Optical Studies at High Pressures

A miniature diamond cell facilitates high-pressure optical studies.

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The scientist has long been interested in the nature of atomic and molecular forces. Recently this interest has been focused on short-range forces such as the perturbing effects of interacting neighboring atoms or molecules. These perturbations are a function of the interatomic or intermolecular distances.

For systematic study of these perturbations in condensed systems, a means of varying the atomic distances is required. The most important factors affecting interatomic and intermolecular distances in solids are temperature, pressure, and geometrical configuration. The variation produced by temperature changes is limited by the expansivity of the material and by its thermal stability. For solids, the temperature range cannot exceed the limits imposed by the melting point and the absolute zero of temperature. For some purposes wide changes in temperature are undesirable because of the concomitant change in the thermal energy involved. It is generally not feasible to change the geometrical configuration in such a way that controlled variation in interatomic distances results. Pressure is the only factor which is not severely limited in its use for producing systematic spacing variations. Moderate pressures of the order of 50 kilobars can usually produce relatively large changes in distance without causing significant changes in the thermal energy.

Besides rearrangements and changes in phase induced by high pressures, there are several effects which are caused simply by the greater proximity of neighboring molecules at high pressures. For example, the presence of dipolar or multipolar electric moments in surrounding molecules may distort the electron cloud of a given molecule. Interpenetration of electron clouds of different molecules may occur. Such distortions affect the internal energy levels of the molecules, inducing changes in the absorption spectrum of the system.

Information about the nature of interaction forces between molecules in a compressed substance and about possible pressure-caused internal distortions of the molecules can often be obtained directly from the absorption spectrum. Indeed, the ability to apply pressures as high as 150 kbar in infrared, visible, and ultraviolet spectroscopy, x-ray crystallography, and microscopy now offers the investigator an effective tool for probing the behavior of atomic and molecular forces. The application of very high pressures in optical studies has been greatly facilitated by the development of a miniaturized apparatus which fits easily into the small sample areas of commercial optical equipment. Our purpose in this article is to describe briefly the development of this miniaturized apparatus and to discuss some of the results obtained with it.

Development of the High-Pressure Cell

The most common methods of developing high pressures are based on intrusion of a piston in a cylinder. Several devices in which this method is used to develop high pressures have been constructed and adapted for use in spectroscopy and crystallography. One early device for studying the structures of high-pressure polymorphs consisted of an x-ray camera enclosed within the high-pressure vessel itself (*1*). Helium gas was the pressure-transmitting fluid, and a beryllium window permitted x-rays to enter the vessel. The maximum pressure that could be exerted in this device was about 5 kbar. A marked improvement was made by Lawson and his co-workers (*2*), who constructed a miniature beryllium vessel and later a miniature diamond vessel. The maximum pressure attained with the latter seems to have been about 30 kbar. In a later high-pressure x-ray device diamonds were used in an anvil-type squeezer (*3*). Drickamer and his co-workers (*4*) devised a pressure cell for studying the effect on infrared absorption of pressures up to 12 kbar. However, in their apparatus the spectral range was limited by the cutoff of the sapphire windows. An ingenious bomb device in which an alkali halide serves as both pressure medium and window has been developed by Drickamer (*5*). With this device pressures as high as 200 kbar have been attained, but, so far, the studies have been restricted to the higher frequencies. Wilkinson (*6*) has modified Drickamer's design and has developed a device for use over wide ranges of frequency and temperature.

The choice of material for the high-pressure-cell window is extremely important. Of the various possible materials, diamond, which combines high compressive strength and excellent transmission properties over a wide range of wavelengths, has been the one used most successfully. In early experiments at the Bureau of Standards (*7*) the piston chamber was a cylindrical hole drilled in a diamond parallel to two polished, flat, parallel faces. Because of various difficulties inherent in this design, the apparatus now being used (*7, 8*) (see Fig. 1) was constructed on the principle of Bridgman's anvil apparatus. Designed to be mounted in a commercial infrared beam condensing unit which has a highly restricted focal area, the cell is only 25.4 millimeters long. Channels surrounding the diamond cell and drilled in the steel supporting block allow circulation of liquids or gases for regulation of temperature. Temperatures ranging from −30° to +175°C have been used. A small thermocouple may be inserted through one piston and placed in contact with the diamonds for measuring temperature.

To minimize problems of axial alignment the two diamond surfaces are purposely ground to have different surface areas. Square and irregular octag-

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onal diamond surfaces have been used. The area of the smaller of a typical pair of diamond surfaces is about 0.5 square millimeter.

Natural diamonds may be classified in two main categories, known as types I and II, which differ in their transmission properties. It is the type-II diamonds, transparent to wavelengths of 35 μ except for an absorption band near 5 μ, that are selected for use in the high-pressure cell. The diamonds withstand extremes of temperature (*9*) and pressure (*10*) without noticeable change in transmission, but apparently they do have regions of stress and strain, and eventually, with continued use at room temperature and routine pressures of 50 kbar, they deteriorate.

Pressure, Its Nature and Measurement

The limited amount of information available at present indicates that the pressure exerted on the specimen is probably not hydrostatic. Until further evidence is available, the uncertainties concerning the specific nature of the pressure will be kept in mind, and the stress endured by the specimen will be described by the general term *pressure*.

The value for the pressure (*11*) exerted on the specimen is obtained by dividing the applied force by the area of the smaller of the two diamond faces. Frictional forces are neglected. The force is determined by measuring the compression of the spring. If greater precision is necessary, the thrust transmitted by the specimen may be measured by determining the resistance of a small coil of manganin wire placed under the thrust bearing. Pressures in the diamond cell are greatest at the center and least at the edges. This gradient is quite useful since it allows simultaneous observation by microscopy of several polymorphic phases occurring in the same field of view, the denser phases always occurring toward the cell center.

The question of the hydrostatic nature of the pressure and the magnitude of pressure gradients near the edges of the specimen make it advisable to check the pressure calculated as force per unit area by a calibration based on a phase change for a given substance at known hydrostatic pressure and temperature. Transitions of inorganic substances—for example, the transition in $NaNO_2$ at 14.5 kbar (*12*) and the transition in KNO_3 at 2.3 kbar (*13*)—have been so used.

Experimental Techniques

With the diamond cell, handling the sample is very simple. After the specimen has been placed between the diamond anvils, the pressure is repeatedly raised and lowered until sample extrusion ceases. Fortunately the sample that remains is usually sufficiently thick (on the order of 15 to 20 microns) to yield a reasonably characteristic spectrum. For detailed study of very strong absorption bands the specimen may be diluted with an alkali halide. When extrusion has ceased, spectra are recorded, beginning with the spectra at maximum pressure. The changes that occur in the spectrum under these experimental conditions are usually reversible. However, in a few cases, at pressures exceeding 50 kbar, irreversible changes apparently occurred; new bands appeared at high pressure and remained when the pressure was reduced to 1 bar. These irreversible changes, which have not yet been subjected to detailed study, may have been caused by chemical reaction or production of a dense phase. In some instances the transition occurred over a narrow pressure range (±0.3 kbar), with only one phase present at any time. In other cases, two or more

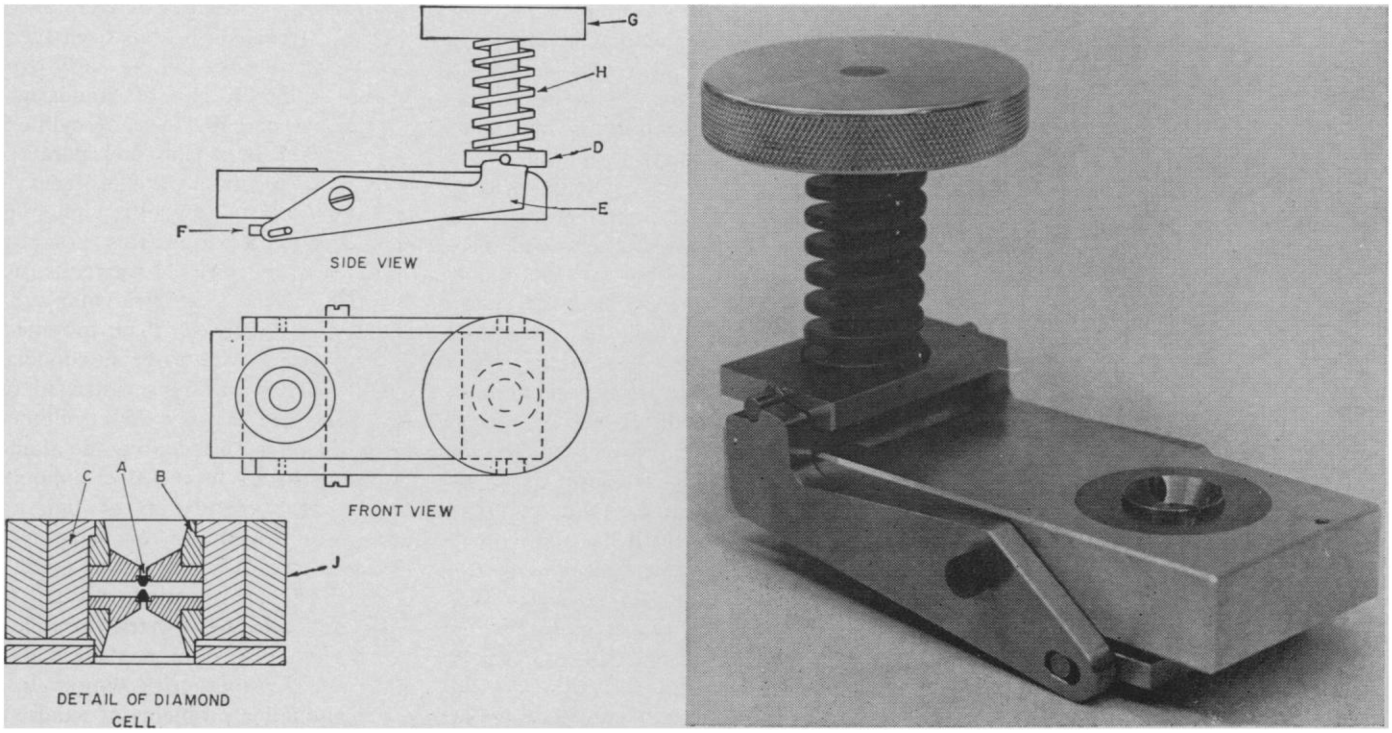


Fig. 1. (Left) Schematic diagram of diamond squeezer for studies of transmission spectra in the infrared, visible, and ultraviolet, to pressures of 150 kbar. *A*, Diamond; *B*, stainless steel piston; *C*, hardened steel insert; *D*, presser plate; *E*, lever; *F*, thrust plate; *G*, manually operated screw for compressing spring; *H*, calibrated spring. (Right) Photograph of the high-pressure cell.

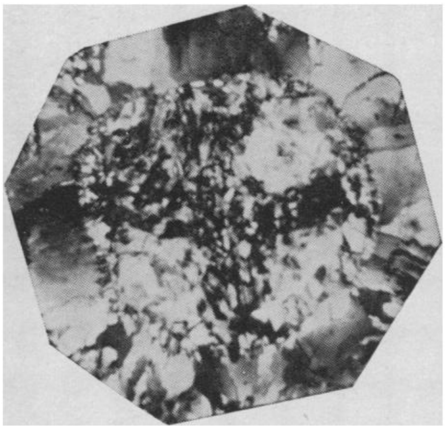


Fig. 2. Potassium nitrate transition under crossed Nicol prisms.

phases were present simultaneously over a rather wide pressure range, indicating the presence of rather marked pressure gradients or considerable metastability. The reproducibility of results and the lifetimes of the diamond anvils depend heavily on proper alignment of the anvil surfaces prior to each run.

Experimental Results and Their Interpretation

Microscopy of solids and liquids. With microscopic techniques the diamond "squeezer" high-pressure cell has been used for investigating the nature and optical characteristics of polymorphic changes in transparent solids. Liquids under high pressure have also been examined. With a polarizing microscope the specimen can be viewed in polarized white or monochromatic light. In general the techniques used in optical mineralogy to obtain optical constants of a compound may be used with the pressure cell. Differences in indices of refraction, birefringence, light absorption, anisotropism, optical character, and so on provide a means of distinguishing two or more phases present in a sample. For example, a transition may first be observed as an island emerging at the center of the diamond, where the pressure is always greatest. With increasing pressure the island spreads out, forming a disc that represents a boundary between two phases having different indices of refraction (*14, 15*). In birefringent materials, transitions, such as the change from noncubic to cubic phase, can be detected by observing the changes in the birefringence.

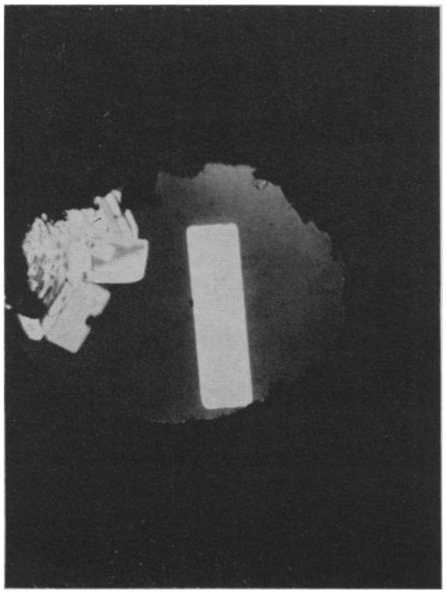


Fig. 3. "Gin-cicle"—ethyl alcohol crystal at pressure of approximately 25 kbar and room temperature.

Some materials show differences in absorption when observed in monochromatic or white light. The high-pressure phases of silver iodide exhibit marked differences in intensity in the region of 0.470 μ (*14*). Thallium bromide (*14*), when observed in white light in the pressure range 40 to 90 kbar, changes color reversibly from near-white through lemon, orange, and red, to opaqueness.

Crystal-growth phenomena can also be studied in the diamond cell (*14*). The phase transition occurring in potassium nitrate at about 2.3 kbar (*13*) is shown in Fig. 2 as it appears when observed with crossed Nicol prisms. The high-pressure phase within the circle can readily be distinguished from the low-pressure phase by the differences in birefringence, crystal size, crystal orientation, and indices of refraction at the phase boundary. The crystals in the low-pressure area have a preferred growth orientation: their longest dimension is parallel to the direction of the pressure gradient. Changing the pressure produces a growing crystal front which has the appearance of a liquid interface.

A thin aluminum-foil gasket with a hole smaller than the area of the diamond window is required for pressure experiments on liquids. Although this technique has only recently been developed, several interesting phenomena have been observed. A drop of water, contained by the gasket, froze to a solid when subjected to pressure. As the pressure was varied, two crystalline phases, ice VI and VII, were observed (*16*). Examination, by microscope, of ethyl alcohol in the diamond cell at approximately 25 kbar and room temperature revealed growth of a rectangular birefringent crystal, a "gin-cicle," shown in Fig. 3. When dry ice was subjected to pressures on the order of 25 kbar, the solid in equilibrium with both gas and liquid was observed. The refractive index of the liquid CO_2, like that of H_2O at room pressure, exceeds that of the solid. Many of the common laboratory liquids, such as ethyl ether, carbon tetrachloride, benzene, and acetone, have been examined in the pressure cell. With careful manipulation of the pressure, the growth of crystals can be observed, and even recorded by a movie camera. Clearly, this technique provides easy access to regions of phase diagrams otherwise observable only with more elaborate apparatus and considerably more tedious techniques.

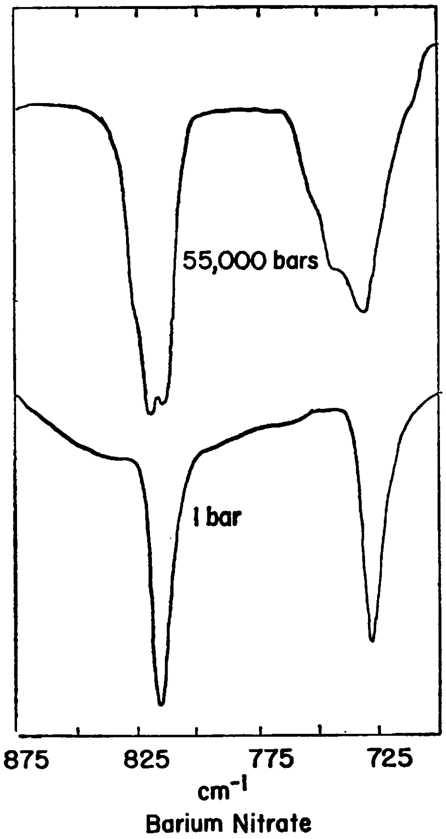


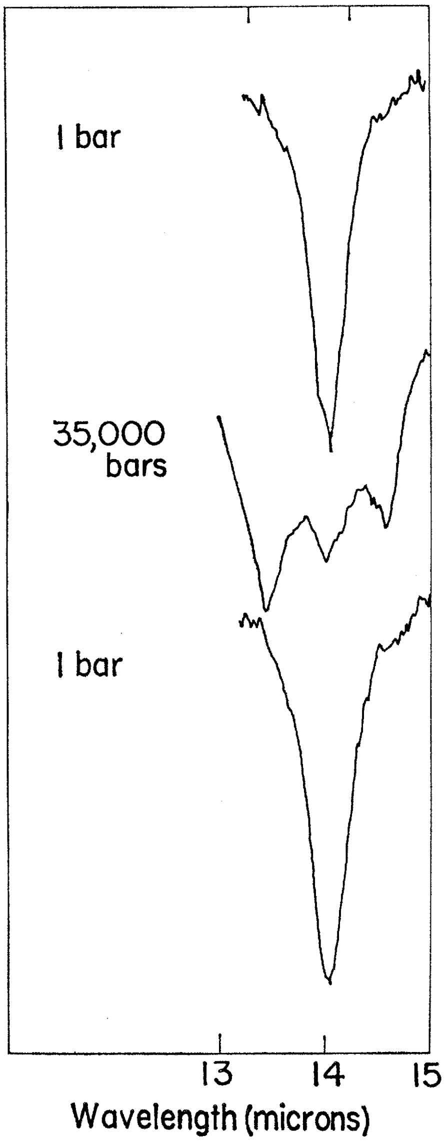
Fig. 4. Discontinuous shift of 815 cm^{-1} out-of-plane bending frequency of nitrate ion at phase transition occurring in $Ba(NO_3)_2$.

Since anvils made of diamond show less distortion under compression than anvils made of any other material, gradient variations caused by anvil deformation are minimized in the diamond pressure cell. It thus provides a unique method for studying pressure gradients of transparent materials being compressed between two flat parallel surfaces. Although misalignment of the anvils is a serious source of error, the alignment can be easily determined under the microscope by observing the attitude of the interference fringes, and realignment is easily achieved by means of set screws in the piston.

The highest pressure always occurs at the center of the diamonds. The change in area of a phase transformation with change in anvil pressure gives a measure of the gradient. The transition boundary line expands more slowly toward the diamond edge as the pressure increases, indicating that the gradient is steeper as the edge is approached. Near the diamond edge the gradients can be tremendous, and it is in this area that diamond failure usually occurs.

After reversible phase transitions of several inorganic salts and low-molecular-weight organic compounds had been observed in the diamond cell, investigators became curious about the behavior of polymers under similar conditions. Early work (*17*) on the hydrostatic compression of a number of polymers had disclosed only the reversible transition, at a pressure of approximately 5.5 to 6.5 kbar, of polytetrafluoroethylene (Teflon) (*18*). The tentative conclusion from this preliminary work was that phase transitions in polymers are not common. However, optical observation of Teflon in the diamond pressure cell at room temperature (*19*) disclosed an abrupt, nonreversible transition from a relatively homogeneous optical field to a highly aggregated field of low birefringence. A shift from the bright interference color, characteristic of photoelastic strain in many polymers, to gradual darkening of the entire field as pressure increased signaled the onset of a transformation. Once the transformation commenced, it proceeded catastrophically, usually accompanied by a loud snapping noise. The occurrence of a phase change seems the most likely cause of the observed transition.

Spectroscopic studies in the infrared region. In general, the infrared spectrum of a substance shows a number of changes on application of pressure; these include shifts of absorption bands from their positions at 1 bar, occurrence of new bands, splitting of bands resulting from a change of symmetry, and changes in apparent band intensity. These effects may occur discontinuously as a result of pressure-



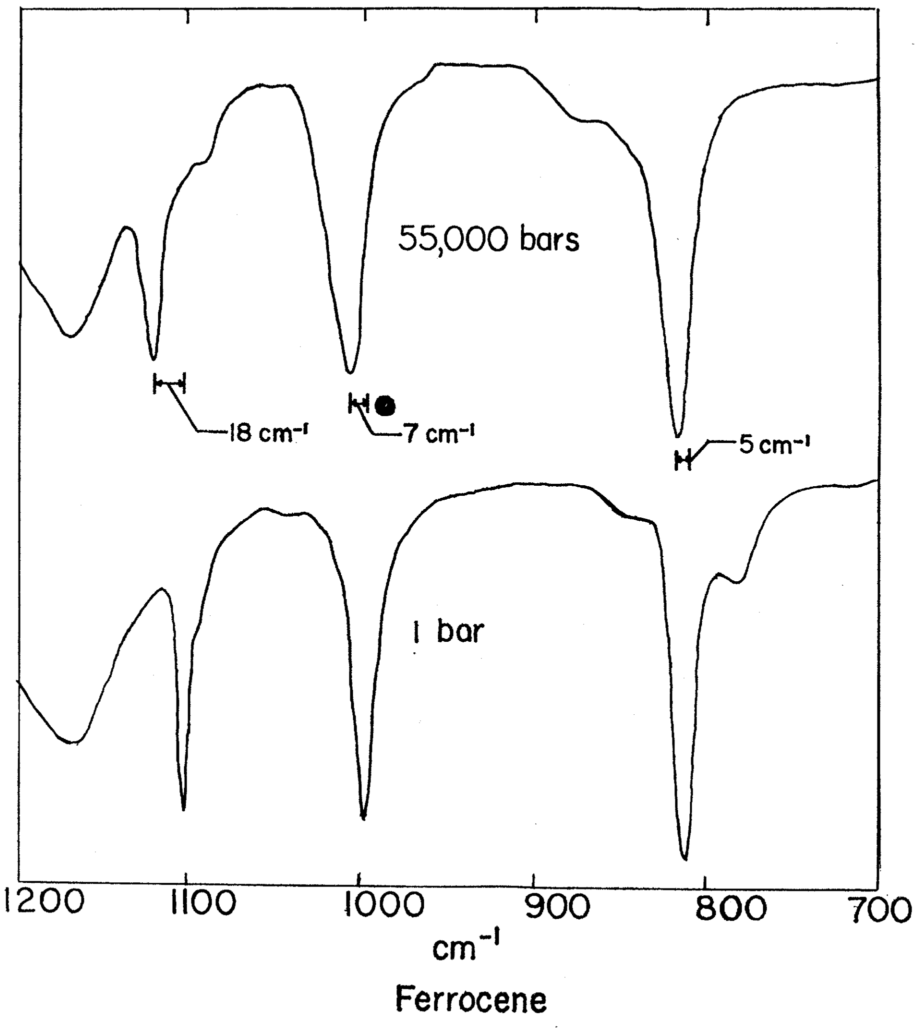


Fig. 5 (left). Pressure-induced splitting of inplane bending frequency of carbonate ion in calcite. Fig. 6 (above right). Effect of pressure on infrared spectrum of ferrocene.

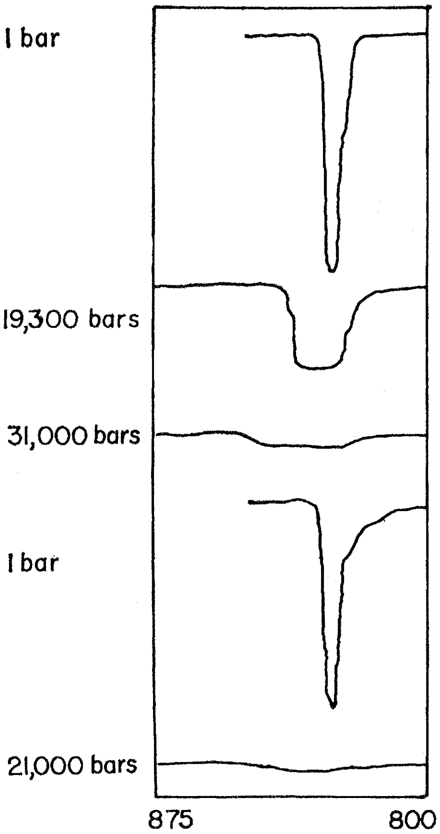


Fig. 7. Apparent disappearance of nitrite-ion bending frequency in $NaNO_2$ under pressure, through two cycles.

induced phase changes, or continuously because of a pressure-induced change in bond environment in a given phase. The band shifts observed to date range up to a maximum of ± 10 waves per centimeter (± 10 cm^{-1}) per 10 kbar of pressure, with greater shifts sometimes occurring for substances that involve systems of hydrogen bonds. Appreciable changes in the apparent intensity of many bands are observed even at relatively low pressures—for example, 10 kbar; at higher pressures the changes are proportionately larger. The change in intensity is specific with respect to both the nature of the substance and the mode of vibration.

The effect of a pressure-induced phase transition on the infrared spectrum of an ionic solid may be illustrated by the behavior of barium nitrate: the 815 cm^{-1} out-of-plane bending frequency of the nitrate ion undergoes a discontinuous shift at the phase transition (see Fig. 4). The effects on the infrared spectrum of pressure-induced phase transitions have also been observed for $NaNO_2$, KNO_3, $AgNO_3$, ferrocene [$Fe(C_5H_5)_2$], ice, $CaCO_3$, semicarbazide hydrochloride, and methylamine hydrochloride.

Infrared spectra of calcite ($CaCO_3$) at elevated pressures (*8*) reveal the appearance of a new band which shows marked pressure-dependence of intensity, reversible splitting of one band into two components and of another band into three distinct components, and frequency shifts for two of the bands. Figure 5 reveals the splitting of the in-plane bending frequency of the carbonate ion into three components.

Relatively weak hydrogen bonds are considerably more sensitive than normal covalent bonds to increase in pressure. Compression of the O . . . O distance in a hydrogen-bonded structure strengthens the hydrogen bond and should result in an abnormally high out-of-plane O–H bending frequency and a low carbonyl frequency. This effect has been observed in the spectrum of succinic acid (*10*). In general, most of the large shifts in frequency observed for pressures below 50 kbar occurred when hydrogen bonds were present in the structure. Similarly, shifts of bands to longer wavelengths that have persisted at pressures greater than 10 kbar have, in the main, been observed only when hydrogen bonds have been present in the structure.

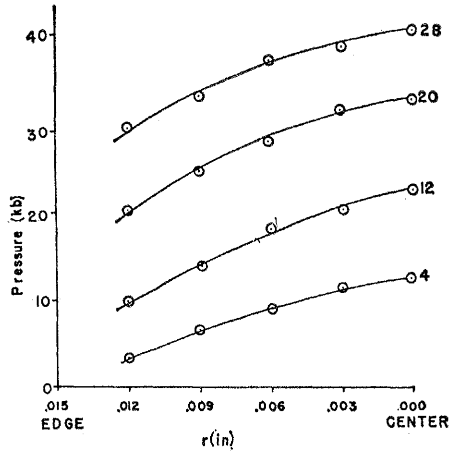


Fig. 9. The radial pressure gradient across the diamond surface at applied pressures of 4, 12, 20, and 28 kbar. The shift of the 19,000 cm^{-1} peak is determined at the points indicated. This peak shift is converted to a pressure by assuming a shift of −80 cm^{-1} per kbar. (This is the shift observed in our laboratory when the spectrum across the entire diamond surface is determined as a function of the applied pressure; it agrees with the shift reported by Drickamer.)

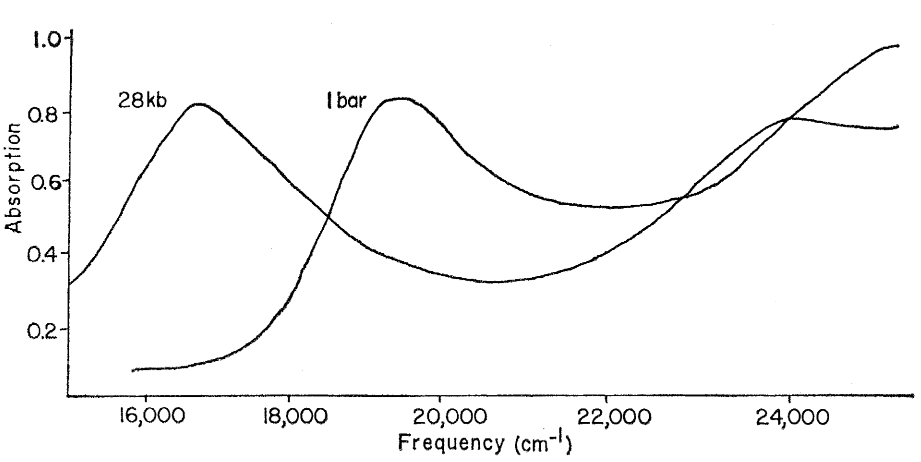


Fig. 8. The visible spectrum of nickel dimethylglyoxime (diluted with 2 parts of sodium chloride), illustrating the shift of the 19,000 cm^{-1} absorption band due to an applied pressure of 28 kbar.

The structures of dense forms of ice have been of considerable interest since the complexity of the system was revealed by Bridgman (*20*). The spectral changes that occur as water is subjected to increasing pressure and decreasing temperature have been studied. The frequency shifts and intensity changes observed (*7, 21*) for the stretching, bending, and libration modes are consistent with the interpretation that the hydrogen bonds responsible for the open structure of ice I collapse under high pressure to form the close-packed structure of dense ice, in which the effect of hydrogen bonding on the vibration modes is only a minor one.

The unusual bonding in ferrocene and the rather definite assignment of its relatively simple vibrational spectrum immediately suggested that a study of the effect of pressure on its spectrum should be made (*22*). A pressure-induced transition occurring at a pressure near 10 kbar is indicated by the shift to higher frequencies of the band assigned to the CC symmetric ring-stretching vibrational mode. The changes in the vibration spectrum—

namely, the intensity changes associated with small frequency shifts of the absorption bands—are continuous before and after the transition. The frequency shifts in the absorption bands are illustrated in Fig. 6. It should be noted that the vibrational frequencies assigned to metal-ring and CC modes of vibration are the most sensitive to changes in pressure.

The effect of pressure on the intensity of bands has been studied by calculating the integrated areas. The pressure effect is expressed by the ratio of these areas. Integration of areas is only justified for bands which are reasonably free of overlap. For most substances studied in our laboratories the intensity of the bands decreases with increasing pressure, or remains the same.

Occasionally, drastic changes occur, such as the apparent disappearance of the nitrite-ion bending frequency on application of high pressure to $NaNO_2$, shown in Fig. 7. The interpretation of this marked, but reversible, change is not yet complete, but clearly the change is not simply a microcrystalline orientation effect. The disappearance of the band may be the result of some internal structural reorientation.

Interpretation of the pressure-induced changes in the infrared spectra in terms of the structures of the specific substances has generally not been possible (*10*). A shift to higher frequency can be qualitatively interpreted as resulting from an increase in the relative importance of repulsive forces of neighboring molecules. Conversely, a shift to lower frequency indicates that the attractive forces of neighboring molecules are exerting the greater influence on the atoms. Most of the shifts to lower frequencies observed to date have been for substances which have hydrogen bonds in their structures. Such bonds are the result of relatively weak attractive forces. Pressure, then, by increasing the attraction, increases the strength of the hydrogen bond. Even for hydrogen bonds, however, there must be some pressure at which the repulsive forces exceed the attractive forces; shifts to higher frequencies should then take place.

If the cases in which hydrogen bonds are present in the structure are excluded, it is clear that an applied pressure of the order of 40 kbar has relatively little effect on the position of most vibrational bands. Apparently such pressures do not produce significant changes in the modes of vibration responsible for the spectra. Similiarly, any phase changes that occur do not alter greatly the bond configuration, although the space-group symmetry of the unit cell may change.

At pressures of the order of 40 kbar the decrease in volume for the organic materials studied is approximately 20 percent. Since the interatomic distances of atoms involved in the bonds do not change appreciably, the changes in intermolecular distances must be large. The available data indicate that the bonds are relatively insensitive to this change in intermolecular spacing. However, for pressures exceeding 50 kbar, changes in structure occur more frequently. Such a structural change has been observed (*10*) in *p*-nitrophenol at 160 kbar in studies made with the diamond cell. The relatively large changes in integrated intensities which occur for pressures up to 50 kbar (for example, for $NaNO_2$, as discussed earlier) suggest that relatively large changes in dipole-moment derivatives are occurring for a number of modes of vibration.

Spectroscopic studies in the visible and ultraviolet regions. The diamond cell can also be used to study the visible and ultraviolet spectra of materials under high pressure. However, the diamonds to be used in these studies must be carefully selected, since not all type-II diamonds are transparent in the 2200- to 3500-angstrom region. Application of pressure can produce the following changes in the electronic absorption spectrum of a substance: shifts in the position of the absorption band

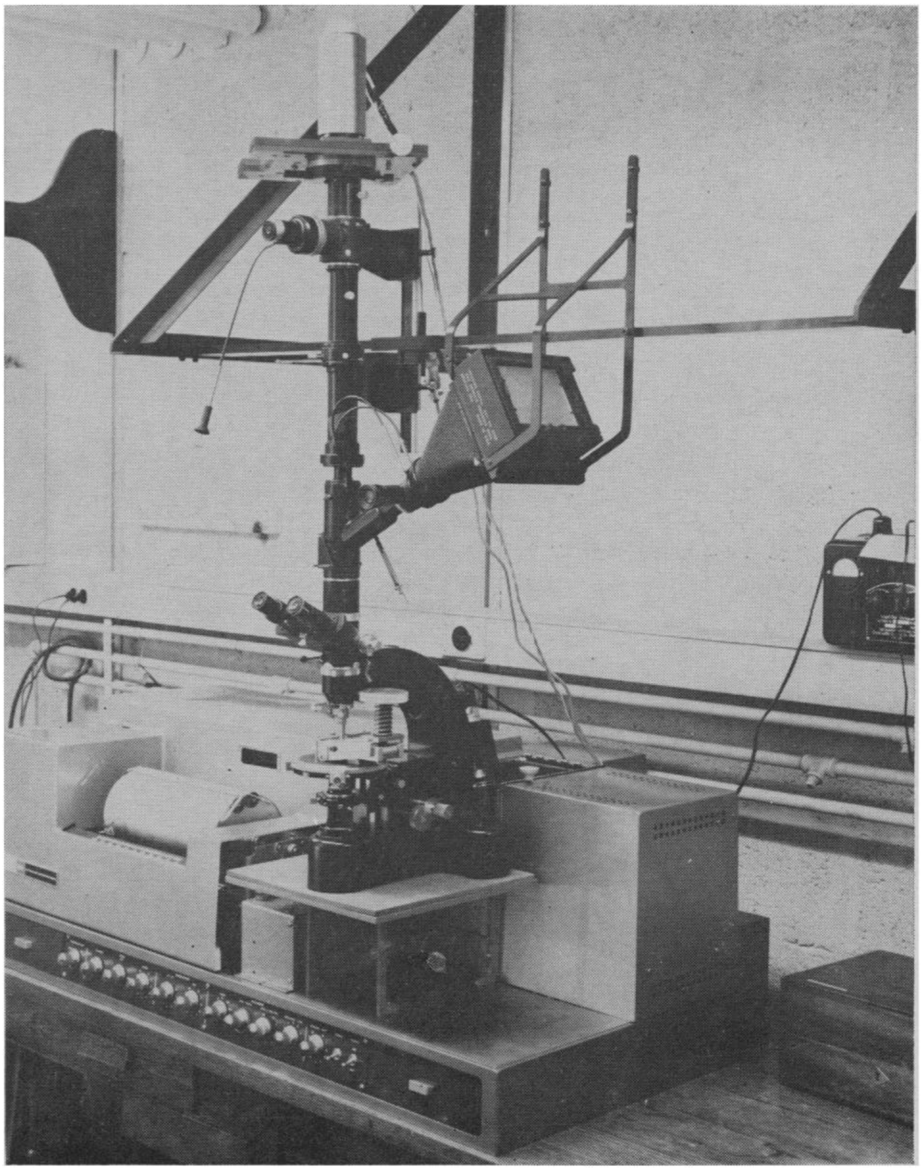


Fig. 10. Microscope-spectrophotometer.

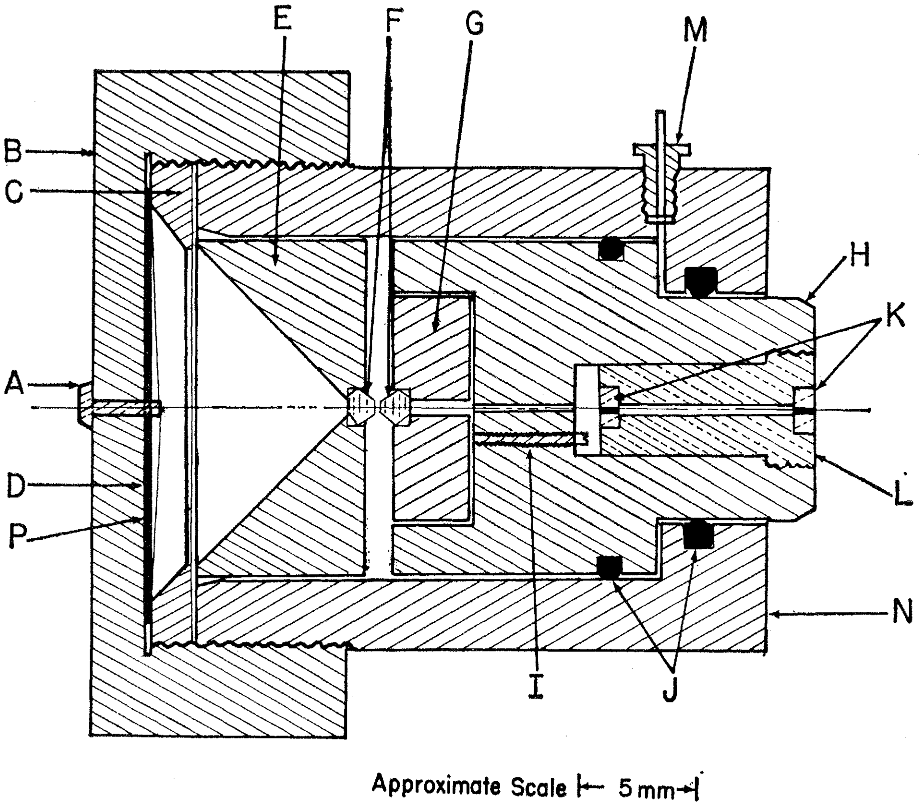


Fig. 11. Simplified schematic cross section of the high-pressure x-ray camera. *A*, Beamstop; *B*, cap; *C*, thrust washer; *D*, photographic film; *E*, hardened steel entablature; *F*, diamonds; *G*, movable steel seat for diamond; *H*, piston actuated by hydraulic pressure generated by means of external pump; *I*, alignment screw; *J*, O-rings which seal space occupied by hydraulic liquid; *K*, cylindrical hole through which x-ray beam enters; *L*, brass insert containing pinholes; *M*, fitting through which hydraulic fluid is introduced; *N*, steel body; *P*, light-tight cover for film.

to either higher or lower frequency, band splitting, changes in intensity of existing bands, and appearance of new bands. As is the case for pressure-induced changes in infrared spectra, these changes may occur either continuously or discontinuously, depending on whether the bond environment in a given phase is altered or an actual phase change occurs. Band shifts of 150 to 250 cm^{-1} per 10 kbar are common for transition-metal complexes.

For the free transition-metal ion, the separation between degenerate electronic energy levels can be calculated from the interelectronic repulsion and described in terms of Racah parameters A, B, and C. The splitting of the degenerate energy levels of the valence electron of the transition-metal ion in a complex is a function of the strength of the crystal field. Optical absorption bands observed for such complexes can be related to the strength and symmetry of the crystal field and to the Racah parameters. For either octahedral or tetrahedral fields, the strength of the crystal field varies as R^{-5}, where R is the metal-ligand distance (*23*). The intensity of the crystal field and the splitting of the degenerate energy levels should then be pressure-dependent. Indeed, for isotropic compression the crystal field should vary as $\rho^{5/3}$. Therefore, absorption bands which depend on the strength of the crystal field should show a shift to higher energies with increase in pressure.

Although crystal-field theory in its simplest form implies the validity in the crystal of the free-ion values of B and C, a significant amount of covalency between ligands and metal ion almost always occurs, resulting in a spreading of the charge cloud of the metal ion and a decrease in interelectronic repulsion. Pressure increases the covalency (*24*) and thus perturbs the ligand levels. A first-order approximation of the effect of pressure on covalency can, then, be obtained through study of the Racah parameters as a function of pressure.

Measurable splittings of crystal-field peaks resulting from spin-orbit coupling have been observed (*25*) for a number of complexes, although for the first transition-metal series spin-orbit coupling is usually not large. The size of this splitting increases with increasing pressure.

Studies of the effect of pressure on electronic absorption spectra have not been restricted to transition-metal complexes and their internal *d-d* transitions. Inter- and intramolecular charge-transfer spectra (*26*) and interband transitions in elements and ionic and molecular crystals have also been investigated as a function of pressure. Extensive work in these areas has been done and recently reviewed by Drickamer (*27*) and his colleagues.

Pressure-induced metal-metal interaction may also occur and has been suggested as the explanation for the spectral changes observed with nickel, palladium, and platinum dimethylglyoximes (*28*). Pressure-induced spectral changes in nickel dimethylglyoxime observed in our laboratory (Fig. 8) are similar to those reported by Drickamer (*28*). The large shift in frequency and the distinctive color change with pressure make this compound very useful for determining the pressure distribution across the diamond surface and thus may afford a means of cell calibration. The microscope-spectrophotometer recently devised, and discussed in the next section, makes it possible to record spectra of very small areas of the sample. The diamond surface can then be scanned, and the change in pressure from cell center to edge can be noted from the change in frequency observed. Figure 9 shows a mapping of the pressure gradient across the diamond cell for nickel dimethylglyoxime in NaCl.

The most prominent feature of the effect of pressure on the electronic absorption spectrum of ferrocene is the large shift of the band at 434 mμ to higher frequencies, accompanied by a definite increase in band intensity. Apparently no frequency shift occurs at the pressure-induced transition; rather, the slope of the pressure-versus-frequency relationship changes.

The microscope-spectrophotometer. The microscope-spectrophotometer mentioned earlier has only recently been designed and constructed (*29*). Its principal components are a Perkin-Elmer 350 spectrophotometer and a high-performance Leitz optical microscope (Fig. 10). Spectra in the region 400 to 2800 mμ can be obtained for

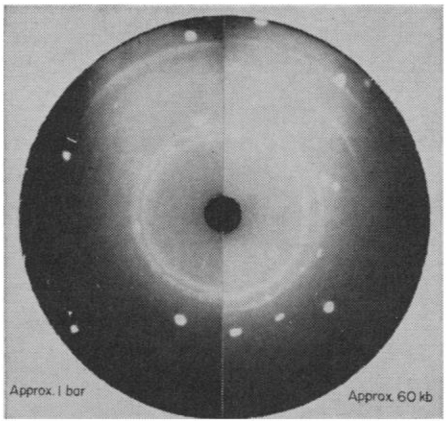


Fig. 12. X-ray powder patterns of thallium at low and high pressures (large film cassette).

sample areas as small as 18 μ in diameter. The pressure gradients known to be present in the diamond cell can therefore be studied spectroscopically as well as visually. As mentioned earlier, the combination of microscope and spectrophotometer makes calibration of pressure distribution across the diamond surfaces possible. Figures 8 and 9 show data obtained with this instrument.

Many substances undergo remarkable color changes with pressure. Some of these changes occur over very narrow pressure ranges. Because of the pressure gradients in the diamond cell, areas of markedly different color may be present simultaneously. With the microscope-spectrophotometer the regions of different color can be examined singly. The instrument has been modified for photographing the region that is being studied spectrographically.

Phosphorescence and fluorescence studies. Preliminary work has also been done on instrumentation for studying the effect of pressure on fluorescence and phosphorescence. The small area of the diamond cell makes it necessary to find a means of reducing the loss in light energy. This factor, together with pressure gradients in the cell, indicates that studies of transmission fluorescence are more feasible than studies of reflectance fluorescence. The fluorescence spectrum of anthracene excited by the mercury line at 3650 angstroms has been recorded at room temperature over the range 4000 to 6000 angstroms, for two pressures: 1 bar and 30 kbar. The primary pressure-induced changes in the spectrum are a decrease in intensity and a slight shift in wavelength. The spectrum of copper-activated zinc sulfide showed, on application of pressure, a decrease in band intensity and marked broadening of the band.

X-ray crystallographic studies. The design of the high-pressure cell used in spectroscopic studies in the infrared region has been modified to permit study of x-ray diffraction patterns of a powdered sample to pressures of at least 60 kbar (*30*). Figure 11 shows a simplified schematic cross section of the high-pressure x-ray camera used for this purpose. Zirconium-filtered molybdenum radiation passes through the axial hole (*K*) in the piston (*H*), through both diamonds (*F*), and through the specimen compressed between the diamond surfaces. Diffraction rings from the powdered specimen diverge through the diamond in the entablature (*E*) and are recorded on the film (*D*) placed inside the cap (*B*) and held securely between cap and thrust washer (*C*). Various improvements of this basic design have been made.

Two salts and two metals known to have transitions at widely differing pressures were chosen (*30*) for a study to determine if a transition could be detected by this technique and what structurally significant crystallographic data could be obtained. For the two salts, silver iodide and potassium iodide, the transitions were quite apparent, the high-pressure patterns were readily indexed, and the lattice constants, densities, and total volume changes obtained agreed well with the structural data available in the literature (*1, 12, 31*).

For one of the metals, bismuth, the powder pattern of the specimen at high pressure was very complex, probably because of the simultaneous presence of more than one high-pressure form. The powder pattern of the high-pressure form of the other metal, thallium, (apparently the first x-ray diffraction study of this phase) was readily indexed as face-centered cubic, corroborating earlier predictions (*32*). The calculated change in volume agrees well with Bridgman's data (*33*). X-ray powder patterns of thallium at low and high pressures are shown in Fig. 12.

Lattice measurement of high-pressure polymorphs of alkali halides have been made by means of the high-pressure x-ray camera. High-pressure phases of RbF (*34*), CsF (*35*), and KF (*35*) have been detected; the normal face-centered cubic structure is converted to a simple cubic structure at elevated pressures.

Summary

The development of a miniaturized high-pressure cell which is useful to pressures of 150 kbar and fits easily into the small sample areas of commercial optical equipment has greatly facilitated optical studies at high pressures. With this cell the nature and optical characteristics of polymorphic changes in transparent solids and liquids have been investigated. A microscope-spectrophotometer with which absorption spectra of small areas of the compressed sample can be obtained has been devised. A camera attachment provides a convenient means of recording the visual observations. X-ray diffraction powder patterns have been recorded for low- and high-pressure forms of several substances, and new high-pressure forms have been discovered in some cases. The wide range of problems in which the cell is applicable, its miniature size, and the relative simplicity of the experimental techniques involved in its use make the development of the diamond cell a marked advance in high-pressure technology.

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Science and Federal Programs: The Continuing Dialogue

Academic values can be extended in the context of major support derived from public sources.

James A. Shannon

To address this distinguished group is not only an especial honor, but also a welcome opportunity to express some personal views on certain aspects of a matter which is demanding increasing attention from all of us. I refer, of course, to the vital and complex relationships evolving out of the federal government's major involvement in the support of science. I am prompted to an informal exploration of this subject by the superb presentation of the problems of this relationship and the wise conclusions drawn in the recently issued report of the Committee on Science and Public Policy of the National Academy of Sciences, developed under the able chairmanship of George Kistiakowsky.

In the present stage of national consideration of these matters, I think this report is most timely and contributory. I believe it also to be clear confirmation of the important historic function of the Academy in providing advice to the federal government and leadership to the scientific community in matters vital to the advancement of science in the national interest at a time of important change. My comments have been engendered by reflecting upon the issues of "federal support of basic research in institutions of higher learning," as presented in the Kistiakowsky report.

It is now possible to view the progress and support of science in some perspective after a period of intense growth and change. It is also possible in this process to see issues emerging which are broader than research and technological development—broader than science itself, for they encompass major national needs relating to higher education and the very basis of scholarly activity. It is my hope that these remarks will evoke discussion, now and henceforth, and sharpen our perception of the issues. This, in turn, may contribute to the further resolution of the continuing dialogue relating to national policy on science and its support. It is through this continuing dialogue that valid concepts must come for guiding the legislative and executive branches of government, as well as the scientific community and its institutions, in the formulation of sound policies.

The Appeal to Science in Times of National Crisis

History reveals that science and technology have been of particular concern to the federal government in times of national crisis, when urgent national problems reveal deficits in our knowledge. Although the founding fathers of our nation were preoccupied with science and its role in government, no lasting federal relationships were established until the Civil War. The need to provide for scientific assistance and advice in a time of peril is in a very real sense the event contributory to the founding of the National Academy of Sciences. In a similar manner medical research in the Public Health Service had its birth in the threat of grave epidemics during the great period of immigration in the 1880's, in the context of beginning scientific knowledge and capability deriving from the germ theory of disease. Thus, the Hygienic Laboratory, originally set up at the port of New York, evolved into the National Institutes of Health.

World War I was the next major crisis that compelled the federal government to call on the nation's scientists in a large-scale manner. The existence of a burgeoning industry bereft of basic scientific support from abroad led to a search for technological and scientific aid from American scientists and institutions for the solution of war-born problems. Accordingly, the Academy established the National Research Council as a practical

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The author is director of the National Institutes of Health, Bethesda, Md. This article is adapted from an address delivered 28 April before the National Academy of Sciences, Washington, D.C.