The diamond cell stimulates high-pressure research

Diamond-anvil pressure cells and an accurate way to measure high pressures have expanded research in many areas, including electrical properties, radioactivity, crystallography and spectroscopy.

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Scientific advances can be made either in a dramatic and revolutionary manner or in a slow evolutionary way, sometimes covering a span of several years. An example of the latter process is the diamond-anvil pressure cell, which in about a decade and a half has developed in stepwise fashion from a rather qualitative instrument to the sophisticated quantitative research tool it is today, capable of reaching static pressures in the megabar range.

The amount of research being carried out with diamond cells has expanded rapidly in the past few years, and we can not hope to cover all aspects of this research in an article of this nature. However, we will mention what we believe are the important elements, including the introduction of three new techniques: the ruby fluorescence pressure-measurement method; advanced laser techniques in the area of spectroscopy, and the development of hydrostatic capability to 104 kbar in the diamond cell. Other important factors have been the diamond cell's miniature size, portability, adaptability to other measurement apparatus, and, finally, extreme pressure and temperature capabilities extending into the megabar range and to 3000°C. It may be used in a wide variety of experiments because the cell body can be modified appropriately for the particular experiment of interest, thus finally enabling the physicist to use the pressure variable as he has used the temperature variable in the past to expand his knowledge of the physical world about him.

To establish a frame of reference we show in the Table on page 46 a range of pressures found in the world about us. From these data it is apparent that the new tool is of major importance to the field of geophysics, as well as to other areas. Knowledge of the Earth's deep interior remains largely theoretical, being derived from observations on or near the Earth's surface and the study of seismic-wave behavior. Laboratory measurements that may unlock the secrets of the Earth's mantle and possibly its outer core now appear feasible.

Rising pressures and accuracies

In the days of Percy Bridgman's pioneering work (around 1909 to 1961), many current scientific experimental techniques were not available; for those that were, measurement sensitivity in many cases was so low than one had to employ large pressure-generating systems to attain the pressures required for significant physical changes. The complexity of attaining the pressures, along with problems of making desired experimental measurements, kept the number of workers in the field very low. Applications were limited to a very few areas that could be readily measured, such as compressibility, electrical resistance, polymorphism, and *pvt* relations.

As pressure is simply force per unit area, very high pressures can obviously be obtained either by greatly increasing the force on a material or decreasing the sample size on which the force is applied. In 1959, the diamond-anvil pressure cell—which makes use of the latter concept—was developed at the National Bureau of Standards; it was used initially for microscopic and infrared studies, followed a few years later by x-ray crystallographic studies. Although this cell was limited in pressure range, and there was no reliable method of determining the pressure generated in the device, work at NBS and other laboratories continued on its development and applications because of the ease with which it could be employed to obtain high-pressure data.

In 1972 the discovery at NBS of the ruby fluorescence method of measuring pressure allowed, for the first time, a rapid, convenient means of measuring accurate pressures in the cell and also resulted in the understanding of the variables needed for attaining ultrahigh pressure. The consequences of this development are extremely significant—an enormous static pressure range, which can be measured with previously unattained precision, has now become routinely available for the study of materials by a wide variety of experimental techniques. Moreover, a knowledge of sophisticated pressure technology is no longer required by the user. He can now concentrate on the experiment at hand, whether it be in x-ray diffraction, spectroscopy, electrical resistance or some other area. Figure 1 illustrates one such complete system for observing a sample and measuring the pressure.

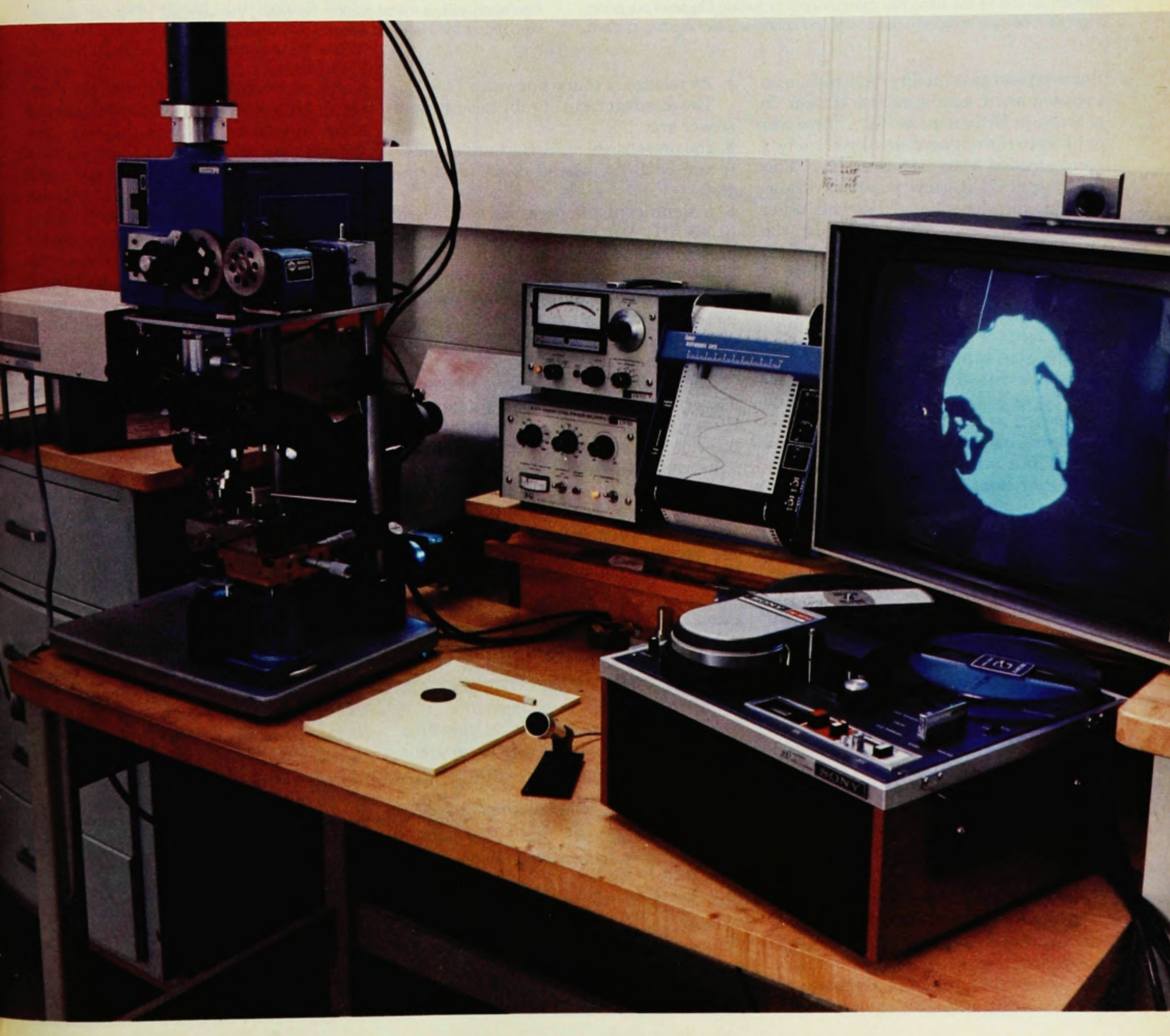
In this article we present a general discussion of the diamond-anvil high-pressure cell and include a description of the instrument and the ruby fluorescence method of measuring pressure. We also discuss important aspects of the development of the cell that ultimately led to the production of megabar pressures. Then we survey what has been done already in this rapidly expanding area of research, and discuss some new opportunities that show great potential.

Diamond-cell concept

The original diamond cell was conceived at NBS by Charles Weir and his group[1] in 1959. It consisted of two small

The complete high-pressure system in the authors' laboratory at the National Bureau of Standards. This photograph shows the microscope, monochromator, recording apparatus, TV camera and monitor. Figure 1

The authors are scientists at the National Bureau of Standards in the crystallography section, of which Stanley Block is chief.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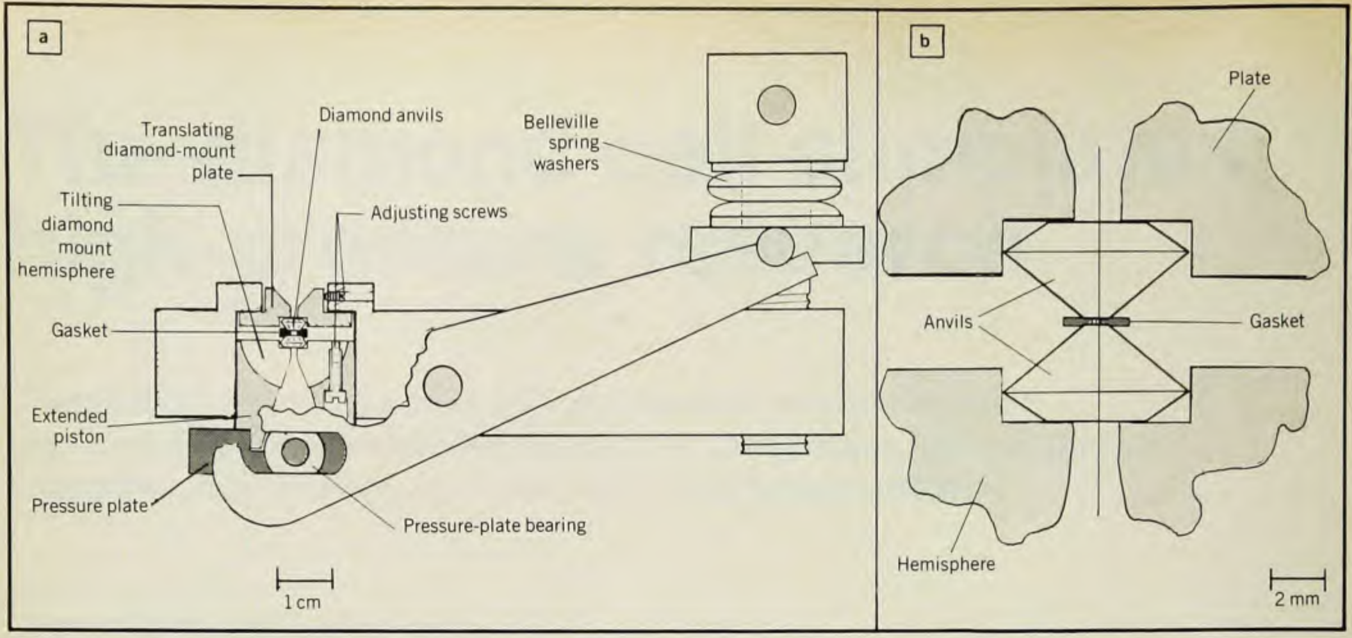

An ultrahigh pressure diamond cell. The complete cutaway cross-section (a) shows the essential components including the anvil supports, alignment design, lever-arm assembly and spring-washer loading system. The detail (b) shows an enlargement of the opposed diamond anvil configuration with a metal gasket confining the sample. The cell was developed at the National Bureau of Standards. Figure 2

single-crystal gem-quality diamonds in an opposed-anvil configuration similar in concept to Bridgman anvils. Force was applied to the opposed-anvil system by a spring-loaded lever-arm assembly. This device quickly became popular; various designs, developed at NBS and other laboratories, were used both in the above-mentioned applications and in other areas, particularly in the study of phase transitions by x-ray powder-diffraction methods. However, with continued use, the instrument's limitations soon became apparent. The cell and its various modifications had limited pressure capabilities. Also there was no convenient way to measure pressure: Estimates involving force per unit area calculations *were* made, but these were very crude due, in part, to the approximately parabolic pressure distribution across the flat. Later, increased accuracy was attained by adding a second phase, such as sodium chloride, and, utilizing the pressure dependence of its lattice parameter. But this method depended on x-ray measurements requiring as much as 300 hours to obtain one pressure point—a procedure with obvious disadvantages.

Ruby-fluorescence technique

In 1972 a rapid, convenient, and simple method of measuring pressure that uses the pressure dependence of the sharp ruby R_1 fluorescence line was developed at NBS.[1] Although several fluorescing materials were studied for this purpose including Al_2O_3 (0.5% Cr), $YAlO_3$ (0.2% Cr), YAG (0.4% Cr_2O_3), and others, ruby appears to be the best available material because of:

- its high intensity per unit volume,
- its acceptable pressure dependence (0.36 Å $kbar^{-1}$), and
- its relatively sharp linewidth (7.5 Å).

The disadvantages of ruby as a pressure sensor are:

- the presence of an R_1R_2 doublet (6942 Å and 6928 Å) instead of an ideal singlet,
- a significant temperature coefficient (0.068 Å$°C^{-1}$) in the same direction as the pressure dependence, and
- a thermal line-broadening effect that causes the R_1 and R_2 lines to overlap with increased temperature and limits the use of the individual R-lines for pressure calibration to less than 200°C.

The composite line can be used with decreased precision to higher temperatures. A redeeming feature is that the pressure and temperature dependences to a first approximation have been found to be linear and additive to 300°C and 30 kbar.

An interesting point is that although the thermal expansion and compressibility of ruby behave normally, the pressure and temperature shifts of the fluorescent line are both unexpectedly in the same direction—towards the red. No theoretical explanation of these shifts is available. Simple considerations based on our current understanding of the point-charge model of crystal-field theory predict a positive pressure dependence with respect to energy—a shift toward the blue with increasing pressure. It appears that the dynamic effects caused by wave function overlaps may be much more significant than the static lattice constant effects. Basically this means that increased shielding, due to the effective decrease in lattice constant with increasing pressure, modifies the parameters used to describe the ion in the crystal-field picture; in particular we are concerned with the changes in the Racah parameters B and C. The linear changes required in these parameters still remain a puzzle.

The linewidths also provide useful information because in a hydrostatic envi-

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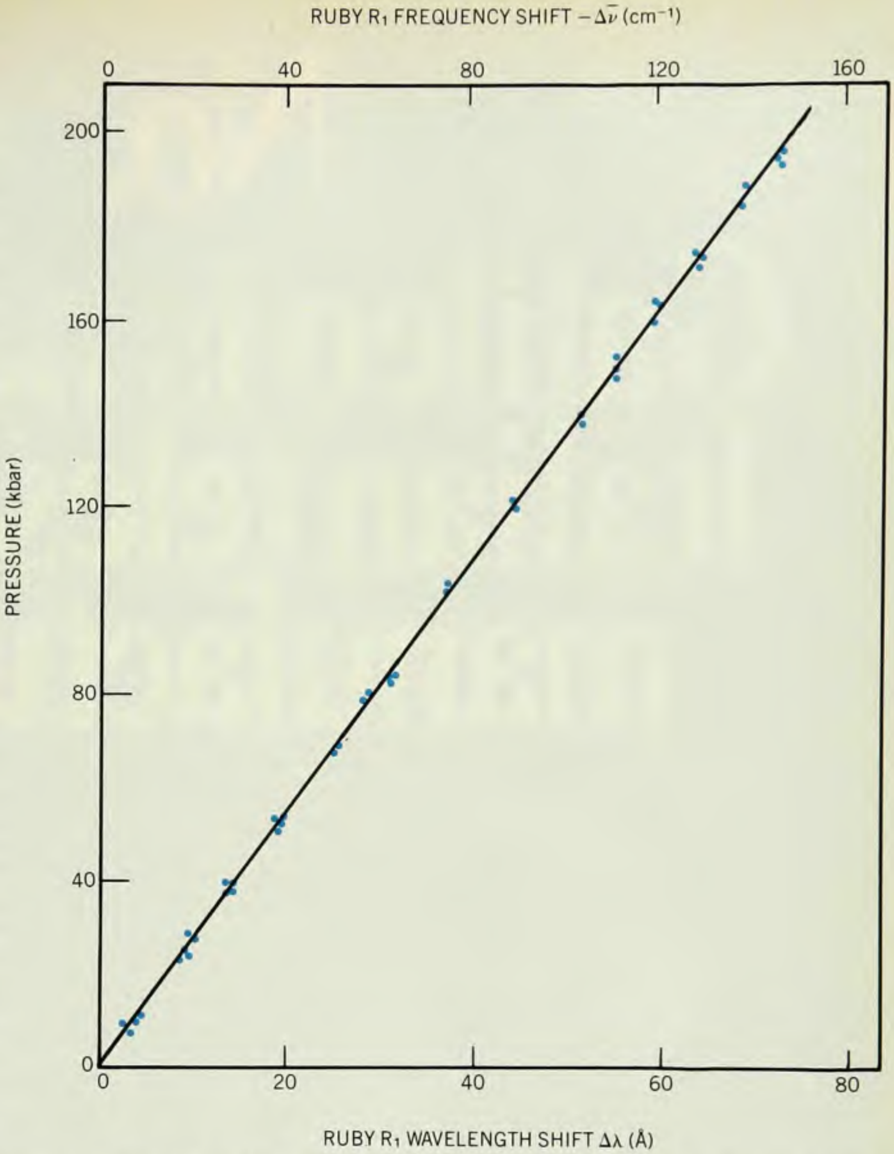
A spectrum of high pressures occurring naturally

Pressure (kbars)	Examples
1	Deepest part of ocean—Marianas Trench
10	Mohorovicic discontinuity, Crust–mantle interface
1.37×10^3	Wiechert–Gutenberg discontinuity, mantle–core interface
3.64×10^3	Center of Earth
1×10^8	Center of Sun

The use of "bar" and "kbar" throughout this article follows the current common practice of workers in the field. For the uninitiated we note that 1 bar = $10^5 N/m^2$ (or pascal) = $10^6 dyn/cm^2$ = 0.9869 atm = 1.0197 kgf/cm^2. The international standard (SI) unit of pressure is the pascal, or newton per square meter.

ronment the lines sharpen slightly with increasing pressure, whereas as soon as the environment becomes nonhydrostatic, nonuniform stresses on the ruby result in strongly broadened lines.[1] Ultimately the R$_1$ and R$_2$ lines coalesce with increasing nonhydrostatic stress.



Pressure calibration at 25°C of the ruby R$_1$ fluorescence line at 6942 Å as a function both of wavelength and of wavenumber or frequency (cm^{-1}). Figure 3

Although the optical fluorescence technique for pressure measurement was developed initially for the diamond anvil cell, it should be noted that the method is applicable to any pressure cell with optical access. Harry Drickamer has informed us that his group at the University of Illinois recently converted the calibration of their optical cells to the ruby shift because of the convenience of making the pressure measurement in spectroscopic apparatus along with the added improvement in accuracy of the measurement.

The use of this rapid pressure measurement technique has added to our understanding of the operation of the cell itself and of the cell design variables on which the production of ultrahigh pressures depends critically.[1] Figure 2a shows a schematic cross-sectional diagram of an ultrahigh pressure diamond cell. The heart of the anvil assembly is shown in the detail, figure 2b. It consists, as did Weir's original cell, of two single-crystal gem-quality diamonds in an opposed-anvil configuration. The culets of the two gemstones have been ground off and the exposed surfaces polished to form flats between which specimens are compressed. Force is applied by a lever-arm assembly similar to that of the original design. Loads are generated by the simple rotation of a screw, which compresses Belleville spring washers of known load capacity. These washers can be placed in series or parallel to vary the magnitude and sensitivity of the load as desired. Because the area over which the load is applied is approximately 0.75 mm^2, very high pressures can be produced with the application of moderate loads. The compressive strength and hardness of diamonds are extremely high; so they are able to support the required loads generally without failure.

Although the technique of squeezing powdered material between the two flats enables pressures as great as 350 kbar to be attained, large pressure gradients exist in the sample, ranging from one atmosphere at the edge of the flat to a maximum at the center.[1,2] In this approximately parabolic distribution of pressure, the presence of large shear stresses has always cast serious doubt on the interpretation of the desired measurements. However, the presence of uniaxial stress on the sample has also been useful in determinations of strain and the strength of materials as a function of pressure. These properties can be determined by measuring the ellipticity of diffraction rings obtained when the x-ray beam traverses a sample perpendicular to the loading axis of the diamond anvils.[3] To eliminate the problems resulting from nonhydrostaticity, techniques were developed at NBS originally by Alvin Van Valkenburg for encapsulating the sample in a fluid to provide a hydrostatic environment.[1] The fluid is retained between the anvil flats by the small metal gasket shown in figure 2b. The gasket hole is approximately 0.25mm in diameter and 0.1mm in thickness. At NBS, pressure-transmitting fluids have been developed that are capable of producing hydrostatic environments to as high as 104 kbar.[1]

Generating megabar pressures

The important criteria for attaining pressures in the ultrahigh pressure range are:

- the ability to align the anvil flats both axially and horizontally with accuracy,
- maintaining this alignment rigidly under the loads necessary to produce ultrahigh pressures, and
- minimizing stress centers in the anvils due to surface inhomogeneities. These criteria are met in the present design.[1] Whether the loads are generated by springs, by hydraulic rams, or by other means is immaterial as long as the above conditions are met. We prefer the spring-loaded lever arm because of the ease of loading the cell with a sample, the ease of changing the force uniformly and continuously, the ability to change the sensitivity of the force control, and the resulting mobility of the cell.

The requirement of maintaining anvil alignment under pressures imposes restrictions on the design of the cell. The body of the cell must be made of material sufficiently high in strength to prevent bending and thus affecting this alignment. We use hardened (RWC-55) 4340 alloy steel to meet this requirement. The support for the table of the diamond anvil must be made of extremely hard material to prevent deformation under the resultant forces and thus possible misalign-

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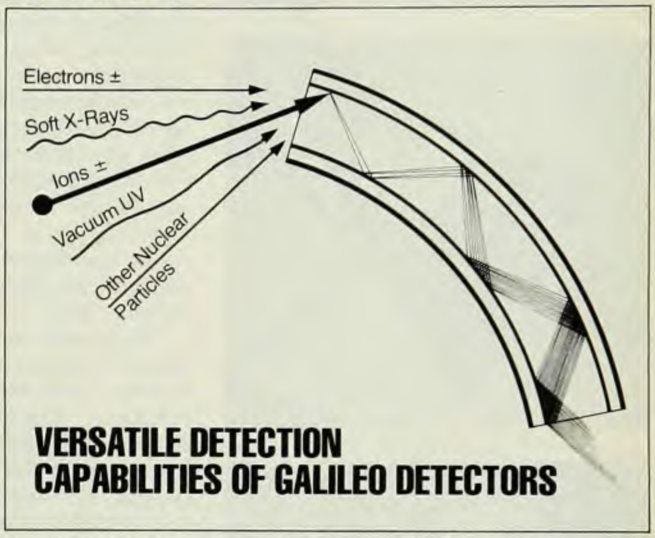

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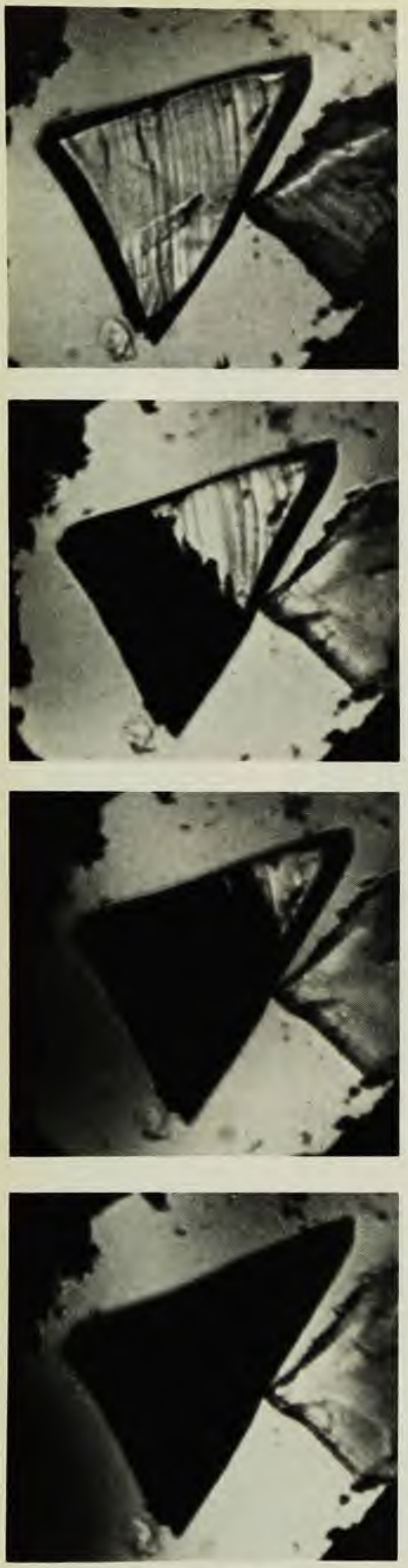


A single crystal of zinc sulfide at 150 kbar in the diamond cell is transformed, in this sequence, to a black opaque phase, which is electrically conducting. The adjacent object is a crystal of ruby that acts as the pressure sensor. The Inconel gasket, which measures approximately 0.5 mm along its major axis, contains the pressure transmitting fluid. Figure 4

ment of the two anvil flats. These materials can be either hardened metal alloys or superhard materials, such as boron carbide or tungsten carbide, which are used with a thin sheet of nickel foil to separate the anvil from the hard material. As an improvement on earlier versions of the cell, the piston in which one of the diamond anvils is set has a longer sleeve, again to prevent misalignment of the flats.

As long as the major requirement of keeping the diamonds aligned during the pressure experiments is maintained, the body can be made from any material suitable for the particular experiment. Obviously, when measuring magnetic properties, one must make the body of the cell of nonmagnetic material such as a beryllium–copper alloy. If one wishes to carry out high-temperature studies in a controlled way the cell body can be made out of a high-temperature, high-strength material such as Waspalloy. A furnace can be installed in the region around the diamond anvils and the temperatures varied at will.

The pressure cell, no more than about 12½ centimeters in length, fits in the palm of one's hand and can reach ultrahigh pressures. The pressures can be determined very rapidly, as the diamonds are transparent in the region of 6942 Å where the ruby fluorescence lines occur. Only a very small ruby fragment, as small as 1% of the total sample volume, is necessary for a pressure measurement. Thus, there is little or no interference by the ruby sensor with other desired measurements. The line shift can be measured by a suitable spectrometer with at least an 8 Å/mm reciprocal dispersion to give a precision of ±0.5 kbar to the measurement.

The system shown in figure 1 consists of an x–y–z stage for mounting the pressure cell, a polarizing microscope, and in our case a ¼-meter monochromator with an echelle grating used in the 8th order to increase the precision of the wavelength measurement. In this apparatus a mercury arc lamp is used to excite fluorescent emission in the ruby fragments. More recent techniques employ different types of lasers for this purpose. There is also a low-light-level television camera with a silicon-diode array extending the optical observation range to 1.1 microns, so that phenomena such as the semiconductor-to-conductor transition in materials such as gallium phosphide and silicon can be observed very readily on a TV monitor and can also be recorded on video tape.

Before one can assign meaningful values to pressures in the ultrahigh pressure regime, a pressure scale must be defined. At present the best pressure scale above 300 kbar (provided that optical access is available) appears to be the shift of the ruby R_1 line. In a series of studies the pressure shift of ruby was determined initially by calibrating against the freezing pressures of a series of pure liquids in the low pressure range below 30 kbars, and ultimately to 291 kilobars by the use of the lattice parameter of sodium chloride and its equation of state as proposed by Daniel Decker (figure 3).[1,4] At 291 kbars NaCl transforms to the CsCl structure (B_1–B_2 transition) and marks the limit of well determined pressure calibration. The R_1 line-shift $dp/d\lambda$ is 2.74 kbar $Å^{-1}$, and the quadratic term is not detectably different from zero.

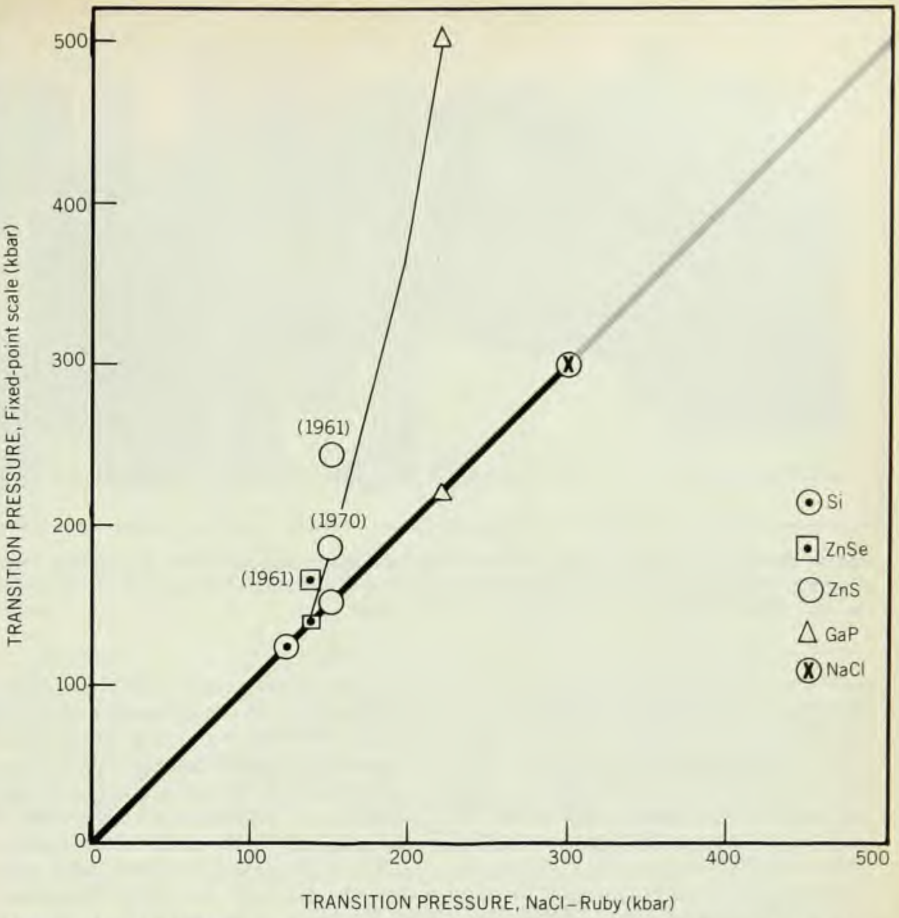
Fixed points

The most common measurement made under ultrahigh pressures is that of electrical resistance. Therefore, a series of fixed points based on large resistance changes of several orders of magnitude, usually associated with a phase change to the metallic state, has been used to establish a fixed-point scale.[5] Unfortunately, the B_1–B_2 transition of sodium chloride yields too small an electrical change to be a good candidate for this fixed-point scale.

The first experiments we carried out after the ruby calibration work were determinations of the semiconductor–conductor transitions of several materials. We observed the change in optical absorption to an opaque phase characteristic of the metallic state, as shown in figure 4 for a single crystal of zinc sulfide.[1] The interesting results are presented in figure 5, where the pressure we determined by the ruby scale in 1975 is the abscissa and the ordinate is the former pressure scale. The historic trend in pressure values has resulted in the fixed-point scale being revised downward several times, as the graph in figure 5 indicates.

At the moment, the highest accepted transition pressure for electrical measurements is that of gallium phosphide. Earlier reports indicated that this transition occured in the ½-megabar range. However, more recently, several independent determinations of this GaP transition have verified our results shown in figure 5. Francis Bundy has determined the transition electrically, and he puts the transition in the 230–240-kbar range.[6] He used compacted sintered diamonds as Bridgman anvils in an apparatus designed for electrical resistance measurements and has attained pressures of over 400 kilobars based on EuO as a fixed point. Because the diamond tips are nonconducting, he used a gasketed system in which gold electrodes are separated by the sample. Clarke Homan has also measured the GaP transition electrically in a Bridgman anvil-type press with variable lateral support and places the transition at 220 kbar.[7]

Still another problem to be considered during the selection of materials to be used as fixed points is the physical and chemical nature of the material itself. In the case of EuO, for example, A. Jayaraman, who has carried out numerous valuable experiments with the diamond cell and has attained the highest reported pressure of 400 kbar for an ungasketed system, reported two transitions: one at about 300 kbar and the other in the region of 400 kbar.[8] Obviously this material should be considered a likely candidate as a fixed point in the 300–400-kbar region of the scale. However, there are indications that EuO has a wide range of stoichiometry depending very much on its impurity level,[9] which affects the transition pressure and thus makes it a very poor fixed point. There is general agreement on the B_1–B_2 transition in NaCl at 291 kbar, and even though it is not electrically detectable with great sensitivity this appears to be the highest reliable fixed point at the present time. A good candidate for a fixed point above 300 kbar is boron phosphide, which is supposed to have a metallic transition in the region of 400 kbar. Neither Bundy nor we have observed this predicted transition in boron phosphide. Bundy carried out electrical measurements in his Bridgman anvil press with sintered-diamond-tipped pistons up to 400 kbar, and we have made visual observations on single-crystal boron phosphide in the diamond cell up to 575 kbar. Therefore, at the moment the highest reliable fixed point with a large change in resistance is gallium phosphide at approximately 220 kbar.



Transition pressures for various materials. This graph compares the fixed-point scale and the ruby–NaCl scale. The points designated "1961" refer to the original fixed-point scale, and those with "1970" refer to the 1970 revised scale. Figure 5

Linearity assumption

For the present we rely on a linear extrapolation of the R_1 pressure dependence to measure pressures in the ultrahigh pressure regime. When more accurate equations of state of other materials that are both transparent and exhibit no phase change become available, then a better measure of the linearity in the higher pressure range can be obtained. A good candidate for such a material appears to be magnesium oxide.

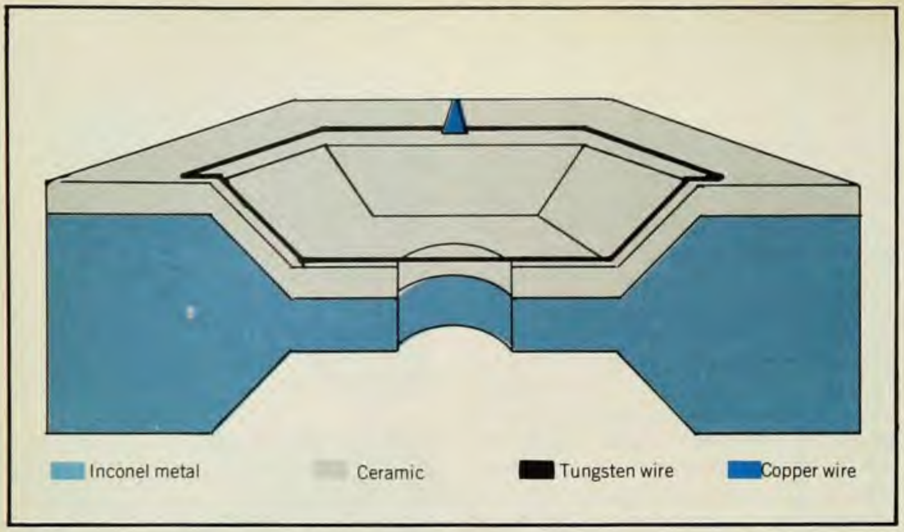
H. K. Mao and Peter Bell report the attainment of pressures in the megabar range based on the assumption of continued linearity of the ruby shift.[10] They built a diamond-anvil pressure cell based, in principle, on the NBS design, but with some modifications. Having placed a small ruby crystal on a thin metal foil between the anvils, they applied force to the anvils and squeezed the ruby into the metal foil. They used a laser in the epi-illumination mode to excite the R lines and measured a shift of 370 ångstroms. With the assumption that R_1 line linearity is still valid in this range, the shift corresponds to a pressure of 1.02 megabar, which is the highest reported for the diamond cell.

Electrical properties

Until very recently no electrical measurements were made in the diamond cell. Mao and Bell developed a method for measuring electrical resistance and estimating resistivity in an ungasketed system, and, more recently, we have developed a method for measuring electrical resistance in a gasketed diamond cell. The gasketed system has two advantages. One is the ability to make the measurements in a hydrostatic system; with a methanol–ethanol mixture the hydrostatic range currently extends to 104 kbar. The other advantage is that a gasket, which acts as a confining belt, must be used to attain the maximum pressures. Figure 6 shows a gasket system that we, along with Dick Forman, have developed for making electrical measurements in the cell. The electrical circuit consists of the metal gasket, an insulating ceramic layer, and a very fine tungsten wire laid across the gasket hole. The sample then makes contact with both the wire and the gasket, completing the circuit. We have carried out studies on semiconductor–conductor transitions, using such a gasket, and have found that the observed abrupt change of optical absorption does, as expected, correlate with the order-of-magnitude changes in resistance at these points. Electrical and optical studies can be carried out concurrently in a diamond anvil cell.

Superconductivity is one field of study where the increasing impact of the diamond cell should become more noticeable. Of the 39 known superconductive elements, approximately one-third are superconducting only under elevated pressure. Application of pressure can cause the transition temperature either to increase or decrease for transition metal superconductors. In all nontransition metals, on the other hand, it appears to decrease with increasing pressure. At the Naval Research Laboratory a diamond-anvil-type pressure cell has been designed that operates down to temperatures of 0.03 kelvin and pressures up to 100 kilobars.[11] The sample is contained in a beryllium–copper gasket, and the magnetic moment (and thus the Meissner effect) is measured by a SQUID magnetometer. The pressure on the sample is obtained from a knowledge of external gas pressure and with calibrations determined from a one-parameter fit to previously measured superconducting transitions in the low-pressure range. Dave Gubser and Alan Webb have used this equipment to study the superconducting transition temperature of aluminum up to 62 kilobars.[12] At 62 kilobars the transition temperature was reduced to 0.075 kelvin from the ambient value of 1.8 K.

At the other extreme is the possibility of doing high-temperature studies. We have studied sulfur to 800°C, controlling the temperature to ±2°. At this tem-



Gasket for electrical resistance measurements in the diamond cell, seen here in a cutaway view. The ceramic adhesive can be replaced with an alumina-filled epoxy coating, which gives similar results. Optical studies can be carried out concurrently. Figure 6

perature sulfur becomes opaque under pressure.[1] The highest temperatures in the diamond cell were obtained by L. Ming and William Bassett using laser heating.[13] With a pulsed ruby laser they produced temperatures as high as 3000°C, and a YAG laser proved capable of sustained 2000°C temperatures. Using the pulsed ruby laser on fragments of graphite suspended in sodium chloride at pressures of approximately 200 kilobars, they were able to transform graphite to diamond. Bundy's study of the direct conversion of graphite to diamond employed a small belt press and the discharge of capacitors through the sample for heating[14]; he estimated that the temperature needed for the transition was 3000°C. This is the basis for the temperature quoted by Ming and Bassett. Bassett's laboratory has been very active in the design and application of diamond anvil cells, with an approach that leads to further miniaturization of the cell. In the early days, gaskets were avoided, with the idea of obtaining the highest pressures; Bassett estimates that the highest pressure attainable in the ungasketed system is about 350 kilobars.[2] Above this value, he thinks, elastic deformation in the anvils is responsible for the extreme loss in efficiency in the apparatus. We have found, on the other hand, that the use of a gasket is one of the primary conditions for the attainment of higher pressures.

Radioactivity

In 1973 the University of Rochester group reported[15] and discussed the pressure dependence of the radioactive decay constant of Be^{7}. In 1947 Emilio Segrè and Raymond Daudel suggested that the decay constants of radioactive nuclides decaying by electron capture could be altered by changing the electron density in the vicinity of the nucleus, and an obvious method of doing this is to vary the pressure on the sample. Kenneth Bainbridge observed the difference of decay rate on Te^{99} before and after subjecting it to pressures of 100 kilobars. W. B. Gogarty used a similar technique to measure the effect of pressure on the decay rates of Be^{7} and Ba^{131}. W. K. Hensley, Bassett, and J. R. Huizenga, however, using a diamond-anvil cell, were able to measure the decay rate constant of Be^{7} at pressures up 270 kilobar, *in situ.*[15] The Be^{7} decays to Li^{7} when electron capture converts a proton to a neutron. Hensley, Bassett and Huizenga found a relatively linear change in $(\lambda - \lambda_0)/\lambda$ as a function of pressure, and estimated the increase in the decay constant of Be^{7}O with pressure from electronic wave functions of the free Be atom. They calculated a 0.35% increase in electron density at the nucleus of the free beryllium atom. The decrease of radioactive decay rate can also serve as a method of pressure measurement for a system in which optical access is not possible. The change in decay rate should be linear and the resultant radiation hard enough to penetrate the sample housing.

Crystallography

The diamond-anvil cell was soon used for x-ray powder diffraction measurements because carbon has a low atomic number and is thus very transparent to x rays.[1,2] Later, during the period from 1965 to 1968, the NBS group developed a single-crystal method based on the use of a beryllium cell body and the precession technique to overcome the limitations of the powder method.[1] Benzene II was the first crystal structure determined *in situ* by high-pressure single-crystal x-ray diffraction techniques.[1] Benzene II is a high pressure polymorph of benzene, stable above 12 kbar. It can be grown either from solid benzene I at room temperature and 12 kbar, where it invariably grows as a twinned crystal, or from the liquidus at 310°C at about 25 kbar, where it forms a good quality single crystal suitable for x-ray study. This structural work was soon followed by similar studies on high-pressure forms of Ga-II, Cs-II, CCl_4-III, KNO_3, and several other crystals.[1] Later, smaller diamond-anvil cells were developed by others, including Roger Fourme,[16] Leo Merrill[17] and Dave Schiferl so that they could be used directly with standard single crystal x-ray equipment. The cell can be used with Bond geometry (measuring the diffracted beam on both sides of the origin, thus eliminating the zero error) to obtain very accurate lattice parameters, and we have used the cell in this way to obtain the anisotropic compressibility of α-lead azide and silicon.[18] The results show that $\Delta V/V_0$ can be measured with a relative standard deviation of 4×10^{-5}. This error is negligible compared to the relative uncertainty in the pressure measurement, which is about 2½% at 20 kilobars. The accuracy of the method is usually limited by crystal perfection and stability. For most crystals the uncertainty in values of the linear compression will be below 10%.

Spectroscopy

The rapid acceptance of the diamond cell for spectroscopic investigations has been due mainly to the following characteristics:

- its relatively low cost,
- its high-pressure capability,
- its miniature size and portability, and finally
- the ease of adaptability to commercially available spectrophotometers.

At NBS the diamond cell was originally conceived for the study of pressure effects on infrared spectra of inorganic materials. Success in that application created immediate interest in other laboratories[19]; a group at Argonne National Laboratory under James Ferraro quickly adopted the technique and extended its application to the far infrared range for the study of lattice vibrations, and contributions in the area of infrared spectroscopy as well as Raman scattering were made at the University of Maryland under Ellis Lippincott. Important advances were also made by Jimmy Brasch and Robert Jakobsen at Battelle Memorial Institute in the study of organic liquids by infrared spectroscopy employing gasketed techniques.

Infrared absorption measurements with the diamond cell require the use of an off-axis ellipsoid beam condensing system and diamond windows (anvils) that transmit in this range of the spectrum. Although diamonds transmit more or less throughout most of the electromagnetic spectrum, certain types have better transmission properties than others. Type II diamonds are always used as anvils or "windows" for pressure studies in the infrared because their only strong

X-Ray Heads from W-J.

50 kV and 75 kV target potential with 1 and 2 mA beam current X-ray heads are available from Watkins-Johnson Company.

Either end- or side-transmission window grounded cathode tubes may be specified. Or, for closer optical coupling, a 75 kV grounded transmission target X-ray head can be supplied.

All heads are housed in radiation-shielded, hermetically sealed packages. These packages contain the X-ray tube and high voltage and low voltage power connectors which mate with WJ-2340 Series Source Control Units. In this configuration, the heads produce 0.2% X-ray output stability over any 24-hour period.

In grounded cathode tubes, multigrid electron guns control and maintain target current stability. Control grid settings are capable of maintaining target current stability from 100 to 2000 microamperes.


75 kV, 1 mA
(GROUNDED TARGET)


75 kV, 1 mA
(NOT GROUNDED)


50 kV, 1 mA
(SIDE WINDOW)


50 kV, 1 mA
(END WINDOW)

Grounded cathode X-ray heads use indirectly heated, thermionic cathodes which are insensitive to filament power variations and depend only on grid potential for changes in target current. Fast grid response makes these tubes suitable for grid pulsing to a 200 kHz repetition rate.

Grounded target tube heads are of the filamentary cathode type and target current is controlled by filament emission. A wide range of target materials is available, including: tungsten, moly, copper, silver, chrome, rhodium, gold and tantalum.

Source control units to power all X-ray heads are available from Watkins-Johnson.

Complete technical information, including data sheets and application notes, is available from the W-J Field Sales Office in your area or from X-Ray Applications Engineering in Scotts Valley, California at (408) 438-2100, ext. 257.

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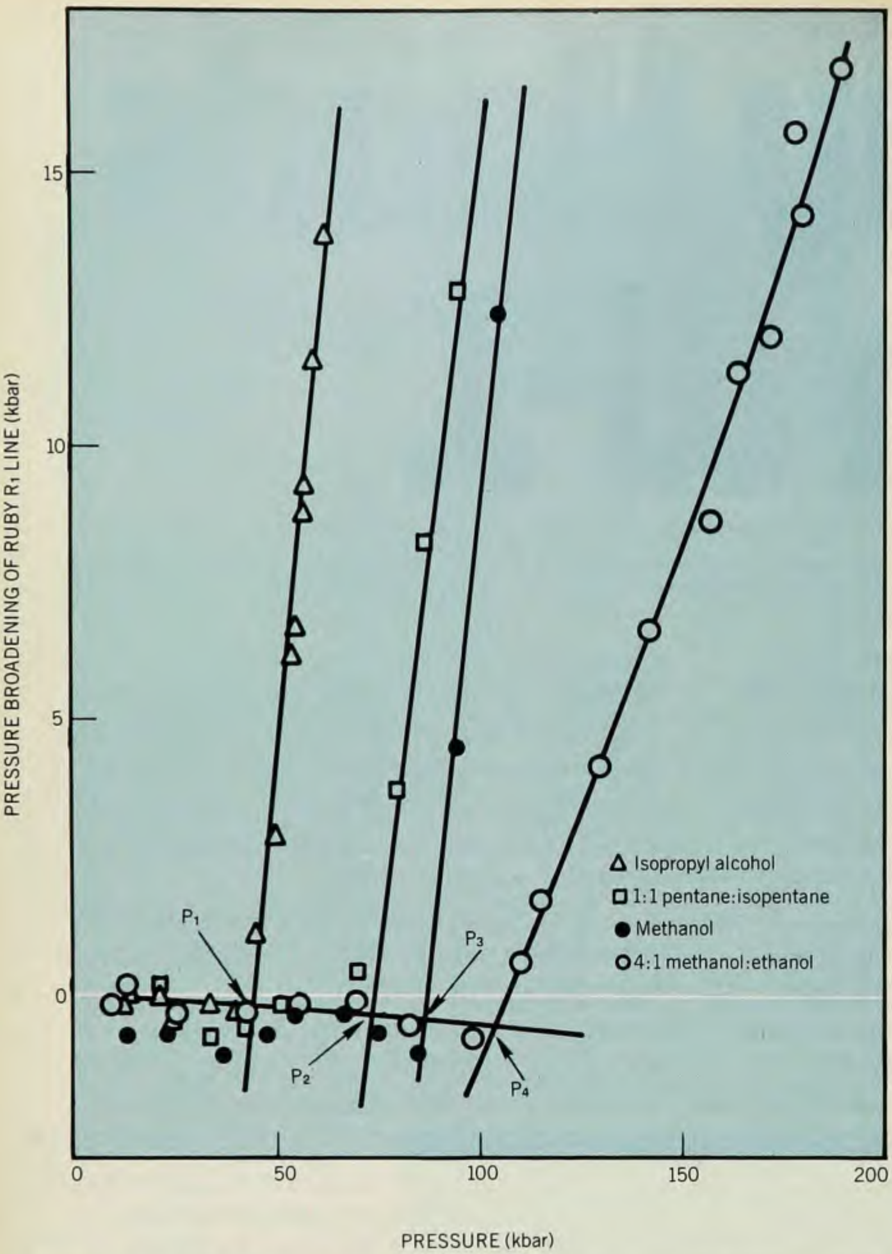

Pressure broadening of the sharp ruby R_1 fluorescence line for various pressure transmitting liquids relative to the one-atmosphere linewidth. Figure 7

absorption is in the region 1800 to 2600 cm^{-1}.

Until recently the majority of spectroscopic measurements with diamond cells was made in the mid-infrared and far-infrared regions. The sample has usually been ungasketed and therefore in a nonhydrostatic environment. The reported pressures were usually estimated from load-per-unit-area calculations, although other techniques have been used. For these reasons much of the reported data obtained in this way are somewhat qualitative.

Significant improvement in the quality of spectroscopic measurements can be made today by the introduction of advanced hydrostatic techniques employing gaskets and appropriate fluid pressure-transmitting media, and by the use of the optical fluorescence ruby pressure measurement method.

Raman scattering has already received considerable attention. Successful measurements have been made at NBS on the polymer Teflon and the semiconductors Si and GaP, employing laser techniques with the diamond cell.[1] These are studies designed to increase our understanding of the pressure-induced phase transitions exhibited by such materials. Of particular importance for their scientific interest are the semiconductors Si and GaP and many others, which undergo a polymorphic change to a metallic state. Work of this type is currently being carried out by Ben Welber at IBM's Thomas J. Watson Research Center, with extensions into the absorption, reflectance, and photoluminescence areas.[20] We have learned also that Brillouin scattering measurements were recently made in a gasketed diamond cell by Bassett and Edward Brody at the University of Rochester; feasibility tests with NaCl crystals yielded satisfactory measurements of elastic constants with an accuracy of 1% at pressures up to 35 kbar. This group used the ruby method to measure pressure.

Liquids and lubricants

As we mentioned earlier the ruby also serves as a sensor of stresses in samples. One of our first uses of the ruby technique was to measure the glass transition of a series of liquids in order to find a liquid that had a higher hydrostatic limit than the pentane–isopentane mixture proposed by Bridgman. The R_1 and R_2 linewidths show an observable decrease as a function of the pressure in the hydrostatic region. Then, as illustrated in figure 7, there is an abrupt increase in linewidth indicating that the liquid has become a glass. We found that the pentane–isopentane mixture has a glass transition at 70 kbars, and that a methanol–ethanol mixture remains hydrostatic to approximately 104 kbar.

The power of molecular vibrational spectroscopy can be used to determine structural changes in lubricants subjected to conditions prevailing in a bearing contact, that is, under very high pressures. One important question to be answered is the physical and chemical state of a lubricant prior to the occurrence of "traction," which is when it loses its lubricating qualities. This condition has been generally associated with the onset of vitrification of the material. The ruby technique has been found particularly useful in determining glass transition pressures by line-broadening measurements. In fact, it appears to be the only procedure currently available for this kind of measurement in the range of pressures above 30 kbar. With the new diamond cell technology, Peter Lauer and M. Peterkin of the Sun Oil Co. have recently completed infrared emission and ruby luminescence studies on certain lubricating fluids, and have thus obtained new insight into our understanding of the phenomenon of traction induced by high pressures. Lauer and Peterkin find that traction appears to be a consequence of a very viscous adhering fluid film in the conjunction region, rather than that of a collection of brittle, glassy particles as has been commonly thought. It is clear that in this area of lubrication, significant developments will take place within the next few years.

In this respect, work on lubrication is typical of all the other fields mentioned in this article. We believe that in each area important advances will be accomplished by application of the new diamond-cell techniques. The story is by no means ended; higher pressures will very likely be generated. All the designs so far have used unsupported diamond anvils. We know that the pressure capabilities of simple carbide anvils were appreciably increased by surrounding supports, and this same principle should apply to the diamond anvils. The time is not far off when pressures well into the megabar range will be readily available to the physicist.

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