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**Optical Measurements on Hydrogen
at Ultrahigh Static Pressures
(Summary Report for NRIP W233)**

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Optical Measurements on Hydrogen at Ultrahigh Static Pressures (Summary Report for NRIP W233)

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OPTICAL MEASUREMENTS ON HYDROGEN AT ULTRAHIGH STATIC PRESSURES (SUMMARY REPORT FOR NRIP W233)

by

R. L. Mills and D. H. Liebenberg

ABSTRACT

This report summarizes the results of a two-year New Research Initiatives Program (NRIP) aimed at developing apparatus and techniques for studying hydrogen and other gases under ultrahigh static pressure in diamond-anvil cells. The following goals were achieved: we established a facility in which precision optical measurements can be made; we built special diamond cells for use at low temperatures; we devised procedures for loading cells with gases at high density; we carried out preliminary visual, x-ray, and spectral studies on various gases at pressures up to 50 kbar; and finally, having demonstrated the feasibility of our NRIP, we sought and obtained other sponsorship on a continuing basis.

I. INTRODUCTION

Diamond-anvil cells were first developed at the US National Bureau of Standards (NBS) in the late 1950s, but the diamond cell became a precision instrument only recently with the advent of ruby-fluorescence in situ pressure measurements.¹ At the Carnegie Institution Geophysical Laboratory,² solid samples have now been compressed in diamond cells to a static pressure of 1.7 Mbar (170 GPa).

Because little effort was being directed toward studies of gases at ultrahigh static pressures, we proposed* to enter this important field under the Los Alamos Scientific Laboratory (LASL) New Research Initiatives Program (NRIP). Our goal was to establish in LASL Group Q-10 a facility for measuring the optical properties of solidified gases at static pressures up to 0.5 Mbar using diamond cells. In particular, we intended to concentrate on the hydrogen isotopes because (a) they represent the simplest diatomic molecules and are of keen interest to theorists, (b) information about deuterium-tritium fuel at extreme pressures and temperatures would be useful in refining schemes to produce thermonuclear energy, and (c) results at ultrahigh densities might lead to a better understanding of the transition to metallic hydrogen.

Our NRIP proposal to study gases at ultrahigh pressures in diamond cells was funded in fiscal year (FY) 1977 at \$60k under Program Code W233. Citing encouraging results after the first nine months,** we applied for second-year support and received \$66k in FY 1978. Following is a summary report of our activities. Several interim reports have also appeared.³

II. EXPERIMENTAL

A. Personnel

1. New Hires. When NRIP approval was first announced in July 1976, we began searching for a postdoctoral candidate with experience in diamond-cell technology. We recruited D. Schiferl, then a postdoctoral appointee at Stuttgart, Germany, who had made x-ray studies using diamond cells both at Stuttgart and the University of Chicago. Schiferl worked on our NRIP from 1 August 1977 through 31 July 1978, when he joined LASL Group M-1, and was instrumental in setting up x-ray diffraction equipment and determining structures.

*R. L. Mills and D. H. Liebenberg, "Optical Measurements on Hydrogen at Ultrahigh Static Pressures," Los Alamos Scientific Laboratory NRIP proposal (January 1976), LASL internal document, unpublished.

**D. H. Liebenberg and R. L. Mills, "Optical Measurements on Hydrogen at Ultrahigh Static Pressures," Los Alamos Scientific Laboratory progress report NRIP W233 (June 1977), LASL internal document, unpublished.

During the summer of 1978, R. A. LeSar (Harvard) worked in Q-10 as a Graduate Research Assistant and made contributions to our NRIP in the field of x-ray diffraction and infrared and Raman spectroscopy.

2. LASL Collaborators. We were fortunate in having the assistance at Los Alamos of J. C. Bronson (Q-10), who designed some of the apparatus, and L. C. Schmidt (SD-5), who did the demanding machine work. We assisted R. D. Taylor and J. O. Willis (both Q-10) in making Mössbauer studies in diamond cells. We also collaborated at LASL with D. T. Cromer (CMB-5) on x-ray measurements and L. H. Jones (CNC-4) on infrared and Raman experiments. We cooperated with H. J. Fullbright (M-1) in setting up an energy-dispersive x-ray system for diamond-anvil cells at the nondestructive test facility. B. W. Olinger (M-6) loaned us several diamond cells for preliminary experiments.

3. Outside Advisors. Our original proposal was written under the assumption that G. J. Piermarini, NBS, Washington, DC, would collaborate with us. Although Piermarini visited Los Alamos in FY 1976 to act as advisor during the planning stages, it was not possible for him to take part in the experiments. Also visiting from NBS and giving general counsel on our project in FY 1976 and again in FY 1978 was P. M. Heydemann.

In FY 1977, A. vanValkenburg from the Carnegie Institution Geophysical Laboratory spent several days in Los Alamos demonstrating diamond-cell technique. Serving also as valuable advisors from the same institution were P. M. Bell and H. K. Mao who visited in FY 1978. On three occasions they hosted visits from us to their Washington, DC, laboratory, and twice carried out ruby-fluorescence pressure measurements on our cells.

E. M. Brody, who pioneered Brillouin-scattering measurements in diamond cells at the University of Rochester, Space Science Center, was invited and came to Los Alamos in FY 1978 to discuss his sophisticated experimental techniques and to explore the possibility of future collaboration.

B. Apparatus

In a diamond-anvil cell, force is usually applied by screw-driven spring washers that bear through a lever arm on a pair of small (1/3-carat) diamonds. A strong metal gasket between the diamond faces is used to confine the specimen and add radial support to the diamond tips. The gasket may also contain a mixture of alcohols, to serve as hydrostatic medium, and a ruby chip, to act as pressure gauge.

When excited, the ruby R_1 and R_2 lines fluoresce in the visible red region. These lines shift as a doublet to longer wavelengths almost linearly with pressure. By relating the lineshifts to sodium chloride x-ray cell constants, which, in turn, have been determined as a function of pressure, workers at NBS have established a new scale called the ruby pressure scale.¹ The ruby scale was recently extended into the megabar region by intercomparison with shock-wave data on metals.⁴

It was our original intention to operate with shopbuilt diamond cells and borrowed optical equipment. Although we were able to pick up a few surplus items, it soon became clear that most of the precision optical and electronic instruments needed for our special applications would have to be purchased as funds became available from related programs. Some of the expensive machine work was also charged to other projects. Our mode of operation obviously caused delays during the two-year course of research, but we realized our primary objective, that of creating a facility where high-quality work in diamond cells can be carried out at LASL.

Fig. 1.
Mao-Bell diamond-anvil cell sectioned to indicate tungsten carbide (WC) backing plates for diamonds in sleeve (cylinder) and plunger (piston). Force is applied to lever arm by spring-loaded screw on left. Gasket (washer) is shown with capillary tube for high-pressure gas filling.

1. Diamond Cells. Our first diamond cell, shown in Fig. 1, was built from plans furnished by Mao and Bell,² who have since reached a record static pressure of 1.7 Mbar in a cell of similar design. We used the Mao-Bell cell to make preliminary measurements on gases at room temperature and, with spot cooling by a jet of Freon, at slightly reduced temperatures. The entire cell mechanism was later mounted in a vacuum jacket equipped with cryogen flow lines for cooling the sample volume down to 200 K. We could not reach lower temperatures with this arrangement because our refrigeration was insufficient to remove the large amount of heat that the diamonds were able to

conduct from the massive mechanism into the sample. A second Mao-Bell cell was recently completed and will be used in conjunction with the two-stage system described below.

A Bassett-type diamond cell was borrowed from LASL Group M-6. This cell has a large screw drive for applying force directly to the diamonds. It is smaller than a Mao-Bell cell and can reach pressures of 200 kbar. The cell has been used in Q-10 for Mössbauer studies of the phase transition in cobalt-doped iron.

On loan from the University of Chicago was a Schiferl-Jamieson-Lenko diamond cell, which features wide-angle windows, but is limited to about 100 kbar. This cell was modified for single-crystal x-ray work on a diffractometer (Picker).

The smallest cell in our collection is a Merrill-Bassett diamond cell, designed at the University of Rochester. It features three small adjusting screws that load the diamond anvils through steel and beryllium backing plates. We made our first x-ray diffraction measurements with a borrowed cell of this type and have since built an improved model using stronger beryllium that should allow us to reach 100 kbar. The new cell has hemispherical backing plates with absorption corrections that are independent of diffraction angle. We also designed a vacuum jacket and flow line for cooling the entire cell to liquid-nitrogen temperature.

We recently built a fifth type of diamond cell designed to operate inside a cryostat for carrying out optical and x-ray studies at low temperatures. Figure 2 is a photograph of the cryostat with the top removed. The diamonds are forced together by thin-walled steel compression and tension tubes that are vacuum jacketed, extend 50 cm from the cold pot, and are hydraulically driven by a screw-thread oil injector as shown in Fig. 3. In preliminary tests with liquid nitrogen, the 4.7-l cryostat cooled the sample area by conduction to 80 K, allowing a working time of over 30 h. With liquid hydrogen in the pot we held a 40 K temperature for 9 h. We plan to study the melting curves and solid-phase diagrams of various light isotopes to over 200 kbar using a combination of cooling baths and electrical heating.

We built a prototype two-stage diamond cell to be filled initially with high-density gas inside our piston-cylinder device.⁵ The diamonds were mounted in a small sleeve and plunger that lock together by a ratchet-type set

Fig. 1. The diamond-cell cryostat is shown in the process of being assembled. The cryostat is a small, compact, and highly reliable device that can be used to study the properties of a sample at low temperatures.

the sample is placed after each 0.1 mm increase in pressure. Tests indicated that the sample could hold against a force of 1000 psi to contain a sample at a starting pressure of 20 kbar.

2. Optical Equipment. A system of optical optics is needed to view samples in diamond cells. We purchased a 100- to 200-power high-quality microscope (Nikon) to make the two kinds of observation that are required routinely, namely, the measurement of gasket compression and the determination of frequency shift with pressure in the ruby fluorescence lines. Our microscope was modified so it could be removed from its base and mounted on various cells and cryostats for close-range viewing. We acquired several other microscopes for fabricating and assembling cell parts.

A 40-mW helium-cadmium laser (RCA) was used as an economical source of 441.6-nm radiation to pump fluorescence in the ruby chip. We analyzed the fluorescence spectrum with a 1/4-m spectrograph (Jarrell-Ash), purchased as a compromise in efficiency, resolution, and cost. Using a motor-driven grating,

Fig. 2. Cooling the diamond-cell cryostat with liquid nitrogen. Windows in cap (top center) permit optical and x-ray measurements. Tension and compression members run inside vacuum-jacketed tailpiece (lower center) and are driven by screw-thread oil injector.

photomultiplier tube, amplifier, and oscilloscope unit, we were able to determine the P_1 and P_2 lines to ± 0.25 nm with a resolution of ± 0.15 nm. A high-resolution spectrograph was later developed to give a resolution of ± 0.05 nm.

We purchased an oscilloscope with a built-in computer, a 100-MHz oscilloscope, and a high-resolution spectrograph. The oscilloscope was used to monitor the signal from the photomultiplier tube and the spectrograph. The computer was used to control the spectrograph and the oscilloscope. The oscilloscope was also used to monitor the signal from the photomultiplier tube and the spectrograph.

Fig. 4.

Fig. 4.
Block diagram of optical system showing arrangement of various components.

When the spectrograph was used in the normal mode, the resolution was ± 0.15 nm. The resolution was improved to ± 0.05 nm when the spectrograph was used in the high-resolution mode. The spectrograph was used in the high-resolution mode for the measurements of the ruby lineshift with pressure at various temperatures. The spectrograph was also used for the measurements of the ruby lineshift with pressure at various temperatures.

We adapted several diamond cells for use on the automatic circle diffractometer in LAFS Group CMB-5. Similar modifications were made for mounting cells in the Group CNC-4 infrared and Raman spectrometers.

Our small piston-cylinder device⁵ was assembled in a 9000-kg press (Carver) and mounted on the optical table for calibrating the ruby lineshift with pressure at various temperatures. The piston contained a sapphire window through which a helium-cadmium laser beam

could enter and the excited fluorescence from a ruby chip could exit as the chip was compressed hydrostatically with fluid ^4He at precisely known pressures.

C. Techniques

It is relatively easy to load gasketed diamonds with specimens of liquids and solids at room temperature and to produce ultrahigh static pressures on compression, but gas samples are so compressible that unreasonably large gasket deformation will result unless the initial filling is at high density. The new experimental procedures that were developed under our NRIP involved primarily schemes for loading diamond cells with high-density gas.

The first method we attempted was that suggested in our NRIP proposal and described recently both in a LASL Disclosure Paper* and in a published article.⁶ Briefly, a horizontal hole was drilled through the metal gasket and an ultrafine filling tube was soldered in place as shown in Fig. 5, whereupon the gasket was positioned between the diamond faces and a slight sealing force was applied while high-pressure gas was introduced through the tube. With additional force we closed off the filling hole and trapped the sample so it could be compressed further. We later modified the technique to reach higher densities by nesting the gasket in a cooling coil through which cryogens could be passed. The gasket, with attached flow tubes, was aligned in a Mao-Bell diamond-anvil cell, previously mounted in a jacket that could be evacuated. By monitoring the vacuum we were able to detect gas leaks and control the anvil force so it was just sufficient to seal the diamonds while gas at a pressure up to 3 kbar was admitted at ~ 200 K.

We developed a second technique in which the entire diamond-anvil cell was immersed in liquefied sample gas. After the cell had cooled and liquid filled the gasket, a clamping force was applied to the submerged cell to seal the specimen at liquid density. In cases where the gases are costly (such as xenon) or hazardous (such as carbon monoxide) the sample can be liquefied in a small volume defined by an indium ring that encircles the diamonds and seals

*D. H. Liebenberg, R. L. Mills, J. C. Bronson, and L. C. Schmidt, "Gasket for High Pressure Diamond Anvil Cell," Los Alamos Scientific Laboratory disclosure worksheet S-49,937 (April 1978), LASL internal document, unpublished.

Fig. 5.
A steady hand is needed to solder a 0.15-mm diam capillary tube into a gasket.

against the backing plates. With one diamond slightly retracted from the gasket, the cell is cooled and the specimen gas is introduced through a capillary into the indium ring where it condenses and fills the gasket. The diamond faces are then clamped, trapping the sample.

We also devised a two-stage filling procedure in which the small sleeve-and-plunger assembly that supports and guides the diamonds in a Mao-Bell cell (see Fig. 1) is removed, fitted with an unsealed gasket, and is inserted in a vessel that can be charged with sample gas to pressures from 2 to 20 kbar. In this high-pressure environment, the diamonds are advanced toward each other to seal the gasket and are locked in final position by a friction fit or by a ratchet, such

as that indicated in Fig. 6. The loaded diamond assembly is then removed and reinstalled in the Mao-Bell mechanism for further compression. This technique was described in a LASL Disclosure Paper,* where it was emphasized that the method can be used to pressurize any solid sample with helium and thus maintain hydrostatic conditions to pressures well above the present 100-kbar limit where alcohols freeze.

*R. L. Mills, D. H. Liebenberg, J. C. Bronson, L. C. Schmidt, and D. Schiferl, "Two-Stage Pressure System," Los Alamos Scientific Laboratory disclosure worksheet S-50,629 (July 1978), LASL internal document, unpublished.

Fig. 6.
Pointing out ratchet grooves on plunger that lock it into sleeve (immediate front). Mechanism with diamonds and gasket is first inserted into piston-cylinder device (shown disassembled) for loading with high-density gas.

III. RESULTS AND DISCUSSION

A. Ruby Pressure Scale

At liquid-nitrogen temperature, helium remains fluid at pressures up to about 15 kbar, where freezing takes place. We used helium as a pressurizing medium in our piston-cylinder apparatus to compress ruby hydrostatically and measure its fluorescence lineshift as a function of pressure at both 75 and 300 K. We were plagued by equipment failure at low temperature, but at room temperature, wavelengths were determined to ± 0.05 nm with a 1/4-m spectrometer and pressures were obtained to $\pm 0.3\%$ from hydraulic readings on the press.

Recently Mao and Bell² reported the ruby calibration curve to be

$$P = 3808 \left[\left(\frac{\lambda_p - \lambda_0}{694.2} + 1 \right)^5 - 1 \right], \quad (1)$$

where P is the pressure in kilobars, λ_p is the wavelength in nanometers of either the R_1 or R_2 ruby fluorescence line at pressure P , and λ_0 is the corresponding zero-pressure value. In our low-pressure region where $(\lambda_p - \lambda_0) \ll 694.2$, Eq. (1) reduces to Piermarini's¹ linear relationship

$$P = 3808 \left[5 \left(\frac{\lambda_p - \lambda_0}{694.2} \right) + 1 - 1 \right] = 27.4 (\lambda_p - \lambda_0). \quad (2)$$

Up to our highest achievable pressure of 10 kbar, we confirmed Eq. (2). Since Eq. (2) was based on the x-ray-determined sodium-chloride pressure scale, we indirectly verified that scale also.

During the course of our NRIP we were unable to build windows that held pressure above 10 kbar. Our urgency to extend ruby calibrations to lower temperatures decreased following a recent report⁷ of calibration data at pressures up to 10 kbar and temperatures down to 4 K. In the future we plan to check the ruby pressure scale in a diamond cell by intercomparison with accurately known melting curves of helium,⁸ hydrogen,⁹ and nitrogen¹⁰ to 20 kbar.

B. Preliminary Studies of Solids and Liquids

In diamond cells, particularly those designed to reach the highest pressures, it is extremely important to align the diamond faces parallel to each other and perpendicular to the line of force, otherwise the risk of fracturing diamonds is high. It is also important to verify that the diamonds remain aligned under pressure. We did this by observing that phase changes in various solids, which serve as pressure standards in the range 2 to 200 kbar, proceeded uniformly from the center of the diamond faces outward as force was applied. The technique is illustrated in Fig. 7.

To gain familiarity with the Mao-Bell cell, we compressed water at room temperature and observed the freezing transition to ice VI at 10 kbar and the solid transformation to ice VII near 20 kbar. Pressures were deduced from literature values.¹¹ After the ruby-fluorescence pressure system was built, we compressed an alcohol mixture to 60 kbar in the Mao-Bell cell to study background satellite lines in the apparatus. From microscope measurements, we found the focussed laser spot to be about 10- μ m diam. We also measured hole symmetry as a function of ruby-determined pressure in gaskets containing compressed liquids. A slight change in birefringence was observed when carbon tetrachloride solidified under pressure. Figure 8 shows similar measurements in progress.

C. Visual Studies of Gases

The first gas we experimented with was carbon dioxide at normal tank pressure to demonstrate that gas could be introduced through a capillary into a gasket, then sealed, liquefied under pressure, and finally solidified at room temperature. In one experiment, we were able to condense and seal CO₂, along with a ruby chip, in a Mao-Bell cell and take it to the Carnegie

Fig. 7.
Diamonds (visible through small hole in side of sleeve) are checked for alignment under pressure in Mao-Bell cell.

Fig. 8.
A wrench (right hand) is used to increase pressure in a Mao-Bell cell while transitions in the specimen are viewed through a microscope.

Institution, where we determined from the ruby spectrum that the pressure was 10 kbar. The pressure was eventually raised to 30 kbar, which was a record at that time for static compression of gases.

In later experiments, gaskets were filled through fine capillaries with carbon dioxide and with argon to initial pressures greater than 1 kbar at temperatures slightly below room temperature. Subsequent compressions to pressures over 30 kbar were achieved and photographs of the freezing fluids were taken to check for birefringent solids. We found, however, that it is extremely difficult to see birefringence in anisotropic crystal specimens by simply looking through diamond cells with crossed polarizers. Under stress the birefringence of the relatively thick diamonds tends to swamp that of the sample.

As an extension of the above experiments, the diamond anvils in our vacuum-jacketed Mao-Bell cell were cooled locally to 200 K by circulating

liquid nitrogen around a beryllium-copper gasket, which was then filled through a capillary with deuterium gas at 3 kbar. We squeezed the gasket to close off the capillary and transported the loaded cell to the Carnegie Institution where further compression gave a pressure of 45 kbar. Our attainment of this record static pressure in D_2 and the results of a similar study on CO_2 were recently reported in the literature.⁶

None of our gaskets with capillary filling tubes survived pressures over 50 kbar. Blowouts invariably occurred near the capillary port. We attributed the failures to two main causes: first, the gasket was simply weakened by drilling and soldering; and second, to accommodate a filling tube, the gasket had to be made thicker than the optimum initial value of 0.25 mm. We therefore were obliged to devise the alternative filling procedures that involve immersion of the cell in liquid or a high-pressure gas.

D. X-Ray and Spectral Studies of Gases

We adapted the Merrill-Bassett diamond cell for use with a precession x-ray camera and used our technique of complete immersion to fill the gasket with liquid nitrogen. The sample was compressed, warmed to room temperature, and examined by x-ray diffraction. We found that a high-quality single crystal of nitrogen had formed in the hexagonal-close-packed structure ($\beta-N_2$) with the c axis aligned perpendicular to the diamond faces. The lattice constants were determined from twelve (hkl) reflections using a least-squares orientation program for an automatic four-circle diffractometer (Picker). The results were $a = 3.629 \pm 0.004 \text{ \AA}$ and $c = 5.890 \pm 0.01 \text{ \AA}$, giving a molar volume 30% smaller than that near the triple point. From P-V-T data¹⁰ on N_2 obtained in this laboratory, we calculated that the sample pressure was 25.1 kbar at 296 K. We also measured the relative x-ray intensities of the various reflections and found them to be unchanged from values at 1 bar. It appears that at our high pressure and temperature the molecules librate about the c axis at the same 56-deg precession angle as at low pressure and temperature. A paper describing our results has been accepted for publication.¹²

Our Merrill-Bassett diamond cell with special high-strength beryllium backing plates was filled with liquid nitrogen by immersion, sealed, and compressed to 36 kbar on the ruby pressure scale. (Pressures ten times higher have since been attained with this method in a Mao-Bell cell). Preliminary

x-ray analysis at room temperature showed two crystals of nitrogen in a new orthorhombic structure closely related to that of β -N₂.

Using our modified technique with indium sealing ring, we filled a second Merrill-Bassett cell with liquid carbon monoxide and, at room temperature, observed that the sample solidified between 18 and 22 kbar. This is in conflict with a published¹³ melting curve for CO, measured to 2 kbar, which extrapolates to a room-temperature freezing pressure of 60 kbar. Preliminary x-ray measurements indicate that the CO structure at 22 kbar is analogous to that of orthorhombic N₂, reported above.

An energy-dispersive powder x-ray diffraction system was set up at LASL Group M-1 by Schiferl who did the following work in collaboration with M-1 personnel: check-out runs were made at 1 bar on aluminum, copper, alpha-uranium, and nickel, with the nickel run extending to moderate pressure in a Bassett-type diamond cell; a first attempt was made to obtain a 1-bar energy-dispersive pattern from a fairly large sample of americium-243, but it was unsuccessful because of high gamma radiation background; powder patterns were transferred to a PDP-11 computer (Data General) for plotting and analysis in which a Bayesian deconvolution scheme was used to separate overlapping peaks.

In conjunction with others in LASL Group Q-10, we used a Bassett-type diamond-anvil cell to study the high-pressure phases of iron through Mössbauer effect. The sample was an iron disk doped with cobalt-57 and placed in an Inconel gasket with an alcohol pressure medium and ruby chip. Data were obtained at 0, 90, and 106 kbar. At 106 kbar a few percent of the sample transformed from the α (bcc) phase into the nonmagnetic ϵ (hcp) phase. Figure 9 is a photograph of the experimental setup.

Just as our NRIP was terminating, we carried out the first spectral studies made on gases in diamond cells. We found from Raman and infrared measurements that the stretching-mode frequency of N₂ and CO molecules increases with pressure. Interpretation of other features in the vibration spectra must await complete solution of the new orthorhombic crystal structures.

Fig. 9.
Indicating chart of Mössbauer spectrum
obtained from cobalt-doped iron sample
(forceps) in diamond cell at low tem-
perature.

IV. CONCLUSIONS

We achieved our main goal of establishing at LASL a facility in which optical properties of solidified gases can be measured at ultrahigh static pressures in diamond cells. Quality instruments, mounted on a large optical bench, now permit good visual observations and spectral measurements to be made. We have built diamond cells in which pressures can be varied at low temperatures and we have devised techniques for filling the cells with high density gases.

Our original scheme for loading cells through a high-pressure capil-

lary in the gasket allowed us to reach a final pressure in deuterium of about 50 kbar, the highest static pressure so far reported for this gas. To attain higher ultimate pressures, however, we have devised two new loading procedures. The first of them involves sealing a gasket while the diamond assembly is immersed in liquefied sample. In the second method the diamonds are sealed in an atmosphere of high-pressure sample gas.

Using the first method of liquefied gases, we loaded several cells with nitrogen and carbon monoxide and produced pressures in the solid phases of 40 kbar. X-ray diffraction measurements made at room temperature in the region of 22-25 kbar disclosed that N_2 is hexagonal closest-packed while CO is probably orthorhombic. Nitrogen appears to transform to the orthorhombic structure around 30 kbar. Preliminary spectral studies of the same samples indicate that the vibrational frequencies of these molecules increase with pressure.

We have not yet demonstrated the second method, that of filling diamond cells in auxiliary vessels at high gas pressures, but we have built various components of the system and subsequent tests were encouraging. The high-density gas technique is especially useful for hydrogen and helium isotopes,

where the liquid densities are low. These isotopes should also prove valuable as hydrostatic media in pressurizing other samples in diamond cells over a wide range of temperatures and pressures.

Our NRIP grant served to establish an important facility at LASL for studying gases at ultrahigh static pressures in diamond-anvil cells. The program is continuing partly under the aegis of the Department of Energy, Office of Basic Energy Science, Division of Materials Sciences, and partly under the Division of Military Applications.

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H. W. Johnson (M-1) took the photographs for Figs. 3, 5, 6, and 9 and prepared the prints. The photographer for Figs. 2, 7, and 8 was W. L. Headdy (ISD-7).

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