Observation of macroscopic current and thermal anomalies, at high temperature, by hetero-structures on thin and long Constantan wires under H_2 gas

Francesco Celani[1,2], G.Vassallo[2,3], E. Purchi[2], F. Santandrea[2], S. Fiorilla[2], A. Nuvoli[2], M. Nakamura[2], P. Cirilli[2], A. Spallone[1,2], B. Ortenzi[1], S. Pella[1], P. Boccanera[2], L. Notargiacomo[(2,4)].

[1] INFN-LNF, Via E. Fermi 40, 00044 Frascati-Italy
[2] ISCMNS, Latium#1 Group, Via Cavour 26, 03013 Ferentino-Italy
[3] DICGIM-Eng, Università di Palermo, Viale delle Scienze Edificio 6, 90128 Palermo-Italy
[4] Dip. Chimica Università "La Sapienza", Pz. A. Moro 5, 00185-Roma-Italy

Abstract
Since 2011, we introduced in LENR Research field the use of a Constantan alloy to absorb and adsorb proper amounts of H_2 or D_2 (concentrated and/or mixed with noble gases of low thermal conductivity) and to generate thermal anomalies even at low temperatures (>200°C wire temperature). Based on this idea, we developed a reactor with a core of sub-micrometric layered Constantan wires that produced measurable excess power and showed result with some reproducibility. During the years, we modified this base configuration with the purpose of improving both the reproducibility and the Anomalous Heat Effect (AHE). We used fiberglass sheaths for ensuring electrical insulation and found out, by chance, that this material even improves the performance of the reactor. In the most recent configuration, we studied the effects of the addition of Fe nanolayers to Constantan wires and of several small knots along their extension, resulting in a larger excess power growing with wire temperature increasing. Finally, we detected a new anomalous electric effect, consisting in the generation of a spontaneous voltage between the ends of a floating wire in the reactor, enhanced and stabilized by Fe presence. At the end we added some speculations/similarities about Rydberg matter, as developed by Leif Holmlid (Univ. Goteborg-SE) and Collaborators, with some of our results.

Keywords: calorimeter, Constantan, sub-micrometric surfaces, H_2 adsorption/absorption, iron, second law of thermodynamics, LENR.

1. Constantan alloys as H_2-dissociation catalyzers

Our investigations concerning the ability of metals such as Palladium (Pd) and Nickel (Ni) to absorb D_2 and H_2, in connection with anomalous heat generation at high temperatures, received a new impulse with the introduction of the Constantan alloys in the LENR research field in 2011.
Our original idea was to individuate a low-cost material able to replace the very expensive (and mechanically weak) Pd in LENR experiments.

	ΔE (eV)
$Ni_{0.3750}$ - $Cu_{0.6250}$	+3.16
$Ni_{0.6250}$ - $Cu_{0.3750}$	+2.86
$Ni_{0.8125}$ - $Cu_{0.1875}$	+2.10
Ni	+1.74
$Ni_{0.1825}$ - $Cu_{0.8175}$	+1.57
$Ag_{0.8125}$ - $Pd_{0.1875}$	+0.57
$Ag_{0.625}$ - $Pd_{0.375}$	+0.51
$Ag_{0.1875}$ - $Pd_{0.8125}$	+0.51
Pd	+0.42
Cu	-1.11
Ag	-1.42

Table 1: Catalytic power of different metals and alloys with respect to the reaction $\boldsymbol{H_2 \rightarrow 2H}$, computed in Density Functional Theory **[**20**]**.

We pointed our interest to the family of (Copper-Nickel) Constantan alloys as materials that could fit our purposes because of their ability to dissociate molecular Hydrogen [**1**]. In particular, we selected a low-cost commercial material called ISOTAN44, with atomic composition $Cu_{55}Ni_{44}Mn_1$ (Isabellenhütte Heusler, Germany). Together with a measurable H_2-diffusion coefficient at high temperature, this material offers good mechanical resistance against the aging effects of the thermal cycles and the H_2 absorption/desorption. Moreover, it has very large values of (calculated) catalytic power with respect to hydrogen dissociation, shown in Table 1.
We demonstrated experimentally that Constantan at nano/micrometric size and at low temperatures ($T > 120$ °C, in comparison with about 2000 °C for Tungsten) is able to catalyze the dissociation reaction $H_2 \rightarrow 2H$ and absorb/adsorb (at least) atomic Hydrogen even inside the bulk of the lattice, apart surface. The demonstration was reported in Ref. [**1**], chapter IV, points 18 and 19, as following: *18) To get deloading we put the cell under dynamic vacuum and increased the temperatures. 19) After several hours, we got the original starting value of $R/R_0=1$, meaning that the test was fully successful.* The fact that H_2 *decreases* the resistivity of Constantan was first reported in Ref. [**2**].

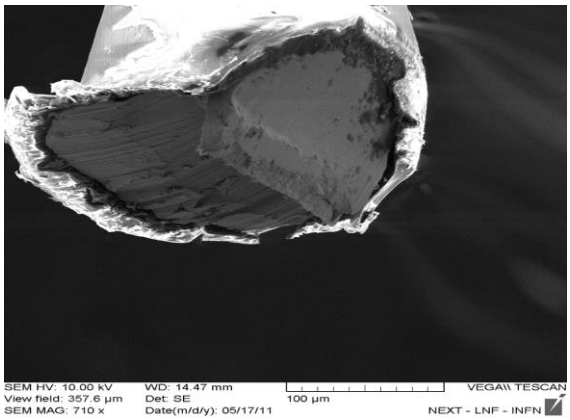

Figure 1: SEM image of the cross section of the constantan wire as provided by Isabellenhütte Heusler. The plastic cover of the wire is visible as the light area rounding the wire.

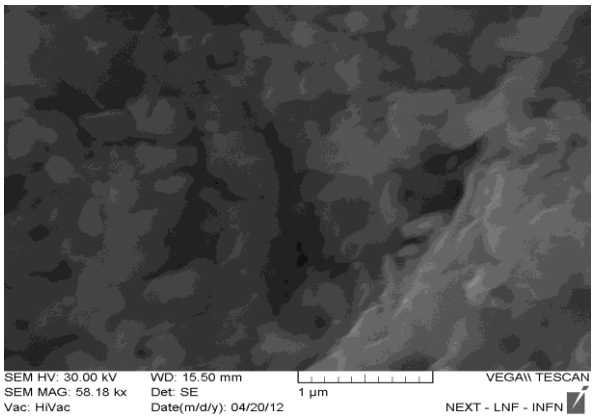

Figure 2: SEM image of the constantan wire surface at micrometric scale after repeated high-power pulse treatments.

For our experimental set-up we employed Constantan wires of length $L = 100$ cm and diameter $\Phi = 0.1 - 0.2$ mm (Figure 1). To increase their effective surface available for catalytic processes, the wires were subjected to specific thermal/electric treatments that created sub-micrometric and multilayered structures at the surface and deeper in the bulk (Figure 2). The sub-micrometric structures were just created by oxidation, with a threshold temperature of 600 °C in free air. Such structures are vaguely similar to hetero-structures.

The treatment includes electric high peak power pulses (20 kVA/g of material) with a rise time $T_r < 1$ µs, corresponding to a current density $J > 50$ kA/cm² even neglecting skin effects. Such pulses induce extremely fast thermal treatments (warming→cooling) and shock waves. A rough evaluation (by fast photo-camera) of light color emitted from the wire revealed a surface temperature even larger than 1000 °C in some specific tests. At the end of the process we obtained glassy materials at the surface.

The treatment just described produces sub-micrometric geometries, a sort of chaotic mixture of Ni, NiO, Cu, CuO, $Ni_xCu_yO_z$, reducing/avoiding, at the same time, the usual (deleterious) self-sintering processes due to the high temperatures. SEM observations revealed that the wires so treated had a large number (up to 700 in some samples) of multilayered structures with thickness of 20 -100 nm.

The number of layers was **roughly** characterized by preliminary experiments using 10, 20, 50, 100 pulses, by SEM and "oblique" cross section of the wire. Among others, we observed that the "distance" between layers DECREASES increasing the number of pulses. Sadly, the original documents (papers and CD) of such introductive test, located in another laboratory, were destroyed by a "third part" on February 2015 together with other materials and documents.

Our treatment was inspired by "*Melt Spinning and Quenching"* metallurgical process, largely used by Prof. Yoshiaki Arata and his Collaborators (Osaka and Tohoku Universities, Japan) to produce *nanomaterials* (Pd, or Pd_xNi_y, both dispersed into a matrix of ZrO_2 at 65% concentration) for his Solid State Fusion devices under interaction with pressurized (up to 60 atm) D_2/H_2 at 150-300 °C [**3**]. In the quenching process their cooling rate was over 100000 K/s. The main aspect of Arata's technique was the "ultra-fast quenching" to get glassy-like materials. Arata used fast rotating Cu disk where the mixture of Pd (35%) and Zr (65%) was dropped from the melted state (about 1600 °C). We employed, instead, ultra-fast powerful electric pulses with fall time <1 µs. Anyway, we needed just cooling from about 900 °C down to 650 °C. With very long and thin wires it is easy to perform it in short time, just by "natural cooling", because of the dependence of emitted power as T^4 (in K degrees), i.e. the well-known Stefan-Boltzmann law.

2. First generation experiments: the introduction of Constantan wires.

The dissipation reactor we realized to perform the tests with the new generation Constantan wires consisted of a mica sheets (used in electrical heating elements) support on a central Stainless Steel (SS) tube ensuring electrical insulation, on which two wires, one active (the surface-modified constantan wire) and the other supposed inert (Ni-Cr control wire), were parallel and helicoidally rounded. The Ni-Cr wire (because intrinsically stable against oxidation or other stresses) was used to give power to the reactor itself (indirect heating). The core of the reactor was contained inside a borosilicate Schott Duran glass tube with 3 mm thick wall. Temperatures at the external glass wall and inside the reactor were detected by means of several Type K, SS-screened (diameter 1.5 mm), MgO insulated, thermocouples [**1**]. Calibrations were made by noble gases (He, Ar) with different powers applied to the inert wire.

The first test was conducted in an atmosphere of H_2/Ar mixture in the ratio 75/25 at 7 bar of total pressure. The power input was 48 W. Figure 3 shows the behavior of the measured quantities with time. In green color are shown the temperature of the external borosilicate wall, while in red the temperature of the mica inside the reactor. The key monitor parameter is the ratio R/R_0 between the resistance of the wire at a given temperature T and that at room

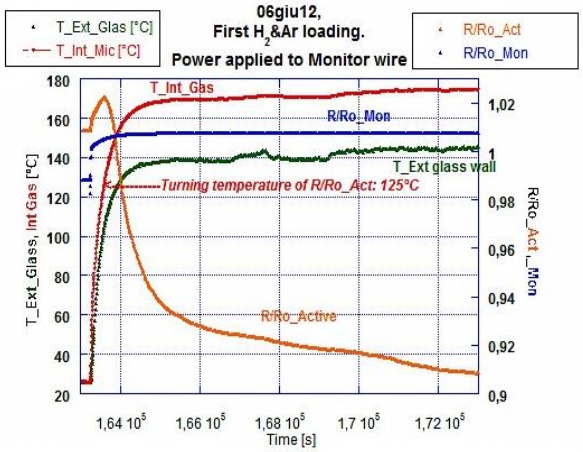

Figure 3: Time behavior of the measured quantities during the first loading by H_2/Ar mixture: T of the external glass (green), T of the internal mica support (red), R/R_0 of the inert wire (blue), R/R_0 of the active wire.

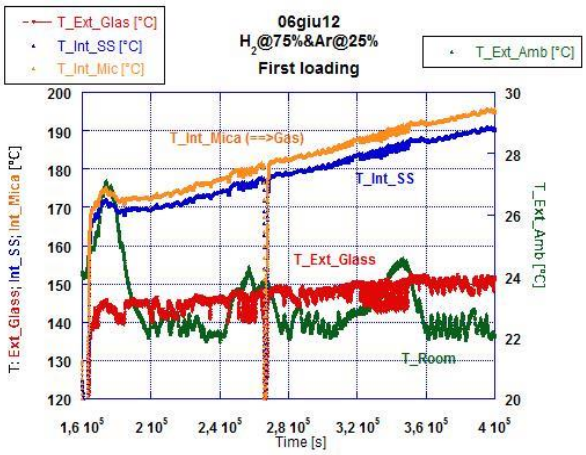

Figure 4: Temperature of the external glass wall (red), the internal SS tube (blue), the internal mica support (orange) and the ambient (green) as a function of time.

temperature T_0. For Constantan, this ratio, because of Hydrogen interaction, decreases with increasing temperature and time. In blue we indicate R/R_0 for the inert (Ni-Cr) wire and in orange R/R_0 for the active (Constantan) wire. We just recall that one of the key characteristic of Constantan is its excellent resistivity stability ($\pm 1\%$) from -75 up to 500 °C.
We observed that when temperature inside the reactor reached 120 °C, R/R_0 of the active wire dropped down to 0.92 in about 2500 s and to 0.88 in 100000 s. Correlated with this decrease of the resistance, we observed also an increase of the excess power at the output of the reactor. Correspondingly, all temperatures related to the reactor grew. External glass temperature increased from about 140 °C to 150 °C; SS tube temperature from 168 °C to 190°C and gas temperature from 170 °C to 195 °C. These variations are not related to room temperature changing. Instead, room temperature instabilities somehow helped the anomalous heat generation, introducing non-equilibrium conditions. In fact, after long time room temperature went back to its initial value, while heat production continued increasing.
During the several tests performed in Frascati with main instrumentation by Agilent (and many ancillary home-made instrumentations), the excess power ranged between 2 up to 12 W (few times) at the reference value of 48 W of input power. When taking place, the typical values of excess power were in the range of 5-10 W. We found no difference in operating the reactor in Constant Current regime, mostly used, and in Constant Voltage regime.
On the occasion of the National Instruments Annual Meeting in USA (NI-Week, August 2012, Austin-TX-USA), the reactor was disassembled from Frascati Laboratories-Italy, shipped and there reassembled, working in a public demo for three days. We also observed the highest values of maximum excess power for this experimental set-up: about 21 W with indirect heating (power applied on the inert wire) and about 25 W with direct heating of the active wire against an input power of 48 W. Just after the NI Week, the reactor was again shipped to South Korea for our participation at the ICCF17 Conference at Daejeon. Even there, overcoming the new strict-rules conditions of the air travel from USA (because of safety rules, no gas inside, apart from air, and/or no vacuum/pressure conditions were allowed), the reactor functioned properly with quite reproducible results: 5 ÷ 15 W of anomalous heat excess with 50 W of electric input power. The values were lower than in the test performed during NI-Week. Moreover, for safety reasons, the reactor was operated for most of the time in Constant Voltage regime, both at NI-Week and ICCF17.
When we went back to Frascati, after several cross checks, we realized that the NI system (HW/SW set-up on the whole) in our hands underestimated the value of electric input power in the regime of Constant Voltage by 11.11% in the range of input power of 40-60 W, i.e. that used in the experiments. Considering such unexpected problem, the real values of AHE power would change to: 8-20 W at Ni-Week, 0-10 W at the ICCF17 Conference (supposing similar HW arrangements).
We remark that all the data were and are correct in Constant Current regime.
The reported lower values are however closer both to our starting values in Frascati and to the results of the subsequent experiments performed by the Martin Fleischmann Memorial Project group but using a batch of Constantan wire with starting *composition different from the old batch* prior to 1970 that we used in the first series of experiments [see next section for further details].
About the overall better performances during the NI-Week, in absence of any systematic study we can only suspect a positive effect from an accident happened during the preparation of the set-up: some vapors of silicon oil, from the rotary pump, went inside the reactor chamber. We also tried to remove the possible residual deposits by heating the wires.
Anyway, such accident, according to us, was a further strong indication about the *catalytic origin* of the AHE effect, at least with our materials and operating points.

3. Second generation experiments: the addition of glass

The successive series of experiments exhibited an unsatisfactory overall reproducibility. Using SEM/EDS/ICPMS analyses, we found out that the first batches (produced before 1970) of raw material we used in our experiments had a composition different from those later used. Analyses revealed a Fe contamination in the order of 1000-5000 ppm, and locally up to 10000 ppm.

Because of a budget cut in the late 2013, we were forced by external events to redesign and reschedule our experiments with the purpose to study again and more deeply some of the most interesting effects obtained in the past and, if possible, to increase the AHE.

In the new experimental set-up we modified the geometrical disposition of the wires inside the reactor [**4**]. The wires were no longer two, but three: a 500-layers Constantan wire, a 2-layer Constantan wire and a Pt wire for control and monitoring purposes. They were inserted inside fiberglass sheaths ($L = 100$ cm, $\Phi_{ext} = 1$ mm, produced by SIGI-Favier, Italy-France Company), with each fiber having a mean diameter of 5 μm, and closely braided together. The braid was then twisted around the central SS support that was likewise covered with a fiberglass sleeve with internal diameter 12 mm. As before, the core was inserted into the thick-wall borosilicate glass tube previously used.

Since February 2013, all the sheaths were embedded in a $Sr(NO_3)_2$ solution and further decomposed in SrO by thermal treatment. Strontium is a material with a *Low Work Function for electron emission* ($W = 2.59$ eV), similar to the Calcium oxide used by Yasuhiro Iwamura at Mitsubishi Heavy Industries Laboratories (Yokohama-Japan) since 1999. Electron emitter materials are empirically recognized to have "beneficent effects" on LENR reaction. The effect of Ca, Ba, Sr, Mg has been studied by us, in electrolytic environment, since about 1995. Iwamura, independently, adopted CaO in his "famous" transmutation device (2002, JJAP) by flowing Deuterium gas. Moreover, he showed that MgO is not effective, similarly to our electrolytic experiments.

We calculated the emitted power using Stefan-Boltzmann law (emission proportional to T^4, in K) for the radiated energy from the glass wall and Newton's law (proportional to T) for the energy dissipated by convection.

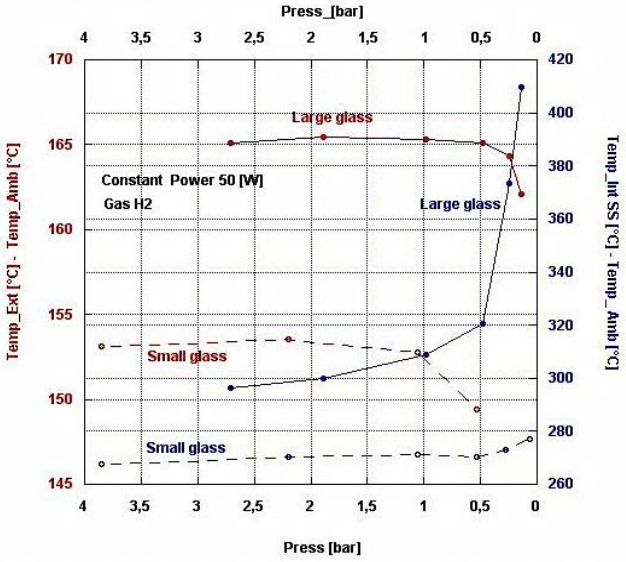

Figure 5: Data comparison between tests conducted with a small and a large amount of glass in the reactor. In red we display external glass temperature, in blue internal SS tube temperature after subtracting ambient temperature. Under the same conditions, temperature is higher when more glass is employed.

During the tests several uncontrolled and unexpected phenomena occurred - included a spontaneous overheating that damaged the 500-layer wire - and the results were unclear. Therefore, we decided that the only way to clarify the role of the fiberglass in the process was to add a larger amount of glass. The SS tube, with the wires twisted around, was inserted inside two more glass hoses.

For the calculation of the heat excess, we imposed that the tests carried out with a smaller amount of glass were the threshold, i.e. the blank. Even with such a conservative constraint, the comparison between the two experiments showed that glass has intrinsic co-effects in the generation of anomalous heat. In Figure 5 we compare the temperatures at external wall and at internal SS tube in the two cases of small and large amount of glass. We note that, under the same conditions of pressure and input power, temperature in the second case is clearly larger than the corresponding values for the experiments with a lower glass content in the reactor.

4. Effect of fiberglass on H storage

The experiments we carried out clarified that borosilicate fiberglass that we used as electrical insulator plays a role in the generation of heat excess.

We individuate the mechanism responsible for it in the adsorption property of (borosilicate) glass, which was observed by Prof. Irving Langmuir (USA, Nobel Laureate in Chemistry in 1932) since 1920 during his studies on Hydrogen dissociation at high temperatures by Tungsten (W) wires (>2000°C, at H_2 low pressures). The Hydrogen atoms, produced by the dissociation of molecular Hydrogen by means of the catalytic action of our sub-micrometric structured Constantan wires on the reaction (at quite low temperatures, about 200°C), are largely adsorbed onto the surface of the micrometric glass fibers, forming a thin film. Moreover, according to one of our Colleagues (private communication) long-time expert in Fischer-Tropsch type reactions, the oxides (in the specific case made by Fe, K, Sr, B) "locked" inside glassy materials (like fiberglass) are quite stable for long time (months) even in reducing environments and at high temperatures. The stability effect against the "evaporation" of light elements (like K) is further enhanced by Mn (present, in the type of Constantan that we used, at 1% concentration).

Langmuir measured that the density of Hydrogen atoms adsorbed onto the surface of a glass bulb (presumably of type borosilicate) kept at low temperature (about 90 K) is of the order of 10^{15} atoms/cm^2. In his experiments, the dissociation was obtained through a hot W filament in H_2 atmosphere and the fraction of dissociated molecules depended on pressure and temperature: lower the pressure and higher the temperature, larger the fraction ([**5**], [**6**]).
In our experiments the effective surface of each sheath is larger than 1 m^2. The total surface of the used fibers could be larger than 50 m^2, corresponding at about 10^{20} – 10^{21} adsorbed atoms according to Langmuir's relation.
The H atoms concentrated onto the glass surface by adsorption are much closer to each other than the Hydrogen atoms moving in the bulb as a gas, increasing so their probability of recombination in the molecular form. This reaction is largely exothermic with the release of 4.52 eV to the environment.
Moreover, the recombination time is in the time regime of so-called Femtochemistry (about 10^{-15} s). The experimental demonstration that several chemical reactions have reaction time extremely short (10^{-12}-10^{-15} s) has been performed since 1980 by Prof. Ahmed H. Zewail (Egypt-USA, Nobel Laureate in Chemistry in 1999) using ultra-short Laser pulses [**7**]. Obviously, with so short times, the peak power of recombination is extremely large, 10^{12}-10^{13} times larger than mean power at steady-state conditions.
According to this reconstruction, the net effect of the introduction of glass in the reactor is the increase of the rate of the chemical reaction of Hydrogen recombination. Therefore, adsorption property of glass appears to be a co-factor in the generation of heat excess in addition to the main unknown LENR process of non-chemical origin.
We just recall that almost all of the chemical reactions have energy, at best, of 4.5 eV. In our case, the effect lasted for several weeks and its integrated value is very far from the product of energy times the amount of material involved.
We also suppose that adsorption may enhance absorption of atomic hydrogen in constantan lattice, supporting in this way the main LENR process of heat generation. Actually, the possibility that the presence of an H film closely surrounding the wire favor the diffusion of atomic hydrogen inside the metal is not to exclude. In conclusion, further investigations aimed to clarify the effects and the role of glass in such kind of phenomena are necessary.

5. The hypothesis of energy localization

In 1954 Enrico Fermi (Italy, Nobel Laureate in Physics, 1938) and his coworkers J. Pasta and S. Ulam with the help of M. Tsingou performed, at LANL-USA, the numerical simulation of a discrete nonlinear system using the computer MANIAC I [**8**]. The dynamical system they studied consisted of 64 one-dimensional oscillators coupled to the nearest-neighbors by nonlinear force terms. Fermi's expectation was that the excitation energy associated to a normal node would have distributed along all the normal modes after a sufficiently long time interval, that is the system would have evolved toward a state of energy equipartition. Surprisingly, energy remained localized to few modes and showed a sort of periodicity, returning most of it to its initial mode.
Prof. Brian Ahern (previously at DARPA-USA) has recently revisited the Fermi-Pasta-Ulam problem/paradox, proposing it as a candidate for explaining some of the complex phenomena occurring in LENR experiments [**9**]. While in most solids the atoms reside in parabolic potential wells and therefore undergo simple harmonic motion, generally at high frequency and low amplitude, in some materials atoms are subject to a non-parabolic potential, corresponding to nonlinear force terms, that leads to nonlinear vibrational modes of large amplitude and low frequency. Hence, Ahern proposes that energy localization may take place in structures with a small number of atoms. Both properties – countable number of atoms and nonlinear coupling – are possessed by nanoparticles of size 3-12 nm (the "right" dimension suggested by Y. Arata; later experimentally reconfirmed by A. Takahashi-A. Kitamura, Univ. Kobe-Japan, in experiments of LENR by interaction of D_2 and nanoparticles at high temperatures). In nanoparticles, a large fraction of atoms is located at the surface and is subject to nonlinear binding forces with the internal atoms.
The transition to the new regime would be triggered by a pulse of energy that the cluster can receive from thermo-mechanical oscillations of the surrounding medium or from electrical pulses. As a consequence, a very small number of atoms in the cluster acquire a significantly greater amount of energy than they would in conditions of thermal equilibrium. Locally, the large oscillations manifest as hot regions. A close similarity with the phenomenon of *oscillons* in granular media can be noticed [**10**]. We note that, in our experimental conditions (i.e. specially the effect of glass fiber sheaths), the, local, pulse of energy could be provided by the $H+H->H_2$ recombination reaction
Energy localization can clarify catalysis processes, usually associated to the lowering of the activation energy of a reaction. According to the depicted scenario, few excited atoms, corresponding to a locally hot region, make their energy available for the activation of chemical reactions that could take place only at higher temperature if the cluster was absent. Ahern sustains that energy localization could also explain the initiation of LENR reactions in H_2/D_2 saturated nanostructures. As a consequence, energy localization circumvents the second law of thermodynamics, since nanoparticles act as Maxwell's demons able to convert part of their thermal energy into valuable chemical energy potential.
The violation of the second law is apparent, because not applicable to ensembles with a small number of particles. We quote Maxwell's words [**11**]: "*The truth of the second law is ... a statistical, not a mathematical, truth, for it depends on the fact that the bodies we deal with consist of millions of molecules... Hence the second law of thermodynamics is continually being violated, and that to a considerable extent, in any sufficiently small group of molecules belonging to a real body.*" Violations of the second law at nanoscales have also been observed experimentally as occasional short-time (less than 2 seconds) fluctuations around the thermal equilibrium state ([**12**], [**13**]).

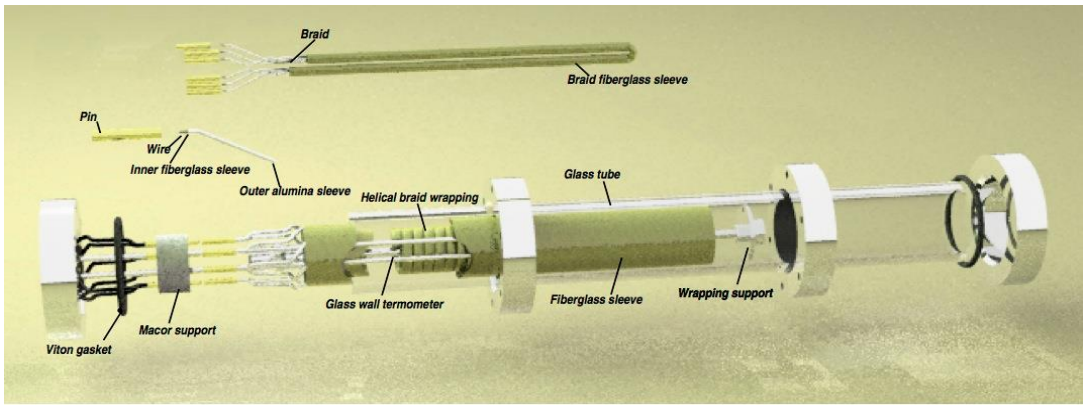

Figure 6: Schematic of the third generation experimental set-up.

The catalytic action of nanostructures at the surface of our surface-modified Constantan wires can partially explain the thermal anomalies we found in our experiments, as they enhance H_2 dissociation even at temperatures $T << 800$ °C.
If further confirmed, the energy localization would be the mechanism for coordinating the casual thermal motion of particles in nanometric regions of matter into localized high-energy oscillations.

6. Spontaneous voltage generation

In our experimental set-up we can control only two wires at the same time. For this reason one of the Constantan wires is not connected to the Data Acquisition System (PIXIe, NI) and left unconnected ("floating"). However, we measure periodically its resistance by means of a general-purpose high sensitivity multimeter (Fluke 187) to evaluate the amount of adsorbed Hydrogen. When the wire is heated in the presence of Hydrogen, its resistance ratio can decrease up to 0.7. Anyway, for what we know from "open literature", any systematic study on the relationship between the amount of Hydrogen absorbed and the decrease of Constant resistance is not available. We have just qualitative data about the correlation of the two quantities.
On June 25, 2014, we noted just by chance that the floating Constantan wire generated by itself a macroscopic voltage of the order of hundreds of microvolts that resulted function of many parameters: temperature, type of gas, pressure, resistance ratio. The highest measured values were about 1400 μV for the tension and 120 μA for the current with duration of only few hours, while stable outputs were about half.
We remind that the spontaneous tension cannot be ascribed to the usual Seebeck effect, because we considered only one single wire and not a junction of two different materials as in the thermocouples.

7. New third generation experiments: the effect of Iron

In previous experiments we found out that Iron contamination in the wires had a positive influence in terms of stability and excess power of the reaction. Hence, we decided to develop a procedure to add Iron of nanometric sizes to the surface of constantan wires and even deeper into the bulk for some microns during our thermal/electric treatments for the preparation of the nanolayers.
From a chemical point of view, Fe is characterized by a solubility of Hydrogen into lattice that increases largely with temperature: in 100 g of material, from 0.37 cc at 400 °C to 7 cc at about 1000 °C. To fully exploit such Fe property, the reactor had to reach higher temperatures than we previously obtained. For this reason, we added another sheath over the usual borosilicate glass one, made of alumina (Al_2O_3), with a higher melting temperature ($T_{max} = 1200$ °C). Figure 6 shows a complete schematic of the reactor and in Figure 7 we report a picture of it, taken during the execution of one of the several experiments conducted.

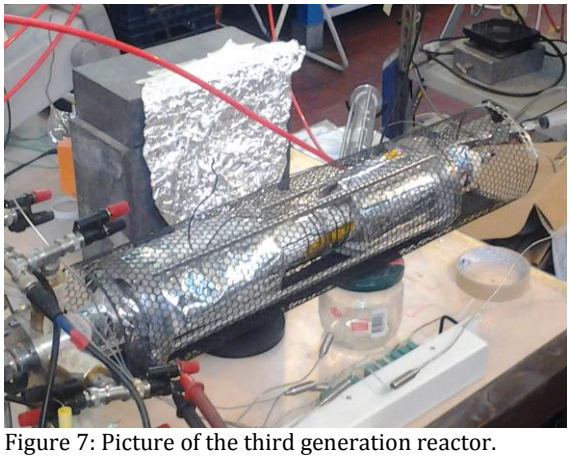
Figure 7: Picture of the third generation reactor.

To increase wire temperature at constant input power, we used a mixture of H_2 with other low thermal conductivity noble gases (Ar, Xe). The effectiveness of such mixture was verified by comparing the results about heat excesses.
With the new procedure, fully developed at INFN-LNF, we produced 20-40 Fe thin layers, similar to multiple hetero-structures, at wire surface. Moreover, we introduced further non-equilibrium conditions in the wire by making several (up to 20) knots with hole diameter 0.3-2 mm. These knots represent local geometrical variations of the path of the current flowing in the wire and are crossed by the lines of the magnetic field they generate. Because of the large currents (up to 2.3A) we inject in the wire, they are place of large thermal non-homogeneities. The tests we carried out with all

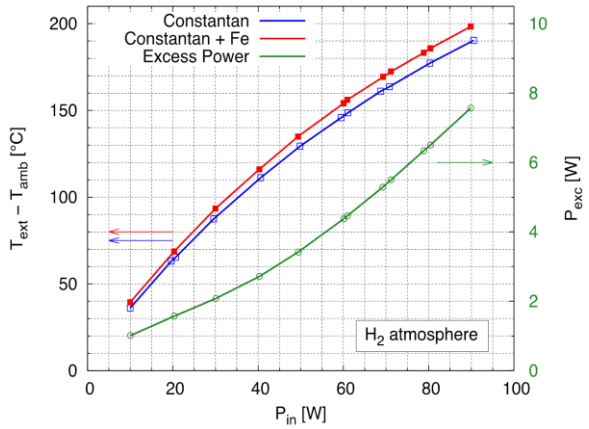

Figure 8: Tests performed in H_2 atmosphere for the configurations with knots with (red) and without (blue) Fe addition. The difference of power between the two configurations is displayed in green.

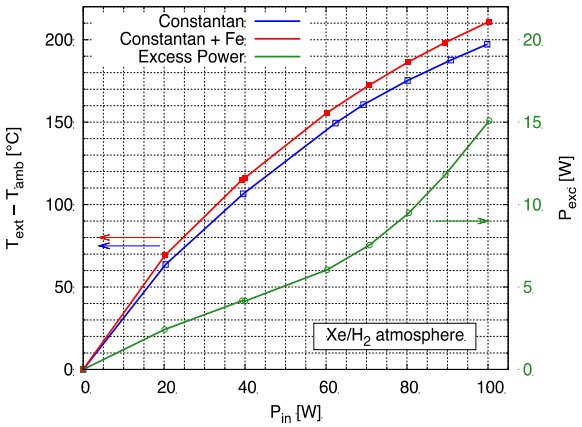

Figure 9: Tests performed in gas mixture atmosphere of Xe (1.4 bar) and H_2 (1.7 bar). The meaning of the colored curves is the same of Figure 8.

different combinations of elements (wire with/without Iron/knots) showed that the new configuration (Iron plus knots) offers measurable advantages in terms of Hydrogen absorption and Anomalous Heat Excess.

As usual, we calculated very conservative estimations of the excess power, imposing as blank the corresponding result obtained with the configuration with no Iron in the wire. The best result (by Xe/H_2 mixture) was 15 W against an input power of 100 W. The local temperature of the wire was estimated, through the Pt wire, in around 800 °C.

In Figure 8 we report the results of the tests carried out in Hydrogen atmosphere. $T_{\text{ext}} - T_{amb}$ is plotted as a function of the input power in the case of standard Constantan wire (blue) and Fe-added constantan wire (red). In green we indicate the excess power of the configuration with Iron with respect to that without it. Clearly, excess power grows with temperature. This behavior was confirmed by the experiments with Xe/H_2 atmosphere, where larger wire temperatures were reached (Figure 9). Wire temperature was estimated through SS-support temperature T_{ss} measured by the thermocouples (Figure 10). For comparison, while at an input power of 90 W excess power is about 7.5 W by pure H_2 atmosphere, this raises up to 15 W by gas mixture.

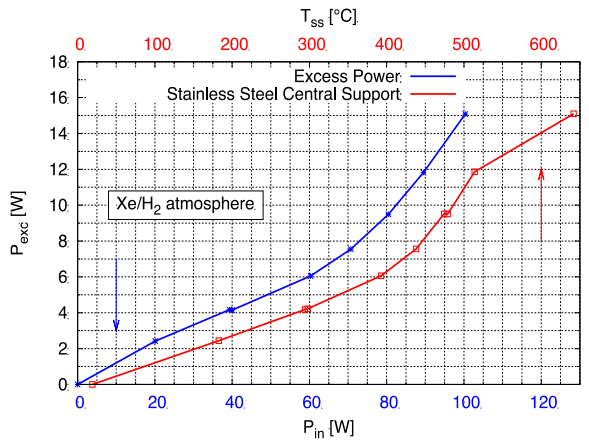

Figure 10: Tests performed in gas mixture atmosphere of Xe (1.4 bar) and H_2 (1.7 bar). The temperature of the SS internal support is showed in red. The difference of power between the configuration with Fe and without Fe is in blue.

We also verified the presence of a spontaneous voltage in the non-powered wire in the reactor. In wires having several knots with hole diameter smaller than 1 mm and filled with Iron at nanometric size, we observed in gas mixture atmosphere currents up to 150 μA and voltages up to 1900 μV, stable over long times. We compared current generation for different wires with the same number of knots and measured values about 2.2 times larger with Iron addiction. In particular, we ascertained as extremely important for maximizing the effect the local presence of Iron in the knots.

8. Discussion on the indetermination of temperature measurements.

As regards the **thermometric experiments** and the relative indetermination of the results, we used 3 different approaches/typologies/analyses:

A) Experiments performed in 2012-2013, i.e. the so-called first series.
B) Experiments performed during 2014, in which we studied the effect of **fiberglass** addition, as presented at *MIT March 21-23, 2014 Colloquium on Cold Fusion effects*.
C) Experiments concerning the effect of **Fe addition** together with a wire geometry with several knots (main argument at ICCF19, April 2015).

First of all we recall that the AHE are considered real if, and only if, there are simultaneous increases of both the internal and external temperatures of the reactor, at a given input constant power used as reference.

For the experiments of **type A** we adopted the approach of performing calibrations by inert gases, mainly He or Ar before H_2 addition. He has a thermal conductivity similar to H_2. Ar has a lower value of such parameter, about 7 times.
The improvement of the overall performances using a low thermal conductivity gas, i.e. increasing the wire temperature at constant input power, has been discovered by us since 2010, employing both Pd and/or Ni wires. At that time we used flow-calorimetry and the effects were out of doubt. The main drawback was the low response time of the system: 2 measurements/day at most. With isoperibolic-type measurements we could make up to 5-6 experiments/day.
Because we used a mixture of H_2 and Ar in the real experiments, we carried out the same procedure for He/Ar mixtures. Furthermore, in the old experiments, we realized that one of the reference "good working points" was at an electric input power of 48 W. As a consequence, the results made public are mainly at the input power of 48 W (few times 50 W). All the works performed at different input powers were not shown or discussed in public and used only for internal discussions in the working group.
The main disadvantage of such approach is the large indetermination, usually quantified in ± 1 W and in some specific conditions up to ± 2 W. The typical excess power when the system showed "useful" effects was in the range of 5-10 W during the test performed at Frascati Laboratories using the Agilent DAQ. In conclusion, the detected excess power, even in the worst situation, is out of doubt.
As regards the experiments of **type B**, they actually consisted in the comparison of 2 different experiments (always at the same power of 50 W but varying the pressure of H_2 inside the chamber from 3.8 down to 0.5 bar at low glass content and from 2.7 down to 0.1 bar for large amount of glass) *by dismantlement of the internal set up for the addition of further glass fibers*. In this case the comparison is more difficult. Anyway, the difference on both the external (about 16 °C, from 149 to 165 °C) and most internal temperatures (over 50 °C, from 270 to 320 °C) at 0.5 bar of pressure is so large that one can hardly infer that the results are meaningless or invalid. In short, adopting for the calculation of the true effective area of the reactor just a value of length = 10 cm, diameter = 4 cm and for the (convective) Newton component a value of 15, we conservatively imposed that the experiment with low amount of glass is the blank, i.e. equal to the input power of 50 W.
In such condition, the excess power of the configuration with large amount of glass seems to reach a value as large as 11.7 W.
In conclusion, even supposing an indetermination of ± 3 W, the effect seems to be real.
About the experiment of **type C**, the comparison is performed in a very conservative way. We have two Constantan wires, with the same length and diameter, both with several knots, where the only difference is the addition of at most few mg of Fe inside the knots of the "active" wire. Fe is added through a very diluted solution of $Fe(NO_3)_2$ in HNO_3 (at about 5% of concentration), 18 times, for 14 knots. In such a way Fe is deposited in sub-micrometric layers. After such treatments, the knots show strong ferromagnetic behaviors. Each wire is put inside a borosilicate glass sheath and again inserted in an Al_2O_3 sheath ($T_{max} = 1200$ °C). The sheaths are twisted each other, about every 2 cm. Moreover, they are inserted in one more, large diameter sheath. In such a geometrical configuration it is very difficult that temperature differences arise because of some geometric effect: only "internally-generated energy" can be their source.
For such kind of set-up power indetermination can be easily kept < 1 W.

9. Conclusions

The observation of a single-wire spontaneous voltage generation in our experimental set-up, apart the aimed increase of AHE amount (using Fe in the most recent specific case), represents one of the (unexpected) result of our recent research activity. The phenomenon consists in the generation of a voltage between the extremities of the non-powered wire in the reactor.
The effect was first revealed almost casually in the second-generation reactor with a large amount of glass. Even more, the successive addition of Iron nanolayers and small knots in the wire (third generation reactor) increased and stabilized the magnitude of the generated voltage (up to 1900 μV) and current (up to 150 μA).
As concerns the anomalous heat production, Iron has a beneficial effect because of its solubility of H_2 in the lattice largely increasing with temperature, while the knots are meant to create further non-equilibrium conditions inside the reactor. With such new wire features, we obtained larger excess powers.
From our observations and experiences we deduce that anomalous heat excess and spontaneous voltage generation are somehow related to the following conditions, or at least to some of them:

- Temperature as large as possible, obviously avoiding material sintering.
- Large Hydrogen absorption/adsorption by means of catalytic materials, i.e. nanomaterials.
- Hydrogen flux as large as possible from regions at high concentration to regions at lower concentration.
- Presence of elements with Hydrogen concentration increasing with temperature, like Fe.
- Presence of non-equilibrium conditions as large as possible: this is the main condition for getting any type of thermal or electrical anomaly.

We highlight that wires with good performances in terms of heat excess showed remarkable values of spontaneous voltage. One key aspect to be clarified is the role of Strontium (Sr) in the generation of the spontaneous voltage. Supposing that the effect is due to some motion of electrons from the powered-wire toward the non-powered one, i.e. a thermionic emission or a process similar to it, an electron-emitting material like Sr (due to its Low Work Function)

might give a large contribution to it. Unfortunately, we performed no measurement of wire voltage for the old set-up with no Sr deposited on the glass sheaths and targeted tests are therefore needed.
As regards Iron, we found out that the used fiberglass sheaths (by SIGI) may contain a small fraction of Iron (< 2%) and Iron oxide (< 1%). Hence, a certain amount of Iron was already present in the second-generation experiments.
In this article we have also formulated some hypotheses about the mechanisms leading to thermal excesses in our experiments. We have focused on Hydrogen dissociation/recombination reactions, individuating three combined processes:

- The catalytic properties of Constantan help molecular Hydrogen dissociation.
- The produced atomic hydrogen is partly adsorbed at fiberglass surface. Adsorption favors Hydrogen recombination (exothermic chemical reaction) but could also promote hydrogen absorption into the metallic lattice.
- If demonstrated, energy localization at nanoscales would enhance Hydrogen dissociation by converting thermal mechanical energy in valuable chemical energy potential.

The next step of our activity is aimed to deeply investigate spontaneous voltage generation and possibly identify its nature and the variables that are related to this anomalous effect as well as to get its maximization.
As concerns the better performance of the reactor after the accident with vapors of silicon oil, we think it to be somehow related to the recent *"Breakdown of Richardson's law…."* found in the electron emission from heated carbon nanotubes [**14**]. In this study, the authors measured an emission density at large temperature ($T \approx 1800$ - 2000 K) more than one order of magnitude higher than that expected with the normal thermionic emission at macroscopic level. We just hypothesize that the heating of the wires in presence of silicon vapor/deposit may have led to the formation of carbon nanostructures at the surface, acting as enhancers of the anomalous effects produced in our reactor.
Further inspired by the experimental design of such important paper, we observe that the pointed shape of the nanotube is also found in some of the nanostructures present at the surface of our Constantan wires after the thermal/electric treatments. As a consequence of the supplied power or even of the energy localization mechanism if real, hot pointed-shaped nanostructures could be also responsible of an electron emission whose current manifests even at temperatures (averaged on macroscopic extensions of the wire, as measured by the thermocouples) smaller than 600 °C, the threshold of the known thermionic emission. We remind that also in Iwamura's experiments the anomalous effects, in the specific case "transmutations", disappear if the size of the nanoparticles is too large or the Low Work Function material used (CaO) is changed to another with higher values of Work Function (MgO) [**15**].

** Addendum: after the ICCF19 Conference, in May 2015, we become aware that Prof. Leif Holmlid (Göteborg University, Sweden) suggested the use of Iron, at nanosize, as cofactor in its Deuterium catalyzer (so-called "*hydrogen transfer catalyst"*), to increase the amount of the so-called, ultra-dense, Rydberg matter in its specific reactor by Inertial Confinement Fusion (ICF) processes. He aimed, and demonstrated experimentally possible by high quality and sophisticated charge particle measurements, to produce very large excess power (energy gain over 1000) just using Deuterium gas (made ultra-dense by a proper catalyst) as initial fuel and a table-top Laser as stimulator for the fusion processes. His main ideas are resumed in the recent Patent application EP 2680271A1 [**16**].
Moreover, Prof. Friedwardt Winterberg (Nevada University, USA), the well-known expert in ICF at International level, suggested the use of a magnetic field to increase the amount of Rydberg matter in Holmlid's experiments [**17**]. We just observe that our knots (carrying a sufficiently large current), filled with Fe and/or Fe oxides at nanosize, can represent a simple/first step, experimental set-up, to match some of such requirements.
We guess that the ultra-short time of $H + H \rightarrow H_2$ recombination reaction with a range of hundreds of femtoseconds could help the stimulation of LENR effects (extremely high peak power), especially in our set-up where we have at the same time:

- Sub-micrometric structured Constantan (large production of H);
- Large amount of fiber glass where to "store" and recombine H;
- Large electron emission as a consequence of the use of Low Work Function materials and of the increased field emission due to the low dimensionality (the trigger of the system).

We would like to inform that in some specific test where we used pure D_2 and/or Xe/D_2 mixtures (ratio 10/1) at mild pressures, we observed a certain increase of "gamma" radiation by a NaI(Tl) gamma detector, energy range 25-2000 keV (model LB125 by Berthold). Such increase happened mainly during the *variations* of operating temperatures of the system, i.e. increasing or decreasing input power. The effect lasted for several hundreds of seconds. Again, one other effect due to non-equilibrium situations. The first detection of such phenomenology happened on June 2012: was reported in a meeting on LENR held at the Italian Parliament (July 2, 2012) and discussed at the ICCF17 Conference (Daejeon, South Korea) on August 2012.
Considering the fact that such effects happened mainly using Deuterium, we can suppose that even in our experimental set-up there are places where Rydberg Matter, as supposed by Leif Holmlid, could give some (low intensity in our situation) "signal" during non-equilibrium conditions.
Further systematic work has been planned in the next experiments.
Finally, some of the Authors of this report, considering the experimental evidence that in several of the LENR experiments (worldwide performed since 1989) there is no consistence between the AHE detected and the usual nuclear

particles emitted, have the “feeling” that some of the LENR are related, for some aspects, even to the so-called Dark Matter (theoretically/experimentally necessary to explain the Universe, although its existence has not yet clearly demonstrated) and emission of new type/exotic particles like the *WIMP* (*W*eakly *I*nteracting *M*assive *P*articles). Even studies devoted to explain the large discrepancies in observations involving heat and helium released from the Earth (heat measured compared to He is too large by a factor of 20) suppose the existence of new kind of particles and related reactions [**18**].

Acknowledgements: Work partially supported, since 2011, by a (High-Tech) Metallurgical Company of NE-Italy.

References

[1] F. Celani et al., "Cu-Ni-Mn alloy wires, with improved submicrometric surfaces, used as LENR device by new transparent, dissipation-type, calorimeter," in *ICCF17*, Daejeon, South Korea, published in *Journal of Condensed Matter Nuclear Science* 13, 56-67, 2014, ISBN: 978-1-63439-142-9, ISSN: 2227-3123.

[2] W. Bruckner et al., "Oxidation behaviour of Cu-Ni(Mn) (constantan) films," *Thin Solid Films* 258 (1995), 252-259.

[3] Y. Arata and Y.C. Zhang, "Development of “DS-Reactor” as the practical reactor of “Cold Fusion” based on the “DS-cell” with “DS-Cathode”," in *ICCF12*, Yokohama, Japan, published in *Condensed Matter Nuclear Science*, 2006, 44-54, World Scientific, ISBN: 978-981-256-901-1.

[4] F. Celani et al., "Are specific glass surfaces co-factors for generation of anomalous effects, by catalytic materials, under H2 gas at high temperatures?," in *2014 MIT Colloquium on Cold Fusion effects*, March 21-23, 2014, http://www.coldfusionnow.org/wp-content/uploads/2014/03/Celani-2014-CF-LANR-MIT.pdf.

[5] I. Langmuir, "Flames of Atomic Hydrogen," *Ind. Eng. Chem.*19 (6), 667-674, 1927.

[6] F. Celani et al., "Further progress/developments, on surface/bulk treated Constantan wires, for anomalous heat generation by H2/D2 interaction," in *ICCF18*, Columbia, MO-USA, 2013, http://hdl.handle.net/10355/37367.

[7] The Nobel Prize in Chemistry 1999, http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1999/press.html.

[8] E. Fermi, J. Pasta and S. Ulam, "Studies of Nonlinear Problems," *Document LA-1940*, 1955.

[9] B. Ahern, "Energy Localization: The key to Understanding Energy in Nanotechnology & Nature," http://lenr-canr.org/acrobat/AhernBSenergyloca.pdf.

[10] P. B. Umbahnhowar, F. Melo and H. L. Swinney, "Localized excitations in a vertically vibrated granular layer," *Nature* 382, 793-796, August 1996.

[11] Ed Gerstner, "Second law broken," *Nature* (2002, July), http://www.nature.com/news/2002/020722/full/news020722-2.html.

[12] G. M. Wang, E. M. Sevick, E. Mittag, Searles D.J. and D.J. Evans, "Experimental Demonstration of Violations of the Second Law of Thermodynamics for Small Systems and Short Time Scales," *Physical Review Letters* 89, 2002.

[13] J. Gieseler, R. Quidant, C. Dellago and L. Novotny, "Dynamic Relaxation of a Levitated Nanoparticle from a Non-Equilibrium Steady State.," *Nature Nanotechnology AOP* 9, 358-364, 2014.

[14] X. Wei, S. Wang, Q. Chen and L. Peng, "Breakdown of Richardson's Law in Electron Emission from Individual Self-Joule-Heated Carbon Nanotubes," *Scientific Reports* 4 (5102), 2014, http://www.nature.com/srep/2014/140529/srep05102/full/srep05102.html.

[15] Y. Iwamura, S. Tsuruga and T. Itoh, “Deuterium Permeation Induced Transmutation Experiments using Nano-Structured Pd/CaO/Pd Multilayer Thin Film,” in *2014 MIT Colloquium on Cold Fusion effects*, March 21-23, 2014, http://newenergytimes.com/v2/conferences/2014/MIT/Iwamura-MIT-2014.pdf.

[16] L. Holmlid, "Method and apparatus for generating energy through inertial confinement fusion," EP2680271A1, Jan. 01, 2014, https://data.epo.org/publication-server/pdf-document?pn=2680271&ki=A1&cc=EP.

[17] F. Winterberg, "Ultra-dense deuterium and cold fusion claims," *Physics Letters A* 374, 2766-2771, 2010.

[18] F. J. Mayer and J. R. Reitz, "Thermal energy generation in the earth," *Nonlin. Processes Geophys.* 21 (2014) 367-378.

[19] F. Celani et al., "Experimental results on sub-micro structured Cu-Ni alloys under high temperatures Hydrogen/Deuterium interaction," in *X International Workshop on Anomalies in Hydrogen-Metal Systems*, Pontignano - Italy, 2012, published in *Chemistry and Materials Research* 3 (3), 2013, ISSN 2224- 3224 (Print), ISSN 2225- 0956 (Online).

[20] S. Romanowski et al., "Density functional calculations of the hydrogen adsorption on transition metals and their alloys. An application to catalysis.," *Langmuir* 15 (18), 5773-5780, 1999.