Metallic Hydrogen: A Game Changing Rocket Propellant

Final report, Phase I NASA NIAC: Isaac F. Silvera

The objective of this research is to produce metallic hydrogen in the laboratory using an innovative approach, and to study its metastability properties. Current theoretical and experimental considerations expect that extremely high pressures of order 4-6 megabar are required to transform molecular hydrogen to the metallic phase. When metallic hydrogen is produced in the laboratory it will be extremely important to determine if it is metastable at modest temperatures, i.e. remains metallic when the pressure is released. Then it could be used as the most powerful chemical rocket fuel that exists and revolutionize rocketry, allowing single-stage rockets to enter orbit and chemically fueled rockets to explore our solar system.

Here, we propose a new method to catalyze the transformation to the metallic state. Our plan is to inject electrons into solid molecular hydrogen under pressure; this would weaken the intermolecular bonds, enabling metallization at a much lower pressure than required for the a pure hydrogen sample. A major advantage of this approach is that it could enable scaling to produce the large amounts of hydrogen needed for rocketry. Early studies at ambient pressure and low temperature showed that electrons can be injected into solid hydrogen and localized in the lattice. The presence of electrons can be detected by studying the near infrared absorption spectrum, which develops new absorption lines when electrons are localized in the lattice.

A large barrier of order 1 eV exists between the molecular phase and the metallic phase, as indicated in Fig. 1. Once in the metallic phase the barrier inverts and should prevent back-conversion to the molecular phase. The idea that we are pursuing is to disturb the lattice of molecular hydrogen with an impurity that can be present at low pressures. The impurities weaken the bonding and lower the potential barrier. Above a certain pressure the molecular solid transforms to the metallic phase and once in this phase the impurity either leaves the system or is unimportant, but the barrier preventing conversion to the molecular phase remains.

The general understanding of the metallization process of hydrogen is that (at high pressure) as the pressure increases the intramolecular proton-proton bonds weaken. This is supported by studies of the molecular vibration of hydrogen as a function of pressure; with increasing pressure the vibrational frequency decreases, attributed to charge transfer out of the bond to the electronic band. This charge overlaps the molecule and weakens the bond, self-consistently.

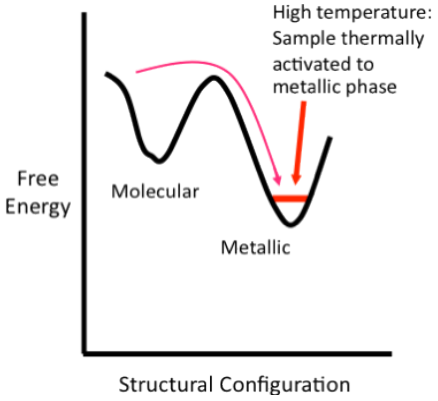

Fig. 1. Configuration diagram of hydrogen for pressures below the transition to the metallic phase. Once in the metallic phase the diagram reverses so that there is a barrier preventing conversion from the atomic metallic to the molecular phase.

In the original experiments on electrons embedded in hydrogen an open solid sample was irradiated with high-energy protons to produce electrons and the resulting infrared spectra were interpreted as arising from electrons localized in cavity like states in the lattice. This geometry is not possible at high pressures as the hydrogen is sealed in a hole in a metallic gasket between two diamonds in a diamond anvil cell (DAC), as shown in Fig. 2.

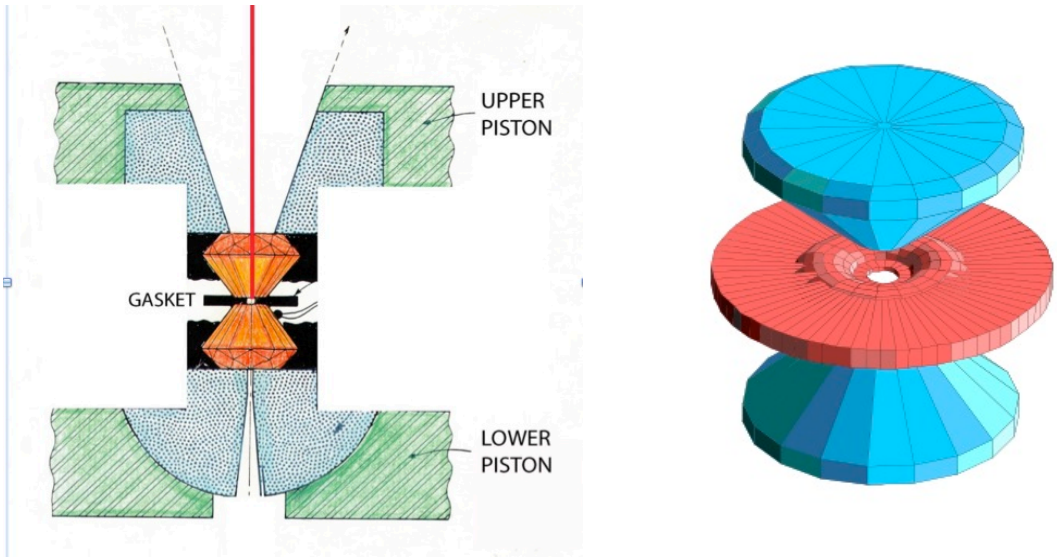

Fig. 2. On the left is the heart of a diamond anvil cell. A sample is confined in the hole in the gasket between the two diamond anvils. On the right is shown two opposing diamonds with a pre-indented gasket.

Our idea was to prepare an electron source inside the hole in the gasket that contains the high-pressure hydrogen and inject the electrons into the hydrogen, at low temperature. If a conductor with a sharp tip having a submicron radius of curvature is placed at a sufficiently negative potential it will emit electrons by Fowler-Nordheim field emission.

We have extensive facilities with high pressure DACs and experience with cryogenic hydrogen loading at pressure. There are three additional requirements to build up of this initial demonstration: 1. Prepare a Fourier transform infrared (FTIR) system for this research, 2. Prepare the e-source, and 3. Conduct measurements to show that the electrons are indeed embedded in the hydrogen and remain stabilized in the lattice with increasing pressure.

The first stage was conducted by integrating a commercial FTIR to a cryostat, so the IR spectra could be measured in pressurized samples. We modified a commercial system (Nicolet 6700) to extract a beam and focus on the DAC in a purge box (to remove water vapor spectra), increasing the signal by a factor of 5 by using a Schwarzschield objective that we built, as a condenser. This system allows FTIR, Raman, and ruby fluorescence measurements (for pressure determination).

For the field emission tip (FET) we first planned to use as sharp etched tungsten tip, as we had experience in making these, and attach it to the inside wall of the metallic gasket using

focused ion beam techniques. Although a test in vacuum showed very nice electron emission at a negative voltage of a few hundred volts, when tested in liquid nitrogen the tip rapidly damaged. This is due to emitted electrons ionizing atoms or molecules that then are attracted to the negative tip, bombard and erode it.

We then decided to use metallic carbon nanotubes (CNTs) that have diameters of tens of nanometers, and even if the end is damaged they continue to emit (it is like a smoking cigarette). We entered into collaboration with Prof. Z. Renn of Boston College as with his experience and facilities he was confident that the CNTs could be grown on the inner wall of the gasket, as shown in Fig. 3a. Unfortunately, when we were ready with our DAC and gasket, we found that Prof. Renn had (unexpectedly for us) moved to the University of Texas and would be delayed in carrying out his part. As his new facilities were substantially delayed in construction, the collaboration ended and we attempted to grow CNTs on the gasket wall ourselves, by at high temperature a technique in a liquid flux. We had limited success and could only get emission at very high voltages (kilovolts) in vacuum and eventually terminated this development.

Finally we came up with a new method to achieve our goals. We could purchase functionalized CNTs from a commercial enterprise. If not functionalized (charged surfaces) the CNTs bond together in large clusters (~50 microns dimension) and are not useful for us. Several procedures were tested. Functionalized CNTs can be distributed in a water solution and droplets on a gasket can evaporate leaving isolated CNTs, about 15 microns long. We developed a new kind of compound gasket made of two half foils of stainless steel, shown in Fig. 3b. These foils are indented between the diamonds and then separated to have a flat side and an indented side. CNTs can be distributed on the flat surface of one of them (Fig. 3c) and then the gasket can be reassembled and further pressed to clamp down on the CNTs hanging over the edge of the hole (Fig. 3d). A test gasket has been successfully made and evaluated in vacuum. We built a test facility to measure the emission current with an electron collector feeding into an electrometer. The compound gasket emits at several hundred volts with a measured current of 0.2 microamps, more then sufficient for our requirements,

At this stage we are preparing an experimental run. A new gasket is being made and shall be mounted in a DAC to be loaded with hydrogen. An electronic circuit has been built that provides a signal when the FET is emitting (but cannot measure the current as the emitted electrons are embedded in the sample). Our procedure will be to load the sample with electrons at liquid helium temperatures at modest pressures (at higher temperatures and zero pressure, the electrons diffuse out of the solid hydrogen due to their large zero-point motion). We shall then increase the pressure and measure the stability of the electrons against diffusion, as a function of temperature. This measurement will be performed in a gasket with a reasonably large hole (50-100 microns diameter) to optimize measurement signal. However, for very high pressures, smaller diamond flats and holes in gaskets are used. We shall then carry on this development to the highest pressures to seek the goal of metallization. The effect of the electrons on the hydrogen can be observed by monitoring the internal vibration mode of the hydrogen, the so-called vibron, which should deviate strongly in properties from those of a pure hydrogen solid.

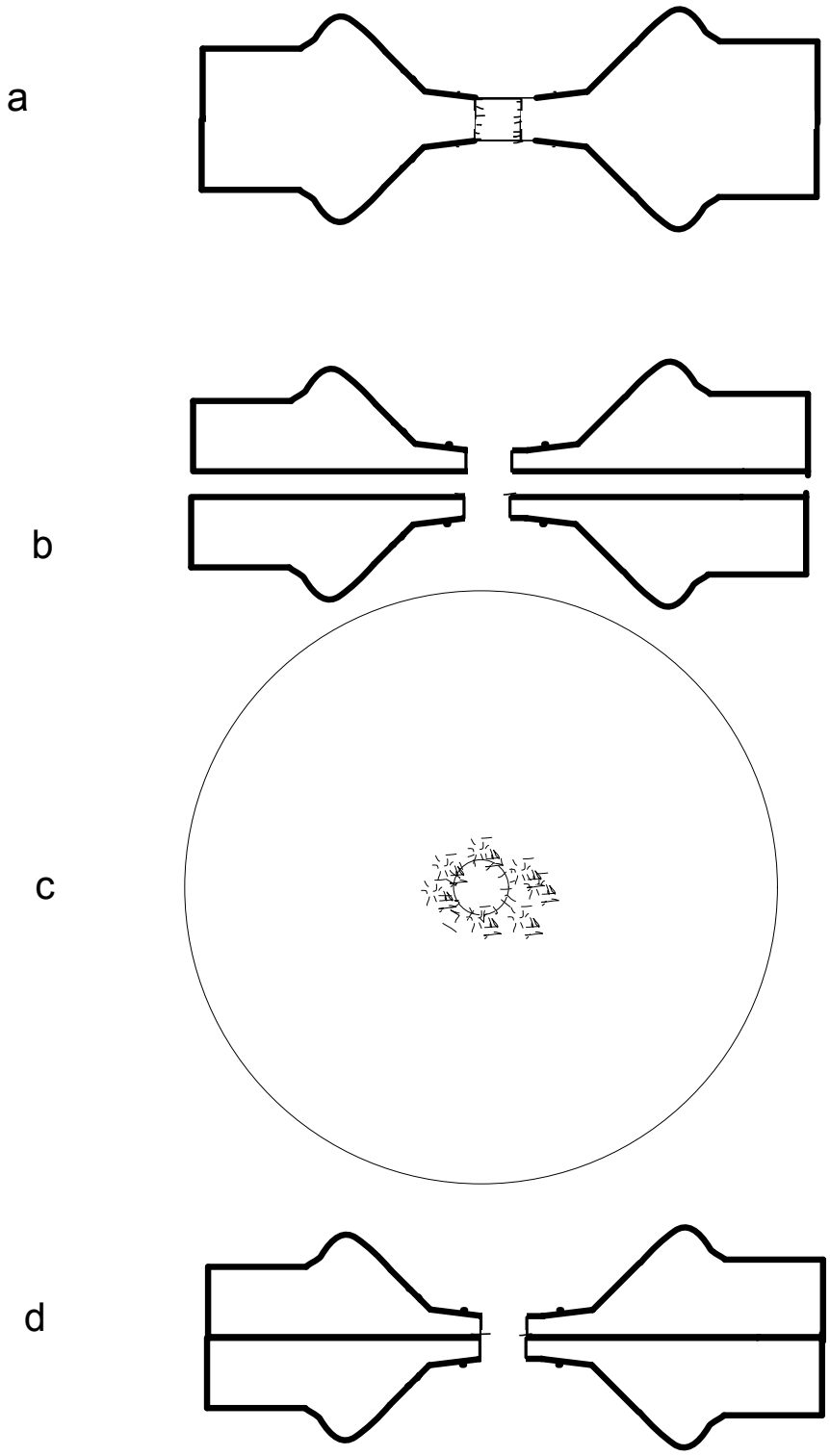

Fig. 3. A conventional gasket (a), and a compound gasket. In (b) we show two separated foils of the indented gasket; (c) shows the functionalized CNTs on the flat surface; (d) shows the CNTs in the mid-plane compressed between the two foils and making electrical contact with the gasket. A typical hole diameter in the stainless steel gasket is 50-100 microns and thickness is half the diameter.