New Phases
of Molecular and Atomic Hydrogen
under Extreme Conditions

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Recently I have had the opportunity of visiting a number of EPS countries as EPS Travelling Lecturer and in the following, I shall cover some of the research results that were presented on the tour. The article should not, however, be regarded as a review of the field, as it deals principally with our research in Amsterdam. The tour was funded by the Dutch Physical Society and supported by the institutes visited, a list of which is shown in the panel opposite.

In the past few years, great progress has been made in research on the simplest of all molecular and atomic condensed matter systems: hydrogen. Molecular hydrogens (H_2, D_2) have been subjected to static pressures approaching a million atmospheres, demonstrating a new phase and nearing the pressure where they should become atomic metals. The fascinating behaviour of atomic hydrogen which was first stabilized a few years ago as a neutral low temperature gas (*Europhysics News*, May, 1980), has been steadily revealed, and, experiments are now being designed in which this substance may be pressurized (10^{-3} atm is considered high) to densities where it may demonstrate Bose-Einstein condensation (BEC).

High Pressure Molecular Hydrogen

Until recently, high pressure studies of molecular hydrogen and deuterium were restricted to about 10-20 kbar by the available techniques. The development of the diamond anvil cell (DAC) as an easy-to-use experimental tool has, however, increased the pressure range by about a factor of 50 — to the megabar range. The heart of our DAC is shown in Fig. 1. Two diamonds, no larger than 3-4 mm across, are aligned so that the culets, the small flat faces, are accurately parallel. Between the culets is placed a hard metal gasket with a central hole in which the sample and a grain of ruby used to measure the pressure are contained. When the diamonds are pushed together, the metallic gasket plasti-

Fig. 1 — The heart of our diamond anvil cell used to study molecular hydrogen at high pressure and low temperature: D, diamond; C, cylinder; G, gasket; R, indium dam.
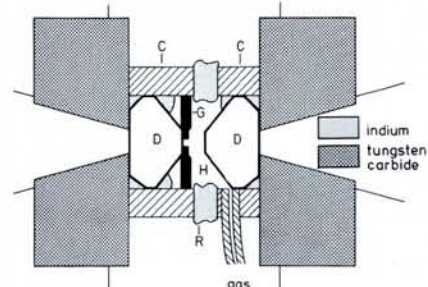
cally flows and the sample is sealed in the hole, the pressure increasing as its volume decreases. Because the area of the culet is small, $\lesssim 1$ mm^2, a modest force gives rise to enormous pressures and because of the strength of the diamond anvils, these pressures can be contained without breakage. The diamonds are optically transparent so that the sample and ruby grain can be directly observed. Pressures are derived by analysing with a spectrometer the ruby phosphorescence in the red, the R-doublet, when excited by a laser. The frequencies of the line centres shift almost linearly with pressure which simplifies calibration.

Our diamond cell can be used in a cryostat enabling studies to be made at temperatures down to $T \cong 1$ K. To load a hydrogen or deuterium sample a small cylindrical chamber has been built around the diamonds and sealed with a dam of indium which offers little resistance to their translational motion. The cell is cooled to just above the freezing temperature of the sample ($T_m \cong 14$ K for H_2) and the chamber is filled with liquid, condensed through a capillary. This liquid is frozen and then sealed in the gasket for study. The most important study technique we have utilized is Raman backscattering. The highest pressures for H_2 is 600 kbar at $T = 1$ K.

At low pressure, the solid molecular hydrogens have a unique property: the molecules are in almost free rotor states so that the rotational energy is given by $E_J = B\,J(J+1)$ where B is the rotational constant (59.3 cm^{-1} for H_2 and 29.8 cm^{-1} for D_2) and J the rotational quantum number. Because of the low temperature, the molecules only occupy the $J = 0$ (para-H_2, ortho-D_2) or $J = 1$ (ortho-H_2, para-D_2) levels. The wave functions are spherical harmonics, $Y_{JM}(\theta, \phi)$, and since Y_{oo} is a constant, the $J = 0$ molecules are spherically symmetric. As a consequence, p-H_2 behaves, for example, as solid argon or helium. In addition to rotational motion, the solids have translational excitations consisting of phonons and vibrons (internal molecular vibrations).

A decade ago, Raich and Etters[1] predicted that at a sufficiently high density the ball-like molecules of p-H_2 or o-D_2 would spontaneously deform and the crystal would orientationally order. This deformation is due to the admixing of higher rotational states, mainly $J = 2$ into the $J = 0$ ground state. The mixing is due to the anisotropic interactions, dominated by the electric quadrupole-quadrupole (EQQ) interaction, characterized by the coupling parameter $\Gamma = (6/25)\, e^2 Q^2 / R^5$. Here Q is the EQ moment and R the intermolecular separation. The wave function mixing parameter is $\varepsilon \sim \Gamma / \Delta E_J \sim \Gamma / B$. As B of D_2 is half that of H_2, the broken (rotational) symmetry phase (BSP) transition should occur at much lower pressures in D_2 than in H_2 as the rotational admixtures will be larger. Raich and Etters' calculation corresponded to a critical pressure of 60 kbar for the phase transition in o-D_2.

Experimentally we believed that the BSP transition could be observed from the Raman spectrum. At low pressure, the $J = 0 \rightarrow 2$ rotational exciton gives rise to a sharp three-line spectrum at $E \sim 2B$ whereas in the high pressure ordered phase, the spectrum should change dramatically as the orientational excitations are librational in nature.

Initial measurements[2] up to 150 kbar showed no sign of the predicted phase transition in o-D_2. However, an unexpected mode repulsion of the roton-phonon modes was observed at $p \sim 50\text{-}60$ kbar as seen in Fig. 2. Further developments enabled higher pressures to be achieved; finally the BSP was observed at $p = 278$ kbar[3]. Here the rotons are observed to split into two broad bands below the critical temperature. The extreme broadening of the rotons in the region of 200-278 kbar is attributed to lifetime broadening of the
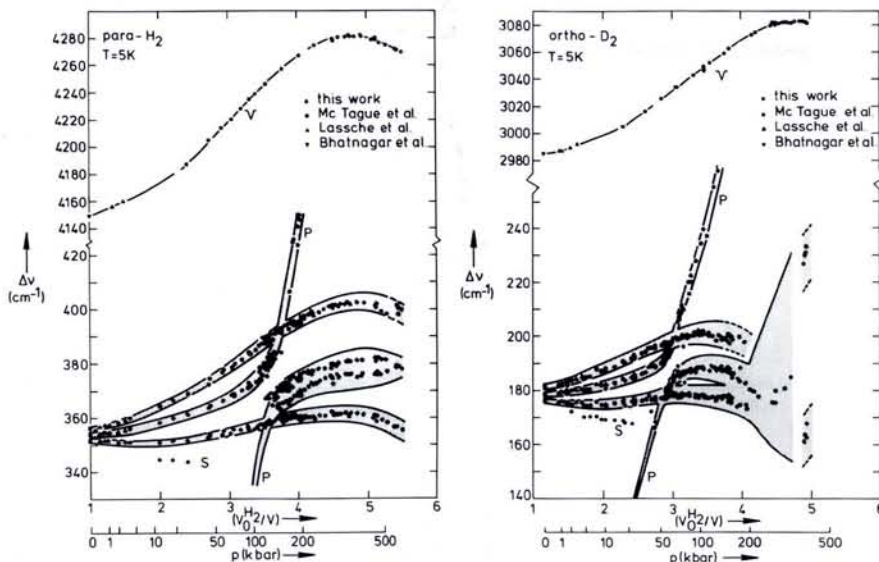
Fig. 2 — The frequency of excitations in solid p-H₂ and o-D₂ as a function of pressure or molar volume, relative to the zero pressure volume of H_2 (23.16 cm³/mole). The shaded regions indicate the width of the Raman transitions. V is the vibron branch, P the phonon branch and S a spurious strain induced transition.

rotons. A zone boundary roton which becomes soft and eventually is responsible for the phase transition[4]) opens up a relaxation channel at $p \sim 200$ kbar. The BSP has still not yet been observed in p-H₂ up to pressures of 600 kbar. Recently Aviram, Goshen, and Thieberger[5]) predicted the observed critical pressure of the BSP in o-D₂ by Monte Carlo simulation techniques, but the same calculation predicts the phase transition in H_2 at a pressure within the range already studied.

The Equation of State

The equation of state (EOS) of hydrogen (pressure vs volume) to ultra high pressures is not only of interest in itself, but is also necessary for any meaningful theoretical interpretation of pressure experiments as the interactions depend explicitly on the molar volume. Until recently, the EOS was known to about 25 kbar. Measurements in a diamond cell have now been made to

about 200 kbar at room temperature by Shimizu et al.[6]) by Brillouin scattering and by us[7]) to about 400 kbar at $T = 5$ K.

The technique we used was a simple and straightforward measurement of the pressure and volume. The pressure was measured from the ruby phosphorescence and the volume by determining the volume of the cylindrical sample $(V = Ad)$, which is not easy as it will be of the order of 10^{-6} cm³ only. The area, A, was measured by microphotography, the thickness, d, by means of fringes due to optical interference of light between the diamond culets. The experimentally determined EOS is shown in Fig. 3. H_2 and D_2 are expected to have essentially the same intermolecular interactions, and as these are the principal factors in determining the EOS, the difference observed between H_2 and D_2 at low pressure can be ascribed to an isotope effect arising from the difference in zero-point pressure of the two light molecules. The measure-
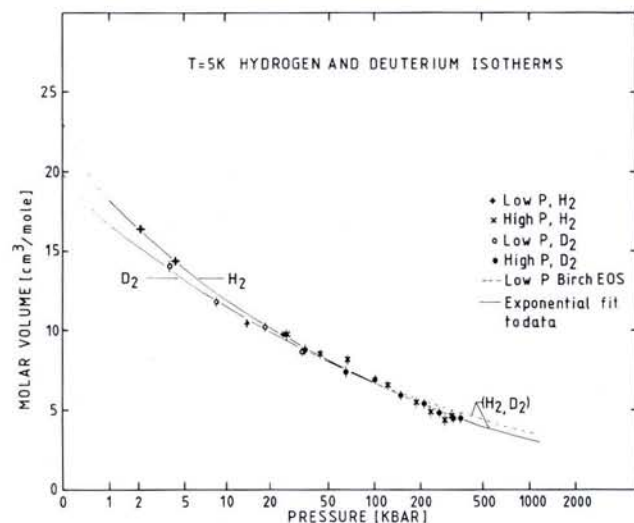

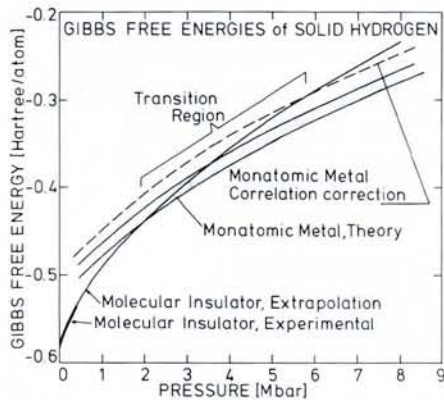Fig. 3 — The T = 5 K isotherms of H_2 and D_2 as measured with a DAC.

Fig. 4 — *The Gibbs free energy of molecular and metallic hydrogen used to predict the critical pressure of the phase transition.*

ments agree well with the known EOS up to 25 kbar. The EOS function can be fitted using an exponential repulsive isotropic pair potential with the usual weak van der Waals long range attractive part. The ability to arrive at a good fit with such a potential gives some confidence in extrapolation of the EOS to even higher pressures.

The EOS can be used to predict the pressure at which H_2 will have a transition to an atomic conducting state. This will occur when the Gibbs free energy (G) of the molecular state is equal to that of the metallic state. The p-V information can be used to construct G of the insulating state which is extrapolated to high pressure into a region where it crosses the theoretical G of the metallic phase. The latter has a large possible spread in value owing to the many calculations needed, and the uncertainty in the value of the correlation energy. The plot in Fig. 4 shows that the critical pressure is at least 1.9 Mbar and perhaps as high as 6 Mbar. It is not yet clear that these pressures can be achieved in a diamond cell as the diamonds tend to flow and break for $p \geq 1.5$ Mbar.

Gaseous Atomic Hydrogen

A description of how atomic hydrogen was stabilized appeared in *Europhysics News* of May 1980, so that here I shall

describe the process only briefly and review recent developments. By polarizing the atomic electron spins, the neutral hydrogen atoms in the gaseous state are forced to interact on the non-binding triplet potential. Polarization also suppresses recombination. A gas of spin polarized hydrogen (H↓) is collected in a low temperature cell ($T \leq 0.5$ K) in a high magnetic field ($B \cong 10$ T) to maintain spin polarization. Walls of the cell are coated with a thin film (~ 200 Å) of superfluid ^{4}He or a mixture of ^{3}He-^{4}He. Because of the weak attractive forces between H↓ and liquid helium, the surface coverage of H↓ is restricted. This is vital since recombination to H_2 occurs principally on the surface. The H↓ atoms are in the hyperfine state |a> and |b> shown in Fig. 5, which have lifetimes of minutes to hours depending on density, field, temperature, etc. They are expected to remain gaseous down to $T = 0$ K. Atomic deuterium has also been stabilized, but at a much lower density. Whereas so far, the maximum densities of H↓ are $n \cong 3 \times 10^{17}$/cm^3, for D↓, they are in the range $n \cong 10^{14}$/cm^3.

H, with its electron spin of 1/2 and nuclear spin of 1/2, behaves as a composite boson and one of the most interesting current goals is to achieve conditions for Bose-Einstein condensation (BEC) of H↓. At the low densities involved, the ideal gas relationship for the critical temperature should be appropriate:

$$T_c = 3.31 \; (\hbar/mK) \; (n/g)^{2/3} \qquad (1)$$

From this we see that a density of 5×10^{17}/cm^3 corresponds to a T_c of $\cong 10$ mK whereas a density of 1.6×10^{19}/cm^3 corresponds to 100 mK.

The lower temperatures are not easily achievable owing to recombination heating, so substantially higher densities must be produced. The problem here is that the growth of the density when filling a cell with H↓, is limited by recombination on the helium surfaces: when the recombination rate is equal to the filling flux, the density no longer increases. A detailed analysis shows that the recombination arises due to

the admixture of the electron up spin into the ground state, $|a> \cong -|↓↑> + \alpha|↑↓>$, shown in Fig. 5. This admixture $\alpha = a/4\mu B$, where a is the hyperfine constant and μ the Bohr magneton, can be suppressed with a magnetic field, but even for $B = 10$ T, where $\alpha \cong 10^{-3}$, its effect is dominating.

A suggestion by Statt and Berlinsky[8] was that the recombination rate of H↓ would be greatly reduced with a gas of pure state $|b> = |↓↑>$, which we symbolize by H↓↑. This requires that the nuclear relaxation time T_1 from $|b>$ to $|a>$ be very long, as was expected from theory. It should be possible to produce H↓↑ by recombination enrichment, as a gas of 50-50 $|a>$, $|b>$ states would be depleted of the $|a>$-states by recombination. Collisions of atoms in states $|a> - |a>$ and $|a> - |b>$ can result in recombination to H_2 but $|b> - |b>$, the pure Zeeman state, cannot. This leaves a gas of electron and nuclear polarized hydrogen.

Cline, Greytak and Kleppner[9] recently produced such a sample of H↓↑ using recombination enrichment so that much higher densities should now be within reach. Our earlier attempt[10] at this was thwarted by rapid relaxation, the source of which has now been traced to grains of ferromagnetic impurities embedded in the copper walls of our cell. However, using a clean, etched cell we have now been able to achieve nuclear polarization of 99.8%[11].

To produce high densities a lower density gas of state $|b>$ is first produced which is then compressed — no easy feat, because the recombination heating, even when bottlenecked, is substantial at high densities. Nevertheless, with our current knowledge of hydrogen, arrived at from experiments at lower densities, we have grounds now for believing that densities can be achieved at which BEC may occur.

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Fig. 5 — *The hyperfine states and energy of atomic hydrogen as a function of magnetic field; a is the hyperfine constant.*