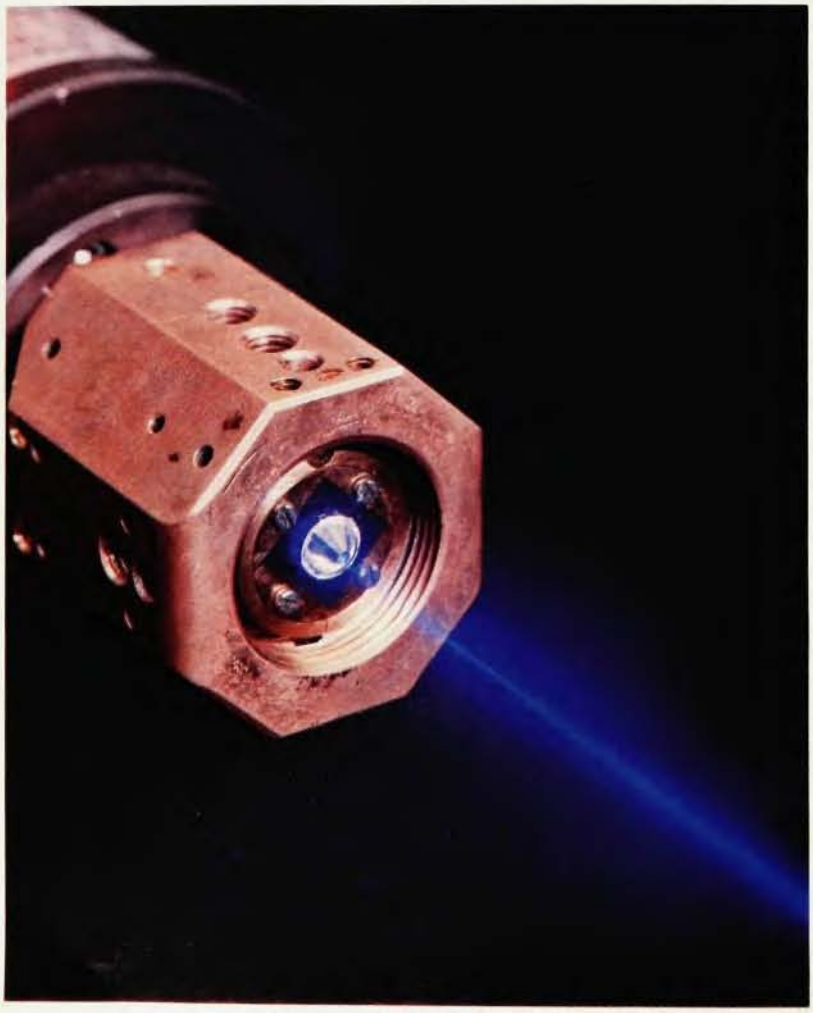
High-pressure research with synchrotron radiation

As diamond anvils subject solids to pressures beyond a million atmospheres, synchrotron x rays find new phase transitions between states of different crystallographic structure.

Earl F. Skelton



Diamond anvil from the only high-pressure apparatus yet operated on a synchrotron-radiation beam line at cryogenic temperatures. The gem-quality diamond is mounted as shown in figure 2 and placed in a housing made of a beryllium–copper alloy. The blue laser beam emanating from the diamond is used both to align the apparatus and to measure the pressure. (NRL photograph.) Figure 1

High-pressure research has undergone a quiet revolution over the past 15 years. This is a result of the creation and evolution of the diamond-anvil cell, an inexpensive, compact and transparent tool that allows one to perform a wide variety of experiments on materials subjected to extreme static pressures. By working with samples that measure only 0.1 mm on a side, the diamond-anvil cell can reach and hold pressures in excess of a million atmospheres.

Unfortunately, conventional x-ray structural studies on such microscopic samples require extremely long exposure times—tens or even hundreds of hours. However, by replacing the conventional x-ray tube with the extremely brilliant synchrotron radiation source, one can cut these times by three to four orders of magnitude: Exposures less than a second in duration have produced useful x-ray diffraction patterns. Thus, thanks to the synchrotron, physicists are now doing high-pressure experiments that otherwise might have been unthinkable.

In this article I discuss energy-dispersive x-ray diffraction measurements on samples at extremely high pressures. I will look at examples where changes in pressure or temperature induce phase transitions, some of which occur so quickly that the only way to study their kinetics is with synchrotron radiation. Information from such studies has, to mention just one significant result, helped to unravel the transition mech-

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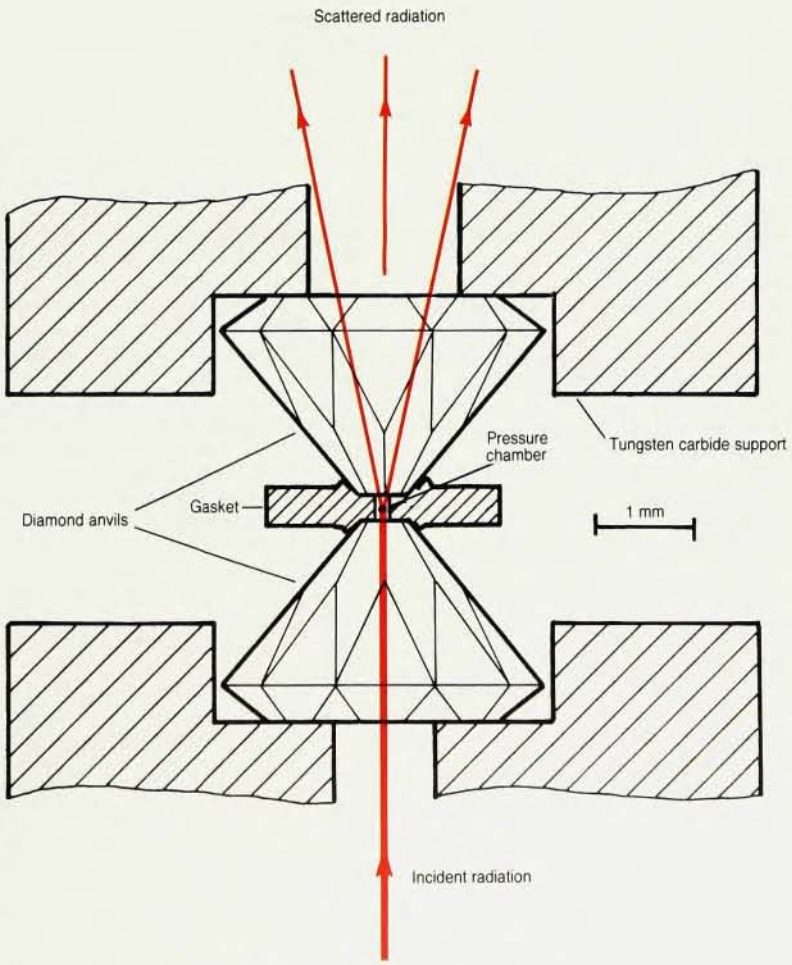
anism in the geologically important mineral fayalite.

Work with diamond-anvil cells and synchrotron radiation is going on not only in the United States, but in Europe and Japan as well, where teams of high-pressure physicists have set up large-volume presses on synchrotron beam lines. A Japanese group studying the pressure-induced conversion of graphite powder into diamond recently produced the first *in situ* structural data that gives information on the kinetics of the process.

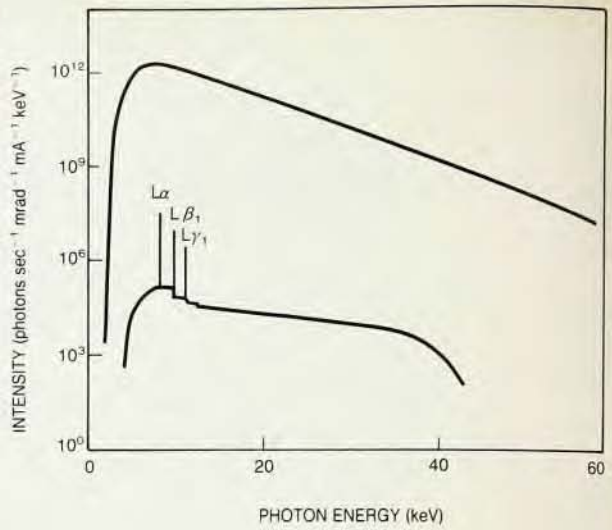
Pressure is an extremely important thermodynamic variable, both in terms of understanding physical properties of materials and in the fabrication of new forms, or polymorphs, of existing materials. The role of pressure in, for example, the newly discovered superconductivity in organic charge-transfer salts based on the cation molecule ditetramethyltetraselenafulvalenium (TMTSF) would appear to be critical, for all but one of these salts are superconducting only at elevated pressures. Classic examples of technologically important polymorphs are diamond and cubic boron nitride, which form only under high pressure.

Pressure is the most efficient means of altering interatomic dimensions without affecting other physical properties, such as thermal energy or chemical environment. Most modern physical theories are based on atomic force models, which depend, in turn, on interatomic distances and crystallographic symmetry. To develop and test these models, one wants to be able to alter the distances and symmetries experimentally. Controlling temperature is a way of doing this, but the temperatures that one can routinely achieve in research laboratories today are roughly an order of magnitude less



Major components of a typical diamond-anvil cell, shown here schematically. The pressure chamber is about 0.1 mm in diameter.

Figure 2



Comparison of spectra. The top curve represents the spectrum available from the SPEAR storage ring at SSRL, corrected for helium, beryllium, carbon and aluminum absorbers in the beam path. The lower curve represents the spectrum from a typical tungsten-target x-ray tube. (From reference 6.) Figure 3

effective than the pressures that one can also readily attain. Moreover, one can apply pressure isothermally, thus not altering the thermal energy of the system and simplifying the interpretation of any resulting changes. For example, changing the temperature of most materials by one thousand centigrade degrees, which is easy to do in the laboratory, will produce a fractional change in length of a few tenths of a percent; on the other hand, pressures of a few hundred thousand atmospheres, which are also easy to generate, will cause most materials to undergo fractional length changes of several percent.

To learn more about materials and their physical properties, it is important not only to identify critical thermodynamical coordinates, but also to monitor, from a crystallographic or structural point of view, how materials transform from one phase to another. It is with such information on transition kinetics that scientists will be able to accelerate new transitions and inhibit reverse transitions, so that they may form desirable high-pressure polymorphs and retain them at atmospheric pressure. Until recently, such information was very difficult to obtain, but, as I will explain below, the extreme spectral brilliance of synchrotron radiation is changing this.

The diamond-anvil cell

Until the mid-1960s, virtually all high-pressure research used massive hydraulic presses. Since then, the diamond-anvil cell has revolutionized the field. There are now diamond-anvil cells of a variety of designs, but they all share certain basic features: a mechanism for aligning the surface faces as well as the axes of a pair of gem quality diamonds, and a mechanism for bringing these anvils together in a controlled manner. (See figures 1 and 2.) Because the working surface area of the anvil faces is typically less than 1 mm^2, modest loads, usually generated with manually driven screws, can produce pressures of tens of gigapascals, the current static pressure limit being 172 GPa. (The S.I. unit of pressure, the pascal, is defined to be 1 N/m^2; thus 1 bar, which is 0.9869 atm, is 10^5 Pa; and 1 GPa, or 10 kbar, is 145 038 psi.)

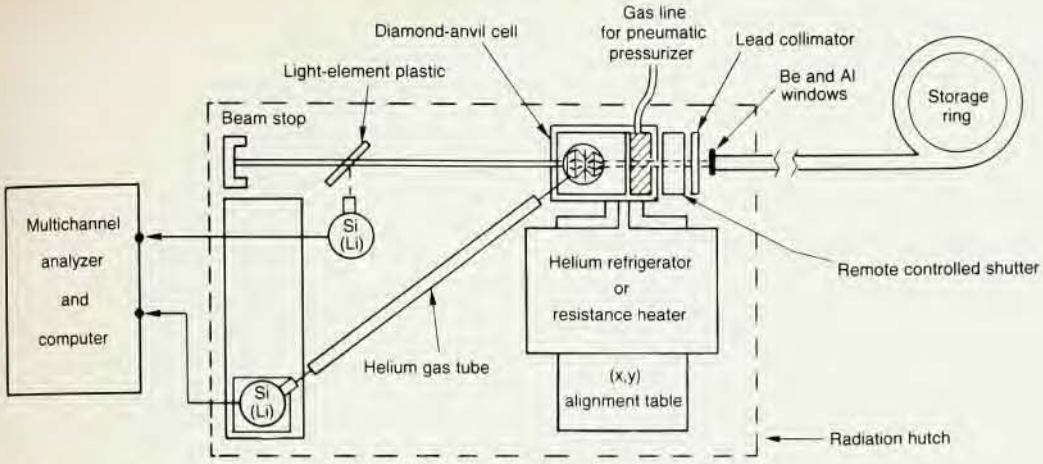
The pressure in a diamond-anvil cell is generally measured by including a pressure calibrant with the sample or samples of interest. Materials such as copper, silver, gold, sodium chloride and cesium chloride, for which the equations of state are reasonably well known, are typical calibrants. Pressure-induced shifts not involving phase changes can also serve as measures of pressure. Two examples of useful pressure-dependent quantities .are the wavelength of optical fluorescence radiation from ruby and the superconducting transition temperature of lead or tin.

The diamond-anvil cell has three important advantages over the older high-pressure systems of comparatively large volume: simplicity, compactness and transparency. Because of its miniature size, the diamond-anvil cell is easy to transport from lab to lab and to operate in a variety of special environments. This feature also makes the diamond-anvil cell easy to heat or cool. At one extreme, pulsed lasers have heated diamond-anvil cells to temperatures of several thousand kelvins, while at the other extreme, a He^3–He^4 dilution refrigerator has cooled a diamond-anvil cell to 30 mK.

The most important advantage of the diamond-anvil cell, however, is the relative transparency of the diamonds to a wide range of electromagnetic radiation. The diamond anvils are thus windows into the pressure chamber, and through them one can perform Brillouin and Raman scattering experiments, as well as measure optical absorption and reflection, all as a function of both pressure and temperature. Of even greater importance perhaps, is the fact that x radiation may be brought to and from the pressure chamber with relatively little attenuation; as a consequence, the diamond-anvil cell is now the most extensively used instrument for studying the effect of pressure on structure.[1]

Diffraction of x rays. Although physicists have designed and built a few cells to study single crystals, most high-pressure x-ray experiments use polycrystalline samples. In a typical set up, filtered radiation from a sealed-beam x-ray tube illuminates the sample chamber, and the forward-scattered radiation is recorded photographically over a limited range of diffraction angles, typically from $\pm 20°$ to $\pm 30°$. The resulting image contains information on the structure of the sample. Some researchers have replaced the film cassette with a position-sensitive photon detector, thereby producing the electronic equivalent of a powder photograph.[2]

Typical heights and diameters for the cylindrical pressure chambers in diamond-anvil cells are in the 100 micron range. Thus, working volumes on the order of 10^{-3} mm^3 must contain the sample, pressure calibrant and any hydraulic fluid or other pressure-transmitting medium. To obtain useful structural data from such small samples requires long exposure times if one uses conventional radiation sources. As an extreme example, a series of pressure calibration measurements[3] on



Layout of a diffraction experiment with temperature control. The electron storage ring that supplies the heterochromatic synchrotron radiation for this energy dispersive x-ray diffraction experiment is about 17 m from the beryllium and aluminum windows. A lithium-doped-silicon detector on a (z,ϕ) alignment table monitors the diffracted x-rays. Figure 4

four elemental metals—copper, molybdenum, palladium and silver—required exposure times ranging from 100 to 400 hours. Although the exposure period varies from experiment to experiment, tens to hundreds of hours are not uncommon for conventional x-ray sources and conventional film techniques.

One way to step up the rate of acquisition of structural information from a diamond-anvil cell is to use the higher-energy x-ray photons available in the bremsstrahlung from an x-ray tube, and to analyze the energies of the scattered x rays in a fixed geometry. For this method, which is known as energy-dispersive x-ray diffraction, a tungsten-target tube is advantageous because of its more uniform heterochromatic radiation.[4,5]

The Bragg relation, two forms of which I give below, specifies the conditions that must be satisfied for diffraction:

$$\lambda = 2\,d_{hkl}\,\sin\theta$$
$$E\,d_{hkl}\,\sin\theta = hc/2$$

Here d_{hkl} is the spacing between the (hkl) crystallographic planes, θ is the Bragg angle, h is Planck's constant, c is the speed of light, and λ and E are the x-ray photon's wavelength and energy. In angular-dispersive diffraction, the x-ray wavelength λ is fixed, usually at one of the characteristic wavelengths emanating from an x-ray tube, and one scans the angle θ to obtain structural information such as the spacing d between the planes. In energy-dispersive x-ray diffraction, one holds the Bragg angle θ constant while scanning the x-ray energy E, usually with an energy-sensitive photon detector.

Need for synchrotron radiation

Replacing the conventional x-ray tube with a rotating-anode source further increases the rate at which one can acquire structural information, but measurement times are still prohibitively long in many instances. An obvious way to cut exposure times significantly is to use a synchrotron radiation source. Figure 3 shows a recent comparison between the spectrum available on the Stanford Synchrotron Radiation Laboratory heterochromatic, or white-beam, line and that available from a tungsten-target x-ray tube. Clearly, over most of the useful energy range from about 10 to 60 keV, the synchrotron radiation source provides more than six orders of magnitude more photons.[6]

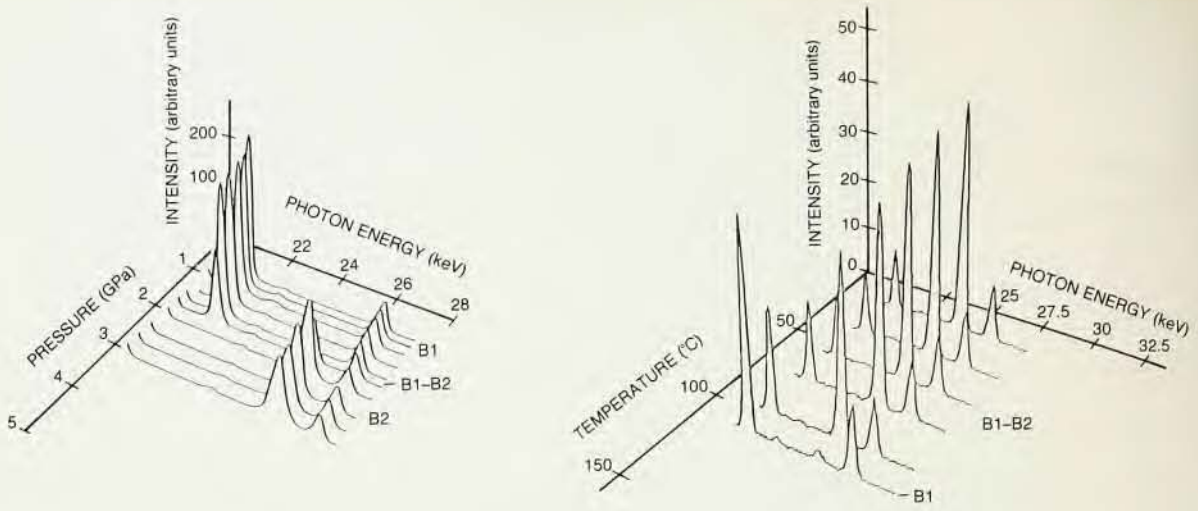
Two other advantages of the synchrotron radiation source involve beam divergence and intensity-versus-energy profile. The divergence of a beam from a conventional radiation source is generally so large that one must perform experiments close to the source point, usually within several centimeters. In contrast, the divergence of the typical synchrotron radiation beam is in the milliradian range, and experiments are usually tens of meters from the source point. The intensity of synchrotron radiation varies smoothly with energy and is well known, whereas the intensity profile of bremsstrahlung from an x-ray tube is complicated by the presence of characteristic lines.

Since the initial high-pressure work using energy-dispersive x-ray diffraction at DESY in Hamburg,[5] high-pressure research programs have been underway at most of the hard-x-ray synchrotron rings throughout the world—at the Stanford Synchrotron Radiation Laboratory,[7] at the Cornell High-Energy Synchrotron Source,[8] and at the Japanese National Laboratory for High-Energy Physics, the "Photon Factory", in Tsukuba.[9]

The experimental set-up and operational procedure for energy-dispersive x-ray diffraction with a diamond-anvil cell are relatively straightforward. The cell is centered in the synchrotron radiation beam and an energy-sensitive photon detector is fixed at some—usually low—angle as shown in the figure above.

The absorption properties of diamond and, of course, the sample itself determine the lower limit of usable photon energies in energy-dispersive x-ray diffraction in a diamond-anvil cell. One usually collects data above 10 keV. Two factors determine the upper limit: the number of high-energy photons available in the synchrotron radiation beam, and the efficiency of the detection system. The former depends upon the radius of the synchrotron ring, the energy of the orbiting electrons, and the electron beam current; the latter is controlled predominantly by the stopping power of the detection crystal. The efficiency for most Si(Li) detectors falls below 20% above 60 keV, whereas that for the intrinsic germanium detectors generally remains above 80% up to 100 keV. However, spectra recorded with germanium detectors are usually complicated by the presence of shadow peaks, due to photons that have lost a fixed amount of energy by exciting germanium atoms. Most reported high-pressure energy-dispersive x-ray diffraction spectra based on synchrotron radiation lie in the 10- to 60-keV range. Figure 5 shows some typical spectra, which I discuss below.

When using conventional radiation sources, it is usually acceptable to change the pressure manually; however, to work safely and to be able to follow short-lived phenomena, when one is using a synchrotron radiation source it is better to control the pres-



Diffraction spectra showing B1-to-B2 phase transitions in potassium iodide induced by changes in pressure (left) and temperature (right). (From reference 10.) Figure 5

sure remotely. By adding well-developed heaters and coolers that make possible the remote control of the temperature of the chamber containing the sample, one has an excellent tool for rapidly obtaining structural information throughout pressure–temperature space.[7] Also, because one usually has only the allotted days or weeks at the synchrotron radiation source to collect data, it is highly desirable to have on-line diagnostic capabilities to perform preliminary analyses. With such information, one can identify and make any necessary experimental modifications while data are still being accumulated. My own research group uses a custom-designed microcomputer system for such work.[7]

Speed of data acquisition. The question naturally arises as to how rapidly one can obtain energy-dispersive x-ray diffraction spectra with synchrotron radiation, and the answer, of course, depends on a number of factors: the photon flux at the scattering center, the size and scattering power of the sample, and the efficiency of the detector and the system that analyzes the data. High-pressure experiments using synchrotron radiation from the Stanford positron–electron accelerator ring usually yield spectra of acceptable quality in one to two minutes—this with the ring operating at energies of 3.0 to 3.5 GeV and beam currents of 20 to 100 mA.

A study of the integration times required to measure a pressure calibration peak in the sodium chloride diffraction spectrum illustrates the accuracy of these experiments. At a recording rate of about 500 counts/second, the standard deviation in the area measured under the calibration peak—its integrated intensity—degraded from less than 1% for measurement periods longer than 5 minutes to about 3% for scans of 10 seconds. The precision in measurement of the peak energy was better than 0.01% for the extended scans and degraded to about 0.04% for the 10-second scans. Integrated peak intensities are measures of crystalline grain sizes, internal atomic positions and thermal vibrational properties. Peak energies correspond to lattice size and symmetry, and therefore are measures of compressibilities, thermal expansivities and structural phase changes.

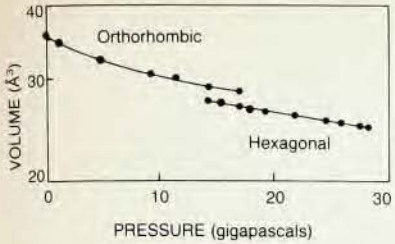
Structural phase transitions

One of the most extensive uses of the diamond-anvil cell is in the study of pressure-induced phase transitions. Energy-dispersive x-ray diffraction with synchrotron radiation is an ideal technique for such studies because of the rapidity with which it can identify the pressures or temperatures of the phase transitions. A common procedure is to monitor the more intense diffraction peaks in the initial phase while changing the thermodynamic variables. When some phase transitions begin, the diffraction peaks of the initial structure begin to lose intensity, while the diffraction peaks of the new phase grow. In this way, one measures the dynamics of the transition.

An example of a structural transition activated by changes in pressure and temperature is the transition from a B1 phase to a B2 phase that occurs in many alkali halide salts. These two phases correspond to the NaCl structure and the CsCl structure, respectively, and the transition between them is usually sluggish. Figure 5 shows energy-dispersive x-ray spectra for potassium iodide. On the left side, the room-temperature spectra appear as a function of pressure, which increases from 0.83 GPa to 3.17 GPa. Below the transition pressure of 1.8 GPa, only the (200) peak of the B1 phase is present, at about 22 keV. At 1.8 GPa the material enters the two-phase region and the (110) peak of the B2 phase is also present, at about 25 keV. A further increase in pressure completes the transition, as is evidenced by the disappearance of the (200) peak. The third strong peak above 26 keV is the (200) peak of sodium chloride, which in this case serves as the pressure gauge.

The right side of figure 5 demonstrates the reverse transition. These spectra were recorded at increasing temperatures as the pressure was held approximately constant at 1.5 GPa. The potassium iodide sample is initially in the two-phase region and remains there until the temperature exceeds 100 °C, whereupon it rapidly converts to the pure B1 phase.[10]

Another example of the power of the diamond-anvil cell used with synchrotron radiation to study phase transitions is provided by some recent experiments on ytterbium at DESY. At high-pressures this element undergoes a valence change from $4f^{14}(5p6s)^2$ to $4f^{13}(5p6s)^3$. This led to the expectation that at elevated pressure YbH_2 would transform from its normal orthorhombic structure to a high-pressure fluorite structure. However, experiments



Volume of a formula unit of YbH_2, as a function of pressure. The low-pressure, orthorhombic phase corresponds to a $4f^{14}$ $(5p,6s)^2$ valence state of ytterbium. The high-pressure, hexagonal phase corresponds to a $4f^{13}$ $(5p,6s)^3$ valence state. (From reference 11.) Figure 6

showed[11] that at 14 GPa, conversion is instead to a close-packed hexagonal structure, a finding that helped clarify the nature of the transition (see the figure above).

Even more recently, researchers at DESY have observed[12] what appears to be evidence of a pressure-induced second-order phase transition in thorium sulfide starting between 15 and 20 GPa. Detailed studies of 12 energy dispersive x-ray diffraction peaks suggest a transformation from the normal B1 phase to a distorted face-centered cubic structure. This transition may be associated with a soft-phonon mode that may explain similar transitions in other materials.

Taking advantage of the speed with which one can acquire data in energy-dispersive x-ray diffraction experiments, workers at CHESS completed in a relatively short time a large number of studies of pressure-induced phase transitions, to wit: Ge, AlSb, BaSe, BaTe, CsI, GaAs, GaP, HgS, HgSe and HgTe. In almost all of these studies, the diffraction-intensity data revealed the crystallographic structure of new high-pressure polymorphs. For example, BaSe and BaTe transform from the B2 structure to the B1 structure at pressures of 6.0 and 5.2 GPa, respectively. Moreover, the mercury chalcogenides, HgS, HgSe and HgTe, transform from the cinnabar structure to the B1 structure, and, at higher pressures for HgTe and HgSe, to an orthorhombic structure.[13]

Another example of how synchrotron radiation has aided in unraveling a particular pressure-induced reaction comes from a study of cuprous bromide. Several years ago, in a search for the possibility of high-temperature superconductivity in CuCl, a dramatic increase in conductivity showed up in this compound at high pressures. There was, however, very tenuous evidence to support an explanation other than superconductivity, namely, a pressure-induced disproportionation reaction that precipitates copper: $2CuCl \rightarrow Cu + CuCl_2$. Due largely to the brilliance of synchrotron radiation, recent experiments[14] at SSRL have provided *prima facie* evidence of this reaction in the isomorphic compound CuBr, making disproportionation seem the more likely explanation of the increased conductivity in CuCl.

Kinetics. Workers at CHESS recently used synchrotron radiation to study the mechanism of the olivine–spinel transition that occurs in the geologically important mineral fayalite, Fe_2SiO_4. By monitoring the relative intensities of selected diffraction peaks, they distinguished between two possible mechanisms for this structural transition: a process controlled by diffusion, involving nucleation and subsequent growth of the new phase, and a martensitic process principally involving cation reordering. The evolution of the peaks in the energy-dispersive x-ray diffraction spectrum, observed[15] during the restructuring, favors the latter transition mechanism over the former.

Another example of a kinetics problem that can only be studied with synchrotron radiation is that of structural phase transitions whose rates are fast compared to the usual measurement time. Many factors control transition kinetics: the pressure, temperature, stress, grain size and the atomic transition mechanism itself. To study the effects of these parameters, one must quantify the kinetics of the transition. If the crystallographic structure is known, then the intensities of the diffraction peaks indicate the relative volume fractions of the various phases. One can use this information to determine the unknown parameters of the Avrami equation, which is an empirical expression that describes the kinetics of a phase transition.[7]

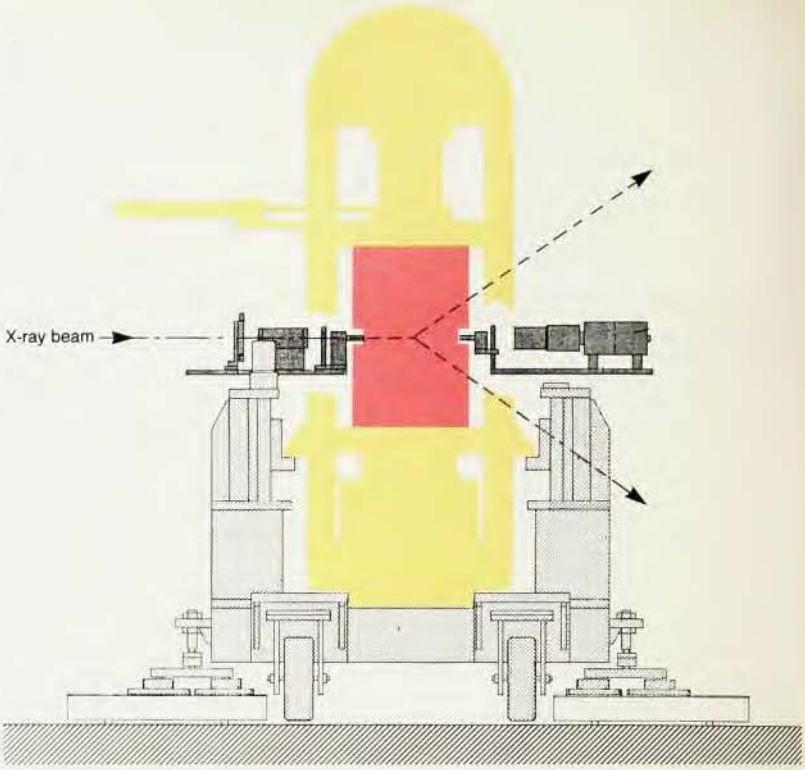
Thus, just as in the case of the fayalite transition, it is critical to be able to monitor signals from the various structural phases for time intervals that are short compared to the transformation time.

Determining structure

In principle, any measurement of the intensities of diffracted x rays gives us information about the locations of atoms within the unit cell. Several groups have summarized[8,16] expressions relating the crystallographic structure factor to intensity data from energy dispersive x-ray diffraction measurements made with synchrotron radiation.

Researchers at DESY have reported high-pressure studies of a number of pyrite structures such as FeS_2 and CoS_2. Because these materials are cubic, the compression of the lattice is reflected in the pressure-induced energy shift of any one of the diffraction peaks. The metal atoms in the pyrite structure are fixed by symmetry requirements in face-centering positions. The sulfur atoms, however, are free to move along the body diagonal of the

Multi-anvil system. The large-volume high-pressure system shown here schematically contains a 500-ton uniaxial press. The high-pressure chamber is about 1.2 m above ground level. The press is now in operation at the Photon Factory in Tsukuba, Japan. (From reference 9.)
Figure 7



cube. Data on 20 diffraction peaks show[17] that a pressure of 4 GPa decreases the metal–sulfur bond length by about 1.3%, but increases the sulfur–sulfur bond length by 2% to 3%.

The availability of synchrotron radiation has significantly enhanced one of the most useful techniques for structural studies: extended x-ray absorption fine structure. A team from the University of Washington carried out the first high-pressure EXAFS experiments. They measured[18] the iron–iron and iron–sulfur bond lengths in FeS_2 at pressures up to 6.4 GPa and found general agreement with earlier x-ray data, thus demonstrating the feasibility of high-pressure EXAFS work. Shortly after these measurements, another group examined[19] the semiconductor-to-metallic transition in gallium arsenide to 22 GPa. Both of these early studies were carried out at SSRL and used diamond-anvil cells to produce the necessary pressures. However, because the diamond anvils are themselves single crystals, they add unwanted structure to the EXAFS spectra through both Bragg scattering and indirect scattering. Consequently, polycrystalline materials such as B_4C or beryllium now stand in for diamond in most high-pressure EXAFS work.

Some recent high-pressure EXAFS studies at DESY focused on the pressure-induced B1-to-B2 phase transition in RbCN. Measurements of the K edge of rubidium in each phase demonstrated[20] that there is a strong coupling between displacements of Rb^+ ions and rotational motions of $(CN)^-$ ions in each phase.

Large-volume systems

As I mentioned above, originally all high-pressure research used systems of comparatively large volume, based on pistons in cylinders, supported anvils or any of a variety of multiple-anvil devices. However, the absorbing materials that separate the high-pressure chamber from the laboratory in these systems complicate the extraction of information from the chamber. In a few instances, however, investigators have succeeded in positioning x-ray tubes to get diffraction data from the high-pressure chambers of these large-volume systems, albeit usually at a rather lethargic pace.

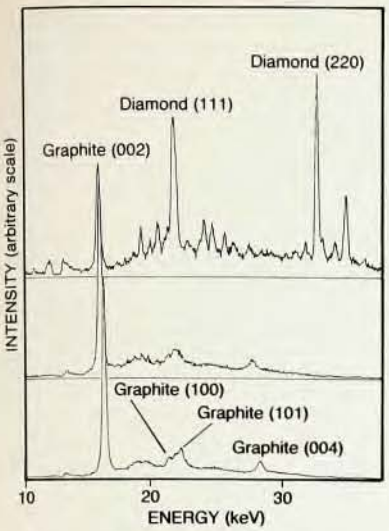
Despite the advantages and popularity of the diamond-anvil cell, a need remains for the large-volume systems. One needs relatively large pressure chambers, for example, to study and perhaps optimize the parameters that govern the production of pressure-synthesized materials such as diamond and cubic boron nitride.

One large-volume system, a belt-type press, was recently installed at HASYLAB, a synchrotron radiation facility at DESY. Sapphire windows in the walls of the high-pressure chamber provide radiation access to and from the sample. One use of this system is to study the kinetics of phase transitions.[21]

A Japanese team has taken the lead in developing large-volume systems by recently installing a 500-ton uniaxial press (figure 7) on one of the beam lines at the Photon Factory in Tsukuba. The press contains cubic tungsten carbide anvils that can produce pressures up to 10 GPa in a volume 4 mm on an edge. The entire system is capable of shifting in three dimensions to adjust the position of the scattering center relative to the beam of synchrotron radiation. The detector can traverse an angle of $\pm 35°$ and can record data in either an energy- or an angular-dispersive mode.[9]

Another important advantage of large-volume systems is that they can operate at temperatures much higher than those that diamond anvils can tolerate. The Japanese press runs at temperatures up to 1700 °C, whereas diamond-anvil cells are usually kept below 600 °C so that the diamonds do not turn to graphite.

As one of its first applications, the Tsukuba press gave the first direct structural evidence of the conversion of graphite into diamond. The three energy dispersive x-ray diffraction spectra in figure 8 are of carbon at a pressure of about 6 GPa. In the two lower spectra, the carbon is in its graphitic form. As the temperature rises from 1200 °C to 1450 °C, going from the middle to the top spectrum, conversion to the diamond phase is evidenced by appearance of the diamond (111) and (220) diffraction peaks. This ability to study the kinetics of synthesis in real time should



Spectra giving evidence of the conversion of graphite to diamond. These spectra were taken at a pressure of six gigapascals, at three temperatures: 25 °C (bottom), about 1200 °C (center) and about 1450 °C (top). Diffraction peaks identified with the diamond structure appear in the top spectrum. (From reference 9.) Figure 8

greatly aid in optimizing the conditions of growth.

Future directions

There seems little doubt that as synchrotron radiation sources continue to become more available to the research community, the number of groups seeking to employ this radiation in high-pressure research will grow. For example, with direct support from the National Science Foundation, there is a program under way by researchers at the Universities of Hawaii and Washington and the Naval Research Laboratory to equip permanently a beam line at SSRL with the electronics and detection instruments necessary for energy-dispersive x-ray diffraction experiments. When this equipment is in place, scientists wishing to perform high-pressure structural studies will need only to bring their diamond-anvil cells, perhaps already loaded and pressurized.

A natural quest for many high-pressure researchers is for higher and higher pressures. One means of pursuing this is through the use of smaller and smaller contact areas. Scientists at Cornell University, for example, are using gasket holes 25 microns in diameter and, in a separate arrangement, diamond anvils with contact areas only 1.6 microns in diameter. With diminishing sample volumes, future researchers will need not only synchrotron radiation from bending magnets, but also the added brilliance of the radiation from wiggler and undulator lines to extract a measurable signal from a sample in a reasonable time. Plans are already under way to use part of a wiggler line at the National Synchrotron Light Source for this purpose when the line becomes available.

Given the accelerated rates of data collection and the increased use of microprocessors to acquire and analyze data, it is reasonable to anticipate the use of these microprocessors to control the pressure and temperature—and thus to fully automated experiments. This will lead to better resolution in pressure and temperature, as well as high-speed *PVT* phase diagrams.

Furthermore, we can expect to see phase transition kinetics studied with time resolutions heretofore unfathomable. Existing multichannel analyzers, operating as time scalars, are capable of monitoring the intensity of an energy dispersive x-ray diffraction peak in millisecond time intervals. By using more brilliant synchrotron radiation sources, based on either insertion devices or higher energy electron beams, microsecond data will also be possible. Researchers will gain new insight as they obtain data from regions closer and closer to the actual phase transition point.

The spatially dispersive EXAFS technique, which is currently under development at SSRL,[22] may obviate the aforementioned problem caused by single-crystal anvils, and permit somewhat more routine EXAFS studies with existing diamond-anvil cells. Similarly, new or improved position-sensitive detectors and charge-coupled devices will lead to enhanced spatial and energy resolution.[23] We can expect that detectors capable of monitoring two-dimensional regions will stimulate high-pressure single-crystal measurements, which, in turn, will permit detailed studies of somewhat more complex crystalline systems. It is entirely reasonable to expect an increase in the number of high-pressure experimenters and in the sophistication of their experiments as more brilliant radiation and more ports become available at synchrotron radiation facilities. Perhaps some day we will see x-ray movies of structural phase transitions.

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References

1. For a review of the design, development and application of the diamond-anvil cell in high-pressure research, see A. Jayaraman, Rev. Mod. Phys. **55**, 65 (1983); Sci. Am., April 1984, p. 54.
2. Y. Fujii, O. Shimomura, K. Takemura,

S. Hoshino, S. Minomura, J. Appl. Cryst. **13**, 284 (1980).
3. H. K. Mao, P. M. Bell, J. W. Shaner, D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).
4. E. F. Skelton, Rept. NRL Prog. **3**, 31 (1972); E. F. Skelton, C. Y. Liu, I. L. Spain, High Press.–High Temp. **9**, 19 (1977).
5. B. Buras, J. Staun-Olsen, L. Gerward, G. Will, E. Hinze, J. Appl. Cryst. **10**, 431 (1977).
6. J. V. Gilfrich, E. F. Skelton, D. J. Nagel, A. W. Webb, S. B. Qadri, J. P. Kirkland, Adv. X-Ray Anal. **26**, 313 (1983).
7. E. F. Skelton, J. P. Kirkland, S. B. Qadri, J. Appl. Cryst. **15**, 82 (1982); E. F. Skelton, S. B. Qadri, A. W. Webb, C. W. Lee, J. P. Kirkland, Rev. Sci. Instrum. **54**, 403 (1983); E. F. Skelton, A. W. Webb, S. B. Qadri, S. A. Wolf, R. C. Lacoe, J. L. Feldman, W. T. Elam, E. R. Carpenter Jr., C. Y. Huang, Rev. Sci. Instrum. **55** 849 (1984).
8. M. A. Baublitz, V. Arnold, A. L. Ruoff, Rev. Sci. Instrum. **52**, 1616 (1981).
9. O. Shimomura, S. Yamaoka, T. Yagi, M. Wakatsuki, K. Tsuji, O. Fukunaga, H. Kawamura, K. Aoki, S. Akimoto in *Proc. Mat. Res. Soc.*, vol. 22, C. G. Homan, R. K. MacCrone, E. Whalley, eds., Elsevier, New York (1984).
10. E. F. Skelton, S. B. Qadri, C. S. Menoni, I. L. Spain in *Proc. 8th Symp. Thermophysical Prop.*, vol. 2, J. V. Sengers, ed., ASME, New York (1981), p. 73.
11. J. Staun-Olsen, B. Buras, L. Gerward, B. Johansson, B. Lebech, H. Skriver, S. Steenstrup in *Physics of Solids Under High Pressure*, J. S. Schilling, R. N. Shelton, eds., North-Holland (1981), p. 305.
12. U. Benedict, J. C. Spirlet, L. Gerward, J. Staun-Olsen, to be published in J. Less Comm. Metals (1984).
13. T. A. Grzybowski, A. L. Rouff, Phys. Rev. B **27**, 7811 (1983); T.-L. Huang, A. L. Ruoff, J. Appl. Phys. **54**, 5459 (1983).
14. E. F. Skelton, S. B. Qadri, A. W. Webb, R. G. Ingalls, J. M. Tranquada, Phys. Lett. **94A**, 441 (1983).
15. M. D. Furnish, W. A. Bassett, J. Geophys. Res. (Solid Earth), **88**, 333 (1983).
16. B. Buras, L. Gerward, A. M. Glazer, M. Hidaka, J. Staun-Olsen, J. Appl. Cryst. **12**, 531 (1979).
17. G. Will, J. Lauterjung, H. Schmitz, E. Hinze, in *Proc. Mat. Res. Soc.*, vol. 22, C. G. Homan, R. K. MacCrone, E. Whalley, eds., Elsevier, New York (1984).
18. R. Ingalls, G. A. Garcia, E. A. Stern, Phys. Rev. Lett. **40**, 334 (1978).
19. O. Shimomura, T. Fukamachi, T. Kawamura, S. Hosoya, S. Hunter, A. Bienenstock, Japan. J. Appl. Phys. **17**, 221 (1978).
20. A. Werner, H. D. Hochheimer, B. Lengeler, Solid State Commun. **45**, 1035 (1983).
21. E. Hinze, J. Lauterjung, G. Will, Nucl. Instrum. and Meth. **208**, 569 (1983).
22. R. P. Phizackerley, Z. U. Rek, G. B. Stephenson, S. D. Conradson, K. D. Hodgson, T. Matsushita, H. Oyanagi, J. Appl. Cryst. **16**, 220 (1983).
23. R. A. Stern, K. Liewer, J. R. Janesick, Rev. Sci. Instrum. **54**, 198 (1983). □