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Research Article

Bird's Eye View of Phonon Models for Excess Heat in the Fleischmann–Pons Experiment

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Abstract

Over the past several years, we have been developing models relevant to excess heat in the Fleischmann–Pons experiment. Here we review some of the key issues, and give an account of some of the progress that we have made. The excess heat effect is prodigious, and ^{4}He seems to be correlated with the energy, but there are no energetic particles seen in amounts commensurate with the energy. This motivated us to seek models which fractionate a large energy quantum, and the lossy spin–boson model appears to do the job. Coherent energy exchange in the fractionation limit and excitation transfer are the mechanisms required which allow us to describe a new set of reactions and associated models which seem to be relevant to the experiments. The resulting models allow us to develop interpretations for numerous experimental observations.

Keywords: Excess heat, Coherent energy exchange, Fleischmann–Pons effect, Theory

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1. Introduction

It has been more than two decades since the announcement of the excess heat effect in the Fleischmann–Pons experiment [1]. In our view, much progress has been made over these many years, and it seems appropriate here to review some of the ideas and approaches that we have been pursuing seeking a coherent theoretical explanation.

On the one hand, a great many experimental results have been put forth which seem inconsistent with what one finds in the nuclear physics and condensed matter physics textbooks. These results have been largely ignored by the mainstream scientific community, probably for several reasons; nuclear physics and condensed matter physics are mature areas of research, and present understanding in both areas appear to rule out the new effects; the effort required to sort through the associated chaff is very large, and the reward that awaits the scientist who puts the effort in is very likely the destruction of his or her career.

On the other hand, the excess heat effect is a very large effect that has been seen a great many times. One would not expect such a strong effect to occur without a good physics reason, which suggests that something very fundamental must be going on. Hence, by all rights we should be able to understand the physical mechanisms involved, and in doing

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so we should expect that known physical law should apply pretty much throughout, perhaps in ways that we had not anticipated. In what follows, we consider a selection of the basic issues that arise in the development of a theoretical model for excess heat.

2. Absence of Energetic Particles

The Fleischmann–Pons experiment as initially described is an electrochemical experiment with a Pd (rod) cathode in D_2O with 0.1 M LiOD, and a Pt anode. Electrolysis has the effect of loading deuterium into the palladium, and a high D/Pd loading is important to see the excess heat effect [2,3]. In some experiments where excess heat is seen, the energy produced is prodigious; if we reference the energy produced to the number of atoms in the cathode, we find results reported in the range of hundreds to tens of thousands of eV per Pd atom. There is no evidence of associated chemical reactions which could produce so much energy, which led Fleischmann and coworkers to conjecture that the effect was nuclear. However, there is no evidence of energetic nuclear products in amounts commensurate with the energy produced. Known exothermic nuclear reaction processes release energy through energetic reaction processes, and the absence of commensurate energetic particles rules out such reactions. Skeptics have made use of this point to cast doubt on positive experimental results, and on the competence of those working on the problem.

From our perspective, there have been more than enough replications of the excess heat effect by different groups using different methods that we are sure that the effect is real. Hence, whatever physical mechanism is responsible for the excess energy must be something new. Since it is new, the best route forward initially is probably to focus on the body of experimental work to try to understand what it is and how it works. The early studies of Miles, Bush and coworkers [4] correlated excess ^{4}He in the gas with the excess energy produced. The ratio of excess energy generated to ^{4}He produced was found to be near 24 MeV [5] (a conclusion which continues to generate controversy even now). This result already allows us to reach a rather strong conclusion about the new physical mechanism.

If the energy produced in a conventional nuclear reaction occurs as energetic particles, and if ^{4}He is involved in the new reaction process, we can ask how much energy the ^{4}He particle is born with. To address this, we note that energetic ^{4}He will occasionally collide with the deuterons in PdD (a picture of one billiard ball hitting another is useful here), producing an energetic deuteron which may collide with another deuteron to produce a fusion reaction. With a neutron detector it is possible to see whether such reactions occur; using textbook results for energy loss rates and deuteron fusion cross sections we can interpret the experimental result in terms of the energy of the ^{4}He particle. What we find from such a study is that from theory fast ^{4}He particles produce secondary neutrons readily even when their energy is modest (this effect has been seen in the experiments of Ref. [6]), and that hardly any neutrons were seen in experiments producing excess energy. We can conclude from such studies that the ^{4}He atom must be born with less than 20 keV of the 24 MeV energy we might associate with the reaction process [7,8].

3. Two-laser Experiment

In conventional nuclear reactions the energy produced appears as energetic particles. The new process associated with excess heat in the Fleischmann–Pons experiment clearly doesn't work this way, which motivates us to ask where the reaction energy goes.

This question is important, and highly nontrivial. On the one hand, there are a great many possible energetic particles in principle that we might look for (photons, electrons, neutrons, nuclei, and more exotic particles), so we need to be sure that none were missed. On the other hand, if not energetic particles, then what should we look for (since we have no previous experience with a process like this in nuclear physics or condensed matter physics)? Although the energy is seen ultimately as thermal energy, intuitively we would expect that the nuclear energy should first be converted into an intermediate form of energy prior to thermalization. Candidates for this include phonons and plasmons.

Indirect evidence supporting the conversion of nuclear energy to optical phonon excitation comes from the two-laser experiment. It was found that excess heat in a Fleischmann–Pons cell could be stimulated with a single weak diode laser [9], but generally the excess heat did not persist once the laser was turned off. Excess heat was found to be stimulated by two weak diode lasers [10], and in this case the excess heat seemed to respond to the difference frequency, and generally persist after the lasers were turned off.

This behavior is consistent with a picture in which the laser stimulation excites (hybrid plasmon-optical phonon) modes which allow the new process to go, and in the single laser experiments the modes are lossy so that the excitation doesn't persist once the lasers are turned off. In the two-laser experiment, strong responses seem to correlated with compressional optical phonon modes with zero group velocity. Since the effect persists after the lasers are turned off, it may be that some of the energy from the nuclear process is being channeled into these modes, and sustaining the excess heat effect [10].

4. Fractionation of a Large Quantum

In the experiments discussed above combined with the interpretations that we have given, there emerges a rather fundamental issue that pertains to the new physical mechanism. In a conventional deuteron–deuteron fusion reaction, we picture the two deuterons tunneling together, and then reacting to produce p + t or n + ^{3}He as reaction products which push off each other converting reaction energy to kinetic energy. In such a picture, energy and momentum conservation local to the deuterons dictates that the reaction energy goes into the kinetic energy of the products, and even tells us what fraction of the energy goes to each particle. In the new physical process under discussion, the experiments seem to point to a new picture in which: the two deuterons tunnel together; a nearly stationary ^{4}He nucleus is produced; the 24 MeV reaction energy goes elsewhere, some of it ends up as optical phonon excitation (in the two-laser experiment); and then the energy is thermalized.

Note that this is not inconsistent with the observation of ^{4}He in the gas phase, since helium can diffuse to the surface in a few hours if created within a few thousand Angstroms of the surface. In some experiments the excess power is found to increase as the operating temperature increases [11]. The temperature dependence is similar to that of helium diffusion in Pd [12], which suggests the interpretation that excess power is limited by helium clogging up the active vacancy sites, which is cleared out by diffusion.

This picture motivates us to ask about a theoretical issue involving the fractionation of a quantum: is it possible for some kind of coherent process to take a very large 24 MeV quantum and split it up into an enormous number of quanta with much smaller (10s of meV) energy. If we take 23.85 MeV and convert it into optical phonon modes at 15.1 THz (63 meV), then we would have to produce about 3.78×10^8 quanta. There is no precedence for such an effect. However, if such an effect existed, then it would become possible to understand the new physical mechanism of the Fleischmann–Pons effect, and obtain a reconciliation with nuclear and condensed matter physics.

5. Energy Exchange between Two-level Systems and an Oscillator

These arguments above motivate us to consider simple models in which two-level systems are coupled to an oscillator. The idea here is that the math associated with a complicated quantum system tends to be a real mess, so that if we replace the complicated quantum system by a simple idealization, then we have the possibility of being able to work the math and gain some understanding of the physical effects under study. So, instead of starting with the complicated physical system that has a four-nucleon nuclear physics problem coupled to a PdD lattice with optical phonon modes and plasmon modes, we abstract the nuclear system into a two-level system, and abstract the condensed matter system into a harmonic oscillator. In the end, our two-level system stands in for any transition in any nuclear system (not just the four-nucleon system), and our oscillator stands in for any optical phonon mode, acoustical phonon mode, plasmon mode, or hybrid optical phonon and plasmon mode. We are interested in whether a large quantum can be fractionated at all, independent at this point of what particular system can do the job.

Before rolling up our sleeves to analyze the problem, our intuition suggests that we should be able to exchange energy well if the transition energy of the two-level system were matched to the oscillator energy. For example, if an atom absorbs a photon we expect the excitation energy to be matched to the phonon energy; otherwise, probably energy exchange does not happen. But then we consider that there are nonlinear process that can occur. There are reports of rare gas atoms being excited in intense laser beams when several photons combine to produce the energy of the excited state. So, in some sense, the question seems to be whether it is possible to exchange lots of quanta efficiently between the oscillator and two-level systems while remaining coherent.

If we assume linear coupling in our model, we find the resulting model outlined in this discussion is one equivalent to one very well known in the physics literature [13] (the spin-boson model); it is written as

$$\hat{H} \;=\; \frac{\Delta E}{\hbar}\hat{S}_z + \hbar\omega_0\hat{a}^\dagger\hat{a} + V\frac{2\hat{S}_x}{\hbar}(\hat{a}^\dagger + \hat{a}). \tag{1}$$

This model has been analyzed in a very large number of papers, and people have found that the model is capable of reasonably efficient coherent energy exchange between the two systems as long as the number of quanta exchanged is not too large (less than 50). We are pleased that there exists in the physics literature a model that shows coherent energy exchange with some fractionation, but it is clear that the spin–boson model will never exchange enough quanta to account for excess heat in the Fleischmann–Pons experiment.

6. Lossy spin–boson Model and Coherent Energy Exchange

So, what limits coherent energy exchange in the multiphoton limit in the spin–boson model? Why can we not fractionate a large quantum, and exchange energy coherently between two-level systems with MeV energy and an oscillator with meV energy?

Well, if we make use of perturbation theory, we can show quickly that what limits the rate for coherent energy exchange in the spin–boson model is destructive interference. Indirect coupling between distant states that are resonant proceeds through all possible pathways, and when we sum the contribution from all the different pathways we find that the cancellation is almost perfect. So, if we would like for a model to have a much larger rate of coherent energy exchange, we need to eliminate this destructive interference.

The simplest generalization of the spin–boson model in which this destructive interference is removed is a lossy generalization of the spin–boson model, where we assume that the oscillator sees loss at the transition frequency of the two-level system [14–17]; the associated Hamiltonian can be written as

$$\hat{H} \;=\; \frac{\Delta E}{\hbar}\hat{S}_z + \hbar\omega_0\hat{a}^\dagger\hat{a} + V\frac{2\hat{S}_x}{\hbar}(\hat{a}^\dagger + \hat{a}) - \frac{i\hbar}{2}\Gamma(\hat{E}). \tag{2}$$

It is not difficult for a physical system to work this way in general. In the coupled nuclear and optical phonon system, we would want to see a nuclear transition mediated by phonon exchange as the basis of the spin–boson part of the model; and then we would want to see phonon exchange to a lossy nuclear or atomic system (where the nucleus disintegrates, or an atomic system in which an electron is ejected, when large quantum is transferred to it). We have analyzed coherent energy exchange in the lossy-spin boson model using different approaches and approximations. It is clear that such models give very strongly enhanced energy exchange rates. We can see this using perturbation theory [18], and using brute force diagonalization of the associated Hamiltonian [19]. We have developed simplified versions of the model that we can analyze in the strong coupling limit [20], and we can evaluate how fast coherent energy exchange occurs when a large quantum is fractionated into however many smaller quanta that we like [21].

The results of these studies so far tell us that it is possible to fractionate a large quantum, and to do it efficiently. The model says that the coupling needs to be very strong to get a fast coherent energy exchange rate for a large fractionation. The coupling strength in this model depends (linearly) on a local phonon exchange matrix element; it depends (square root) on how highly excited the oscillator is; and it depends (roughly linearly) on the number of two-level systems involved as long as each of them interact in the same way with the oscillator. The leverage in this case is in having a lot of two-level systems working together; on the one hand it is impossible within the models to fractionate a large quantum without a very much larger number of two-level systems (two to three orders of magnitude less than the square of the number of oscillator quanta) [21]; and on the other hand if enough two-level systems are involved then it does not seem to be a particularly difficult thing to do.

7. Excitation Transfer

The existence of the lossy spin–boson model tells us that a large quantum can be fractionated such that efficient coherent energy exchange is possible. The model describes a new physical mechanism in which a very large nuclear quantum can be fractionated into a large number of oscillator quanta of an optical phonon mode. But we still have work to do connecting things to a physical picture.

The problem is that there is a substantial Coulomb barrier between the two deuterons so that the associated coupling matrix element is going to be extremely small, so small that no reasonable amount of enhancement by having a lot of them is going to get us into the strong coupling regime enough to fractionate a 24 MeV quantum.

In response, we have been interested in models in which the excitation from an initial set of two-level systems (that are weakly coupled to the oscillator) is transferred to a second set (that are strongly coupled to the oscillator); it is this second set of two-level systems that fractionate the large quantum. Such a model can be written as

$$\hat{H} = \frac{\Delta E_1}{\hbar}\hat{S}_z^{(1)} + \frac{\Delta E_2}{\hbar}\hat{S}_z^{(2)} + \hbar\omega_0 \hat{a}^\dagger \hat{a} + V_1 \frac{2\hat{S}_x^{(1)}}{\hbar}(\hat{a}^\dagger + \hat{a}) + V_2 \frac{2\hat{S}_x^{(2)}}{\hbar}(\hat{a}^\dagger + \hat{a}) - \frac{i\hbar}{2}\Gamma(\hat{E}). \tag{3}$$

For this to work, we need an excitation transfer mechanism. Excitation transfer occurs in the context of spin–boson type models where there are two sets of two-level systems, but the effect requires precise resonances, and the associated rate is slow. However, when such models are augmented with loss, the rates are very much faster [21], and in the case that the second set of two-level systems are very strongly coupled with the oscillator then it is possible to make up quite a large energy mismatch [22].

8. Connection with the Physical System I

If coherent energy exchange between such strongly mismatched systems is predicted by the lossy spin–boson model, one might reasonably ask whether such an effect might be demonstrated by itself in an experiment. For example, suppose we wished to demonstrate coherent energy exchange from an excited lattice to a nucleus, then probably we would want to work with the lowest nuclear transition energy from a ground state. A list of the lowest energy transitions in the stable nuclei is given in Table 1. We see that the lowest energy transition occurs at 1565 eV in ^{201}Hg. If the vibrational excitation were uniform over the sample (e.g., the lowest vibrational mode in some orientation), then we might expect the nuclei to be excited in phase, with the resulting X-ray emission collimated due to a phased-array effect. Such an effect has been observed. In an experiment reported by Karabut, collimated X-ray emission is observed near 1.5 keV in connection with the termination of the discharge current in a glow discharge experiment [24–27]. In light of the

Table 1. Low-energy nuclear transitions from the ground state of stable nuclei, from the BNL online NUDAT2 table.

Nucleus	Excited state energy (keV)	Half-life	Multipolarity
^{201}Hg	1.5648	81 ns	M1+E2
^{181}Ta	6.240	6.05 μs	E1
^{169}Tm	8.41017	4.09 ns	M1+E2
^{83}Kr	9.4051	154.4 ns	M1+E2
^{187}Os	9.75	2.38 ns	M1(+E2)
^{73}Ge	13.2845	2.92 μs	E2
^{57}Fe	14.4129	98.3 ns	M1+E2

comments above, we view the discharge termination as providing a substantial pressure change that excites the lowest compressional mode of the sample (with a frequency in the MHz range). We propose that some of the vibrational energy is coherently exchanged to excite the 1565 eV transition of ^{201}Hg (which we imagine is deposited by the discharge, where mercury is assumed to be an impurity).

Within the framework of the theory outlined above, there are three different models that might be considered. We might take the 1565 eV transition as the two-level system, and then estimate the phonon exchange matrix element to see whether coherent energy exchange might occur. Assuming electric quadrupole (E2) or magnetic dipole coupling with electronic transitions, the resulting phonon exchange matrix element is too small by orders of magnitude to do the job. We might focus on the stronger electric dipole (E1) coupling to more highly excited nuclear states resulting in indirect coupling to the 1565 eV transition. To pursue this we developed a three-level generalization of the lossy spin–boson model and analyzed it in the strong coupling limit (so far not published). The coupling is much stronger in this case, and the analysis that results suggests that a much bigger experiment could be done in which coherent energy exchange would be predicted; however, it is clear that the Karabut experiment does not work in this way.

The third approach is to make use of the donor-receiver model formulation described in [23]; assume that the ^{201}Hg transition is weakly coupled to the phonon mode, and assume that a different and much stronger transition is present and couples to the oscillator. By matching the predictions of such a model with the Karabut experiment, we are able to develop a constraint on the ratio of the product of the zero-phonon and one-phonon exchange matrix elements to the transition energy. To be consistent, this ratio must be on the order of 5 keV or greater if the phonon exchange fraction of the interaction is low.

So, we face the question of what transition can couple so strongly. We have put in much effort to quantify electron-nuclear coupling, and by now we know that it falls short by orders of magnitude. Much stronger coupling is possible in the case of electronic (polarization) transitions, and we have begun to examine such transitions. From preliminary computations, it seems that the strongest of these gives a ratio near 0.1 eV. Our model would predict coherent energy exchange in a Karabut experiment in this case for much higher energy acoustic phonons (in the meV) range, but not for vibrations in the MHz range.

The only possible transition that is consistent with our interpretation of the Karabut experiment, within the framework of the model, is phonon exchange associated with configuration mixing of the nuclear states. This would be expected to occur due to the mass shift of the excited state configurations, as long as the phonon mode were sufficiently highly excited. Such an effect would require a generalization of the lossy spin–boson model so that phonon exchange with the strongly coupled system occurs through a mode rearrangement effect; the associated Hamiltonian would be of the form

$$\begin{aligned}\hat{H} \;=\; & \frac{\Delta E_1}{\hbar}\hat{S}_z^{(1)} + \frac{\Delta E_2}{\hbar}\hat{S}_z^{(2)} + \hbar\omega_0(\hat{S}_z^{(2)})\hat{a}^\dagger\hat{a} + V_1\frac{2\hat{S}_x^{(1)}}{\hbar}(\hat{a}^\dagger + \hat{a}) \\ & + V_2\left(\frac{\hat{S}_+^{(2)}}{\hbar}\mathrm{e}^{i\hat{S}_D} + \frac{\hat{S}_-^{(2)}}{\hbar}\mathrm{e}^{-i\hat{S}_D}\right) - \frac{i\hbar}{2}\Gamma(\hat{E}). \qquad (4)\end{aligned}$$

The oscillator frequency and phonon modes structure change due to the mass shift in such a model, as indicated by the dependence of the frequency on the $\hat{S}_z$ operator, and the presence of Duschinsky operators.

9. Connection with the Physical System II

We have put in much effort over the years trying to understand the excess heat effect in the Fleischmann–Pons experiment in terms of lossy spin–boson models and their generalizations. A direct connection can be made with the donor-receiver model described in [23] assuming that the $D_2/{}^4$He transition is the weakly coupled donor transition. The hard part of the problem has always been the identification of the receiver system. There seem to be two basic approaches to the problem, based on how the models work. Two-level systems that are long-lived work a bit differently than two-level systems that decay rapidly.

Consider two-level systems that are long-lived first. In this case, the donor–receiver model allows the subdivision of the large donor quantum into many receiver excitations, which are converted into oscillator quanta. Metastable nuclear states are very long-lived, but couple poorly with the lattice as equivalent two-level systems. In this case, we have found that the generalization to the lossy three-level system has many of the same properties, so that we expect to be able to couple indirectly to metastable states. In this approach, metastable states with indirect transition energies from the ground state that are most nearly a submultiple of the donor transition energy are favored.

If the upper state of a two-level system decays rapidly, then there is no way to accumulate any real excitation, and hence there is no way to subdivide a donor transition. In this case one can think of the two-level system as being essentially adiabatically polarized by coupling with the oscillator, but deviations from adiabaticity leads to a mixing of the oscillator and two-level system degrees of freedom. It is possible for the strongly coupled two-level system with the short lifetime to mix with the oscillator in such a way that essentially no net excitations occur, but the mixing can allow efficient coherent energy exchange with a lower energy two-level system that is weakly coupled to the oscillator. This is the situation which seems to be the case in the Karabut experiment, but it should be able to work for energy production on equal footing.

All of these lead to the following pictures for excess heat production. In the simplest version of the model for $D_2/{}^4$He transitions, the strongly coupled transition would be associated with configuration mixing of the deuteron ^{3}S and ^{1}D states (which have different masses), with phonon exchange taking place for sufficiently highly excited (Γ-point or L-point) optical phonon modes. Strong mixing of the phonon and nuclear degrees of freedom can result in energy exchange between long-lived states that are weakly coupled to the oscillator, such as the $D_2/{}^4$He (or HD/^{3}He) transition. The reaction energy ends up in the oscillator, and the host nuclei of the lattice largely do not participate.

In the next simplest version of the model, the lattice has impurity nuclei with metastable transitions that are well matched as a submultiple of the $D_2/{}^4$He (or HD/^{3}He) transition energy. The coupling to these states is much weaker, so we still require a strong configuration mixing transition (such as deuteron S/D mixing) to mix the nuclear and phonon degrees of freedom. But now most of the energy ends up going through the metastable transitions. In this case, we might expect to see a small fraction of the energy as gamma emission from the metastable state.

In a light water system, there is much less deuterium, so that the strong configuration mixing based coupling with the oscillator is more likely to be associated with the host nuclei. In this case, acoustic phonon mode excitation would be expected to be more important. The mixing of the nuclear and phonon degrees of freedom once again would allow for the $D_2/{}^4He$ (or $HD/{}^3He$) transition energy to be coupled to the lattice. The same basic model applies. However, the strong acoustic mode excitation in such a model would allow coherent energy exchange with long-lived states generally in the host lattice nuclei. Some of these long-lived states may involved deformed nuclei that have slow fission decay channels. In this case one might expect to see a "lattice-induced" disintegration effect that would favor fission channels with minimum kinetic or excitation energy [28]. Finally, we might expect the subdivision route involving metastable transitions to be allowed in the case of an excited acoustic mode and host nuclei configuration based mixing with the phonons.

Tritium production can fit in nicely in such a picture. Suppose that we have strong optical phonon mode excitation with a metal deuteride, so that mixing between the deuteron S and D states couples with the excited phonon mode. However, suppose the phonon mode is insufficiently excited to allow for a 24 MeV energy exchange, but excited sufficiently to allow for a 4 MeV energy exchange. In this case the $D_2/{}^4He$ transition cannot go freely, but a slightly more complicated $D_2/{}^4He/HT$ transition would be allowed.

10. Connection with the Physical System III

In the analysis of the lossy spin–boson model, we focused on the limit where things work well, which is the situation after things start up. However, the models also talk about the regime where things just get started, which is interesting in its own right.

In the regime where excess heat production works well, there are lots of basis states available to the coupled quantum systems, so that if some are very lossy the system avoids them in favor of less lossy ones. As a result, the model works very efficiently, with little loss. The situation is very different when it first starts up. In this case, there are far fewer states available, and the system is unable to avoid lossy states and their associated decay channels (we noted this in Section 3.4 of [19]).

We might well expect loss from the p + t and n + ${}^3He$ channels of deuteron–deuteron fusion in association with the two deuterons getting close to each other in the process of coherently reacting to produce ${}^4He$. Note that the coherent rate associated with the physical mechanism under discussion is linear in the Gamow factor, so it can be orders of magnitude faster than the incoherent fusion process. However, if the coherent process is not working very well, with a slow associated rate, then we might expect the deuteron–deuteron fusion products to show up as part of an expected decay channel at low level. Excitation transfer of the 24 MeV excitation energy from the $D_2/{}^4He$ transition in the case of acoustic mode excitation would be expected to go into producing real excitation of the very lossy host nucleus excited state. In the case of Pd, we might expect that alpha ejection might result. If it could be observed, it would support the conjecture that excitation transfer occurs in the way we were imagining (which was the reason we encouraged Lipson to see whether low-level energetic alphas could be observed along with the deuteron–deuteron fusion products). Energetic alphas were observed [29] in the 10–15 MeV region. If we think of this excitation transfer process as being something like gamma absorption, then we would imagine that a Bohr state might be formed (as in gamma absorption in Pd near 24 MeV), which would decay through all available channels. The alpha spectrum that results from 24 MeV gamma absorption in Pd looks similar to Lipson's alpha spectrum from PdD. The Bohr state in Pd produces fast protons and neutrons more efficiently than alphas, so we have been interested in energetic proton and neutron emission which should accompany the Lipson energetic alphas. The first sign that the energetic neutrons in the right energy range might be present came from experiments reported by Roussetski [30] in which neutrons near 14 MeV were seen with CR-39 in amounts inconsistent with what was possible for secondary DT reactions. Remaining to be clarified is the situation in regard to energetic proton emission above 10 MeV, which seem not to be present in Lipson's experiments.

A modification of this picture is in order based on Lipson's observations of fast alphas from light water experiments, where excitation transfer of the 24 MeV quantum would not be expected from the $HD/{}^3He$ system. The resolution in this case is that the mixing of the phonon and nuclear degrees of freedom occasional spreads the oscillator distribution sufficiently that energy can be absorbed due to electron–nuclear coupling (involving an outer orbital that is sensitive to vibrational excitation), where the strongest coupling occurs with the giant dipole resonance. Such a mechanism would yield fast alphas on an equal footing with heavy and light water experiments, consistent with Lipson's observations.

11. Connection with the Physical System IV

We discussed a route for tritium production that involved a $D_2/^4$He transition and HT/^{4}He transition, both of which are weakly coupled to the lattice, that could allow for tritium production as a favored coherent pathway if there were not enough mixing with the phonons to transfer 24 MeV of energy. This notion motivates us to think about the ^{4}He/ n+^{3}He channel in analogy with the ^{4}He/HT channel. In previous years, we dismissed the ^{4}He/n+^{3}He channel in connection with excitation transfer and energy exchange mechanisms since the neutron is free. However, the more significant issue is how long the system remains localized. If we suppose for discussion that the relative energy is near zero, then there seems to be no reason that a neutron channel couldn't exist similar to the tritium channel. We are tempted to think of the Wolf experiment in connection with this conjecture [31,32]. The Wolf experiment is interesting in particular since the current density was much lower than for excess heat production, but also low relative to experiments where tritium production was observed (but higher than Wolf had used earlier for neutron measurements).

For completeness we note that p + t/^{4}He and t + t/^{6}He have the potential to be source transitions in place of d + d/^{4}He and p + d/^{4}He discussed above. Given the difficulty of working with tritium in such experiments, these are probably of academic interest only.

12. D_2 and Vacancies

In the new reaction schemes discussed above, the starting point is molecular D_2 or molecular HD in the lattice. The notion of molecular D_2 in PdD is controversial even today, and there are as yet no observations of which we are aware. It has been argued over the years that the electron density is too high in bulk PdD for D_2 to occur, and we are in agreement. If so, then our focus should be on defects, where the electron density can be lower. The simplest example is a monovacancy, and this has been the focus of our attention recently [33].

One can verify that the electron density at the Pd vacancy location is on the order of a factor of two below what is needed for D_2 to form. In principle we then have a solution. However, the situation is more complicated. Unfortunately, D_2 near a monovacancy is unstable if there are any unoccupied octahedral sites surrounding the Pd monovacancy. The configuration with five occupied O-sites and a D_2 molecule seems to be favored, and a recent DFT computation [34] has shown that a caging effect favors a strongly bound D_2 in a relatively high electron density region.

We have proposed the connection of this problem with the observed excess power as a function of loading in the Fleischmann–Pons experiment [33]. Until the D/Pd loading reaches more than 0.80, one would not expect much D_2 in the monovacancies. The D_2 occupation in our initial version of a statistical calculation seems to go up faster at higher loading than the excess power versus loading curve. This is thought to be due to the omission of the eight deuteron configuration in the vacancy. In this configuration, there are six deuterons in octahedral sites, and a D_2 molecule at lower electron density. The conjecture (to be tested) is that the molecular D_2 in this configuration is effectively inert since there is much less screening. If so, then a revised computation of the 7-deuteron configuration D_2 occupation should be much closer to a match for the excess power versus vacancy curve.

So, if vacancies are so important, then how are they produced? In unloaded Pd, it takes on the order of 1 eV to make a vacancy, but adding H or D stabilizes the vacancies. At very high loading (above 0.95) the vacancies become preferred thermodynamically [35]. Unfortunately, the diffusion rate is very slow, so that diffusing even one lattice constant within a month is unlikely near room temperature.

We have conjectured that vacancies form in the Fleischmann–Pons experiment through inadvertent codeposition. Some of the Pd dissolves off of the cathode surface into the electrolyte, and then it codeposits back on over the course of the experiment. Lithium from LiOD in the electrolyte is absorbed into the near surface region [37–42], which may make dissolution of the Pd more likely [43] under anodic polarization (which is sometimes used as part of the loading protocol). Evidence in support of Pd codeposition in the Fleischmann–Pons cathodes comes from observations of Pt on the outer surface layer along with Pd [36]. If the loading happens to be 0.95 or higher, then this codeposition should produce superabundant vacancies [35]. As a result, we would expect the active region in the Fleischmann–Pons experiment to be the outer 100–300 nm of the cathode. If so, then we should re-think codeposition experiments, or seek other materials in which molecular D_2 forms naturally without such heroic requirements.

13. Making Phonons

In the mechanisms reviewed above for $D_2/^4He$ transitions, the generalized lossy spin–boson models indicate that little excess heat is expected until the oscillator is very highly excited. We note that the thermal excitation of the oscillator is insufficient to promote the new process. So, how can we excite the optical phonons?

In the Fleischmann–Pons experiment, the thought is that when deuterium fluxes through the codeposited region near the surface, that the hopping associated with the diffusion is efficient at generating optical phonons. We would expect such a source to be nonspecific in that pretty much all of the phonon modes would be excited, and probably only a small (per cent) fraction of this excitation will be suitable for our needs. Excess heat has been seen to increase roughly linearly above a threshold in many different Fleischmann–Pons experiments, a behavior consistent with how we expect the models to work. A key goal of our modeling effort is to compute the threshold current density directly from the model, but this has not yet been done. As noted above, excess heat was seen to be stimulated in single laser experiments, which we interpret as producing a weak excitation of hybrid plasmon/optical phonon modes. Probably the nuclear energy in these experiments go into these modes, but the modes are likely too lossy to be self-sustaining near 500 THz. In the two-laser experiments, the optical phonon modes are stimulated [9,10]. Excess heat is often seen to persist after the lasers are turned off, which is consistent with the lower loss near 8, 15 and 21 THz. In both single-laser and two-laser experiments, the laser polarization is p-polarization, resulting in the stimulation of compressional modes [44].

Direct stimulation using THz radiation has been discussed by not tried yet. A barrier in electrochemical experiments is that THz radiation is strongly absorbed by the electrolyte. A much needed experiment is one in which the relative strength of the Raman sidebands are detected during excess power production in a two-laser experiment. If the nuclear energy goes into these modes, we should be able to see it in such a Raman experiment.

14. Getting the Helium Out

If ^4He is made as part of the new mechanism, then we would expect helium to accumulate in the monovacancies, reducing the efficiency of D_2 formation. Helium diffusion is slow, so that if the codeposited layer in the Fleischmann–Pons experiment is sufficiently thin then it can diffuse away. If we take the observed profile of codeposited Pt as a indicative of the thickness of the codeposited layer, and use the diffusion coefficient of helium in Pd as representative, we can get a consistency check that much of the helium should diffuse out into the gas within a few hours of having been produced.

However, in experiments where helium accumulation is an issue, we would like to find a way to get it out more rapidly. The largest available leverage in this case is through increasing the diffusion coefficient, by increasing the temperature. Fleischmann and Pons introduced the notion of positive feedback [45,46], wherein a heat pulse associated with calibration was seen to raise the level of excess power. If the temperature increase resulted in enhanced helium diffusion, then we might interpret the effect as simply activating more monovacancy sites.

Storms reported a measurement of the increase in excess power with temperature leading to an activation energy of 670 meV (see [11]), which is essentially the same as the activation energy for helium diffusion in Pd [12].

15. Modeling

A major goal of our research effort is to develop a numerical simulation model for the Fleischmann–Pons experiment. Based on the discussion above, all of the various pieces seem to be available for such a modeling effort. It seems useful to consider briefly what might go into such a model. To begin with, we require an electrochemical model and deuterium diffusion model to account for the loading. One can find such a model in was is termed the hydrogen-evolution-reaction (HER) model, variants of which have been applied to the Fleischmann–Pons experiment. Loading occurs through the Volmer reaction

$$\mathrm{D_2O + M{+}e^- \rightarrow M\,D}_{ads} + \mathrm{OD^-}$$

and deloading occurs through the Tafel reaction

$$\mathrm{M + 2D}_{ads} \rightarrow \mathrm{M + D_2}.$$

So, increasing current leads to more loading, and when the loading increases the chemical potential increases, raising the rate of outgassing. At high current density, the loading is seen to drop in the experiments, which has been accounted for by the Heyrovsky reaction. Unfortunately, there is no experimental evidence that this mechanism occurs in the Fleischmann–Pons electrochemistry, and models which include the reaction are inconsistent with experimental observations of very high loading [47]. As a result, new models are needed. The situation is complicated by the large number of impurities that accumulate on the electrochemical surface. There are also complications in the diffusion coefficient, which is moderately high in the alpha phase, very low in the mixed phase region, and very high in the beta phase.

To model the Pd dissolution and subsequent inadvertent codeposition is largely problematic, since the dissolution and codeposition rates have not been studied in the experiment. However, reasonable models for the vacancy fraction can be developed as a function of the loading and temperature. Since numerous impurities are codeposited with the Pd, the situation is ultimately more complicated (a cleaner system would be a Pd codeposition system, or a different host that allowed D_2 occupation directly).

Some modeling of the phonon modes has been done, and crude models for the excitation of the optical phonon modes have been studied. Phonon exchange matrix elements have been formulated, but so far only a brute force computation of the $D_2/{}^4He$ matrix element has been attempted so far. Dynamical equations for excitation transfer and coherent energy exchange have been developed and studied, leading to models that behave something like experiment. However, at present an effort is underway to develop a new set of self-consistent models.

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