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HIGH-DENSITY HYDROGEN RESEARCH*

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This paper presents three different efforts at Livermore which are proceeding toward a characterization of high-density hydrogen. Two are experimental, aimed at measuring hydrogen's properties at high density. The other is theoretical, with the goal of correlating experimental results with theoretical calculations. The results of all three efforts have proven useful to the understanding of how the molecular liquid phase, initially at a density less than 0.1 g/cm^3 , can be compressed more than tenfold to make the relatively dense metallic hydrogen phase forecast by Wigner and Huntington [1].

Because high compressions and pressures of a few megabars are required, it is natural to study hydrogen with dynamic, as opposed to static, high-pressure measurements. Two kinds of dynamic experiments have been carried out at this laboratory: relatively fast shock compression and relatively slow isentropic compression using a strong magnetic field. Shock compression has made it possible to study material properties at pressures much higher than those so far achieved with static presses. In shock compression a material is suddenly compressed by impact with a rapidly moving projectile. X-ray experiments, such as those performed by Johnson *et al.* [2], show that the high-pressure shocked material comes to thermodynamic equilibrium long before the sample begins to slow down and lose pressure. Probably the equilibration time is of the order of 10^{-12} sec, too small to measure accurately. Following compression the new high-pressure state persists for a few microseconds during which the velocity of the sample and shock are determined. From the measured velocities both pressure and energy can be determined (by using the conservation relations for momentum and energy). Because the initial shock compression is rapid and irreversible, the final equilibrium temperature reached in the shock experiments is greater than that generated by an isentropic compression. For example, a liquid hydrogen sample at atmospheric pressure, shock-compressed to one-fourth its initial volume, would rise in temperature above 5000 K. This temperature rise associated with the shock experiments limits the compression which can be obtained, ruling out the possibility of compressing hydrogen directly to the metallic state with a single shock wave. The value of the shock experiments is that they can test the strength of the interaction of hydrogen molecules at close range. The shock experiments bring colliding molecules close together by combining relatively high density with sharply increased thermal motion. As a result of these two effects, conditions

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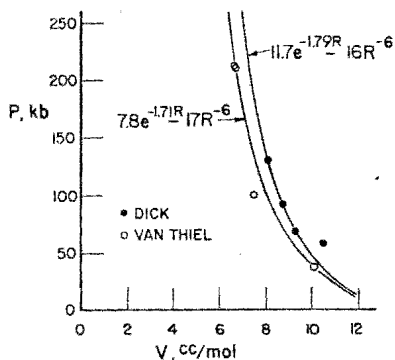


Fig. 1. Pressure generated by shock compression of hydrogen as a function of volume per mole of H_2 . Small differences between hydrogen and deuterium and between slightly differing initial conditions have been taken into account in plotting the data. The points plotted here all correspond to an initial liquid molar volume of $23.8 \text{ cm}^3/\text{mol } D_2$. The two calculated curves are based on the H_2-H_2 interaction potentials indicated. Energies and distances are in atomic units (hartrees and bohrs).

achieved in shock experiments with fourfold or fivefold compressed hydrogen are similar to those which would be reached by more than tenfold compression at a low temperature.

In a series of experiments van Thiel *et al.* [3] shock-compressed deuterium to pressures slightly higher than 200 kbar. The measured data, converted to pressure-volume points using the mass and momentum conservation relations (Hugoniot relations) are shown in Fig. 1 as open circles. The lowest of these open circles is the result of an earlier 40-kbar experiment carried out by van Thiel and Alder [4]. The filled circles are results from Dick's shock-compression experiments at Los Alamos [5]. Shown along with the experimental data are two calculated theoretical curves due to Ross [6]. These calculations are based on the exponential repulsion-inverse-sixth-power attraction (exp-6) form of the pair interaction energy between hydrogen molecules. The two theoretical curves indicate roughly the range of such pair potentials that could be considered consistent with the experimental data. To resolve the systematic disagreement between the two sets of experimental data more shock-compression experiments will have to be carried out.

The second experimental technique, which uses isentropic rather than shock compression, has been pioneered by Hawke [7] and should eventually lead to direct observation of the metal. In Hawke's experiments a cylinder of liquid hydrogen is surrounded by two concentric conducting cylinders. The outermost cylinder is driven inward with a high explosive shortly after a magnetic field has been introduced between the cylinders. The magnetic field serves to transfer momentum from the outer to the inner cylinder. The compression of the hydrogen in this case occurs relatively slowly, in a time order of 10^{-6} sec (perhaps six orders of magnitude slower than in the shock experiment), slowly enough for sound to traverse the sample several times, so that the compression is nearly isentropic. Calculations indicate that the required tenfold compression for conversion of the molecular liquid to the atomic metal will result in temperatures of the order of 2000 K. The plan is to make metallic hydrogen by this slow implosion and to diagnose the presence of the metal with a conductivity measurement. Although this technique has not yet resulted in a successful conductivity measurement on hydrogen, the experimental difficulties are technical ones which can be overcome. Pressures as high as 3 Mbar have been reached by Hawke (but not diagnosed), and a single pressure measurement in the vicinity of 1 Mbar has been found to correspond roughly with the theoretical equation-of-state predictions.

On the theoretical side, considerable progress has been made in understanding the results of the hydrogen experiments. The theoretical calculations proceed in two

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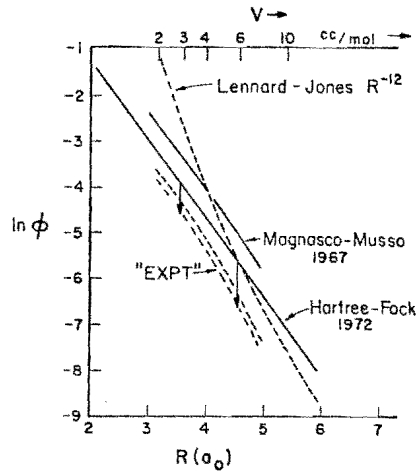


Fig. 2. Estimates of the H₂-H₂ interaction, averaged over angles. Three theoretical estimates of the repulsive part of the energy are shown: the Lennard-Jones repulsion, the Magnasco-Musso repulsion, and the more recent Hartree-Fock repulsion calculated by Tapia *et al.* [10]. When the attractive part of the energy is added in (indicated by vertical arrows), the theoretical estimate lies in the range obtained from shock compression experiments. The two dashed pair potentials correspond to the two potentials indicated in Fig. 1.

steps: First, the forces governing the interaction of hydrogen molecules with each other must be determined; second, the macroscopic properties of a system of many interacting molecules must be calculated from the intermolecular forces. Fundamental calculations of the complete hydrogen molecular interaction still appear to be far in the future. Nevertheless, calculations for the simpler case of two interacting helium atoms show that separate calculations of the repulsive and attractive parts of the pair potential give, when added together, a good description of the total interaction as inferred from experiment and as calculated from theory [8].

A summary of recent theoretical progress for hydrogen is shown in Fig. 2, which shows the angle-averaged interaction energy for two hydrogen molecules as a function of the distance R between their centers. The energy is given in atomic units (hartrees) and the distance scale at the base of the graph (in bohrs) has been converted at the top of the graph to a volume scale (cm³ per mole of hydrogen) by using the volume V which corresponds to a nearest-neighbor spacing R in the face-centered molecular crystal. The total interaction energy as inferred from the shock experiments corresponds to the region lying between the two dashed lines. This experimental determination of the pair potential has an uncertainty of about $\pm 10\%$. The theoretical curves shown are calculations of only the repulsive part of the intermolecular interaction. The old Lennard-Jones inverse-twelfth-power repulsion is much too steep. The repulsion calculated by Magnasco and Musso using just spherical atomic wave functions lies about a factor of two above the more recent calculations which incorporate angle-dependent wave functions [8-10]. When the attractive contribution to the energy is added to the most recent calculations (the curve marked Hartree-Fock)—the result is indicated by the two vertical arrows in Fig. 2—the theoretical potential lies within about 10% of the experimentally determined one. This new result represents substantial progress. Within the 10% uncertainty still present in the experimental results, theory and experiment are now consistent in their pictures of the hydrogen molecule interaction energy.

Now that the experiments and theory agree on the forces in molecular hydrogen, what can the theory tell us about the possibility for making the metallic form? Figure 3 shows the phase transition linking the two phases, molecular and metallic, using the steepest curve consistent with the shock experiments (upper exp-6 isotherm).

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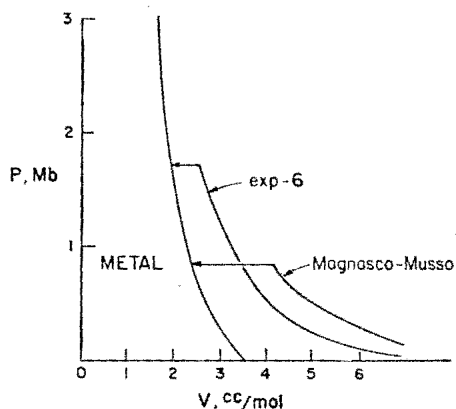


Fig. 3. Zero-Kelvin equilibrium between the body-centered metallic phase and the molecular phase; pressure in megabars as a function of molar volume of H_2 . The Magnasco-Musso repulsion predicts too low a transition pressure. The transition to the metallic phase must lie no lower than the exp-6 isotherm since that isotherm corresponds to the steepest potential consistent with the shock compression experiments.

The metallic isotherm is Roger's [9] modification of the Wigner-Huntington calculation. The transition pressure thus predicted, 1.7 Mbar, is about twice the pressure predicted earlier [9] using the Magnasco-Musso potential. Unless some other metallic structure is more stable than the body-centered crystal, 1.7 Mbar is a lower limit on the pressure necessary to make hydrogen metal. Such a pressure lies well within the range of Hawke's experiment. It is less easy to place an upper limit on the transition pressure; a transition pressure off the scale of Fig. 3 appears to be highly unlikely. Most calculations lie in the vicinity of 2 Mbar. A more definite calculation awaits the resolution of the experimental discrepancies between the Livermore and Los Alamos shock data.

Suppose that metallic hydrogen could be made. What are the chances of preserving it to fashion it into superconducting transmission lines and the like? It is worth noting that relative to the molecular form, the energy stored in the metallic form at low pressure would be enormous, of the order of $2 \text{ Mbar cm}^3/\text{mol}$. This stored energy means that constant-volume decomposition of the metal would result in temperatures of several thousand degrees and pressures of over a megabar. This stored energy would exceed by two orders of magnitude the energy stored in diamond relative to graphite, for example. Because some transitions are so sluggish that metastable phases can be observed, it is worthwhile to consider the rate at which the metal would decay back to form the molecular phase. For some reactions the rate is slow because the mechanism is very complicated on a molecular level. In the case of diamond, for example, the tetrahedrally coordinated carbon atoms have to rearrange to form widely separated close-packed planes of atoms, a gross rearrangement. The mechanism for the breakdown of metallic hydrogen is very simple. Pairs of neighboring atoms need only link up to form molecules. Calculations of the time required for the crystal to decompose are of the order of fractions of a second [11,12], in keeping with the observation that so much stored energy is unlikely. A detailed calculation of the rate has not yet appeared.

Ashcroft has suggested that the obvious instability of the surface to decay could possibly be avoided by plating the metal with beryllium. The possibility of bulk decay would still remain. How stable is the bulk metal? This question involves a detailed study of the mechanism for molecule formation within the crystal. The question to be answered is, Where does the energy go when two atoms form a molecule? If the energy is substantially transferred to neighboring nuclei, the decomposition might well be autocatalytic. If not, and the energy is removed somehow, carried

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by high-energy electrons, perhaps the molecule could gradually decay back into the atomic form without doing permanent damage to the crystal. Although the metastability question deserves further study, the present prospect for preserving the metal for more than a millisecond appears quite remote.

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