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Research Article

First Evaluation of Coated Constantan Wires Incorporating Capuchin Knots to Increase Anomalous Heat and Reduce Input Power at High Temperatures

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Abstract

Anomalous Heat Effects (AHE) have been observed in wires of $Cu_{55}Ni_{44}Mn_1$ (Constantan) exposed to H_2 and D_2 in multiple experiments during the last eight years. Improvements in the magnitude and reproducibility of AHE, and improvements in wire preparation and reactor design were reported by the authors in the present and previous papers. The oxidation of the wires by pulses of electrical current in air creates a rough surface featuring a sub-micrometric texture that proves particularly effective at inducing thermal anomalies when temperature exceeds 400°C. This effect appears also to be increased substantially by deposing segments of the wire with a series of elements (such as Fe, Sr, Mn, K, via thermal decomposition of their nitrates applied from a water solution). Furthermore, an increase of AHE was observed after placing the treated wires inside a sheath made of borosilicate glass (B–Si–Ca; BSC), and even more after impregnating the sheath with the same elements used to coat the wires. (continued in the next page)

Keywords: Air-flow calorimetry, Anomalous Heat Excess (AHE), Electro-migration phenomena, $H_2 \rightarrow 2H$ dissociation by Constantan, H_2 and/or D_2 absorption at high temperatures into Constantan, Low work function materials, Noble gases, Plasma surface interaction, Spontaneous voltage generation along hydrogen-absorbing wires, Surface-modified Cu–Ni–Mn alloy

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(continued from the title page)

The treated wire, comprised of knots and sheaths, was wound around a SS316 rod and inserted inside a thick wall glass reactor. The presence of thermal and chemical gradients is an important factor, especially when considering the noteworthy effect of knots on AHE. The ICCF21 Conference held in June 2018 marked a turning point, when the scientific community showed notable interest in the effects of knots and wire treatments, further increasing confidence in the approach. From that time on, attempts to further increase AHE focused on the introduction of different types of knots, leading to the choice of the "Capuchin" type. This knot design produces very hot spots along the wire and it features three areas characterized by a temperature difference up to several hundred degrees. Efforts were also made to better understand the thermionic effect of the wire, and the spontaneous voltage that arises when a second wire is introduced close by (anode). Eventually a large AHE rise was observed when an extra voltage was introduced between the active wire (cathode) and the second wire (anode) through an external power supply; a truly remarkable effect, despite its short duration due to the wire failure caused by an AHE runaway that melted the wire. This article summarizes the presentation given at the 13th International Workshop on Anomalies in Hydrogen Loaded Metals and reports the latest AHE results obtained from a new reactor design comprised of Capuchin knots and new custom manufactured, enhanced sheaths.

1. Introduction

Over the last eight years, our group observed Anomalous Heat Effects (AHE) in wires of $Cu_{55}Ni_{44}Mn_1$ (Constantan) exposed to H_2 and D_2 Constantan (CN) is a cheap alloy that can provide 1.56–3.16 eV for the dissociation of molecular hydrogen and deuterium, whereas the more studied and expensive Pd can only deliver 0.424 eV [1]. Furthermore, Constantan similarly to palladium can absorb a significant amount of hydrogen [2].

Improvements in the magnitude and reproducibility of AHE were reported by the authors of the present work in the past and related to wire preparation and reactor design [3–5]. The oxidation of the wires by pulses of electrical current in air creates a rough surface featuring a sub-micrometric texture particularly effective at inducing thermal anomalies when the wire's temperature exceeds 300–400°C and local non-equilibrium conditions are promoted.

2. Wire Treatment

The AHE appears also to be increased substantially when deposing segments of the wire with a series of elements such as Fe, Sr, Mn, K, via thermal decomposition of their nitrates, applied from a diluted acidic heavy-water solution. This treatment leads to a mixed oxides coating that dramatically change the magnetic properties of the wires. The coating turns the wire from a-magnetic to ferromagnetic. Our group has speculated also that the coil geometry of knots on the wires may further increase the observed magnetism arising from Iron Oxides containing coating. Remarkably, an increase of AHE was observed also after enclosing the treated wires inside a sheath made of borosilicate glass (B–Si–Ca; BSC), and even more after impregnating the sheath with the same elements used to coat the wires (nitrate impregnated sheaths were first dried and later heated to promote the formation of oxides).

Eventually, the AHE was augmented after introducing equally spaced knots to induce thermal gradients along the wire (knots indeed, become very hot spots when a current is passed along the wire).

Interestingly, the coating appears to be nearly insulating and it is composed of mixed oxides of the corresponding elements (mostly $FeOx$, SrO). After we observed a degradation of the BSC fibers at high temperature, an extra sheath made of quartz fibers was used to prevent the degraded fibers from detaching from the first sheath. Recently the two coaxial sheath assembly has been replaced with a hybrid single sheath developed, in a collaboration between SIGI-Favier and an Italian Metallurgical Company. The latter has not only provided materials, but since 2011 they have also independent cross-checked of some of our results in their own laboratories.

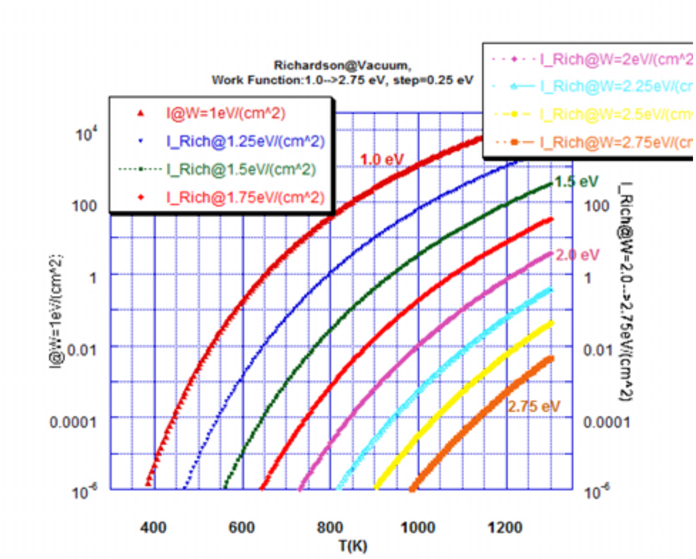

Figure 1. Dependence of electron emission on temperature (300–1300 K) and work function (1–2.75 eV).

The treated wire, comprised of knots and sheaths, was wound around a SS316 tube and inserted inside a thick wall glass reactor. The reactor operates via direct current heating of the treated wire, while exposing it to a 5–2000 mbar of D_2 or H_2 and their mixtures with a noble gas. (In these conditions electromigration phenomena are supposed to occur.)

3. Richardson Law

In 2014, the authors introduced a second independent wire in the reactor design and observed a weak electrical current flowing in it while power was supplied to the first [4]. This current proved to be strongly related to the temperature of the first wire and clearly turned to be the consequence of his Thermionic Emission (where the treated wire represents a cathode and the second wire an anode), in close accordance with the Richardson law.

Also, it must be highlighted that the key parameter of thermionic emission is the work function (Fig. 1); this is usually between 1.5 and 5 eV, and refers to the energy required for the electron emission from a surface:

$$J = A_{\mathrm{g}} T^2 \exp(-\lambda / k_{\mathrm{B}} T),$$

where:

- J the emission current density (A/m^2), Ag= λ_{R}A, λ_{R} is a correction factor depending on the material (0.5–1); $A = (4\pi \mathrm{q_e m_e k_b^2})/(\mathrm{h}^3) = 1.2\times 10^6$ (A/m^{2}K^2), Richardson constant
- $\mathrm{q_e} = 1.6\times 10^{-19}$ C, electron charge; $\mathrm{m_e} = 5.11\times 10^5$ eV, electron mass; $k_{\mathrm{B}} = 8.617\times 10^{-5}$ eV/K, Boltzmann constant.

Our experiments showed that the presence of the thermionic effect and a spontaneous voltage between the two wires is strongly associated with AHE occurrence. This observation led us to find ways to increase electron emission by the deposition of Low Work Function materials (LWFm, such as SrO), on the surface of the Constantan wires.

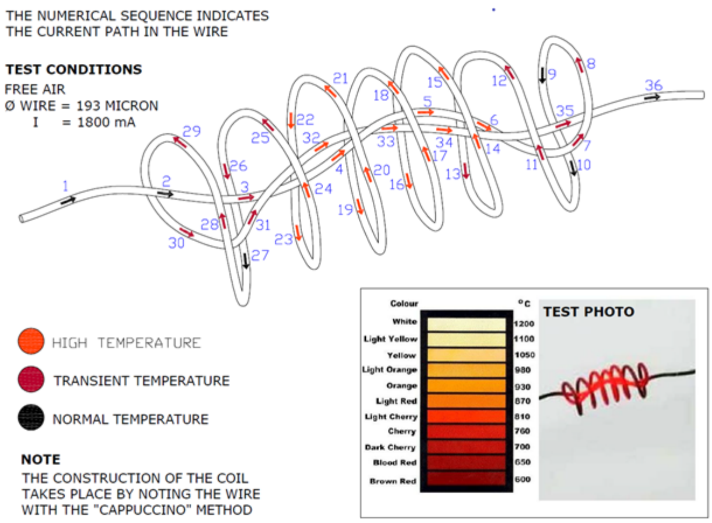

Figure 2. Picture of an eight loop knot heated in air with a direct current ($I = 1800$ mA). Wire of 200 μm diameter. If we estimate the temperature using color, the dark area is likely to be at <600°C, the external spires at about 800°C, while the inmost straight section, may reach 1000°C.

Also, the presence of thermal and chemical gradients is considered as being particularly relevant, especially when considering the large effect of knots on AHE magnitude. These experimental findings were reported at the ICCF21 Conference held on June 2018 and the scientific community showed notable interest in the effects of knots and wire treatments, further increasing the confidence on the described approach.

4. The "Capuchin knot" Geometry

After ICCF21, attempts to further increase AHE focused on the introduction of different types of knots, leading eventually to select the socalled "Capuchin" type (see Fig. 2). This knot design produces very hot spots along the wire and features three areas characterized by a temperature delta up to several hundred degrees. The temperature delta between the external spires of the knot and the internal straight segments may induce also a voltage (V) arising from an Ohmic drop along the wire, and from the different temperature between the inner part of the knot and the external spires. In other words, we may have a significant voltage arises between the relatively cold spires and the internal wire segments (up to 300–400°C hotter than the spires). Taking into consideration this difference of potential, and the emitted electrons from the warmer segments of the wire, we believe that the knot behaves as a diode.

Based on these observations, efforts have been made to better understand the thermionic effect of the wire, and the spontaneous voltage that arises when a second wire is introduced close by (anode). We emphasize that a large AHE rise was noticed when introducing an extra voltage (at low current) between the active wire (cathode) and the second wire (anode) through an external power supply. This is a truly remarkable phenomenon, despite its short duration due to the wire failure (caused by a runaway AHE melting the wire). This effect occurred in particular with 100 μm thick wires, where the voltage drop along the wire may reach 100 V and it is significantly larger with respect to the 200 μm wires. Eventually the authors observed a stunning similarity of the best performing reactor design and a thermionic diode where the active wire represents the cathode and the second wire the anode, whereas the electrodes are separated by fibrous layers impregnated with mixed oxides comprised of iron and alkaline metals.

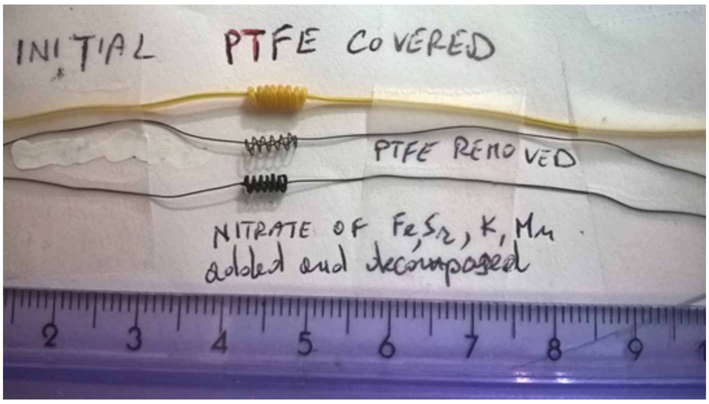

Figure 3. Photo of a typical coil just assembled (*top*), after PTFE destruction (*middle*), after nitrate addition and decomposition to oxides (*bottom*).

In short, preliminary measurements, at reduced pressure, show a current dependence as $V^{1.5}$, resembling the Child–Langmuir law for current emission inside a vacuum diode. The net result of the observations allow us to speculate on a thermionic power converter able to generate electricity through the thermionic emission of a cathode, heated by AHE, and collected by an anode (colder and/or featuring a different work function with respect to the cathode).

5. Preparation of the Knots

The knot preparation starts with a wire of a Constantan variant (Cu55 Ni45) free of manganese. The wire has a PTFE coating (the yellow material shown in Fig. 3). The diameter of Constantan wire is listed in the supplier's specifications as 193 μm We measured it as 197$\pm$3 μm. The external diameter including PTFE is 730 ($\pm$ 5) μm (Fig. 3, top). Decomposition of PTFE sheath is carried out at 550°C in air flow and at 0.15 bar for 10 ks. (Caution: a "water vacuum pump" was used to vent traces of hydrofluoric acid from the decomposition of PTFE). The wires were then dipped in 8% HNO_3 for 5 min and rinsed in distilled water. (Fig. 3 wire in the middle.) Several cycles (5–10) were repeated of deposition of diluted solution of nitrates of Fe, Sr, K, Mn and high temperature decomposition (500–800°C) to oxides. A typical procedure starts with a $\sim$200 cm wire. After preparing the knots (14 knots of eight loops each) the resulting length is $\sim$130 cm.

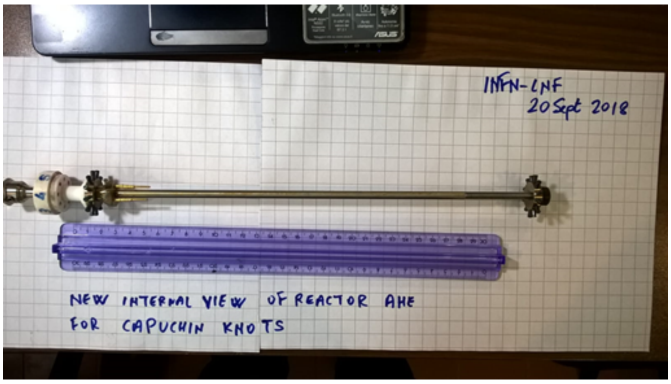

Figure 4. Supports for the wires with knots geometry.

6. Reactor Assembly

The reactor consists of a borosilicate glass tube (D= 33–40 mm, L=400 mm). A central support is used to hold in place wires and their sheaths (Pictures in Figs. 4 and 5). Thermal power was measured with air-flow calorimetry. A calibration was made using an internal tungsten lamp (Figs. 6–8). Details on the calorimetric technique can be found in the ICCF21 presentation.

7. Calorimetry

The air flow calorimeter is calibrated with a tungsten lamp heater (maximum power 230 W), which is under-powered to decrease the emission temperature of the filament. The lamp is inserted into a borosilicate tube with dimensions similar to the active reactor. Both the heater and the reactor are placed in close proximity, and covered by several layers of a 40 μm aluminum foil. The fan is 5 cm wide, operates in suction mode and has a nominal air flow of 4.445 l/s at NPT and 75 Hz. Its rate is monitored (revolutions/second) and logged in the acquisition system (based on a PXIe

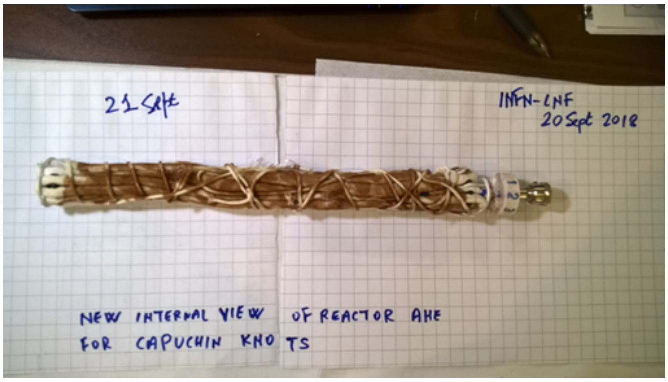

Figure 5. Reactor core, comprised of wires and sheaths made of quartz and borosilicate fibers. This “hybrid” sheath was custom manufactured by SIGI-Favier with the support of a metallurgical company in northeast Italy.

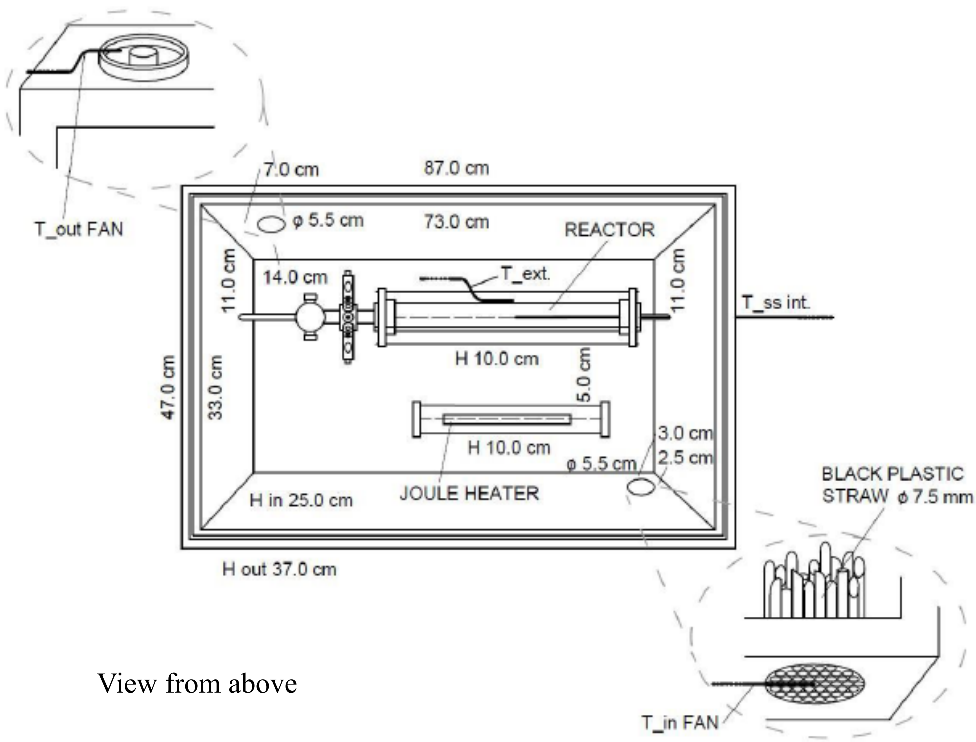

Figure 6. Schematic of the reactor and calorimeter case.

made by National Instruments). The overall average coefficient of heat exchange during calibrations is approximately 0.20°C/W and is consistent with the values of air flux, density, and heat capacity in the range of air temperatures inside the calorimeter (20–60°C). A selection of measurements is reported in Ref. [6] and Table 1 in this work.

The procedure of AHE measurement takes into account:

(a) a calibration by the sealed tungsten lamp,
(b) regular cross-check of accuracy powering a platinum wire resistor inside the reactor (which can be used as calibration resistance inside the reactor),
(c) measurements powering the active wires (CN).

8. Conclusions

Based on calibrations with the tungsten lamp at 10–120 W, the mean calibration constant in the power range of immediate interest (90–110W) was 0.200 ± 0.010°C/W. The calibration constant when powering a Constantan wire comprised of 14 knots (8 loops), has been on average 0.242± 0.010°C/W. This value was obtained at 2 bar of deuterium. When the pressure is reduced to about 0.1 bar a significant increase of the AHE was measured. A few days before the presentation of this paper, we activated a second wire inside the reactor comprised of 32 knots with four wire

Figure 7. Photo of the air flow calorimeter with both reactor (*top*) and calibration lamp (*bottom*).

loops each. Preliminary measurements confirm AHE values obtained in previous experiments with same knot design. Experiments previously reported at ICCF21 gave stable excess power of 6–7 W with an input power of 100–120 W. With the new knot design the excess reaches 20–25 W at similar input power.

Taking into consideration:

- current path in the Capuchin knot,
- size of the knot (few mm),
- large magnetism" of the wire induced by the multilayer coating of FeOx and SrO,
- "boil-off" of electrons at the inner and hotter area of the knot.

We speculate that, when in operation, a magnetically confined plasma may arise inside the knot.

Indeed, the "boil-off" of electrons, due to the low work function of the coating, may lead to a localized non-neutral plasma. The interaction of this non-neutral plasma with the nanostructures on the wires and sheaths will be object of

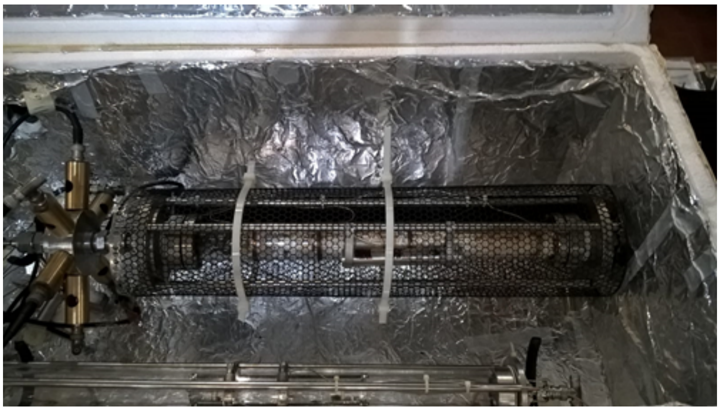

Figure 8. Photo of the reactor including a safety cage.

Table 1. The most significant measurements are summarized in this table (CN, 8N stands for Constantan wire with eight knots; 4N stands for Constantan wire with four knots).

Date DMY, Tot. time meas. (ks, kilo-second)	Type of meas.	P_w(W) V(V); I(A)	T_{in} fan (°C)	T_{out} fan (°C)	T_{SS}, int. React. (°C)	T_{ext} react (°C)	React. Gas Press. (bar)	$\Delta T/P_{in}$ (°C/W); Excess P_w (W)	Note
250918 90 ks	Calib. W lamp	0	21.2	22.4	22.9	22.3	Dynamic vacuum <0.001		Offset due to the fan.
260918 50 ks	Calib. W lamp	70.55	21.42	35.02	43.6	42.9	Dynamic vacuum < 0.001	0.1928	
6 ks	Calib. W lamp	50	21.51	32.15	38.6	37.8	Dynamic vacuum <0.001	0.2128	
7 ks	Calib. W lamp	30.2	22.2	28.5	32.8	32.4	Dynamic vacuum <0.001	0.2086	
7 ks	Calib. W lamp	10*	21.7	24.49	26.6	26.4	Dynamic vacuum <0.001	0.279	
11 ks	Calib. W lamp	120	24.6	48.76	61.7	61.0	Dynamic vacuum <0.001	0.2013	
270918 61.6 ks	Calib. W lamp	110.3	22.42	44.52	57	56	Dynamic vacuum < 0.001	0.2003	**Calibr. Ex-trap.at 100W=0.20**
7.5 ks	Calib. W lamp	90	22.8	40.2	51.5	50.3	Dynamic vacuum < 0.001	0.193	
7 ks	CN, 8N	50.6; -41.41, -1.23	22.6	32.6	291.7	110.7	Air flux, 0.1	0.198	Cleaning 8N
61 ks	Pt	65.6; -58.95 -1.11	21.9	35.67	230.9	99.6	Air flux, 0.1	0.2099 +3W	Calib. Extr. at 60W=0.20
011018 230 ks	CN 8N	91.2 -53.2 -1.71	23.2	42.5	409.9	170.4	D_2 0.92	0.2116 +10W	First loading D_2
021018 80 ks	CN 8N	98.5 -54.8 -1.796	22.7	44.0	426.7	174.4	D_2, 0.90	0.2162 +6.5 W	
031018 56 ks	CN, 8N	93.1 -53.78 -1.73	22.3	44.9	379.1	162	Xe=D_2 0.738	0.2427 +19.9W (cal.0.20)	At RT P =0.45 bar

031018 12 ks	CN 8N	100.6 - 56.0 - 1.795	23.7	47.5	397.7	170.6	Xe=D_2 0.744	0.2365 +18.4W (cal=0.20)	
031018 5ks	CN 8N	100.3 - 55.95 - 1.793	23.2	47.9	400.1	169.6	Xe=D2 0.43	0.2462 +23.5W (cal=0.20)	Press. re- duced
031018 6 ks	CN 8N	100.7 - 56.25 - 1.79	23.5	48.1	416.2	169.7	Xe=D_2 0.24	0.2443 +22.3W (cal=0.20)	Press. re- duced
031018 8.5 ks	CN 8N	100.5 - 55.47 - 1.811	24.3	48.8	443.4	172.3	Xe=D_2 0.107	0.2438 +22.5W (cal=0.20)	Press. re- duced
041018 56 ks	CN 8N	101 - 55.7 - 1.81	23.38	47.92	433.8	171.4	Xe=D_2 0.100	0.2430 +21.7W (cal=0.20)	Counter electr.at GND
041018 9ks	CN 4N	91.2 - 52.8 - 1.727	24.1	45.9	278	187	D_2 3.23	0.239 +17.8W	First time D2 on 4N
041018 6ks	CN 4N	91.05 - 53.3 - 1.708	24.08	46.27	333	191	D_2 0.26	0.2437 +19.9W	Press. reduced

*Larger value of $\Delta T/P_{\text{in}}$ due to the offset arising from the fan self-heating.

deep investigations and reported at ICCF22.

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