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## THE DIAMOND ANVIL CELL AND HIGH PRESSURE RESEARCH

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**Résumé** . - Nous présentons une revue des techniques utilisant la cellule à enclumes de diamant pour la génération de hautes pressions et les recherches en Physique. Nous discutons l'application de ces techniques à quelques problèmes relevant de la Physique du Solide, de la Géophysique et de la Physique des Planètes.

**Abstract** . - The diamond anvil cell techniques for high pressure generation and physical investigations are reviewed. Some pressure studies of interest to Solid State Physics, Geophysics and Planetary Physics are discussed.

### Introduction

In recent years the diamond anvil cell (DAC) has become the most popular pressure generating device.<sup>1</sup> Static pressures of over a million atmospheres can be reached with the diamond cell and a variety of sophisticated high pressure measurements can be performed.

The basic principle of the DAC is very simple. A sample placed between flat parallel faces of two diamond anvils (see Fig. 1) is subjected to very high pressure when a force pushes one anvil diamond against the other. A prerequisite to using the DAC for pressure generation is, that the anvil flats are perfectly aligned axially and set parallel to each other as well. Presently, at least five different types of DACs exist and the variations arise from different ways in which the force — generating and the anvil alignment mechanisms are designed. To generate hydrostatic pressure, a metal gasket with a hole (200  $\mu\text{m}$  diameter) drilled at the center to serve as the pressure chamber has to be introduced between the anvil faces. A small sample (50 to 100  $\mu\text{m}$  in linear dimension and 50  $\mu\text{m}$  thick) is placed in the chamber, along with a tiny fragment of Ruby for pressure calibration.

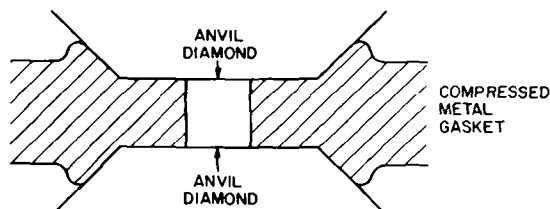


Fig. 1 Opposed diamond anvil configuration with a compressed metal gasket between the anvil flats. The hole (200  $\mu\text{m}$  in diameter and 100  $\mu\text{m}$  in depth) serves as the pressure chamber.

Then the hole is filled with a suitable fluid to serve as pressure medium and sealed by the diamond flats. Force on the diamond is applied by compressing the Belleville spring washers with the screw arrangement (Fig. 2) or other types of force generating mechanisms. The DAC shown in Fig. 2 is suitable for optical, spectroscopic and X-ray diffraction studies. The diamonds for the DAC have to be high quality, flawless, and free from fluorescence if the DAC is used for Raman spectroscopy.

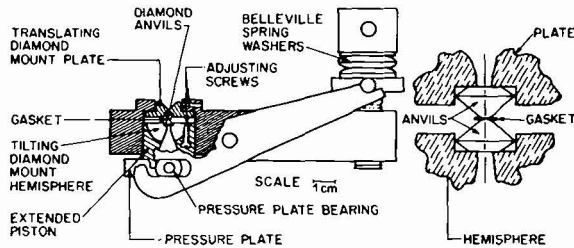


Fig. 2 Diagrammatic sketch of the NBS ultra high pressure diamond anvil cell (DAC) developed by Piermarini and Block (Reference 2). The right side shows the diamond anvil region enlarged.

The pressure generated in the DAC is measured by the Ruby fluorescence technique.<sup>3</sup> The ruby fluorescent emission consists of two well defined peaks at wavelengths of  $6942\text{\AA}$  ( $R_1$  line) and  $6927\text{\AA}$  ( $R_2$  line). These shift to higher wavelengths with increasing pressure and the  $R_1$  shift has been calibrated against standard substances, to construct a pressure-scale. The ruby scale is almost linear up to 300 kbar, and at higher pressures it begins to bend a little bit towards the pressure axis (see Fig. 3). This scale is widely in use at the present time.

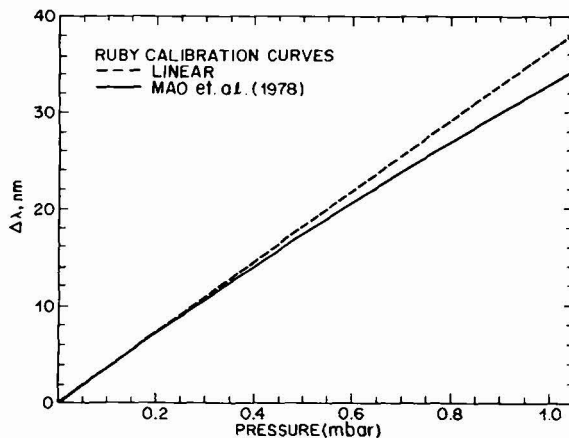


Fig. 3 Pressure calibration with ruby fluorescence technique,<sup>4</sup> using the  $R_1$  line shift. Linear (dashed line) calibration is  $0.365\text{\AA}$  shift/kbar.

A rather remarkable achievement with the DAC is that some simple ingenious techniques have been developed to condense gases into the tiny gasket-hole and trap them for optical, spectroscopic and X-ray diffraction experiments, or for use as a pressure medium.<sup>1</sup> For hydrostatic pressure medium the most popular choice is a mixture of methanol and ethanol in the proportion 4:1. This mixture solidifies around 105 kbar, beyond which it is not a strictly hydrostatic medium, although it is still usable. Rare gas solids appear to be excellent hydrostatic pressure media to a few hundred kilobar pressure and xenon is particularly attractive in this regard because it can easily be condensed with a simple set-up. Also, hydrogen and helium seem to be promising as good pressure media at least up to 600-700 kbars, as judged by the ruby linewidth. These condensed gases will be increasingly used in the future, wherever a nonreactive hydrostatic media is required.

Diamond cells have been adapted for low temperature studies down to liquid helium temperatures (see Ref. 1). For high temperature investigations in the DAC a novel method of heating has been devised, namely laser heating using a YAG laser.<sup>5</sup> If the sample is absorbing at the wavelength of the laser line, it can be very quickly heated to about 2000°C in the DAC, and the temperature measured by optical pyrometry. The technique is especially useful for studying phase equilibria in systems of interest to geophysics, and has been extensively used in such studies. The DAC is the tool par excellence for high pressure spectroscopy and microscopy. Several microspectroscopic techniques have been developed in recent years for absorption and reflection spectroscopy, Raman and Brillouin scattering measurements (see Ref. 1). The DAC is ideally suited for high pressure x-ray diffraction studies, for diamond is very transparent to X-rays. Further, the interfacing of the DAC with the powerful synchrotron X-ray sources,<sup>6</sup> has drastically reduced the tedium of data collection. It has now become possible to obtain powder diffraction data of high pressure phases in a fraction of a second, whereas it used to take hours or even days, with conventional X-ray sources. This has renewed interest in studying phase transitions, kinetic studies and other nondiffraction investigations, such as extended X-ray absorption fine structure (EXAFS).

Despite the limitations imposed by the smallness of the pressure chamber in a DAC, very fine optical techniques have been developed for the measurement of sample lengths and refractive index under pressure.<sup>7</sup> Viscosity of fluids have been measured by the falling sphere method (see Ref. 1). Resistivity measurements in the DAC are perhaps the most difficult, but even here several techniques are available, which are promising (see Ref. 1).

#### **Metallization Under Pressure**

One of the exciting predictions of solid state theory<sup>8</sup> is that, xenon would become metallic at 1.3 Mbar, iodine near 0.2 Mbar, hydrogen at pressures over 3 Mbar and even helium at pressures above 110 Mbar. Cesium iodide (CsI) is predicted to become metallic at 0.8 Mbar.<sup>8</sup> These substances, with the exception of iodine, are all gases at room temperature and atmospheric pressure, but solidify at high pressure. In the solid state they are very good insulators. The DAC has made it possible to experiment on these systems and check the prediction at least in a few favorable situations.

The electronic structure (greatly simplified) for a few elements neighboring xenon is schematically illustrated in Fig. 4, as a function of volume.<sup>9</sup> The levels designated 6s, 5p and 5d are the discrete levels in the atomic state, for the group of elements indicated at the bottom. In the solid state these levels broaden into bands and these bands cross when the volume is decreased. The system is an insulator if

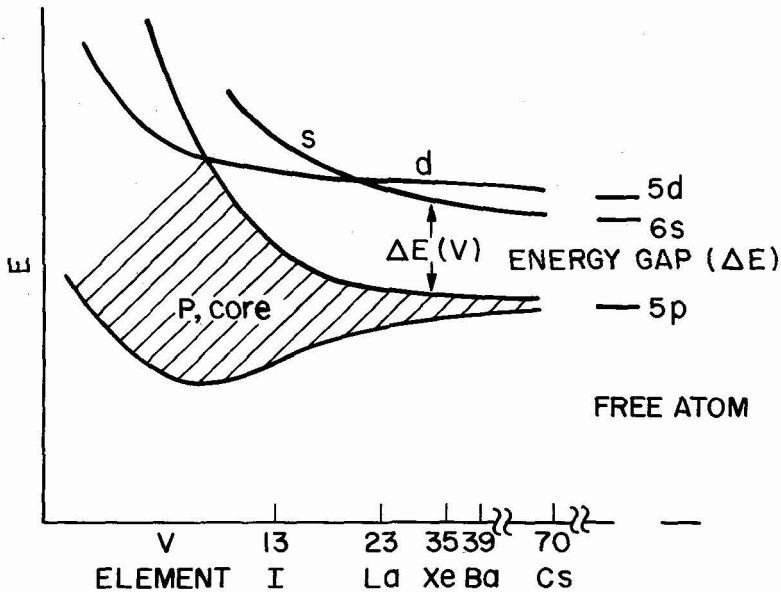


Fig. 4 Electronic structure of elements (Reference 9) surrounding Xenon, in their solid state. The relevant discrete atomic levels are shown on the extreme right. With pressure the volume decreases and the bands broaden and rise in energy, giving rise to electronic structure changes.

there is a gap between a fully occupied state and the next higher band, and metallic if the band is partially occupied, or overlaps with a fully occupied band. At normal pressure both Xe and  $I_2$  (iodine exists as a dimerized molecule and has a closed 5p shell) have a filled 5p band, separated by a gap from the empty 5d and 6s bands and therefore are insulators. With decreasing interatomic distance this gap closes and the 5p and 5d overlap. The expectation then is that both  $I_2$  and Xe should become metallic at high pressure, and band structure calculations have indicated that this event should occur around 1.3 Mbar pressure in Xe and near 200 kbar in  $I_2$ .

Solid Xe is a clear transparent substance and a wide band gap insulator, with a gap of 9 electron volts at ambient pressure. In its progression towards the metallic state, this gap may be expected to decrease with pressure and vanish in the metallic state. In the latter event the material would turn opaque to light, as all metallic substances are, and this can be easily viewed in the DAC. Recent optical absorption spectroscopic measurements on solid Xe to nearly 600 kilobar<sup>10</sup> have indicated, that its insulating band gap decreases to about 4 electron volts, which is in the right direction for metallization with pressure. However, the clear transparency of Xe at 600 kbar is proof that it is still a very good insulator at this pressure. A resistivity measurement performed by Nelson and Ruoff<sup>11</sup> some years ago in a diamond indenter has shown evidence for a metallic transition in Xe at an estimated pressure over 1.3 megabar.<sup>12</sup> It is likely that we have seen metallization in Xe, but further corroboration is needed. The optical absorption edge of CsI has been studied to 600 kbar and from the data it is concluded that metallization in CsI will not occur below 900 kbar pressure.<sup>13</sup>

Iodine is a case in which the transition from insulating to the metallic has been established beyond doubt. It is a molecular crystal with  $I_2$  as the unit, and is an insulator at ambient pressure because of the completely filled 5p band. Two decades ago, Drickamer and coworkers investigated the electrical resistance of iodine under pressure and observed a large continuous decrease in the resistance in the 0-200 kbar region. From this result they suggested that solid iodine becomes metallic under pressure, possibly due to a valence – conduction band overlap. However, the question whether iodine is still a molecular crystal in the metallic state, or it becomes a monatomic metal was unresolved. Only recently high pressure X-ray diffraction studies on iodine with the DAC has settled this question.<sup>14</sup> From the results it can now be stated that iodine becomes gradually metallic in the molecular crystal itself by band overlap, and the metallization process is completed through an abrupt structural transformation to a monatomic lattice at about 210 kbar, where it becomes a p-band metal due to a partially filled 5p band in the monatomic solid. The structure of iodine at three different pressures is shown in Fig. 5 to illustrate the point. The metallization of iodine under the influence of pressure is relevant to gain an insight into the metallization process for hydrogen.

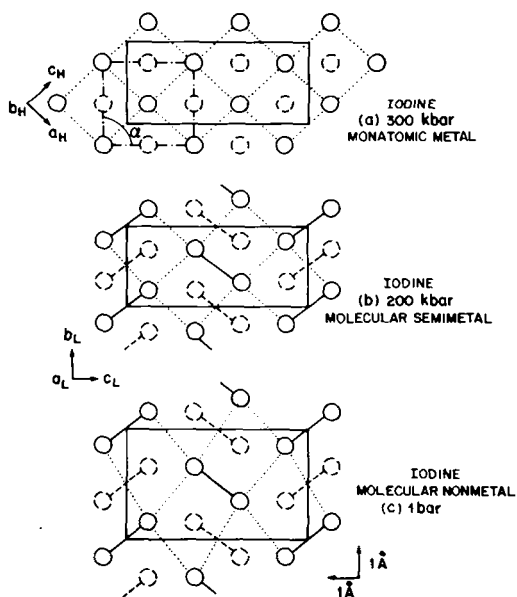


Fig. 5 The structure of iodine at three different pressures, obtained from high pressure x-ray diffraction experiments (Reference 14).

The quest for metallic hydrogen has evoked a lot of interest in the high pressure behavior of solid hydrogen. Hydrogen solidifies to a clear transparent solid near 57 kbar pressure at 298K and is a molecular crystal, with  $H_2$  as units. Solid hydrogen is highly compressible; its density increases sevenfold in 1 to 360 kbar.<sup>15</sup> It is also a very good insulator. Under the influence of pressure, metallization in

solid hydrogen can occur due to the band overlap mechanism in the molecular crystal, or the molecules can break up, leading to a monatomic metal (in the latter event the 1s-band would become half filled and the monatomic solid would be a metal), as mentioned earlier. Theory predicts that metallic hydrogen is likely to be a high temperature superconductor. The high pressure behavior of hydrogen is therefore of fundamental interest and further, it has implications for the internal structure of the giant planets which are believed to be largely made up of hydrogen.

One of the important inputs into the calculations for estimating the transition pressure to metallic hydrogen is the experimental equation of state for the molecular solid. Until recently experimental data on the compressibility of hydrogen extended to only 20 kbar. The DAC has provided pressure-volume data to pressures an order of magnitude greater than the above. Shimizu et al<sup>16</sup> have measured the sound velocities in hydrogen as a function of pressure, by a Brillouin spectroscopy and have used the data to calculate the density of hydrogen as a function of pressure. Van Stratten et al<sup>17</sup> have measured the pressure-volume relationship for solid hydrogen to 370 kbar directly, by measuring the gasket hole diameter with a microscope and the thickness of the hole by an optical interference technique at different pressures. Based on this data an equation of state was obtained and this was used to estimate the transition pressure for metallic hydrogen. According to this estimate the metallic transition pressure could be anywhere between 2 and 6 Mbar, depending upon certain correction factors that go into the calculations. Whether metallic hydrogen could be produced in the DAC or not cannot be answered at the present time, but the high pressure Raman studies<sup>18</sup> show that the intramolecular binding weakens at pressures above 300 kbar.

Since the advent of the DAC, structure determination by high pressure X-ray diffraction, absorption, reflection and light-scattering spectroscopic studies have multiplied. A host of metallic elements, semiconducting materials, molecular crystals and numerous inorganic insulators have been investigated to pressures of several hundred kilobars. A new level of understanding of the physics and chemistry of solids at high pressure is emerging, as a result of these studies (see Ref. 1). The possibility of reaching megabar pressures has stimulated solid state theoretical calculations. These calculations, facilitated by modern computing are able to predict pressure-induced transitions and the electronic band structure at high pressure, to an astonishing degree of precision.<sup>19,20</sup>

### High Pressure and Planetary Interior

High pressure research is relevant to a deeper understanding of our own planet Earth, if not for more basic reasons connected with the physics of matter at high pressure. Inside the earth, both pressure and temperature progressively increase with depth and at the center these are estimated to be 3 million atmospheres and  $\sim 4000^\circ\text{C}$ . It is well accepted that the interior of the earth is differentiated into a core, mantle and crust, with different densities, chemical makeup and pressure-induced phases. Much of the information about the interior of the earth has come from seismological data. However, a detailed understanding of the internal structure of the earth has to come largely from Laboratory high pressure - high temperature studies on the rock forming minerals. In the era prior to the DAC, high pressure - high temperature conditions that would correspond to a depth of about 400 km in the earth's interior could be simulated in the laboratory and extensive studies have been carried out on phase equilibria in silicate minerals.

With the advent of the DAC and laser heating, it has become possible to simulate conditions corresponding to a depth of 2900 km and the diamond cell is like a window to the interior of the earth up to the core-mantle boundary. A large number of high pressure - high temperature mineral studies using the DAC have been done in recent years by several groups, simulating conditions in the lower mantle, right-up to the core-mantle boundary.

As per current knowledge,<sup>21</sup> the silicate minerals (mainly made up of  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{FeO}$  and  $\text{Al}_2\text{O}_3$ ) undergo a series of pressure-induced phase changes, each one resulting in an increase in the density. These density increases can be correlated with the observed velocity profile, giving us a picture of the interior of the earth. Accordingly, the sudden velocity increase near 400 km is believed to be due to a phase change in olivine [ $(\text{Mg,Fe})_2\text{SiO}_4$ ] to the spinel, or to the distorted-spinel phase called the  $\beta$ -phase, and the similar increase in the velocity at a depth of 670 km is tentatively associated with the spinel ( $\text{MgAl}_2\text{O}_4$  structure) to perovskite transition. The perovskite structured phase involving Mg, Fe, Si and O, seems to reign the depths of the lower mantle up to the core-mantle boundary. Possibly there are also some simpler oxides such as nonstoichiometric  $\text{FeO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ , and  $\text{SiO}_2$  in the dense stishovite structure, in the depths of the lower mantle. However, the view that the mantle is made up of a mixture of simple oxides may not be quite correct. That the outer core is predominantly iron is well accepted. Whether there is some lighter element such as sulfur or oxygen in it is still being debated.

High pressure research is also of considerable importance to the understanding of the internal structure of other planets, in particular the giant planets, viz. Jupiter, Saturn, Uranus and Neptune.<sup>22</sup> Rough estimates of the pressure at their center are: Jupiter about 45 Mbar, Saturn about 10 Mbar, Uranus and Neptune about 6 Mbar. The most important problem in the high pressure physics of giant planets is to identify the relevant constituents in their make-up and ascertain the pressure-induced phase transitions in them, to develop thermodynamic models for their interior. Plausible models for Jupiter, Saturn and Uranus are shown in Fig. 6.

Hydrogen is believed to be the dominant constituent in the make-up of Jupiter and Saturn and helium is likely to be present as hydrogen-helium mixture, in the proportion close to the cosmic abundance. The high pressure properties of hydrogen were discussed earlier and the main conclusion was that it would turn metallic at high enough pressure. Accordingly, hydrogen is assumed to be present in the metallic state, in the region enveloping the core of both Jupiter and Saturn, where the pressures should certainly be above the metallic transition pressure for hydrogen. The core designated as rock is primarily magnesium, silicon and iron, in combination with oxygen. The ices in the present context refer to solid water, solid methane and solid ammonia. The ices are probably minor constituents in Jupiter and Saturn but they are believed to be important for Uranus and Neptune. Uranus appears to have a different internal structure, with an envelope made up of molecular hydrogen, helium and methane. At a level corresponding to 70% of the radius, an abrupt transition occurs to an ionic ocean of  $\text{H}_3\text{O}^+ \cdot \text{OH}^-$ , with dissolved  $\text{NH}_3$ . Although pressure here is about 200 kbar, the temperature is well above the melting temperature of water at this pressure. The rock core representing 30% of the radius may be differentiated into an iron core-silicate mantle structure, similar to the earth.

One may ask the question what would be the limit of pressure attainable with the diamond anvils. One thing that will limit the maximum pressure would be a



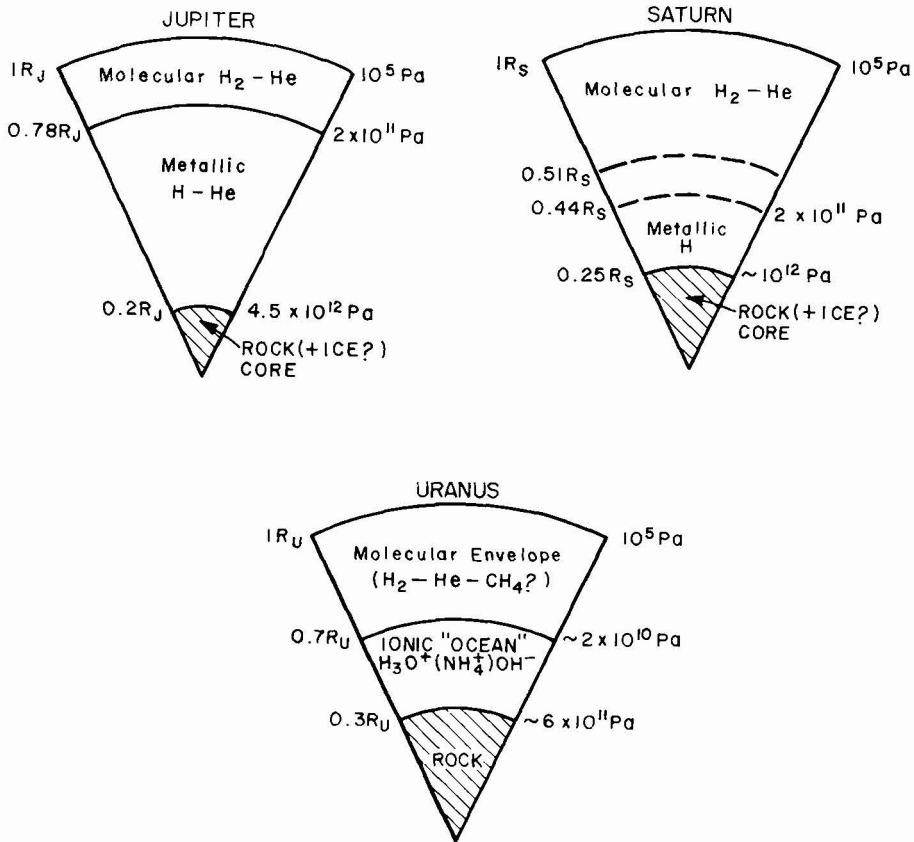


Fig. 6 Models for the interior of the Giant Planets: Jupiter, Saturn and Uranus. The radius ( $R$ ) normalized to 1 are indicated on the left. The numbers adjoining the boundaries are the densities (Reference 22).

phase transition in diamond, possibly to a metallic phase. However, a recent total energy calculation by Yin and Cohen<sup>23</sup> shows that diamond is stable up to 23 Mbar pressure, with respect to a transformation to the  $\beta$ -tin, simple cubic and other well-known close packed structures. It is conservatively estimated that the diamond structure would be stable up to at least 10 Mbar, with respect to any other metallic phase. While this is very encouraging news for the proponents of the DAC, the ultimate pressure that can be reached would be determined by the yield strength of diamond. From plasticity theory it is estimated, that in perfect diamonds pressures of 5 Mbars might be achieved over submicron dimensions.

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