plugs active sites and must be removed. This is discussed further in Section 8. Given the relatively shallow dependence of ΔE around the minimum for this data set, such values used in the above fitting model would not lead to a substantial degradation of the fit.

3. Possible Magnetic Field Dependence

Letts has found that excess power tends to work better when a magnetic field is present generally in his experiments. In looking through the data set associated with the spectrum, the majority of the associated experiments included a magnetic field; however, some were done without a magnetic field. In general we might include the magnetic field dependence in our model through

$$P_{xs} = F(B) \exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right) \sum_j A_j \frac{\gamma_j^2}{(f - f_j)^2 + \gamma_j^2}.$$

Now, in the experiments under discussion the magnetic field strength was always the same when present. Consequently, we might make use of a reduced function of the form

$$F(B) = \begin{cases} 0 & \text{no magnetic field,} \\ 1 & \text{magnetic field.} \end{cases}$$

Letts has conjectured that the excess power should be linear in the magnetic field. However, given that excess power is known to occur with no applied magnetic field, probably a better general fit might be

$$F(B) = 1 + \frac{B}{B_0}$$

if Letts is correct. It will take a dedicated set of experiments to sort this out.

If we eliminate data points with no magnetic field present, the optimum ΔE is again 0.42 eV, and the resulting spectrum is nearly identical (since these points mostly gave zero excess power at the same difference frequency points as existing points). The frequencies of the resonances in this case are 8.3, 15.3 and 20.7 THz.

4. A New Test for Temperature Dependence

In more recent work, Letts (in this case stimulated by Cravens) carried out a two-laser experiment (669u,v) in which temperature dependence was explored. The cathode was first stimulated with two lasers at a difference frequency of 21.0 THz, which occurred at minute 58 while the electrolyte was at 62.0°C. The cathode responded with about 220 mW of excess power that can be seen drifting upward slowly. The lasers were turned off at minute 948, following which the excess power drifted down over the course of about 8 h. The heater power was increased which raised the cell

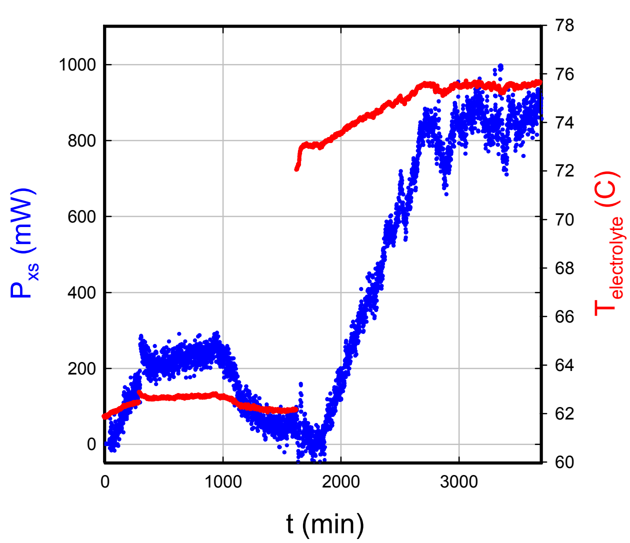

Figure 3. Excess power for experiment 669u,v in mW (*blue*); electrolyte temperature in °C (*red*).

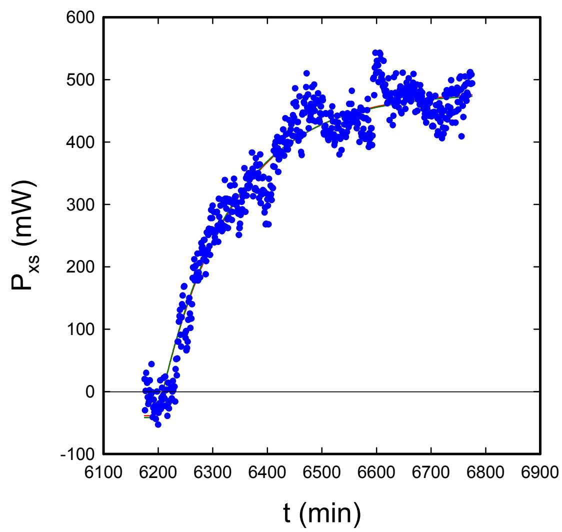

Figure 4. Excess power for experiment 662a (*blue*); analytic models (*red line, green line*).

temperature to 72.05°C at minute 1633. The lasers were turned on again at minute 1849, with a difference frequency of 21.6 THz, which stimulated a second excess power event. The excess power produced in this case was higher, around 840 mW, as can be seen in Fig. 3.

If the difference in excess power is attributed in this experiment only to the different initial temperature as

$$P_{xs} = F(B) \exp \left(-\frac{\Delta E}{k_{\mathrm{B}} T} \right).$$

then the associated value for ΔE is 1.33 eV. If we repeat this calculation based on the electrolyte temperature at the time of the excess heat (which includes the positive feedback effect), then we get 1.27 eV. These values are much higher than we found in the discussion above, and motivates us to go back and reconsider the data set.

5. Examination of a Single Set of Data

When we analyzed the data set previously, the approach that we used was to fit the data to a thermal relaxation model, which was useful to get systematic excess power estimates along with error bars. This procedure is discussed in [14,15].

However, given the temperature dependence of experiment 669u,v discussed above, Letts was motivated to go back through the data once again to see whether this temperature dependence had been overlooked somehow. In order to understand what Letts found, we need to consider an example. Perhaps most illuminating is the case of an experiment labeled 662a, which gave the highest excess power (521 mW) as mentioned in [14]. The analysis of that paper can be summarized as in Fig. 4. We see the excess power increasing following laser stimulation with a beat frequency of 14.75 THz, and the excess power follows the two analytic model results reasonably well. The value 521 mW in this case is the asymptote for the simpler analytic model. Similar data sets following laser stimulation were provided by Letts for analysis at MIT at the time Refs. [14,15] were written.

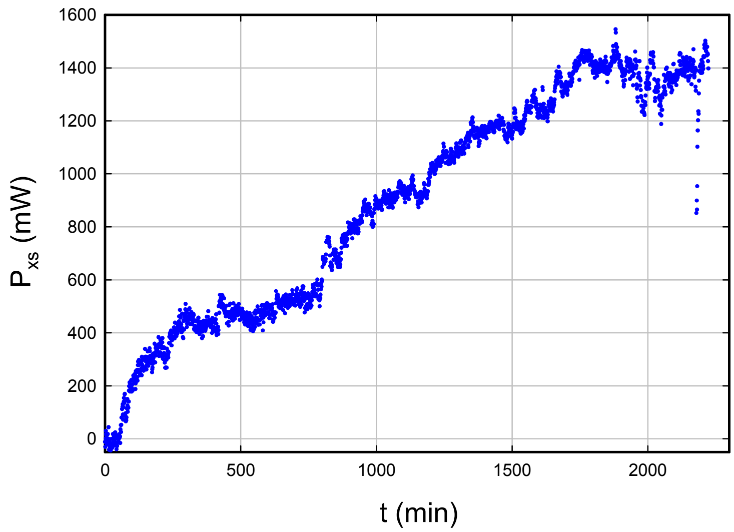

Figure 5. Excess power for experiment 662a (*blue*) for longer time.

However, in this case the experiment was allowed to continue running, so that it is possible to see how close the experiment came to the predicted asymptote. The results are shown in Fig. 5. We see that the excess power subsequently started to rise again.

So, should we use the 521 mW number as was done previously, and which could reasonably be argued to represent the initial level of excess power; or should we use a higher number in the vicinity of 1400 mW? Since Letts was comparing against a predictor based on the ΔE value from 669u,v discussed above, he was expecting the excess power for the elevated temperature conditions of this experiment to be a good bit greater than 521 mW. In fact, the excess power in this experiment ended up going to a level relatively close to what might be expected based on $\Delta E = 1.33$ eV.

The conjecture in this case was that rather than looking at the initial excess power as was done before, perhaps the better thing to do in response to 669u,v would be to make an estimate of the maximum power that the cell seems to equilibrate to.

6. Max Equilibrium Power Spectrum

These arguments led to the construction of a different kind of spectrum from the data. In this case, the maximum equilibrium excess power is reported as discussed above; however, only data sets with magnets present are now included, not all of the data sets used previously were judged suitable, and results from 669u,v are now included. The excess power data points in this case are shown in Fig. 6.

Since the two experiments with very high excess power correspond to runs done at elevated temperature, let us first consider the fitting of the spectrum in the absence of these points. Results are shown in Fig. 7. The minimum error occurs for $\Delta E = 0.54$ eV, and we see that the error in this case is much lower than what we found previously. The spectrum that results is shown in Fig. 8. The peaks in this fit are centered at 8.4, 15.2, and 20.8 THz. This result is consistent given the shallowness of the error curve as a function of ΔE with the earlier ΔE results of Storms, and of

Swartz.

As expected, when the two highest power points are included in the spectrum, the fit becomes dominated by their contribution. This is illustrated in Fig. 9, where the minimum error occurs for $\Delta E = 1.0$ eV. Given this situation there are a number of obvious candidate interpretations. One interpretation might be that the barrier associated with the two-laser experiment is in the range of 0.85–1.05 eV, and we should think of it as being higher than the barrier found in the experiments of Storms and of Swartz.

Another interpretation might be that for the majority of the two-laser experiments the barrier is around 0.6 eV, so that we have reasonable consistency with the experiments of Storms and of Swartz; while the two outliers at higher power do so because some additional and different sites are involved in the excess power production. One could imagine that the excess power in Fig. 5 stays for a while at the lower power value (around 500 mW) perhaps consistent with a lower ΔE number, then increases later on due to extending the reactions to a new batch of sites with a higher associated ΔE.

Finally, there is yet another point of view. Not all experiments show a dependence on the operating temperature. For example, excess heat at SRI in the 1990s seemed not to show any particular sensitivity to temperature. Perhaps it is that the temperature sensitivity shows up when the excess power is "high" relative to the experiment under study (suppose all the active sites available are plugged up with ^{4}He, so that the temperature dependence comes about due to barriers associated with getting the helium out); and there is little temperature sensitivity when the excess power is "low" (suppose that there are many active sites available, so that scrubbing out the helium is not at issue). Certainly this data set would be consistent with such a picture.

7. Mechanism Issues and Vacancies

Over the years much effort has been put into the development of theoretical models for excess heat production. At present there is no consensus within the field as to what reaction or mechanism is responsible. Outside of the field,

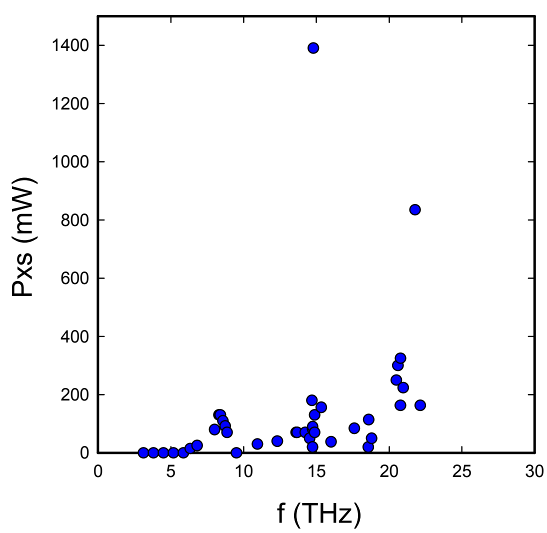

Figure 6. Spectrum of maximum equilibrium excess power as a function of frequency (*blue*).

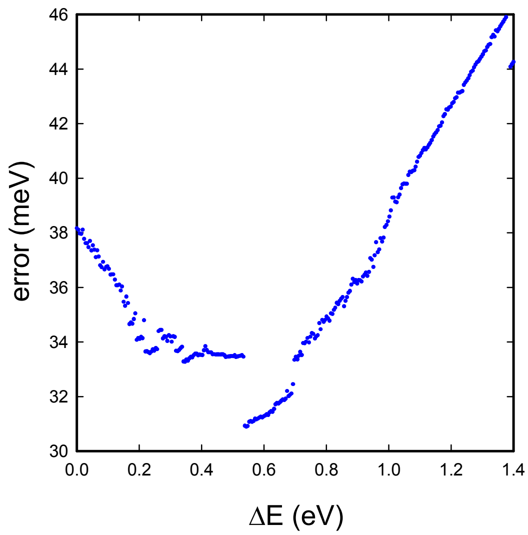

Figure 7. Error in the fit for excess power in mW as a function of ΔE in eV for the spectrum of Fig. 6 without the two highest points.

the scientific community generally still regards excess heat Fleischmann–Pons experiments to be impossible, with all positive results attributable to experimental error. Those in the field at this point are sure it works, and that new physics is emerging in the associated studies.

From our perspective, the issue of how it works can be divided into two sets of issues [16]: conventional issues (electrochemical, materials science, applied physics, and so forth) that relate to loading and how deuterium behaves in the cathode; and unconventional issues that relate to the microscopic reaction mechanism. If we adopt the point of view generally that two deuterons react to make ^{4}He in connection with the new unconventional issues (consistent with theoretical models that we have pursued), then many experimental issues become purely conventional. This is the view we take in what follows.

For example, in order for two deuterons to interact in the first place, they probably need to be physically close to one another. Since the electron density in bulk PdD is too high to support D_2 formation, our focus has been on the lower electron density region available in the vicinity of a host Pd vacancy [17]. The vacancy formation energy in bulk Pd is around 1 eV, which one might think could be related to the ΔE value associated with the excess heat in experiment 669u,v, except that atomic self-diffusion is sufficiently slow near room temperature that it would take a great many years for thermal equilibrium to be established.

When Pd is loaded with hydrogen or deuterium, the vacancies become stabilized more with each additional interstitial until at a loading near 0.95 the vacancies become thermodynamically preferred. This could account for the requirement observed at SRI that the maximum cathode D/Pd loading over the course of the loading history must reach about 0.95 for excess heat to be observed [4]. Even when stabilized, the diffusion rate remains very slow near room temperature; so we contend that the most plausible mechanism for the production of vacancies in these experiments is inadvertent codeposition at high surface loading [16].

8. Active Sites and Helium

From this perspective, the active sites are vacancies, and molecular D_2 formation is expected near room temperature at sufficiently high loading that the other O-sites around the vacancy are occupied (which we suspect occurs above a loading around 0.84). In the two-laser experiment there is codeposition of Au at substantial current density, and it may be that vacancies are formed at high surface deuterium chemical potential similar to Pd and Ni in the case of Au close to PdD. Density functional calculations support the conjecture that molecular D_2 formation occurs in an Au vacancy similar to the situation in a Pd vacancy [18].

If this picture is basically sound, then the active sites of the system are the vacancies, which we expect to be created in the course of the experiment (since Au is codeposited at high current density). According to the unconventional reaction mechanism that we have focused on, the reaction energy is fractionated and transferred to the optical phonon modes prior to thermalization [14,16]. If so, then the ^{4}He produced remains roughly in place where the D_2 molecule had been previously (since the local interaction of the ^{4}He is different than molecular D_2, we would expect some relaxation of the equilibrium position to lower electron density). The ^{4}He produced will eventually "plug up" the active sites [16].

If there were no way to remove the ^{4}He, we might imagine that after some amount of energy is produced that all active sites would end up blocked. We can see from Fig. 11 that the production of 10 kJ corresponds to 2.6×10^{15} ^{4}He atoms, which may be in the vicinity of the number of vacancies present (although we know that sufficient Au is present on the surface to change the color, we do not have an estimate for the associated number of vacancies produced).

To remove ^{4}He atoms from the active sites, we would expect first that we would have to arrange for it to get out of the vacancy, and then for it to diffuse away from the active sites. In the case of He binding in a single vacancy in Pd, there has been a recent density functional calculation by Zeng et al. [19] which gives a binding energy of about 2.4 eV for a single helium atom, about 1.5 eV for two, and about 0.6 eV for three. In a different calculation by Laakmann et al. [20], the binding energy for a single helium atom in a monovacancy in Au is about 2.3 eV. One would expect

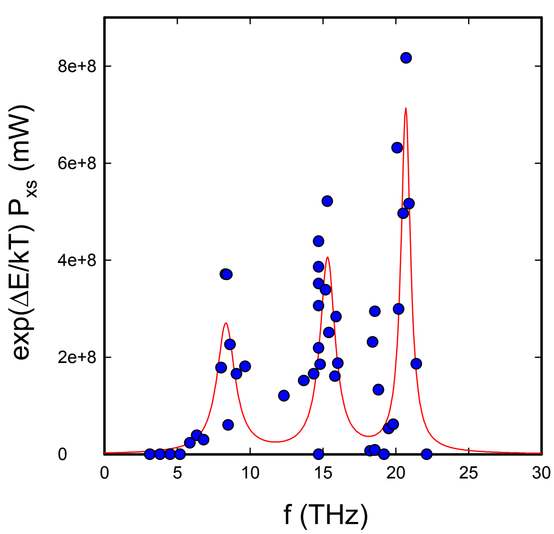

Figure 8. Scaled spectrum without two highest power points compared with empirical model for ΔE = 0.54 eV.

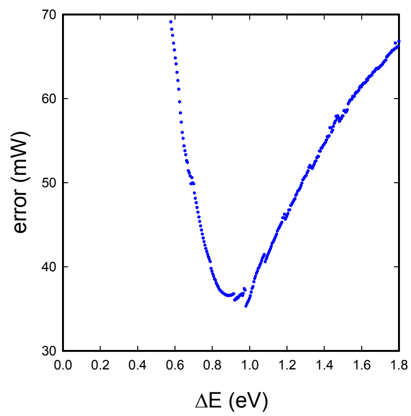

Figure 9. Error in the fit for excess power in mW as a function of ΔE in eV for the spectrum of Fig. 6 including all points.

these binding energies to change in the case of a monovacancy with substantial deuterium occupation.

Next, the helium atoms must diffuse away. Xia et al. (2006) calculated the barrier energy for helium diffusion in Pd as 0.72 eV. A similar value (0.72 eV) is reported by Laakmann et al. [20] for helium migration in Au.

Based on this we might conjecture that the 0.67 eV value for ΔE found by Storms [7], and the 0.63 eV number found by Swartz [8], may be associated with helium diffusion in Pd away from the active sites. The higher ΔE number (near 1.3 eV) associated with experiment 669u,v may be associated with the binding energy of helium in a vacancy (where Pd and Au appear to be similar, and where the presence of deuterium in the other O-sites of the vacancy is conjectured to reduce the binding energy).

Such a picture might be appropriate if the active sites in the two-laser experiment are closer to a nearby surface

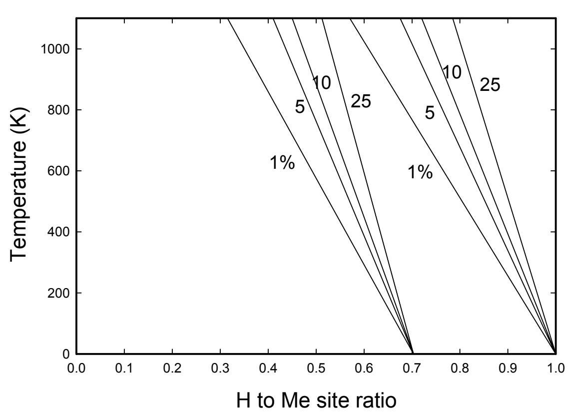

Figure 10. Estimated vacancy fraction in equilibrium in NiH and PdH at different temperatures as a function of loading.

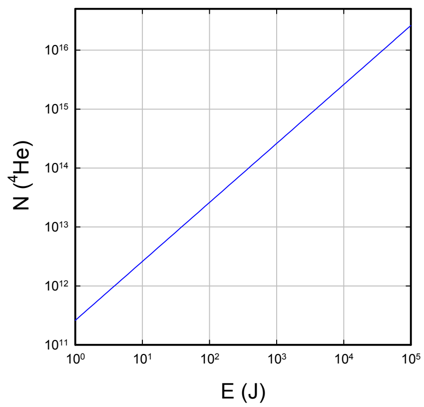

Figure 11. Number of ^{4}He atoms as a function of the excess energy produced.

(so that diffusion is not limiting), while the active sites in the experiments of Storms and of Swartz involve active sites further away from a nearby surface (so that diffusion is limiting).

Of course we would like to see additional experimentation that focuses on the question of the temperature dependence; and also measurements aimed at determining the number of vacancies, deuterium occupation of the vacancies, and showing that molecular D_2 forms under the conditions proposed. Within the basic picture under discussion we can readily identify helium removal and diffusion mechanisms, and we have the ability to pursue relevant density functional calculations; however, at some point we are going to need additional experimental results to have confidence in the proposed picture.

Finally, we note that the excess power in 669u,v is seen to go away (slowly) following beat laser irradiation. This is in contrast to previous experience with the two-laser experiment in which the excess power remains on at the same level when the lasers are turned off.

9. Magnetic Field Dependence

The issue of why excess heat should depend on an externally applied magnetic field deserves some consideration. By now there are several observations of an enhancement of the excess heat with the application of relatively small external magnetic fields, and also a substantial increase in excess heat with the application of a large magnetic field. In addition, excess heat in the two-laser experiment was sensitive to an applied magnetic field with the proper orientation [14].

At issue is why there should be any dependence at all. For example, one would not expect the local $D_2/^4He$ problem to be impacted at all by such weak fields. In the phonon theory, nuclear transitions between a molecular D_2 state embedded in the lattice and the stationary final ^{4}He state is made possible through the fractionation of the large nuclear quantum into a great many low energy phonons [16]. Relatively recently, a new model has been introduced that allows for the computation of physical parameters (such as matrix elements) in connection with the theory [21]. It was noted in the calculation of the **a**-matrix element of the deuteron [22] that the selection rules were consistent with the magnetic field orientation effects observed in the two-laser experiment. The idea is that if the deuteron is involved in the fractionation of the large nuclear quantum, then only two out of the three spin states can participate. A magnetic field can lead to an increase in the number of deuterons that have a favorable spin alignment. In the event that fractionation limits the reaction rate, then the rate is exponential in the number of deuterons with in a favorable spin state. This could account for the extreme sensitivity of excess heat to such weak magnetic fields seen in the experiments.

References

[1] M. Fleischmann, S. Pons and M. Hawkins, *J. Electroanalytical Chem.* **261** (1989) 301, errata **263** (1990) 187.
[2] M. Fleischmann, S. Pons, M.W. Anderson, L.J. Li and M. Hawkins, *J. Electroanalytical Chem.* **287** (1990) 293.
[3] M.C.H. McKubre, S. Crouch-Baker, A.M. Riley, S.I. Smedley and F.L. Tanzella, *Proc. ICCF3* **5** (1993).
[4] M.C.H. McKubre, Cold fusion (LENR) one perspective on the state of the science, *Proc. ICCF15* **1** (2009) xv–xxvii.
[5] M. Fleischmann and S. Pons, Calorimetry of the Pd D_2O system: from simplicity via complications to simplicity, *Proc. ICCF3* (1992), pp. 47–66.
[6] S. Szpak, P. Mosier-Boss, M.H. Miles and M. Fleischmann, Thermal behavior of polarized Pd/D electrodes prepared by codeposition, *Thermochemica Acta* **410** (2004) 101–107.
[7] E. Storms, Some characteristics of heat production using the *cold fusion* effect, *Proc. ICCF4* **2** (1993) 4-1.
[8] M. Swartz, Photo-induced excess heat from laser-irradiated electrically polarized cathodes in D_2O, *Proc. ICCF10* (2003) 213–224.
[9] M.C.H. McKubre, S. Crouch-Baker, A.K. Hauser, S.I. Smedley, F.L. Tanzella, M. S. Williams and S. Wing, Concerning reproducibility of excess power production, *Proc. ICCF5* (1995) 17–33.
[10] F. Celani, Who explained that excess heat could be stimulated by axial electrical current in the demonstration shown at *ICCF17*.
[11] M. Swartz and P.L. Hagelstein, Demonstration of energy gain from a preloaded ZrO_2–PdD nanostructured CF/LANR quantum electronic device at MIT, *Proc. ICCF17* (in press).
[12] D. Letts and D. Cravens, Laser stimulation of deuterated palladium: past and present, *Proc. ICCF10* (2003) 159.
[13] D. Letts and P.L. Hagelstein, Dual laser stimulation and optical phonons in palladium deuteride, in *Low Energy Nuclear Reactions and New Energy Technologies Sourcebook,* Volume 2, J. Marwan and S.B. Krivit (Eds.), Washington, DC, American Chemical Society (2009) p. 81.
[14] P.L. Hagelstein, D. Letts and D. Cravens, Terahertz difference frequency response of PdD in two-laser experiments, *J. Cond. Mat. Nucl. Sci.* **3** (2010) 59.
[15] P.L. Hagelstein and D. Letts, Analysis of some experimental data from the two-laser experiment, *J. Cond. Mat. Nucl. Sci.* **3** (2010) 77.
[16] P.L. Hagelstein, Bird's eye view of phonon models for excess heat in the Fleischmann–Pons experiment, *J. Cond. Mat. Nucl. Sci.* **6** (2012) 169.
[17] P.L. Hagelstein and I.U. Chaudhary, Arguments for dideuterium near a monovacancy in PdD, *Proc. ICCF15,* Rome, Italy, October 5–9, 2009.
[18] L. Dechiaro, unpublished.
[19] C. Zeng, H. Deng, and W. Hu, First-principles approach to the properties of point defects and small helium-vacancy clusters in palladium, *Nuc. Instr. and Methods in Phys. Res. B:* **267** (2009) 3037.
[20] J. Laakmann, P. Jung and W. Uelhoff, Solubility of helium in gold, *Acta Metall.* **35** (1987) 2063.
[21] P.L. Hagelstein and I.U. Chaudhary, Including nuclear degrees of freedom in a lattice Hamiltonian, *J. Cond. Mat. Nucl. Sci*. **7** (2012) 35.
[22] P.L. Hagelstein and I.U. Chaudhary, Coupling between a deuteron and a lattice, *J. Cond. Mat. Nucl. Sci.* **9** (2012) 50.