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HIGH DENSITY HYDROGEN RESEARCH

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HIGH DENSITY HYDROGEN RESEARCH* **

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1. Summary

The interest in the properties of very dense hydrogen has been prompted by its abundance in Saturn and Jupitur, and its importance in laser fusion studies. Furthermore, it has been proposed that the metallic form of hydrogen maybe a superconductor at relatively high termperatures and/or exist in a metastable phase at ambient pressure. For ten years or more, laboratories have been developing the techniques to study hydrogen in the Megabar region (1 Megabar = 100 GPa). Three major approaches to experimentally study dense hydrogen have been used, static presses, shockwave and magnetic compression. Static techniques have crossed the Megabar threshold in stiff materials but have not yet been convincingly successful in very compressable hydrogen. Single and double shockwave techniques have improved the precission of the pressure, volume, temperature, Equation of State (EOS), of molecular hydrogen (deuterium) up to near 1 Mbar. Multiple shockwave and magnetic techniques have compressed hydrogen to several megabars and densities in the range of the metallic phase. The net result is that hydrogen becomes conducting at a pressure between 2 and 4 megabars. Hence, the possibility of making a significant

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**This paper is a written [illegible] invited presentation [illegible] given at the International [illegible] Conference [illegible] Colorado State University, [illegible] Colorado, from August [illegible] amount of hydrogen into a metal in a static press remains a formidable challenge. The success of such experiments will hopefully answer the questions about hydrogen's metallic vs. conducting molecular phase, superconductivity, and metastability.

2. Status of Theoretical Calculations

A. Equations of State

The EOS of molecular hydrogen has been very difficult to calculate due to hydrogen's extreme compressibility and hence large variation in intermolecular spacing. Although it is possible to calculate the forces between molecules, these calculations all involve some approximations whose ultimate justification is based on comparison with the experimental data.[1] In the past, calculations of pairs of molecules have been made and then summed over all pairs in the vicinity. Recently calculations have been made for the system of molecules in a crystal. Preliminary results of these calculations have predicted closing of the band gap which would yield a conducting molecular phase distinct from a metallic phase.[2,3] However, no band overlapp was found in other calculations[4] which were in very good agreement with the experimental results of shockwave experiments.

The variations in the calculated EOS of metallic hydrogen have been much smaller than for the molecular phase. Furthermore, the techniques have been accurate when applied to the naturally occurring alkalli metals.[5] However, there is not yet any diffinative experimental data to compare with theory nor is it certain that the 0K metal will be solid as assumed, rather than possibly a quantum liquid.[1]

B. The Metallic Transition Pressure

The molecular to metallic transition pressure can be estimated from the intersection of the tangent of the Gibbs free energy vs. pressure of the two phases. The intersection is extremely sensitive to small changes in either phase causing wide variation in the predicted transition pressure. Even the relatively small variation in the metallic EOS lead to transition pressure variations of a few Mbars.

C. Properties of Metallic Hydrogen

The expected high Debye temperature (~ 2000 - 3000K), leads to the possibility that metallic Hydrogen would be a superconductor near room-temperature and also that it may be a quantum liquid. The later possibility is at odds with the possibility of a metastable metallic phase. Other factors suggesting non-metastability are the high stored energy (more than an order of magnitude greater than TNT and 2 orders of magnitude greater than diamond vs. graphite), simplicity of reversion to the molecular form and ample energy to drive it. The normal thermodynamic relationship of the melting point of the metallic phase being lower than the melting point of the molecular phase (14K) may or may not apply since molecular and metallic hydrogen are quantum solids and/or liquids.

3. Status of Experimental Approaches

A. Static Presses

Several laboratories throughout the world have undertaken efforts to develop static presses and static techniques in order to compress hydrogen into the metallic state. During the last 10 years, the estimated pressure necessary has ranged from 0.8 to 20 Mbars and the maximum attained pressures have continually increased at the same time the calibration of the static pressure scale has been periodically reduced.

The largest press to be used for High Pressure research is in Russia. The late L. F. Vereschagin constructed a 30 m high press capable of exerting a force of 50,000 tons. However, that press has not yet been used for compressing hydrogen. A smaller press (10,000 tons) has been used to compress a very thin layer of hydrogen with anvils made of carbonado (polycrystaline diamond) (See Fig. 1.) Vereschagin, et al. reported a sharp decrease in resistance at an unknown, but assumed high pressure.[6] They also reported the resistance remained low while some of the force was removed, which they claim indicates possible partial metastability. However, Ruoff argues that the maximum pressure that could have been excited in the reported experiments, was less than 1 Mbar and possibily much less.[7] Claims of insulator to metal transitions in thin films are always difficult to verify. Pressumably the use of the large press will allow experiments with more substantial volumes of Hydrogen and permit more sophisticated diagnostics.

In Japan, Kawaii has developed a high pressure apparatus known as a split sphere (See Fig. 2). His apparatus has the advantage of being able to work with larger volume samples. Kawaii, et al. used anvils made of Al_2O_3 and WC and gaskets made of M_gO in one case and diamond powder in another, to compress hydrogen to high density.[8] Again a decrease in electrical resistance was observed at an unknown but presumed high pressure. They also indicate continued conductivity as force is removed but do not assert that as evidence of metastability. Unfortunately, hydrogen becoming a conductor is not the only possible means of obtaining a conductive path in these experiments. Metallic transitions in Al_2O_3 and M_gO which were used as insulators, have been reported at again unknown, but presumably similar pressures.[9,10] However, the reported transition in Al_2O_3 is also in question as it has been found to remain an insulator to pressures of at least 5 Mbar.[11] A further difficulty is that not only have M_gO and diamond been claimed to become conductors, but the possibility of chemical products with lower transition pressures remains.

In summary, the two claims of observed insulator to metal transitions at high pressure generated by static presses, are not yet completely verified as unambiguous proof of the possible conductive molecular hydrogen phase let alone the metallic phase. Continued efforts by both groups as well as the interesting work being done by A. L. Ruoff at Cornell and I. Spain at the University of Maryland will hopefully lead to complete and detailed results in the future. Ruoff and Spain are using diamonds as their anvils and are methodically increasing the pressures attainable and verifiable at the same time developing sophisticated diagnostics to measure optical, electrical and structural properties of dense hydrogen.

[illegible] Single and Double Shockwave Compression

To date, single and double (reflected) shockwaves have provided the only simultaneously independently measured pressure and density data on hydrogen at pressures above [illegible]. A single shock generated by high explosives [illegible] generate about 150 kbar and [illegible]20 kbar in hydrogen and deurium respectively. A reflected shockwave can achieve about 900 Kbar in deurium. The results of these experiments have slightly narrowed the uncertainty in the EOS of molecular hydrogen at densities approaching the expected density of metallic hydrogen.[12] However, the accompanying temperatures are approaching 1 eV and further compression into the metallic state seems unlikely prior to ionization. Further experiments are being planned at LLL in order to improve the accuracy of the EOS.

C. Multishock and Magnetic Compression

Two approaches have been used in order to use the high energy density of High Explosives (H.E.) to compress hydrogen isentropically. Implosion of hollow H.E. cylinders can achieve pressures approaching 10 Mbar and can compress hydrogen to densities exceeding 15 times the normal solid density provided the energy can be transferred slow enough. Grigor'yev et al., imploded a H.E. driven metal tube on high density gaseous hydrogen (See Fig. 3) and reported 6 pressure-volume points.[13,14] The volumes were measured directly from flash radiographs and the pressures were calculated. The original report and a recent analysis by Gringor'yev, et al. claim the results indicate hydrogen remains in the molecular state up to at least about 3 Mbars.[14] The original work states that a break in the slope of the pressure-volume data, is consistant with a first order change in phase as might be the case for the insulator-metal transition.

Hawke, et al., have used a magnetic field (See Fig. 4) to convert the H.E. energy into compressing hydrogen to pressures greater than 2 Mbar and found that electrical conductivity was observed in the multi-Mbar region.[15]

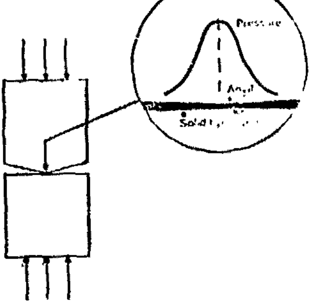

Fig. 1. High pressure anvil technique used by Vereschagin, et al.

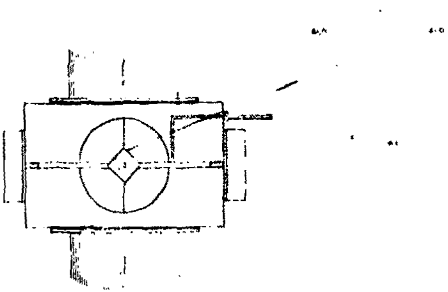

Fig. 2. Modified split sphere apparatus used by Kawaii, et al.

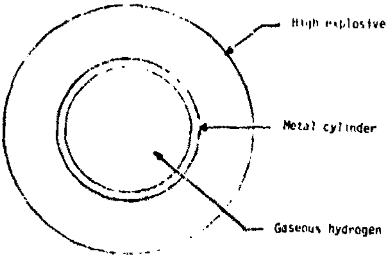

Fig. 3. Multishock implosion device used by Grigor'yev, et al.

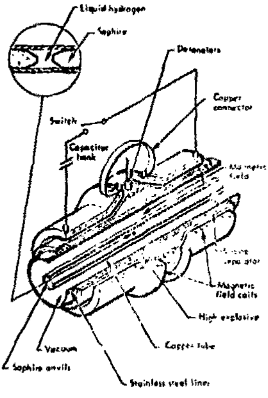

Fig. 4. Magnetic compression device used by Hawke, et al.

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