

ELECTROLYSIS OF LaAlO_3 SINGLE CRYSTALS AND CERAMICS IN A DEUTERIATED ATMOSPHERE

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Abstract

We have measured excess heat in solid state electrolytes, namely $\text{La}_{0.95}\text{AlO}_3$, in deuterium gas atmospheres. We have shown that an excess heat of 50 mW is observed at 550 °C, with an input power of 2 mW. However, at 620 °C, a temperature decrease has been observed. Those results have been obtained with ceramics, and attempts to do the same with single crystals have failed so far. We believe that both positive and negative temperature changes cannot be explained by a chemical reaction within the crystal.

1 Introduction

Following the discovery of "Cold Fusion" in 1989 by Fleischmann and Pons¹, numerous techniques have been proposed to duplicate this original work. In particular Forrat², proposed the use of metal oxides proton conductors as electrolytes, assuming that the reaction will occur in the electrolyte instead of the metal electrode. Following Forrat's idea, several groups³⁻⁶ have performed experiments with solid state electrolytes. The details of the operation of the system employed here have been described at the ICCF5 conference³. Therefore, we will only recall briefly in the next two sections the main important features of this approach

2 Theoretical Approach

Lanthanum aluminate has a perovskite structure with aluminum and lanthanum atoms surrounded by oxygen atoms³. When stoichiometric, the crystal is white, and behaves as a semiconductor, which conductivity increases with temperature. When there are lanthanum vacancies, (for example, with the composition $\text{La}_{0.95}\text{AlO}_3$, the crystal becomes red, and an electron type "n" conductor.) Figure 1 shows the conductivity of a single crystal of lanthanum aluminate with lanthanum vacancies (of unknown quantities) at 567 °C, and 640 °C in an argon atmosphere. When those vacancies are filled with deuterium (or hydrogen), in principle, three deuterons (or protons) can fill every three valent lanthanum vacancy, the crystal becomes white, and intrinsic. In this case, the conduction will only be protonic, and therefore as the mobility of the protons is less than the one of the electrons, the overall resistivity should be higher. However, when an electric field is applied through the crystal, there is diffusion of deuterons towards the cathode, and there can be more than three deuterons in a single lanthanum vacancy. This region of the crystal becomes blue, and it is equivalent to a "p" type conductor. The total conductivity of such a device in a deuterium atmosphere becomes complex. Figure 2 shows the current versus temperature of the same crystal where about 10% deuterium has been added to the argon.

It is interesting to note that in argon (figure 1), i.e. without deuterium in the lattice, the current increases with temperature as expected in the case of a semiconductor. However in deuterium, at similar temperatures, the conductivity is lower. In addition, the current decreases with increasing temperature, an indication that at higher temperature, more deuterium is dissolved in the lattice. At 640 °C and 710 °C, we were limited in voltage by sparking between the electrodes, and the ceramic heater. However at 742 °C, we could go to

higher voltages, namely 300 V, and at this higher temperature and voltage, the current behavior is no more linear with voltage. The overall conductivity being electronic and protonic, at higher voltages, the protonic conductivity becomes more important.

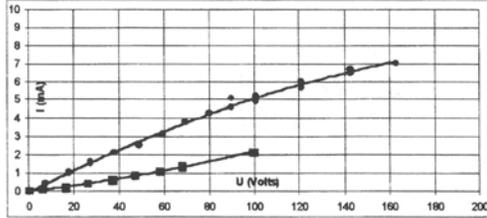


Figure 1 : Intensity current (mA) versus voltage at 567 C (squares) and 640 C (circles), in argon.

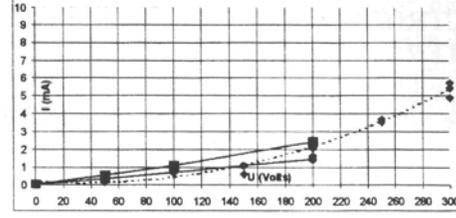


Figure 2 : Intensity current (mA) versus voltage at 640 C (squares), 710 C (squares) and 742 C in argon plus deuterium.

When the crystal vacancies are filled with deuterium, the deuterium ions are close to each other. It is then possible that native atoms are formed when an electron encounters a deuteron, creating for a short period of time an unstable atom. Its main characteristics being that the electron could spin around the nucleus closer to the nucleus as in the muonic atom. In this case, the effective mass of the electron is larger than its rest mass, because of the high density of electrons surrounding it. A reaction might occur that will produce ^4He . This model is quite speculative, but other mechanisms might actually be involved.

Experiments have been conducted with single crystals made with AlO_3 and $\text{La}_{0.95}$ using the Verneuil method and with ceramics made starting with nitrates. In both cases, the starting materials were lanthanum with 5% atomic less than aluminum. They were both of brown color, indicating the presence of vacancies. However it was not possible to measure the actual amount of vacancies. We tried to weight the samples after absorption of deuterium at 800 °C in a deuterium atmosphere for 10 hours, but in spite of the fact that the samples turned white, showing that the vacancies have been filled with deuterium, no significant weight increase was measured. Therefore we assume that there are in fact less than 1% vacancies.

We typically operate the system with two identical samples of same dimensions: 3 mm thick, 15 mm in diameter. After mechanical polishing a 1 μm layer of platinum is sputtered on both sides of the samples. They are then sandwiched between one central cathode, and two symmetrical anodes made of palladium foil (see figure 3). This attachment is placed inside a 35 mm diameter vacuum tube (stainless steel for the first experiments with ceramics, then quartz for the single crystal experiments), at the center of which we have positioned a furnace. After evacuating the chamber at a pressure of 2×10^{-2} Torr, the chamber is filled with gases: either pure deuterium, or pure argon, or a mixture of argon, and 10% deuterium. This last combination allows us to run blank experiments in argon, then to continue in a similar atmosphere with deuterium. The deuterium gas having a different conductivity than argon, at a given furnace power, the crystal temperature will be different. By adding only 10 % deuterium, the thermal conditions are similar in both cases.

Temperatures are measured by a thermocouple positioned near the sample in the gas phase, and by the resistance of the furnace. We calibrate its resistance with the thermocouple, and afterwards we utilize it as a temperature sensor. The advantage of this method being that it is an integration of the heat flux through the walls of the furnace, whereas the thermocouple gives only local temperatures. We have shown by calibration that about 80% of the heat produced in the samples is collected by the furnace. The total pressure being one atmosphere at room temperature.

In order to obtain precise temperature measurements, we operate at constant input power in the furnace, typically between 50 and 100 W, and we calculate the temperature by the

calibrated resistance of the furnace. In order to get good stability, the reaction chamber is

placed inside an enclosure in which temperature is regulated at 90°C , $\pm 0.1^{\circ}\text{C}$. Also all the electronics and the computer interface are placed inside another temperature regulated chamber at 50°C , $\pm 1^{\circ}\text{C}$. We therefore are capable of regulating the input power at better than $\pm 100 \mu\text{W}$, and therefore to measure relative temperatures with a precision of a few hundreds of a degree. Figure 4 shows a diagram of the experimental system.

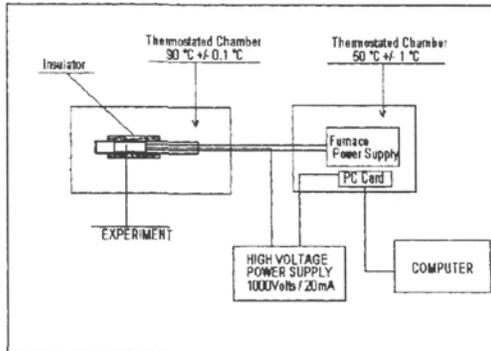


Figure 3 : Schematic of the experimental Setup

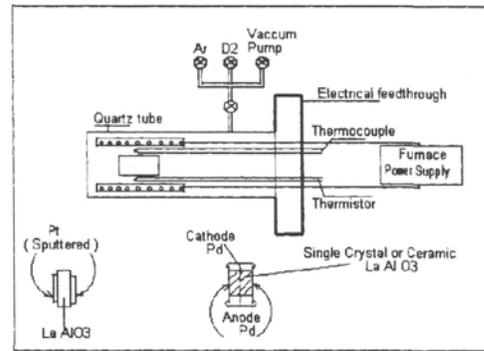


Figure 4 : Details of the chamber containing the samples.

3 Experimental procedure

After evacuation of the vacuum chamber, and introduction of gases (argon, deuterium or a mixture of both), the furnace is heated at a constant input power, in the 50 to 100 W range. When temperature has reached equilibrium, current is passed through the samples, and this input power is measured by the computer. We operate in DC mode or in pulse mode. In this latter case, we have used one second pulses every 60 or 120 seconds. The temperature deduced from the resistivity measurement is recorded continuously. Increases of this temperature is then compared to the expected temperature rise due to Joule heating.

4 Experimental results

4.1 Calibration

Figure 5 shows the temperature versus time at 100 W. At time 40 minutes, the input power is raised to 101 Watts. With an excess power of 1 Watt, the temperature rises 2.9°C .

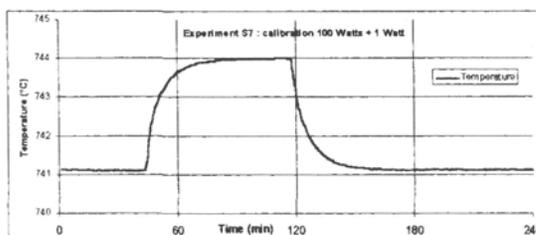


Figure 5 : Furnace temperature when power is changed from 100 Watts to 101 Watts

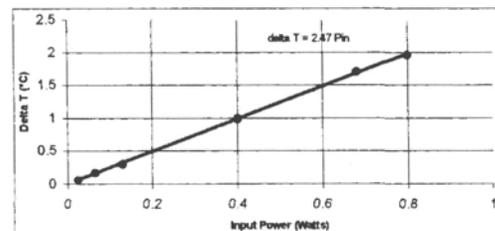


Figure 6 : Furnace temperature increase at 100 Watts, versus input power in the crystal.

In order to check the validity of the temperature measurement, we apply a current through the crystal, and measure the temperature rise as a function of this extra input power in the crystals. Figure 6, shows that this increase is linear, with a slope of 2.47 °C per Watt. This number has to be compared to value 2.9 °C per Watt obtained in the previous calibration where the extra heating power is directly put in the furnace. This indicates that 85 % of the heat generated in the crystal is collected and measured by the resistor of the furnace.

4.2 Experiments with ceramics

Figure 7 shows the temperature increase when a current of 900 Volts and 145 μ A, is passed through the ceramics. The theoretical temperature rise should be 0.4 °C. Upon observation of this curve, it is apparent that there is first a fast increase of temperature, with a time constant of a few minutes comparable to the one observed at the calibration (figure 5), then a slow increase. When the current is stopped, the reverse phenomenon occurs: there is a fast decrease followed by a slow decrease.

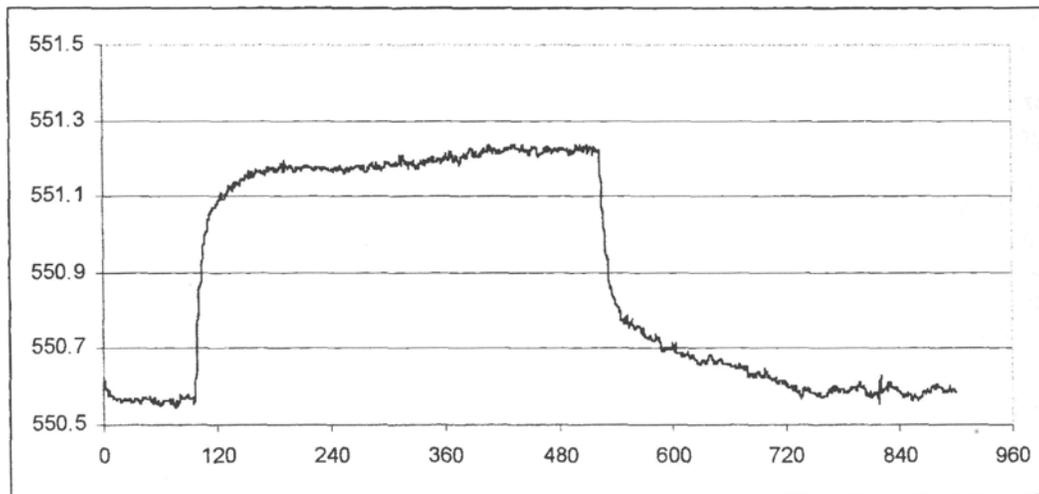


Figure 7 : Temperature rise when a DC power of 135 mW is put through the samples.

In order to eliminate the contribution of the Joule effect, we have performed an experiment using pulsed current. Figure 8 shows results obtained with 900 Volts and pulses of 1 second every 60 seconds. The input power is about 60 times less, and therefore should produce a negligible temperature rise due to Joule heating. However, temperature rises slowly by an amount of 0.17 °C, that corresponds to an excess energy of 50 mW.

In order to study the influence of the various parameters on this effect, experiments have been performed at 900 Volts, with pulses of 1/120, and at 400 Volts with pulses of 1/60 with no significant change in the actual temperature rise. However at 620 °C, we have observed a temperature decrease of the same magnitude as the temperature rise. This surprising result casts some doubts on our results. The low level of excess heat we observe cannot be caused by an artifact in our measurement techniques. We have done experiments under argon that do not show such an effect at any temperature, therefore we exclude this possibility. Also, when using a DC voltage, there is first a temperature rise corresponding to the Joule heating, followed by a temperature drop. Therefore this cannot be analyzed as an anomalous heat dissipation. We also exclude chemical reactions, since this phenomenon lasted in a one of the runs, 24 hours, and the total energy consumed is too

large to be chemical.

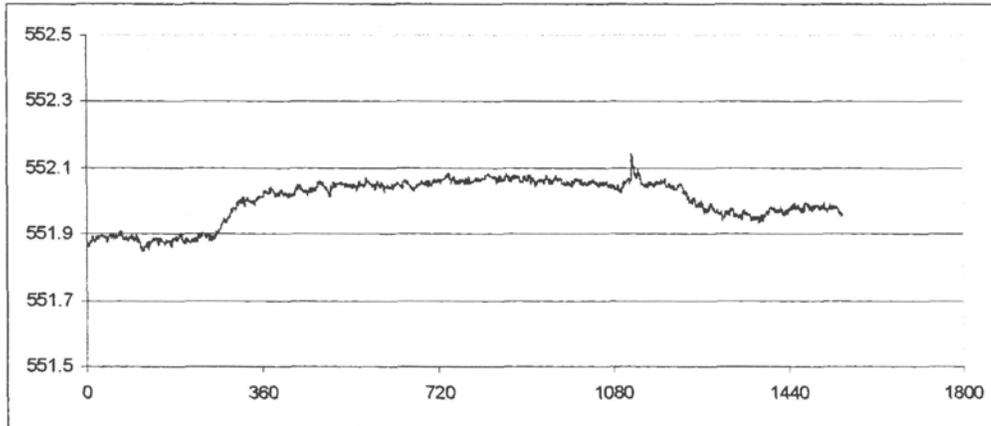


Figure 8 : Temperature rise when pulses of 900 Volts (1 second every 60 seconds, this corresponds to 2 mW) are applied to the samples.

4.3 Experiments with single crystals

Similar experiments with single crystals have shown no effect under any circumstances. We have varied the temperature, the voltage, DC or pulse, and have never seen any effect. This is in contradiction with previous results with single crystals that we had obtained³, but the samples were not the same, and the old batch seems to have worked better than the new one.

5 Conclusion

We have shown that excess heat is produced when a current is passed through a lanthanum aluminate ceramic. The temperature decrease result observed at higher temperature is unexplained yet. More work is in progress in order to amplify the phenomenon and to resolve this surprising result. The key to this approach of Cold Fusion is most likely the manufacturing of samples with large quantities of vacancies.

References

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