Excess Heat Measurement in AlLaO3 Doped with Deuterium

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Abstract:

We show evidence that solid state electrolytes can be used successfully in "cold fusion" experiments. We describe in this work that $LaAlO_3$ single crystals loaded with deuterium produce excess heat up to 10 times the amount of electrical power applied. No significant amount of neutrons has been detected.

1. Introduction

Since the public announcement of the discovery of "cold fusion" in 1989 by Fleischmann et al. [1], most of the experimental research work has been done in liquid electrolytes. However, as soon as 1989, Forrat [2] patented a solid state electrolytic device, with the reaction in the electrolyte. He proposes a process catalyzed by nascent muonic like atoms in polyvalent vacancies compensated by H^+ or D^+ ions in refractory oxides. Mizuno et al. [3] have shown that large quantities of excess heat could be generated in perovskite ceramics in deuterium atmosphere when a slowly varying current is passed through the sample.

It is the purpose of this work to repeat this early work, and to determine the characteristics of the reaction in a better controlled environment.

2. Theoretical point of view

Oxides with the perovskite structure are excellent proton conductors, when metal atoms are replaced by protons [4,5]. They are therefore a good choice for "cold fusion" experiments. In this work we have used $LaAlO_3$ single crystals. Figure 1a shows the unit cell of the stoichiometric lanthanum aluminum oxide. The structure is composed of a lanthanum atom at each corner of the cubic unit cell, an aluminum atom at the center, and an oxygen atom at the center of each face. An alternative description is shown in figure 1b, with an aluminum atom at each corner, a lanthanum atom at the center, and oxygen atoms in the middle of each side.

If a lanthanum vacancy is created (V center or p type semiconductor), the unit cell is shown in figure 1c. Since lanthanum is trivalent, three protons (or deuterons) can replace one lanthanum ion as shown in figure 1d. When a negative voltage is applied, more protons (deuterons) are attracted and can fill up the vacancy.

Figure 1e shows the structure of the cell with interstitial deuterium. Five protons can be placed in a single lanthanum vacancy. The density of deuterons is then close to that of liquid deuterium.

Intrinsic lanthanum aluminum is transparent. When lanthanum vacancies are present, it becomes red (the maximum vacancy concentration being 5%). When vacancies are filled with deuterium, the crystal becomes transparent again ([4,5]).
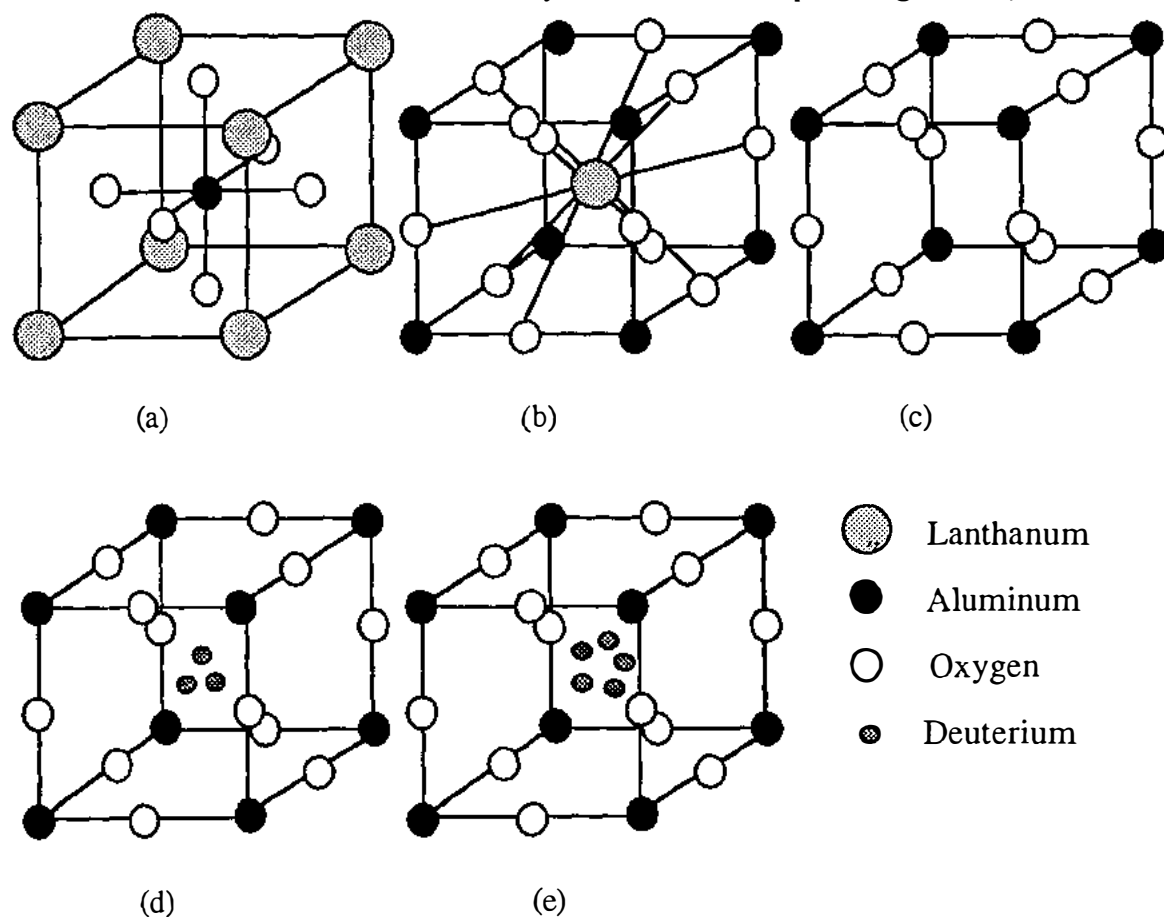

(a)   (b)   (c)

(d)   (e)

Figure 1

The LaAlO₃ perovskite type unit cell. a) The intrinsic unit cell with Lanthanum atoms at the corners and Aluminum at center. b) Same cell with Aluminum at corners and Lanthanum at center. c) Cell with Lanthanum missing creating a V center. d) Cell with Lanthanum replaced by 3 deuterons to compensate vacancies. e) Cell with Lanthanum replaced by 5 deuterons forming F centers.

When the crystal is heated in an hydrogen (deuterium) atmosphere, protons (deuterons) diffuse in the crystal. If a voltage is applied on two faces of the crystal, protons (deuterons) diffuse towards the cathode. Three zones develop, as shown in figure 2. The cathode side has excess interstitial deuterium, so that it becomes blue, (F centers), as described in figure 1e. The middle section is white, because it is stoichiometric, the lanthanum vacancies have been filled by three hydrogen (deuterium) atoms as in figure 1d. The anode side is red because it has lanthanum vacancies as in figure 1c (V centers).

Numerous such crystals can be used as proton conductors, however rare earth aluminates are very well suited because aluminum and lanthanum are both solely trivalent. AlLaO$_3$ proton conductivity has been extensively studied for fuel cell applications ([4]).
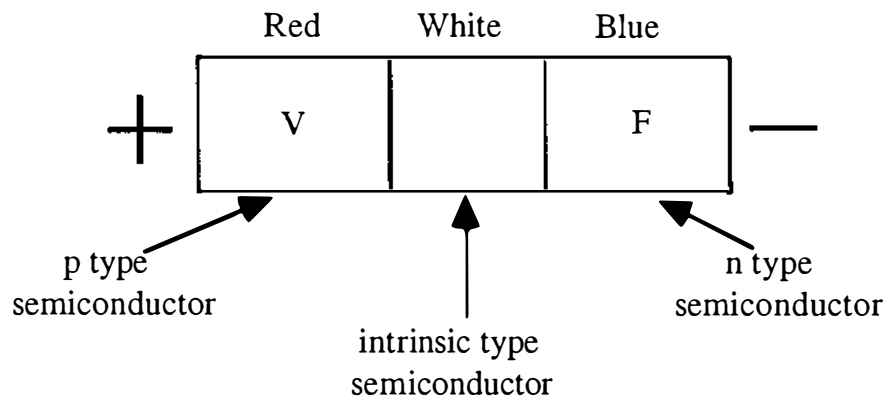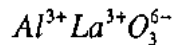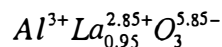

Figure 2

When a voltage is applied through the sample at high temperature in an hydrogen (deuterium) atmosphere, the anode becomes red, because of depletion in proton (deuteron) contents, the cathode becomes blue due to proton (deuteron) enrichment, and the middle returns white because the vacancies are neutralized by the protons (deuterons).

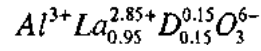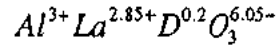The structure of the intrinsic aluminum lanthanate is:

$$Al^{3+}La^{3+}O_3^{6-}$$

and the crystal appears white.

A crystal with 5% vacancies will be red and will have the following structure:

$$Al^{3+}La_{0.95}^{2.85+}O_3^{5.85-}$$

When the crystal is heated in a deuterium or hydrogen atmosphere, ions diffuse in the sample and vacancies are occupied by the deuterium ions, and consequently the crystal recovers its intrinsic white color. The structure of the crystal is now:

$$Al^{3+}La_{0.95}^{2.85+}D_{0.15}^{0.15}O_3^{6-}$$

After application of a voltage an F zone appears at the cathode with the composition:

$$Al^{3+}La^{2.85+}D^{0.2}O_3^{6.05-}$$

Therefore, when a voltage is applied through the sample at high temperature in an hydrogen (deuterium) atmosphere, the anode becomes red, because of depletion in proton (deuteron) contents, the cathode becomes blue due to proton (deuteron) enrichment, and the middle returns white because the vacancies are neutralized by the protons (deuterons) as shown in figure 2.
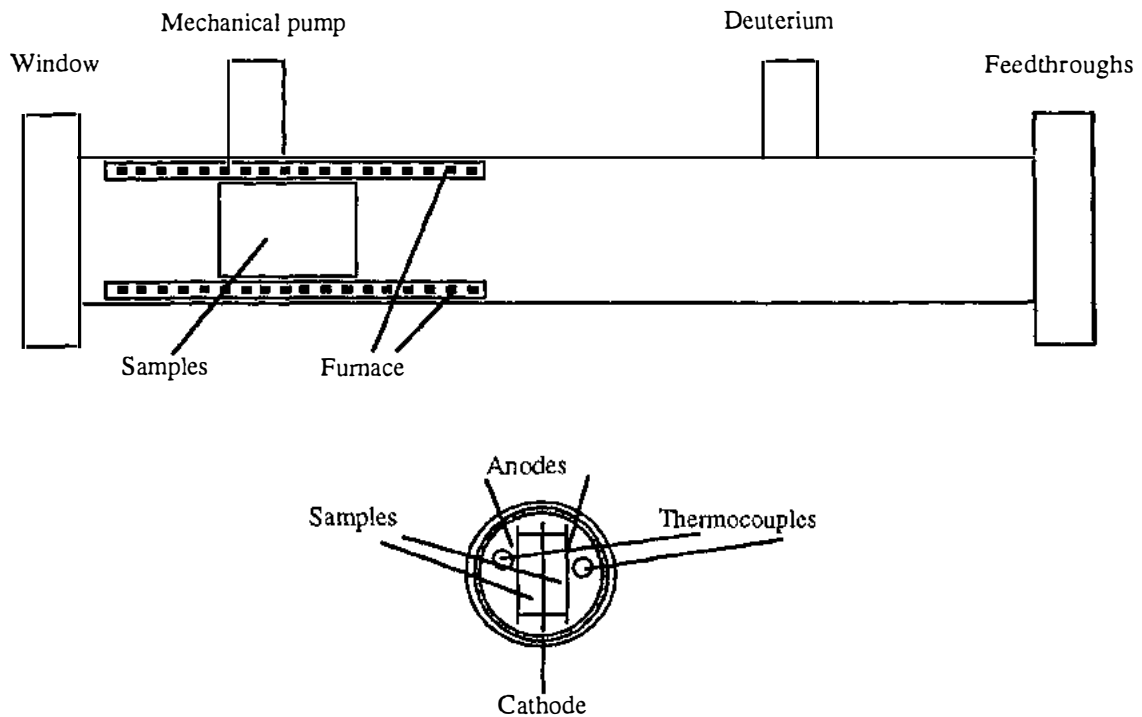

Figure 3
Schematic of the experimental setup. The samples are sandwiched between two palladium foils. They are heated by a cylindrical furnace. Two thermocouples measure temperatures near the sample. A glass window allows viewing of the sample, and a gauge monitors pressure. The cylindrical chamber is 35 mm in diameter and 300 mm long.

3. Experimental set up

The samples we have used are LaAlO3 single crystals with unknown amounts of vacancies, but probably less than 5 %, and in some cases doped with rare earth metals. They have been prepared in the sixties by the flame fusion process. They are cut with a diamond saw: 4 cm^2 in area and 3 mm thick. The first experiments have been conducted with a thin film of gold sputtered on each side. In one occurrence, when the crystal has been heated at high temperature (500-600 C), the gold layer dissolved in the crystal, so later bare crystals were used successfully.

Figure 3 shows a schematic of the experimental set-up. The system is a 300 mm stainless steel tube 35 mm in diameter, positioned horizontally The crystals are sandwiched with 100 µm thick palladium foils. Two chromel-alumel thermocouples measure the ambient temperature near the sample. A window at the other end of the tube allows viewing the sample. A gauge is used for crude measurement of the pressure in the chamber.

The sample is positioned at 250 mm from the flange, so that the feedthroughs do not warm up significantly. A palladium foil is used as cathode between two identical wafers cut from the same crystal rod. Two palladium foils used as anodes are then placed symmetrically on the other faces of the crystals. These two anodes are hold together by a molybdenum clamp. The symmetric design has the advantage of eliminating the problem of the mechanical attachment of the electrodes without producing a short circuit.

Temperature is measured two ways: on one hand, two chromel-alumel thermocouples are positioned in the ambient deuterium gas surrounding the crystal. And on the other hand temperature is deduced from measuring the resistivity of the tungsten wire used in the furnace heater. This resistance has been first calibrated against the two thermocouples, and shown to behave linearly with temperature in the whole temperature range. The advantage of using this second type of temperature measurement is that it is an average temperature and not a local measurement as with thermocouples.

All measurements are made with a PC based data acquisition system. The heating power of the furnace is maintained constant by regulating the applied voltage.

A helium-3 neutron detector is positioned 30 cm from the sample, and its measurements are recorded at all times. An internal source inside the detector produces a signal at a frequency of 0.534. Therefore any neutron emission from the sample should add to this signal.

4. Experimental procedure

The crystals are first heated in air to remove any hydrogen present. After that crystals are red indicating the presence of lanthanum vacancies. It is then heated in deuterium for several hours at about 800 °C. At this point crystals turn white.

Crystals are placed in pairs in order to simplify the attachment as described in the above section. The stainless steel chamber is evacuated using a mechanical pump down to a pressure of 10^{-2} torr. Deuterium is subsequently introduced at about atmospheric pressure. Power of the furnace is raised slowly, without passing current through the crystals. After a few hours, when the desired temperature is reached, and remains stable,

a voltage is applied through the crystal. This is done with four 120 Volts power supplies mounted in series. To avoid any power surge in the crystal when the current is applied, we use the current limitation mode.

Blank experiments have been performed in a similar way, but with a virgin crystal, without any deuterium. We can therefore compare directly data obtained with samples loaded with deuterium and blanks experiments.

5. Experimental results

A blank experiment is shown in figure 4. Sample temperature is deduced from the measurement of the resistance of the furnace. The furnace power is 150 Watts, producing a sample temperature of 545 °C. The electrochemical power is 250 mW (250 V, 1 mA). The temperature rise is 0.5 K.
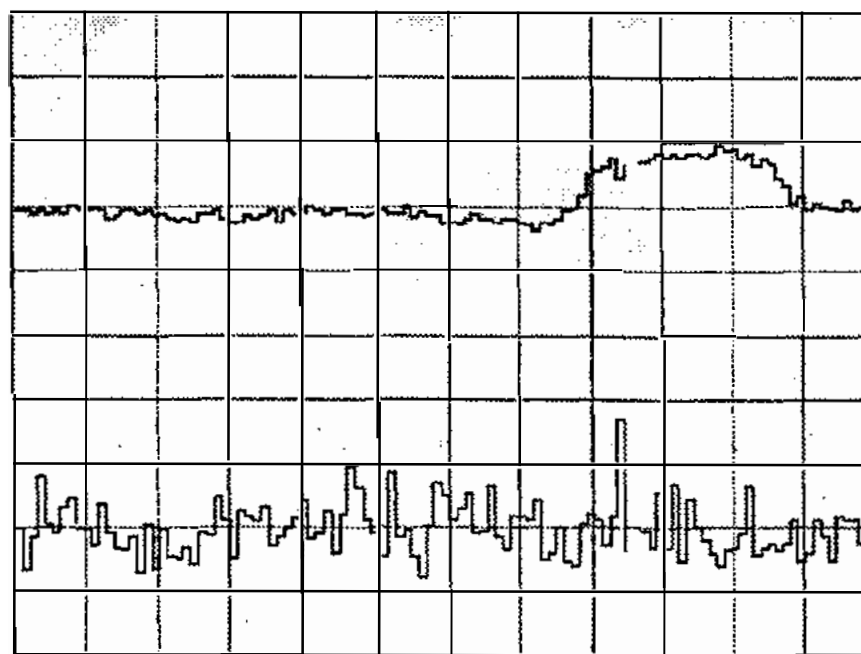

Figure 4
Blank experiment. Top curve: temperature, bottom curve: neutron counter.
Time: full scale 120 minutes. Temperature: full range 5 K.

Figure 5 shows similar curves, but the crystals are doped with an unknown amount of praseodymium, and loaded with deuterium. The furnace power is 150 Watts, and the electrochemical power is 50 mW (250 V, 0.2 mA). The temperature rise is 1 K, and corresponds to 500 mW. The excess energy gain is therefore 10.

The lower curves in figures 4 and 5 represent the neutron counts, and show no sign of increase. However in one occasion a very slight increase 0.1 counts/sec has been measured. We cannot exclude that this signal is due to noise, because further experimentation has shown that the detector is very sensitive to noise.
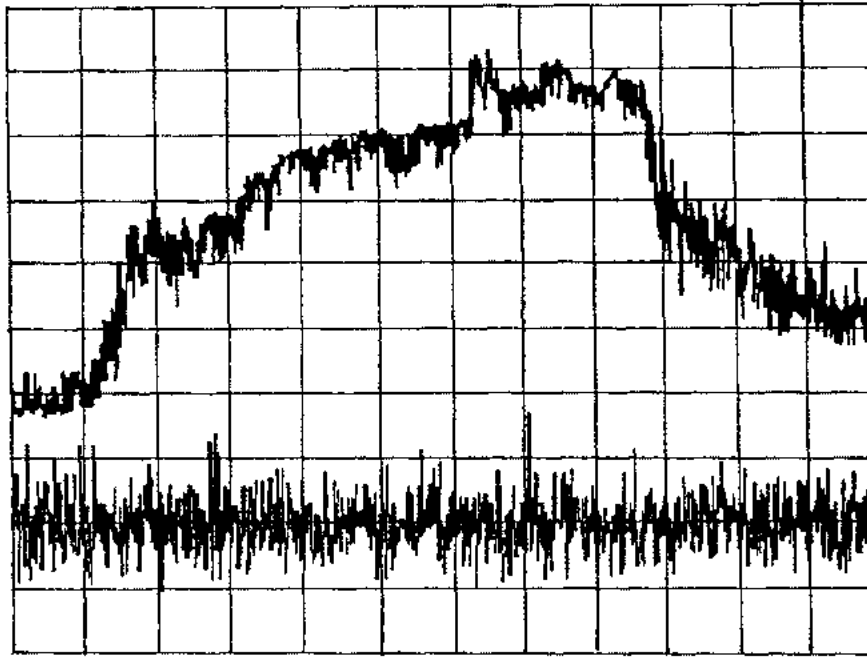
Figure 5

Experiment in deuterium. Top curve: temperature, bottom curve: neutron counter. Time: full scale 18 hours. Temperature: full range 5 K.

An interesting observation is the potential difference between anode and cathode when the voltage generator is disconnected. Values of up to 1.9 Volts have been measured. This indicates that upon application of the initial voltage through the crystal, there is a non-uniform distribution of the deuterium inside the crystal. This voltage decreases with a time constant in the 5 to 10 minutes range.

6. Discussion

A comparison between temperature curves of figure 4 and 5 shows that in the blank experiment, temperature increase is achieved in 3 or 4 minutes, whereas with the active sample the temperature rise happens after at least one hour. This indicates that during the process of passing current through the sample, there is probably diffusion of deuterium inside the crystals.

Experiments have been carried out in a closed cell. So if we assume that all the deuterium molecules have reacted somehow, we obtain an energy of 10 eV per molecule. This is not possible because after the experiment is stopped, there is still plenty of deuterium.

We therefore believe that the reaction mechanism is either nuclear in origin, (in which case it corresponds to unknown reactions since observed fusion ashes lie below the threshold needed to explain the observed heat) or to a new quantum chemistry.

Mizuno et al. [3] have observed similar effects with a SrCeO3 ceramics , that have the same perovskite structure. However, they observe a much larger excess heat of

the order of 10^4, at 300 to 400 °C! The main difference is probably the structure of the sample. We have used a single crystal , whereas Mizuno et al. have used a ceramic that has a polycrystalline structure with grain boundaries.

7. Conclusion

We have shown that excess heat is observed when a current is passed through a lanthanum aluminum oxide crystal with lanthanum vacancies in a deuterium atmosphere. The amount of excess heat has been determined to be up to 10 times the electric power passed through the sample.

We cannot exclude low level neutron emission, but at this point noise can still be the cause of the small signal increase observed.

Solid state electrolytes are excellent candidates for future applications because they operate at much higher temperature than liquid electrolytes. This should make it much easier to generate electricity. Also because of the closed cell configuration, and the possibility of working at low deuterium pressure, it would be possible to measure helium-4 production with an excellent accuracy.

Acknowledgments

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