

Fleischmann-Pons effect studies

RLE Group

Energy Production and Conversion Group

Sponsors "Nuclear Energy Release from Metal Deuterides", SRI International under sub-agreement #33-000075, Period: 3/23/09-9/27/11

Project Staff and collaborators

Peter L. Hagelstein, Irfan U. Chaudhary, Dennis Letts, Dennis Cravens, Michael McKubre, Francis Tanzella, Michael Melich, Rodney Johnson, Lou Dechiaro, and Peter Orondo

Introduction

We have been interested in reports of excess heat in the Fleischmann-Pons experiment [1] for many years, in spite of the controversy that has surrounded research in the area. The basic effect, announced in March 1989, involved a temperature increase in an electrochemistry experiment in which deuterium is loaded into a palladium cathode in a heavy water electrolyte with 0.1M LiOD. The amount of energy produced in some of these experiments is prodigious, with no sign of commensurate chemical reaction products. This prompted Fleischmann to conjecture that the origin of the energy was nuclear, even though there were no commensurate energetic nuclear reaction products.

There are a number of reasons that this is important. From a scientific perspective, this result cannot be accounted for by known nuclear reaction mechanisms (since local conservation of energy and momentum requires that the energy produced be expressed as energetic products), and hence implies new physics. From a practical point of view, this experiments tell us that it is possible to have a clean and compact nuclear energy source, which if in addition could be made cheaply, would have a dramatic impact on major problems (oil, energy, water, among others) facing the world today.

Two-laser experiment

Excess heat in a modified Fleischmann-Pons experiment can be stimulated using a weak laser as found by Letts and Cravens in 2002 (as described in our last year's RLE report), but the excess heat appeared to stay on only while the laser stimulation persisted. We proposed that if excess heat could be stimulated in a two-laser experiment, that the response might depend on the difference frequency, which would allow us to study the response in the THz frequency region and perhaps identify which phonon modes were involved. Letts and Cravens recently demonstrated the effect [2], and much recent work has gone into analyzing and understanding the experimental results.

An example of the excess power response is shown in Figure 1 [3]. In this experiment two weak lasers turn on between minutes 303 and 304, with a difference frequency of 20.66 THz. The total power of the two laser beams is about 26 mW, of which about 15 mW is absorbed. One can see a rapid initial response (that is faster than the calorimeter response) which is an artifact due to a sudden change in the cell potential, which causes the electronics to overcompensate transiently to keep constant input power. A sudden change in the cell potential as a precursor to the initiation of an excess heat pulse has been seen in many laboratories over the years, as was noticed by Cravens some years ago. In our experiment, when the cell potential is changed (with no excess heat production) by reducing the resistance of the electrolyte, a similar transient is seen before the system returns to power balance.

Encouraged by reviewers, we upgraded our data analysis to extract more accurate results for the excess power as a function of the difference frequency. We found that the data could be fit using

simple relaxation models, an example of which is presented in the blue line of Figure 1. The calorimeter relaxation time was found to be about 30 minutes, and the thermal response produced by the lasers in many experiments was slower.

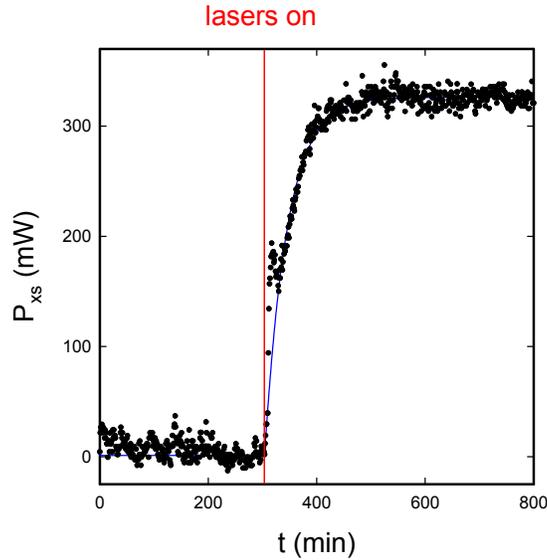


Figure 1. Excess power (mW) as a function of relative time (min) for parts of data set 662N2 and 662O2 (circles), along with a best fit relaxation model (curve). Two lasers were turned on between time 303 and 304, as indicated by the vertical line. The difference frequency is 20.66 THz.

The revised excess power spectrum [3] is shown in Figure 2. We assembled results for the relaxation times of the thermal response (not including the calorimeter relaxation time, which was modeled and accounted for separately) [4], which is shown in Figure 3. We see that the longest relaxation time is found near the resonance at 15 THz. Very little delay is seen in the response near 8 THz. Why there should be a sluggish response in the build-up of excess power is not understood at present.

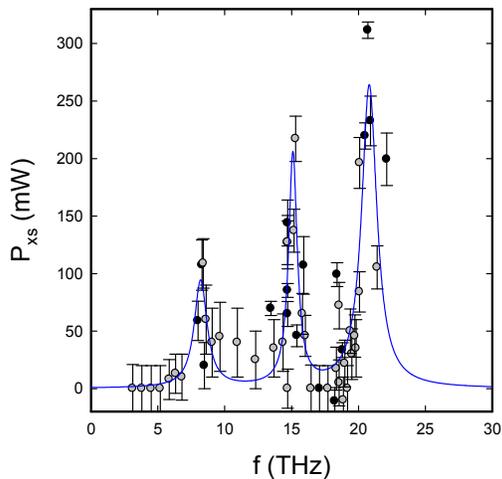


Figure 2: Thermal response for different two-laser experiments as a function of difference frequency.

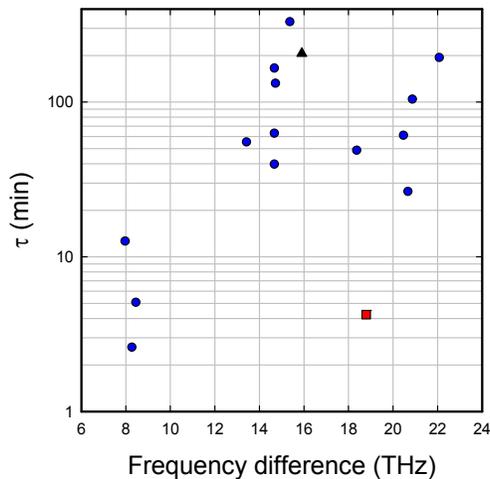


Figure 3: Relaxation time of excess power as a function of difference frequency.

The excess power tends to persist in the two-laser experiment, which indirectly supports the conjecture that energy from the new nuclear process is channeled into optical phonon modes prior to thermalization, and that the excited optical phonon modes in this experiment stimulates the new nuclear process.

Constraints on energetic particles in the Fleischmann-Pons experiment

Last year a series of meetings were held at the Naval Postgraduate School on the subject of theory in connection with the Fleischmann-Pons experiment. Reviews of experimental work on the Fleischmann-Pons experiment were held for outside reviewers, which included theoretical and experimental physicists, chemists, and materials scientists. A number of theoretical approaches were put forth, which stimulated much enthusiastic discussion over quite a few hours. In the end, we ran into what seemed to be a conceptual road block for the outside physicists. The associated arguments and discussions motivated various research efforts, and are worth recounting here.

Evidence for excess heat was presented, discussed, and ultimately accepted in these meetings. Problems began as soon as the discussion turned to the issue of mechanism and theoretical explanation, specifically when the issue of whether the effect was chemical or nuclear was considered. On the one hand, the outside physicists were predisposed to view the problem as chemical in the absence of energetic nuclear radiation commensurate with the energy produced. The lack of chemical products commensurate with the energy as an experimental fact, as well as the prodigious amount of energy (thousands of electron volts per atom of cathode) argued against chemical explanations. The presence of ^4He in amounts consistent with 24 MeV per atom as a preliminary experimental result was tentatively accepted, and provided experimental input around which to begin theoretical speculations.

That is when things hit a conceptual road block. The issue is that local conservation of energy and momentum requires that energy produced in a nuclear reaction comes out as (primarily) kinetic energy of the reaction products; hence if nuclear energy is being made, the energetic particles must be there. The physicists that participated pretty much rejected all new approaches in favor of conventional approaches in which energetic particles are "hidden". The most likely theoretical resolution according to their arguments was that an aneutronic reaction was involved, and that the energetic reaction products slowed down inside the cathode producing nothing observable. The favorite example of such a mechanism discussed was one in which two deuterons somehow tunneled together near the Pd with subsequent recoil between the Pd and resulting alpha. It was argued that a 24 MeV alpha particle slowing down inside the cathode would result in no detectable radiation.

All of this seemed rather discouraging, since from our perspective the most significant feature of the experiment is the production of nuclear energy without commensurate energetic particles. We argued that a 24 MeV alpha source at the watt level in PdD would produce all kinds of radiation, and that if it was present, it would already have been detected. These arguments were rejected with prejudice.

This motivated us to quantify our argument and document it in the literature. We computed expected yields for a variety of reactions which would produce neutrons, gammas, and x-rays. We also reviewed the cold fusion literature looking for experimental results in which excess heat was observed, and penetrating radiation was simultaneously monitored. From a comparison of the experimental observations with the calculated yields, we hoped to be able to interpret the experimental results in terms of the energy of candidate reaction products in the Fleischmann-Pons experiment.

In the end, the most sensitive diagnostic for energetic alpha particles in PdD is from secondary reactions in which an energetic alpha particle collides with a deuteron (giving it a significant fraction of the alpha energy), and then the deuteron collides with another deuteron resulting in a

conventional deuteron-deuteron fusion reaction. We found that the secondary neutron emission from this process should be detectable at very low alpha particle energy [5], as shown in Figure 4.

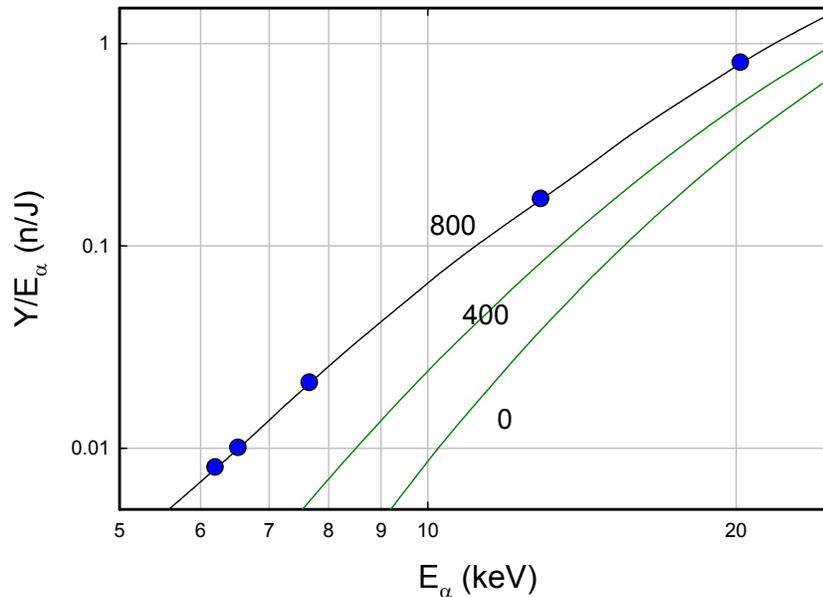


Figure 4. Neutron yield per unit alpha energy as a function of alpha energy. The three lines are predictions assume a screening energy of 0, 400 eV, and 800 eV (low energy deuteron beam experiments are consistent with screening energies between 400 eV and 800 eV). Solid circles are for upper limits or observed neutron emission during excess heat measurements.

In the experiments, neutron emission and excess power are largely not observed to be correlated. In the lowest noise experiments, no neutrons are observed, so the circles in Figure 4 are primarily estimated upper limits (which are near 0.01 neutron/Joule). Such low levels of neutron emission in these experiments indicate that the ^4He which is observed must be born conservatively with less than 20 keV of energy. Since the current experimental result for energy per ^4He is currently near 24 MeV, the new physical process that is responsible partitions less than 0.1% of the reaction energy to alpha kinetic energy.

This result rules out the "hidden" reaction product approach. It also rules out all conventional binary reaction mechanisms involving an alpha particle in the exit channel. The majority of reaction mechanisms that have been put forth over the past 21 years to account for the Fleischmann-Pons experiment can be argued to be inconsistent with experiment according to these limits. Supporting calculations and additional results are described in [6-9].

Molecular D_2 in PdD

Following the announcement of cold fusion in 1989, researchers in condensed matter took an interest in the problem of the formation of D_2 in PdD. There was quickly basic agreement that the electron density in bulk PdD was too high for the D_2 molecule to form. Calculations of D_2 in jellium showed that the molecule falls apart by about $0.06 \text{ e}/\text{Angstrom}^3$, which is less than the lowest electron density due to the Pd atoms alone (which is near $0.09 \text{ e}/\text{Angstrom}^3$ at the O-site). We used simple superposition based on relativistic Hartree-Fock $4d$ orbitals and Clementi $5s$ orbitals to develop the electron density plot of Figure 5 (which gives a surprisingly good account when compared to density functional calculations). This motivated us to investigate the situation in the vicinity of a Pd monovacancy in PdD. Since the Pd is providing so much of the electron

density, we should be able to reduce the electron density by removing Pd atoms. This is shown using a superposition model in Figure 6.

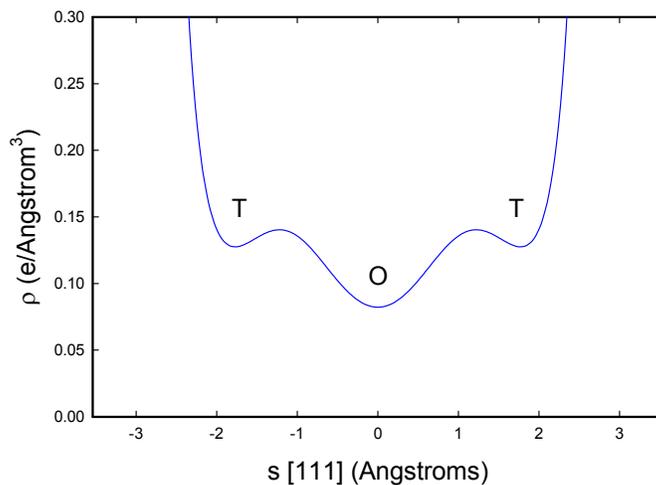


Figure 5. Electron density due to Pd in the vicinity of an octahedral site in the [111] direction based on a simple electron superposition model. The octahedral site is marked with an O, and the tetrahedral site is marked with a T.

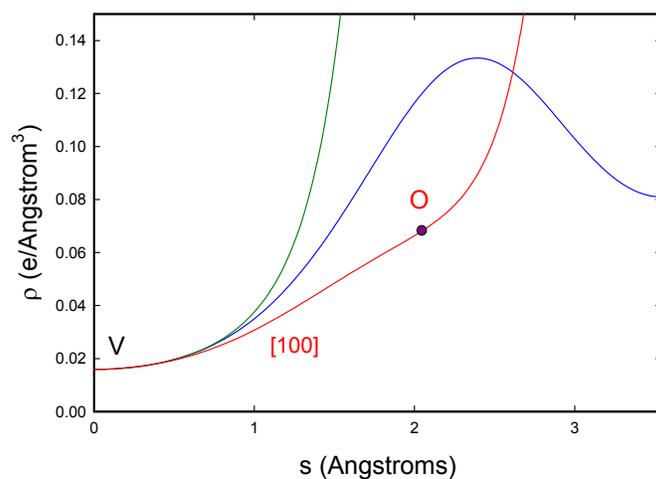


Figure 6. Electron density due to Pd in the vicinity of a Pd vacancy. The nearest octahedral site is in the [100] direction from the vacancy (red), and is marked with an O. The electron density in the other directions are indicated: [110] in green, and [111] in blue.

The Pd electron density at the site of H_2 in molecular PdH_2 (the sigma-bonded singlet ground state) is about $0.03 \text{ e}/\text{Å}^3$. We see from Figure 5 that the electron density near a monovacancy is sufficiently low to support molecular D_2 formation, and that we might look for D_2 in the vicinity of 1 Å in the [100] direction away from the vacancy site [10]. These results have recently been supported by extensive DFT calculations of Dechiario, to be reported on in the future.

Connection with Fleischmann-Pons and Szpak experiments

From our perspective, the key to the Fleischmann-Pons experiment in practical terms is the development of large numbers of vacancies which can host molecular D_2 formation. Since the electron density in bulk Pd is too high, we view most of the cathode as being inert with respect to the new process that produces excess heat and makes 4He .

In the Fleischmann-Pons experiment, we conjecture that some of the Pd is dissolved from the outer cathode surface (a process which is aided by interstitial lithium which codeposits with large amounts of LiOD in the electrolyte), and subsequently codeposits. This is very much an inadvertent process in the Fleischmann-Pons experiment, in that it has historically been uncontrolled, and very little Pd is codeposited (probably on the order of 100-300 nm). This conjecture is consistent with the observation of most of the 4He in the gas phase, since had it formed deeper into the cathode the diffusion rate is too slow for it to make it to the surface.

However, we would expect enormous differences in the number of vacancies developed in the codeposited layer depending on the D/Pd loading when the codeposition occurs. This is easy to understand from the associated energetics. A vacancy in pure Pd takes a bit more than 1 eV to form. As a result, pure Pd tends to have relatively few vacancies (few relative to what we are looking for, that is). If you use electron bombardment to make more, then they anneal over the course of several hours to a level near 0.1%. If hydrogen or deuterium is added, then the effective energy of the vacancy is changed (since the binding energy of the hydrogen interstitial is different near the vacancy), with the result that it is easier to make a vacancy as the loading increases. Near room temperature, vacancies become preferred thermodynamically near a D/Pd loading of 0.95.

What this means is that if the dissolved Pd is codeposited when the loading is very high (at or above D/Pd=0.95), then we would expect the codeposited layer to have superabundant Pd vacancies. Although the vacancies are also preferred in the bulk region, the rate of atomic diffusion near room temperature is very slow so that we would not expect to see many new vacancies form elsewhere in the cathode.

In experiments at SRI during the 1990s, a correlation was noticed between the peak loading that a cathode developed during the several week loading period prior to excess heat observations, and whether the cathodes showed excess heat or not. The result from this study was that cathodes which did not achieve a D/Pd loading of 0.95 showed no excess heat effect, while cathodes that loaded higher than 0.95 did show excess heat. These experimental results are consistent with our arguments above concerning vacancy formation, but as yet we have no direct evidence in terms of quantitative measurements of vacancy concentrations in the codeposited region from Fleischmann-Pons experiments.

Things are different in the Szpak experiment, where the Pd is codeposited at the outset of the experiment onto a copper substrate. Excess heat was reported by Szpak and coworkers immediately following codeposition, in contrast to the Fleischmann-Pons experiment where one had to wait 2-4 weeks before excess heat burst would occur. This also seems to be consistent with our vacancy formation picture, as long as the codeposition is done under conditions of very high D/Pd loading. From this perspective, the Fleischmann-Pons experiment is not a good experiment, because the critical Pd codeposition occurs in an uncontrolled manner; and the Szpak experiment is superior because the Pd codeposition is taken as a key component of the experiment. Based on this, one might expect the Szpak experiment to give better results for excess heat than the Fleischmann-Pons experiment. Yet, from a perusal of the relevant literature, one finds few positive results for excess heat from the Szpak experiment, which has been for us discouraging.

During the past two years, there was a DTRA supported effort which had as a goal the development of a "lab rat" experiment which could be done quickly and easily, and which would

give positive results a large fraction of the time. Part of this effort focused on the Szpak experiment, motivated in part by the shorter cycle time of the experiment (days rather than several weeks), and motivated by a hope of avoiding the serious materials problem of obtaining good cathode samples (which has haunted the Fleischmann-Pons experiment since the early days). Once again, initial attempts to replicate the Szpak experiment seemed to be plagued by a lack of positive results. This was not understood, given the good reproducibility reported initially by Szpak and coworkers. In the experiments of Letts, the initial results were uniformly negative.

This motivated attempts at varying the protocol. In recent years, published versions of the Szpak protocol involved codeposition at low current density (a few mA/cm²), motivated by adherence issues (the Pd flakes off if codeposited at higher current density). Letts reasoned that the low current density would result in fewer vacancies, so he tried experimenting at high current density (hundreds of mA/cm²); the codeposited Pd flaked off. Letts then cut back on the concentration of PdCl₂ in the electrolyte, and ran again at high current density. In this case, the Pd stuck, and excess heat was seen immediately in all of the experiments run using this modified protocol [11].

We went back to the older literature to see what current density was used by Szpak in the early experiments, thinking that perhaps it might be higher (the recent Szpak experiment protocols are for low-level energetic particle emission experiments, and not for excess heat experiments). We found that the current density was not reported in the publications. Pam Boss responded quickly to our request to go back to the old lab notebooks, where she found that in one of these experiments where a record was found, the current density was much higher than more modern versions of the protocol.

Swartz has reminded us recently that he described codeposition experiments at lower Pd concentration at ICCF10, which we had not remembered.

Progress on theory

As we have described in previous RLE reports, we have been working to develop a theoretical model for excess heat in the Fleischmann-Pons experiment. The point of view that we have taken is that we are dealing with a fundamentally new physical process, and that to learn about it we need to turn to experiment. This process is hindered because there have been a very large number of experiments reported, and we tend to have more confidence in some results and less in others (based in part on listening to more than a thousand presentations over two decades, visiting labs, looking at data, talking to experimentalists and theorists, and reading a very large number of papers in the field). We have reported a number of times on the experimental situation over the years [12], and on the implications of the experimental results for theory [13].

The big problem is the production of nuclear energy without the production of commensurate energetic particles. Even to consider such a possibility is outside of what most physicists would consider to be physically reasonable, which is in part why excess heat in the Fleischmann-Pons experiment has met with so much resistance over the years.

In 1989 we envisioned the effect working something like a phonon laser, in which energy extracted from the nuclear levels was somehow downshifted to optical phonon modes, and subsequently thermalized. Phonon lasers have been demonstrated, and optical phonons thermalize efficiently; so, the big issue in such a scheme is how to down-convert from the MeV to the meV. Over the years we looked at many different schemes to accomplish this, including a variety of models with very high-order nonlinearities. We were able to dismiss all such models, as well as modified versions of them. It was only in the late 1990s that we considered models which were based on excitation transfer (which we now consider to be a key mechanism for a successful model), and it was 2002 before we finally found a mechanism that was strong enough to fractionate a large quantum into a very large number of smaller quanta.

The spin-boson model presents us with a good starting place for thinking about the mechanism. This model is made up of a set of two-level systems that are coupled to an oscillator, with the coupling between the two systems linear in the raising and lowering operators of both systems. Excitation that starts in the two-level system can be transferred to the oscillator, and vice versa, as long as the dressed two-level system is an odd multiple of the characteristic energy of the oscillator. This effect is basically what we need: coherent energy exchange between the two-level systems and the oscillator under conditions where the two-level system energy is a substantial multiple of the oscillator energy. In this discussion, we think of the two-level systems as standing in for the nuclear energy levels, and the oscillator as standing in for an optical phonon mode.

In calculations with the model, we found that coherent energy exchange works reasonably well as long as the energy quantum associated with the two-level system is fractionated 50-fold or less (where we need more than a million-fold fractionation to address excess heat production in the Fleischmann-Pons experiment). This motivated us to examine the model to see what was limiting coherent energy exchange when a large quantum was split into a great many smaller quanta. In a perturbation theory calculation it is possible to see clearly that destructive interference limits the rate for energy exchange. If this destructive interference could be lifted, then we would be able to obtain substantial coherent energy exchange rates under conditions of extreme fractionation.

We found a variant of the spin-boson model augmented with an unusual kind of loss in which the destructive interference was removed. This model we have referred to as a lossy spin-boson model, although it is distinct from lossy spin-boson models that one can find in the literature. In literature versions, the oscillator experiences loss in the vicinity of the characteristic frequency, while in the lossy spin-boson model that we have been studying the loss is at the transition energy of the two-level systems.

Back in 2002, we carried out brute force numerical calculations which showed that coherent energy exchange could proceed in this type of model at interestingly large rates when several thousand quanta were exchanged (in contrast to the lossless spin-boson model which gives no energy exchange in such a case). In recent years, we have been building up tools to analyze the model systematically, in order to understand coherent energy exchange under conditions where even larger fractionation occurs. During the past year or two we were able to develop exact solutions for a reduced version of the model, one which we termed a local approximation to the model. The associated Hamiltonian is

$$\hat{H} = \Delta EM + \hbar\omega_0 n + g \left(\hat{\delta}_+^M + \hat{\delta}_-^M \right) \left(\hat{\delta}_+^n + \hat{\delta}_-^n \right)$$

This system models the energy of the oscillator and two-level systems and the loss as in the lossy spin-boson model, but the coupling between the two systems is simplified. We are able to solve this model numerically and analytically in the strong coupling limit where the two-level system quantum is fractionated into a very large number of oscillator quantum. Results are shown for the scaled indirect coupling coefficient V_{eff} (which is proportional to the coherent energy exchange rate) in Figure 7. In the strong coupling limit this rate obeys a scaling law of the form

$$\frac{\Delta n^2 V_{\text{eff}}}{4g\Delta E} = \Phi \left(\frac{g}{\Delta n^2} \right)$$

Within this reduced approximation of the lossy spin-boson model, we can analyze coherent energy exchange quantitatively under conditions of strong coupling where very large fractionation occurs. In this simplified model we can develop accurate estimates for the rate of energy exchange when an MeV quantum is down-converted into an enormous number of meV quanta

[14-16]. We have been working toward a systematic presentation of these models and results in a set of papers that we hope to publish in the coming year.

We have recently put together an overview of this and related models, and how they connect with experiment in a brief review paper [17]. We have succeeded in deriving such models from a more fundamental starting place, which allows us to obtain formulas for computing the phonon exchange coupling matrix elements which appear in the lossy spin-boson class of model [18].

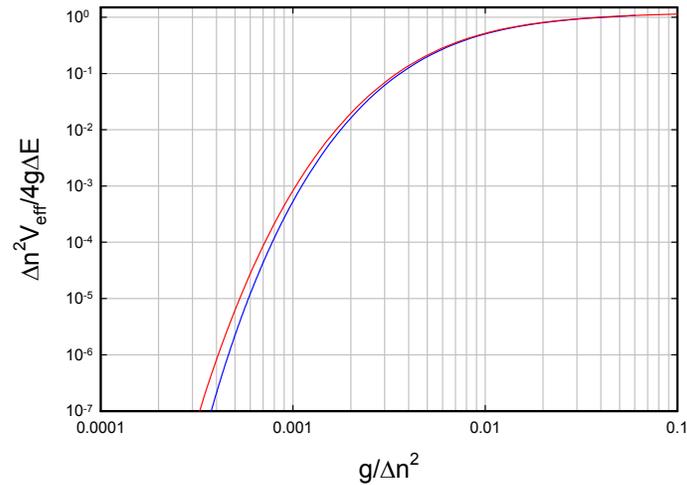


Figure 7. Scaled indirect coupling coefficient as a function of the scaled dimensionless coupling coefficient; strong coupling limit (red line) and numerical calculation for $\Delta n=91$ (blue line).

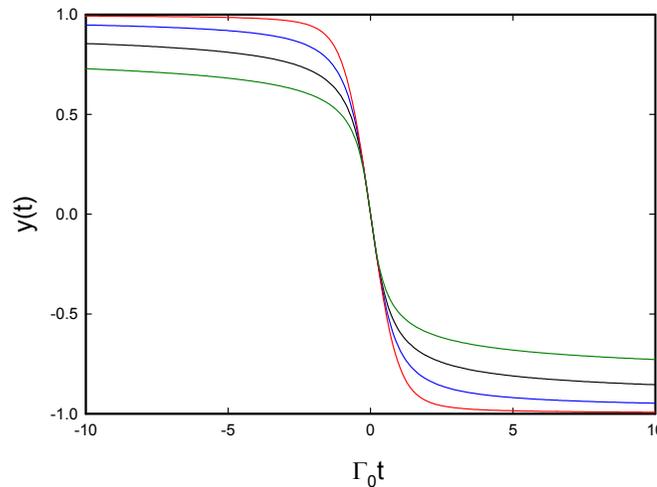


Figure 8. Dynamics of two-level systems in the strong coupling limit with fractionation of the two-level system quantum into a very large number of oscillator quanta; calculations for $\max(g)/\Delta n^2$ values of 0.0003 (green), 0.001, 0.003, and 0.01 (red). When all the two-level systems are excited then $y(t)=1$, and when they are all in the ground state then $y(t)=-1$.

It is possible to estimate the dynamics for this kind of model in a classical approximation, to see how fast coherent energy exchange occurs. Results are shown in Figure 8 for a set of calculations for non-periodic solutions in which all of the two-level systems are initially excited, for a model in which the oscillator is assumed to be highly excited. The de-excitation in this case

happens suddenly, with a peak rate given by $2 \max(V_{\text{eff}})/h\bar{\nu}$. In essence, we have demonstrated that coherent energy exchange occurs in this model in a burst reminiscent of Dicke superradiance, with reasonably high rates even when a very large number of quanta Δn are exchanged per two-level system quantum.

Modeling electrochemical reactions

One of our goals is to develop a simulation model for the Fleischmann-Pons experiment. Since the problem is multidisciplinary, such a model is going to require a surprisingly large number of parts if it hopes to be at all realistic. We require a model for the deuterium chemical potential as a function of D/Pd loading, since it determines the rate of de-loading in the Tafel reaction. We need a model for the diffusion of deuterium in PdD, and kinetic models that describe the loading. Then there are models for Pd codeposition, vacancy formation, vacancy occupation with molecular D_2 , coherent dynamics for the new process, optical phonon mode dynamics, and then helium diffusion to clear out the active sites following reactions. We need estimates for the phonon exchange matrix elements for the different nuclear transitions (some of which now have been estimated from detailed calculations). The overall project is rather broad, but it seems to be doable (although it has been taking many years to put together).

Here we wanted to discuss briefly some of the issues with modeling the electrochemical reactions. In the literature, one can find a set of reactions that are termed the hydrogen evolution reaction model, that describe the loading of hydrogen into different metals. Four steps are generally recognized in base for this model:

1. Volmer reaction: $H_2O + M + e^- \rightleftharpoons OH^- + MH_{\text{ads}}$
2. Adsorbed to absorbed exchange: $H_{\text{ads}} \rightleftharpoons H_{\text{abs}}$
3. Tafel reaction: $2H_{\text{ads}} \rightleftharpoons H_2$
4. Heyrovsky reaction: $H_2O + MH_{\text{ads}} + e^- \rightleftharpoons OH^- + M + H_2$

This model is one of the success stories in electrochemistry. The adsorption and absorption of hydrogen in a variety of different metals has been successfully analyzed and characterized in terms of this model in hundreds (if not thousands) of papers in the literature over the past half century. One can find this model in electrochemistry textbooks.

This model has been used many times to describe the loading of deuterium into Pd in the Fleischmann-Pons experiment. The Volmer reaction and the exchange reaction load the Pd with deuterium, and as the chemical potential increases the adsorbed deuterium combines to make D_2 gas causing de-loading. When the current density is high (over 100 mA/cm^2) the loading is seen to decrease, which some researchers have attributed to the onset of the Heyrovsky reaction.

We attempted to use this model to model cathode loading data that we obtained from SRI. It became clear quickly that the hydrogen (or deuterium) evolution reaction model doesn't work very well for Pd cathodes in the Fleischmann-Pons experiment. At low current density the Volmer and Tafel reaction mechanisms seem to describe things pretty well qualitatively, but a major problem occurs at higher current density. Without the Heyrovsky reaction, the loading is predicted to increase at higher current density, but experiments show it leveling off or decreasing. If we use the Heyrovsky reaction to account for this effect, then we are able to match one data set, and not others. The model for the Heyrovsky reaction works like a "wall" in the loading model, such that when it kicks in at a given loading the model will never allow significantly higher loading, which is not in agreement with the experimental data. Moreover, there is no experimental evidence so far that the Heyrovsky mechanism contributes in a significant way under the moderate loading conditions that have been explored. And if the Heyrovsky reaction is not responsible for the decrease in loading, then some other mechanism must be responsible.

In response, we have put together a number of different models in an effort to have a more satisfactory description of the loading process. Although this modeling effort is not yet complete,

there are a number of effects which can be modeled that improve the agreement. Perhaps the most significant effect comes about from the assumption of an internal Tafel leak rate, in which different cathodes de-load from internal surfaces (the D_2 subsequently escapes through fractures and grain boundaries). The experimental data is consistent with internal Tafel leak rates which can be several orders of magnitude larger than the surface Tafel rate (many of the surface sites can be blocked), and cathodes which have a very low internal Tafel leak rate achieve very high loadings at low current density. There is evidence that lithium in the electrolyte can be adsorbed, resulting in adsorbed lithium near the surface, and we have developed an equilibrium model for this. In some experiments additional additives are present in the electrolyte which result in more adsorbed species, which can increase the loading since the rate of the Volmer reaction is hindered linearly in the number of blocked sites, while the surface Tafel reaction is blocked proportional to the square of the number of blocked sites. The experimental data seems consistent with plugging up of internal leaks with additional LiOD concentration in the electrolyte. These and other issues are discussed further in [19].

Criticisms

Science advances in a number of different ways. New results can stimulate a field, and result in additional progress. Sometimes there are mistakes, which hinder progress, and a necessary part of scientific research must be to identify and correct mistakes when they are made. In this sense, criticisms generally need to be thought about and addressed, and good criticisms can be of great value if they remove errors that stand in the way of progress. In research relating to the Fleischmann-Pons effect, the number of criticisms that have been put forth over the years is very large. It has not been widely appreciated just how much effort has gone into addressing and responding to the technical criticisms, since one often sees issues that were addressed and settled decades ago reappearing as criticisms. It seems useful to consider some of these here.

"The history of LENR research, more commonly known as cold fusion research, is dominated by one prevailing fact, irreproducibility. From the very beginning, this has caused consternation and frustration in all those who have attempted to research and/or study the field. In the 'hard' sciences like chemistry and physics, which is the arena wherein cold fusion plays, no significant scientific progress can ever be made without reproducibility." (from Ref. [20])

Most of the scientific community still believes the excess heat effect to be irreproducible, and the author in writing this provides reinforcement. A reader might imagine that the task that lays before us is to work toward a reproducible experiment, and until then the field should not expect to be taken seriously. Hence, the criticism here is that all cold fusion effects are not reproducible, and as such they do not belong as a part of science.

Following the announcement of 1989, a great many groups tried to replicate the excess heat effect in the Fleischmann-Pons experiment, and the vast majority of them obtained a negative result. Some of us have thought about this a great deal over the years, and with time some clarity has begun to emerge. Perhaps the best way to understand why things didn't work is to examine the conditions under which positive results were obtained. This was done over many years in the case of experiments at SRI, where it was noticed that positive results were obtained only when the cathode D/Pd loading exceeded 0.95 at some point during the several week long loading cycle prior to excess heat bursts (high D/Pd loading is difficult to obtain because the Tafel leak rate is exponential in the loading above 0.60 near room temperature). When seen, the excess heat was proportional to the square of the D/Pd loading above a threshold which was typically near 0.85 in those experiments. Additionally, a delay of 2-4 weeks seemed to be required prior to the observation of the first excess heat burst, as discussed by McKubre recently at ICCF15.

Technical information about the Fleischmann-Pons experiment was not readily available in 1989 when the majority of these early experiments were done. The criteria mentioned above were not deduced until years later. It is said that the success rate in Fleischmann and Pons own lab at the

time was on the order of 10%, so one could argue that even the originators of the experiment at the time couldn't have explained to their colleagues how to do the experiment reproducibly had they been of a mind to do so. Consequently, it would be fair to ask precisely what were the majority of these negative experiments actually doing in 1989? For example, did they reach a D/Pd loading of 0.95 during the initial charging period? Was the loading sufficiently high during the cycling later on when heat bursts might be expected? Was the cathode charging time sufficiently long?

In short, the answer is no in all cases. For reasons that are hard to understand now, the need for high loading was either not appreciated, or disregarded (since it was certainly emphasized at the time). The loading was not monitored in real time during these experiments (as was done later on in many successful ones), and in all but a few experiments no effort was made to determine the loading. The highest D/Pd loading (0.80) of these early replication attempts was reported in the Caltech experiments, but in retrospect this loading is far too low to be relevant for excess heat production. Hence, none of these negative experiments are known to have been performed in an experimental regime that we would consider to be relevant now. In short, the majority of experimentalists in 1989 had no relevant idea of what they were trying to replicate. Continued reference to this work in this day and age is inappropriate. Yes, many labs were not able to replicate the excess heat effect, and that is because to within a good approximation they had no idea of what they were supposed to be doing in the experiment.

Of course the author intends his statement to apply to more than excess heat production, and more than the early experiments of 1989. In this case, there are a number of experiments which have been reported for which the reproducibility is much better. For example, SRI reports excellent reproducibility of excess heat for cathodes that load well enough and long enough to satisfy the criteria they have established; Swartz has for years reported a very high reproducibility in his excess heat experiments with phusors; the Energetics group reported good reproducibility for moderate levels of excess heat in their experiments with Superwaves; Mosier-Boss reports good reproducibility in the case of low-level energetic radiation in codeposition experiments; and earlier in this report we discussed the two-laser experiment and the modified Szpak codeposition experiment, both of which were quite reproducible in Letts's lab.

So, how do we understand the author's statement? Well, he has taken the position that there are no new effects, and that all of the reported observations are artifacts. Excess heat observations (such as in Figure 1), according to this author, can be explained by (random) calibration constant shifts. Presumably the experiments reported in recent years that have shown good reproducibility can be ignored, or are simply rejected by the author.

In the Fleischmann and Pons experiments, the rate of inferred excess heat generation was in the range of 10-20% of total input. (from Wikipedia)

Most scientists believe that the amount of excess heat effect is very small, so that it is plausible that it could be accounted for by calorimetric errors. Some critics have taken advantage of a confusion between excess power and excess energy; for example, it was argued that excess power was unimportant since there might be some kind of strange storage effect, and that excess energy was all that mattered. In this way, an excess power burst with a power gain of 100% over 5-10 hours could be transformed into an energy gain at the 1% level (since the experiment might last for 6 weeks), which could then be dismissed as a tiny effect outside of the accuracy of the calorimeter.

In the Wikipedia statement, we might begin assuming that excess power is being discussed, and that measured excess power in the early Fleischmann and Pons experiments was only 10-20% larger than the input power. However, if we look at their 1990 paper in *J. Electroanal. Chem.*[1], the excess power gains are more than 10x (Figure 9A in that paper). So we presume that we (and perhaps others) have misunderstood the statement as referring to excess power, and that it refers to excess energy instead. As mentioned above, experiments can take months, and during

most of the time there is no excess energy. Once again, we refer to the 1990 paper where we see an energy gain of about a factor of 2x (Figure 10A in that paper), which is certainly not 10-20%. So, clearly we have misunderstood the statement in some way, or else it is simply incorrect.

Thus it would seem that cold fusion calorimetry is currently near or at its limits of accuracy and precision. (from Ref. [20])

The implied criticism here is that excess heat in the Fleischmann-Pons experiment is a small effect, and that those working in the field have not done a good job on their calorimetry. Hence, one should not expect others to accept measurements of excess heat because of inadequate calorimetry.

If excess power production were in fact a small effect, then it would be reasonable to worry about the accuracy of the calorimeter. For example, some of the calorimeters that have been used in the field are accurate between of 10^{-3} and 10^{-2} of the input power (Miles and Fleischmann have recently demonstrated power balance with a Pt cathode control at the level of 10^{-4} [21]), so that there might be reason for concern if the effect were near the percent level. Most of the scientific community still believes that the effect reported is small, so that the existence of the effect is still in question because per cent level effects are presumed hard to measure. This belief is encouraged by this author in what he has written.

This statement is inconsistent with the 10x or greater excess power observations of Fleischmann and Pons in their early experiments [1], and it is inconsistent with more recent work. There are a great many reports of subsequent observations of excess power bursts where the excess power is 50% to 300% of the input power, as well as a smaller number of reports of excess power events with very high power gain between 1000% and 3000%.

So, how do we understand what this author has written? Seemingly this author is of the opinion that researchers carrying out Fleischmann-Pons experiments are not able to develop and calibrate calorimeters that can get the right answer to within an order of magnitude. The great many control experiments that have been done presumably are to be disregarded, or else the random calibration constant shift proposed by the author must somehow know when a control experiment is done, and know to shift so as to give a positive excess power correlated properly with current density, loading, and whether to shift early if the experiment is a codeposition experiment or with a long delay in the case of a Fleischmann-Pons experiment (some of these arguments are discussed in [22]).

"The efficiency of electrolysis will be less than one if hydrogen and oxygen recombine to a significant extent within the calorimeter. Several researchers have described potential mechanisms by which this process could occur and thereby account for excess heat in electrolysis experiments." (from Wikipedia)

The implied criticism here is that the possibility of the calorimetry being compromised by a chemical effect (recombination) as was pointed out by quite a few skeptics back in early 1989. An additional implication from this statement appearing in Wikipedia in 2010 is that researchers working on the Fleischmann-Pons experiment still have not gotten around to addressing the problem. One would think that until this very serious problem (that was pointed out more than two decades ago) gets properly addressed, people working on the excess heat effect should not expect to be taken seriously.

In the early work of Fleischmann and Pons, open-cell calorimeters were used, so that the deuterium and oxygen gas produced in electrolysis would leave the cell. Critics argued that if deuterium and oxygen recombined in the cell, then this recombination would show up as excess power in the calorimetry. In the event that all of the oxygen and deuterium recombined in an open cell, and all of the power generated was measured with unit efficiency, then the calorimeter

would report a excess power of $V/(V-V_0)-1$, where V is the cell voltage (usually between 5-7 volts) and where V_0 is the thermoneutral potential (1.54 volts). For a cell operating at 5 volts, this would result in a 44% apparent excess power. So, the excess power observations of greater than 10x gain described in Ref. [1] could not be due to recombination alone, even though their cell voltage was very low (a bit below 4 volts).

In the recent Pt cathode control experiment reported by Miles and Fleischmann [21], power balance was obtained at the 10^{-4} level in an open-cell calorimeter similar to that used by Fleischmann and Pons in 1989. In this experiment, recombination effects contribute no more than 0.1 mW with nearly a watt of electrical input. Because of this and other results, there is no reason to believe that recombination contributed in any significant way in the early experiments of Fleischmann and Pons.

However, if we suppose that we remain concerned about the recombination of oxygen and deuterium producing errors in open-cell calorimetry, then perhaps we should consider closed cell calorimetry in which all of the oxygen and deuterium is recombined. In 1989, this was even suggested by some of the skeptics as a way to resolve the issue. Millions of dollars were spent on the development of sophisticated closed cell flow calorimeters at SRI, and these were used for a great many observations of excess heat in Fleischmann-Pons experiments. Excess heat bursts were observed in these cells similar to those obtained in open-cell experiments, with a similar dependence on current density and on D/Pd loading.

Given this, how do we understand the statement in Wikipedia? Either the author is not aware of, or simply disregards, the work which has laid the issue to rest long ago. In any event, we should regard it as simply in error.

"Between 1992 and 1997, Japan's Ministry of International Trade and Industry sponsored a "New Hydrogen Energy Program" of US\$20 million to research cold fusion. Announcing the end of the program in 1997, the director and one-time proponent of cold fusion research Hideo Ikegami stated "We couldn't achieve what was first claimed in terms of cold fusion." He added, "We can't find any reason to propose more money for the coming year or for the future."" (from Wikipedia)

Implied here is that the Japanese put in a lot of time, money, and resources into a study of cold fusion, nothing was seen, and that based on the results Ikegami stopped believing in cold fusion. The implication is that the Fleischmann-Pons experiment had been tested by those who believed in it, that there was just nothing there, that a large amount of money has been wasted, and no further efforts should be pursued in the area. The scientific judgment of researchers continuing to study the effect is called into question, and we should learn from this experience that other funding agencies should put their funds into more promising lines of research.

The MITI program was created to focus resources on the two most important excess heat experiments of the early 1990s. One of these was the Fleischmann-Pons experiment, and one was the SRI variant. The Japanese were impressed by the closed cell flow calorimetry pioneered at SRI, and so one of the goals was to get a confirmation of Fleischmann and Pons experiment done in a flow calorimeter. The Japanese were also impressed by the positive results obtained with the SRI version of the Fleischmann-Pons experiment, where excess heat seemed to be able to be reproduced in cathodes that achieved sufficiently high loading, and they wanted to propagate the experiment to many laboratories so that a much larger effort could be applied.

In the original SRI experiment, the source of the palladium was critical in obtaining high D/Pd loading (Pd in some batches from some suppliers worked, while Pd from other batches did not). To circumvent this problem, MITI defined the experiment to be tested as using 0.99999 pure Pd, which would make all samples uniform in replication experiments done at the different laboratories. Once the MITI program got under way, the laboratories were reporting that the cathodes weren't loading, or that they would lose their loading suddenly, and no excess heat was

seen. More than 100 experiments using the MITI protocol gave negative results at SRI over several years of runs.

At the end of the MITI program, there was an effort made at SRI to understand why the experiment wasn't working, given the earlier positive results. From a comparison of the loading curves for the earlier runs that loaded well and gave excess heat with the MITI runs that failed, it began to become clear that there was a problem with the 0.99999 pure Pd cathodes. When the D/Pd loading becomes very high, the chemical potential is also very high, and the corresponding internal D₂ gas pressure becomes very high. The cathodes were breaking as soon as the internal D₂ gas pressure exceeded the yield strength of the pure Pd, which occurred at a loading well below the 0.95 loading needed for a positive result. Through the specification of a modified protocol, failure had been built into this part of the MITI program.

The experiment of Fleischmann and Pons of that time had evolved to a protocol that took advantage of what was called "positive feedback", where the level of excess heat production was found to be nudged higher with each calibration pulse. So, the cathodes were initially loaded near room temperature (where it is easier to get higher loading), and then nudged to higher and higher temperatures near boiling for maximum excess power operation (excess power production in this experiment was found to increase strongly at higher operating temperatures). Unfortunately, the flow calorimeters of that time worked best at a fixed operating temperature. So, the Japanese researchers attempting to replicate the Fleischmann and Pons experiment in the flow calorimeters had to change the protocol to a constant temperature protocol. There were other difficulties, and at some point technical interactions between the MITI program and Fleischmann and Pons ceased. In the end the Japanese did not obtain positive results with their modification of the experiment.

The later years of this program was a time that tested those working in the field. The great hope and enthusiasm that followed the wonderful thing that the Japanese had done in funding an effort in time turned into despair as experiment after experiment gave a negative result. We didn't understand why none of the experiments were showing excess heat in real time, and even the most stalwart in the field were beginning to doubt the positive results that had been obtained earlier. Many people left the field near the end of the program, including Ikegami. When new experiments were run at SRI with less pure, and stronger Pd, there were more positive excess heat results. Fleischmann and Pons continued to report positive results from their experiments not run at constant temperature.

With this in mind, how should we understand what this Wikipedia author has written? Presumably the lesson should be that when an experiment is not so well understood, that probably it is not a good idea to change the experimental protocol when replicating it. The author seems to have chosen to omit the associated context, so that it seems to mean more than it should.

Enthusiasm turned to skepticism as replication failures were weighed in view of several reasons cold fusion is not likely to occur, the discovery of possible sources of experimental error, and finally the discovery that Fleischmann and Pons had not actually detected nuclear reaction byproducts. (from Wikipedia)

Implied here are numerous criticisms, many of which were repeated a great many times back in 1989, but we will focus only on a subset of them here. It is without question that the initial enthusiasm did turn to skepticism; that there were a very large number of replication attempts which failed; and also that reasons were put forth in 1989 deuteron-deuteron fusion is not likely to occur; and reasons which seemed reasonable at the time that the excess heat effect is unlikely. The criticism that we would like to consider concerns the associated arguments. From what is written one might imagine that had Fleischmann and Pons detected nuclear reaction by-products in 1989 that there might be some reason to take their claims more seriously.

In their 1989 paper, Fleischmann, Pons, and Hawkins had included what they claimed was NaI data showing the gamma line from neutron capture on protons, but which instead was an artifact. This error was found immediately, criticized, and it was used to destroy the credibility of Fleischmann and Pons. A few years later (1992) Pons and Fleischmann published HPGe data that showed a high resolution gamma spectrum as well as a time history of the line, but by then there was no longer any interest in the problem. By now there have been reported many observations of low-level neutron emission from metal deuterides, so that low-level neutron emission from PdD (uncorrelated with excess heat) appears to be a real effect.

However, a more important issue concerns the issue of nuclear reaction by-products generally. In the announcement of March 1989 by Fleischmann and Pons, the important effect that was described was a very large thermal effect in their experiment, in which energy much greater than chemical was observed, with no commensurate chemical reaction products, and also without commensurate energetic nuclear radiation. Whatever was responsible, it had to be some new physical effect. Since deuteron-deuteron fusion reaction produce neutrons half the time, and tritons half the time, Fleischmann and Pons were certain that the energy was not being generated through such reactions since neither the neutrons nor the tritons were present in amounts commensurate with the energy.

The possibility that there could be any new effect was of course rejected in 1989. One argument that was made was that the nuclear four-body problem was well understood, and that there was no room theoretically for an excess heat effect of the sort claimed in the experiments. Another was that there was no basis in theory from nuclear physics or from condensed matter physics for the effect. Because of this, skeptics successfully convinced others that the experiments had to be in error. Going further, it was argued that one could put upper limits on the amount of energy produced from neutron measurements, which implicitly rejects the basic effect under discussion.

In the end, this has had an amazing effect, which is the rejection generally of experimental results pertaining to the Fleischmann-Pons experiment by the scientific community. What we know about nature generally we know because of experiment. A cornerstone of the scientific method itself is observation (experiment). The skeptics have been wildly successful in persuading others scientists (who depend on experimental observations for their own work) that experimental observations of any anomalies in PdD can and should be ignored. The willful disregard of experimental observations in this area is now a part of modern science; this, if nothing else, should cause people to think about what is happening.

Despite all details provided in the manuscript and the apparently rigorous procedure, I cannot recommend publication of the manuscript. The main reason is that the manuscript and the associated documentation target the rehabilitation of the cold fusion concept; unfortunately cold fusion has largely been disproved among the scientific community. (anonymous reviewer, 2010)

Our paper on the two-laser experiment [3] was submitted to many journals over the course of a year prior to publication. It was returned from *J Phys C* without review. Another journal had tentatively accepted it, and when we submitted the paper in final form for publication, we received notice from the editor that they had received a late set of reviewer's comments and that the paper was now rejected. This criticism is from the associated review. No response to this criticism was allowed.

References

1. M. Fleischmann, S. Pons, M.W. Anderson, L.J. Li and M. Hawkins, "Calorimetry of the palladium-deuterium-heavy water system," *J. Electroanal. Chem.*, **287**, p. 293-348 (1990).
2. D. Letts, D. Cravens, and P. L. Hagelstein, "Dual laser stimulation of optical phonons in palladium deuteride," *Low-energy nuclear reactions sourcebook, ACS Symposium Series 998*, 337 (2008).

3. P. L. Hagelstein, D. Letts, and D. Cravens, "Terahertz difference frequency response of PdD in two-laser experiments," *J. Cond. Mat. Nucl. Sci.* **3** 59 (2010).
4. P. L. Hagelstein and D. G. Letts, "Analysis of some experimental data from the two-laser experiment," *J. Cond. Mat. Nucl. Sci.* **3** 77 (2010).
5. P. L. Hagelstein, "Constraints on energetic particles in the Fleischmann-Pons experiment," *Naturwissenschaften* **97** 345 (2010).
6. P. L. Hagelstein, "Simple parameterization of the deuteron-deuteron fusion cross sections," *J. Cond. Mat. Nucl. Sci.* **3** 31 (2010).
7. P. L. Hagelstein, "Neutron yield for energetic deuterons in PdD and in D₂O," *J. Cond. Mat. Nucl. Sci.* **3** 35 (2010).
8. P. L. Hagelstein, "Secondary neutron yield in the presence of energetic alpha particles in PdD," *J. Cond. Mat. Nucl. Sci.* **3** 41 (2010).
9. P. L. Hagelstein, "On the connection between K α x-rays and energetic alpha particles in Fleischmann-Pons experiments," *J. Cond. Mat. Nucl. Sci.* **3** 50 (2010).
10. P. L. Hagelstein and I. U. Chaudhary, "Arguments for dideuterium near monovacancies in PdD," *Proc. ICCF15* (in press).
11. D. Letts and P. L. Hagelstein, "Modified Szpak protocol for excess heat," *Proc. of the 2010 ACS topical meeting on LENR* (in press).
12. P. L. Hagelstein, M. C. H. McKubre, D. J. Nagel, T. A. Chubb, R. J. Hekman, "New physical effects in metal deuterides," *Proc. ICCF11* 23 (2005).
13. P. L. Hagelstein, M. Melich, and R. Johnson, "Input to theory from experiment in the Fleischmann-Pons effect," *Proc. ICCF14* (in press).
14. P. L. Hagelstein and I. U. Chaudhary, "Excitation transfer and energy exchange processes for modeling the Fleischmann-Pons excess heat effect," *Proc. ICCF14* (in press).
15. P. L. Hagelstein and I. U. Chaudhary, "Models relevant to excess heat production in the Fleischmann-Pons experiment," *Low-energy nuclear reactions sourcebook, ACS Symposium Series* **998**, 249 (2008).
16. P. L. Hagelstein and I. U. Chaudhary, "Energy exchange using spin-boson models with infinite loss," *AIP topical volume on LENR* (in press).
17. P. L. Hagelstein, "Bird's eye view of phonon models for excess heat in the Fleischmann-Pons experiment," *Proc. of the 2010 ACS topical meeting on LENR* (in press).
18. P. L. Hagelstein, I. Chaudhary, M. Melich, and R. Johnson, "A theoretical formulation for problems in condensed matter nuclear science," *Proc. ICCF14* (in press).
19. P. L. Hagelstein, M. C. H. McKubre, and F. L. Tanzella, "Electrochemical models for the Fleischmann-Pons experiment," *Proc. ICCF15* (in press).
20. K. L. Shanahan, *J. Environ. Monit.* **12** 1756 (2010).
21. M. H. Miles and M. Fleischmann, "Accuracy of isoperibolic calorimetry used in a cold fusion experiment,
22. J. Marwan, M. C. H. McKubre, F. L. Tanzella, P. L. Hagelstein, M. H. Miles, M. R. Swartz, Edmund Storms, Y. Iwamura, P. A. Mosier-Boss and L. P. G. Forsley, "A new look at low energy nuclear reaction (LENR) research: a response to Shanahan," *J. Environ. Monit.* **12** 1965 (2010).