X-RAY CRYSTALLOGRAPHIC STUDIES AT HIGH PRESSURE AND HIGH TEMPERATURE

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Fig. 1 – Cross section of diamond cell (from Finger and King (3))

ABSTRACT

Various diamond-anvil cells have been developed for study of single crystals at hydrostatic pressures as high as 170 kbar. In addition a cell for simultaneous operation at elevated pressure and temperature has been designed. Results obtained with these devices, as well as data from other investigators, have been used to construct empirical relationships describing polyhedral compressibility and thermal expansivity in terms of simple bonding parameters.

INFORMATION ABOUT THE INTERIOR OF THE EARTH is obtained, for the most part, from indirect determination of physical properties such as seismic velocity or density. These properties, whether elastic, optical, electronic, or thermochemical, are dependent on crystal structure. In this report, the types of apparatus used to study variations of structure of single crystals with changes in pressure and temperature are described. Results of experiments are summarized, and empirical relations between bulk and microscopic compressibility and thermal expansivity are presented.

PRESSURE CELLS

Most studies of crystal-structure variation with pressure have been conducted with an opposed-anvil, diamond cell of the type first used by Weir et al. (1*) and revised by Merrill and Bassett (2), Finger and King (3), and Hazen and Finger (4). As shown in Fig. 1, the sample chamber of the single-crystal, diamond-anvil cell is formed by a gasket of hardened stainless steel approximately 0.1 mm thick with an 0.3 mm diameter hole. The gasket is pressed between two 10-point (0.1 carat) diamonds with anvil faces 0.5-1.0 mm in diameter. The diamonds are supported by backing disks of beryllium that are held by steel supports. Pressure is applied by clamping the steel parts with screws. The contents of the sample chamber include the single crystal to be studied, a fluid for transmission of hydrostatic pressure, and small chips of ruby for pressure calibration with the fluorescence of the R_1 line of ruby (5).

The choice of a pressure-transmitting fluid depends upon the sample to be studied and the desired pressure range. For most inorganic materials and minerals a 4:1 mixture of methanol and ethanol is used as this mixture remains fluid to a pressure of 100 kbar (6). For studies above 100 kbar, no conventional fluids are known; however, cryogenic liq-
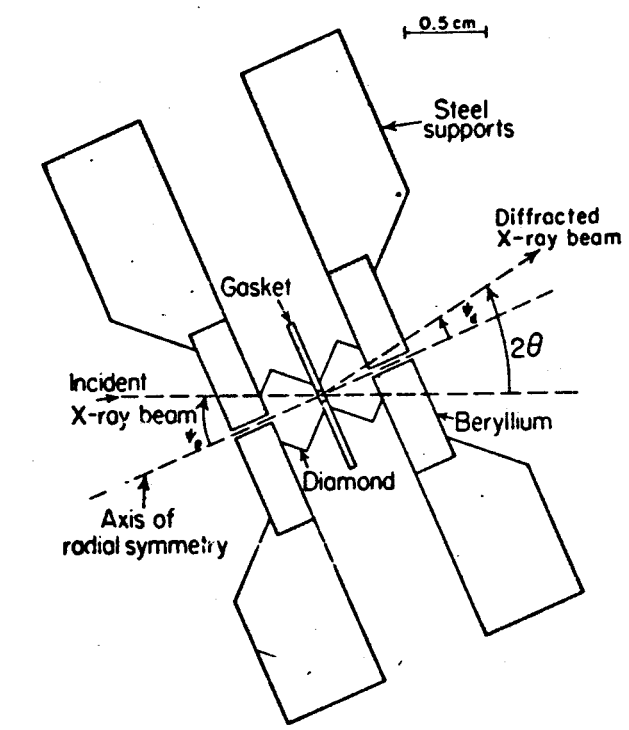
uids at high pressure and room temperature form solids that support very little shear stress (7). A pressure cell with solid neon as the pressure-transmitting medium has been developed (8, Fig. 2) and used to study FeO to a pressure of 170 kbar (9). With suitable modification of the apparatus, it is likely that hydrostatic pressures as high as 500 kbar will be obtained with the use of helium or hydrogen as the medium. These cells have an additional advantage in that the lattice constant of the medium can be used as a very precise internal pressure calibration.

The types of apparatus used to study single crystals at high temperature and room pressure have been reviewed by Finger and Hazen (10) and in the references cited therein. The only successful attempt to design and build a cell for controlled, simultaneous high pressure and temperature is described by Hazen and Finger (11,12) and Finger and Hazen (13). As shown in Fig. 3, a heater and thermal shielding have been placed around the diamonds of a cell very similar to the design used at room temperature (Fig. 1). A major difference is the use of boron carbide backing disks without visual access rather than beryllium. Consequently, the ruby fluorescence method of pressure calibration cannot be used, and an internal, X-ray pressure calibration is employed. This cell has sustained, for periods of several weeks, temperatures to $400^\circ C$ and pressures to 30 kbar – conditions that duplicate most of the crust of the earth.
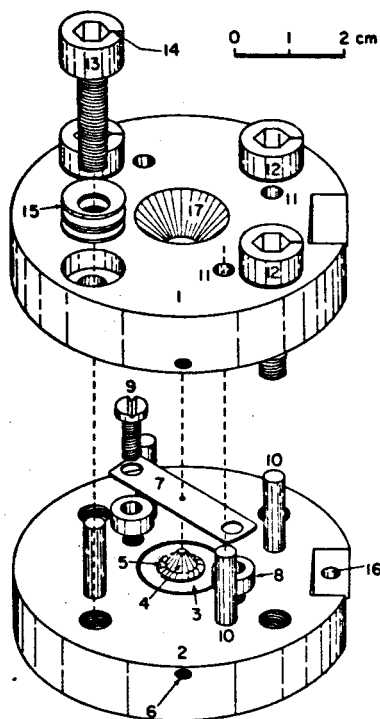
Fig. 2 - Modified diamond-anvil pressure cell for study of single-crystal samples loaded cryogenically. Parts: 1, 2, end plates; 3, Be support discs; 4, diamond anvils; 5, epoxy cement; 6, set screws for diamond alignment; 7, gasket; 8, spacer; 9, gasket holding screw; 10, alignment pins; 11, alignment hole; 12, 13, screws for raising sample pressure; 14, fiducial mark; 15, Belleville washer; 16, hole for mounting screw; 17, X-ray access cone. Figure adapted from Mao and Bell (8)

Fig. 3 - High-pressure, high-temperature cell. Adapted from Hazen and Finger (11)

RESULTS

Diamond-anvil, high-pressure cells of the type described above have been used to study the crystal structures and lattice parameters of approximately 35 materials at room temperature and pressures greater than 10 kbar. The compression results for individual cation-anion polyhedra in these materials were combined with the lattice compression data for simple structures with no variable positional parameters where polyhedral compression may be calculated from lattice compression. The resulting data (10,14) showed that the polyhedral compression, β , of each type of cation polyhedron was essentially independent of structure type and can be represented by

$$\beta = 0.133(4)\underline{d}^3/(\underline{s}^2\underline{z}_c\underline{z}_a) \quad \text{Mbar}^{-1} \qquad (1)$$

where $\underline{d}$ is the mean cation-anion bond distance; $\underline{s}^2$ is an "ionicity" term defined as 0.5 for oxides, 0.75 for halides, 0.4 for sulfides, selenides and antimonides, and 0.2 for carbides; and $\underline{z}_c$ and $\underline{z}_a$ are the formal charges of the cations and anions, respectively. Figure 4 is a plot of the compressibility versus volume for more than 100 substances in 19 different structure types. All points are reasonably close to the line except four circles corresponding to CsCl-type structures in which the cation-cation distance is only 15% greater than the cation-anion spacing. It is likely that the
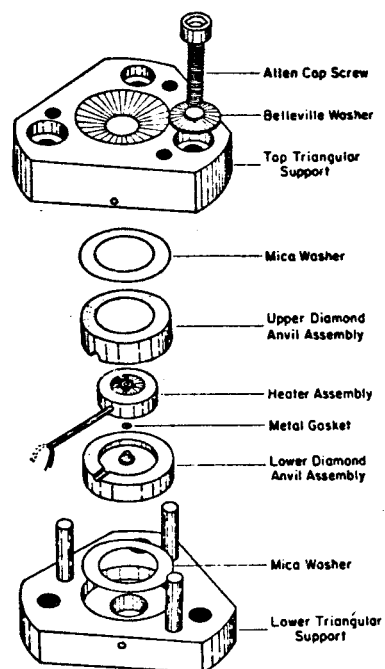
cation-cation repulsions of this structure lead to a smaller compressibility than predicted. In addition, the predicted compressibilities for most tri- and quadri-valent materials appear to be too large (9); nevertheless, Eq. 1 is a useful empirical relationship for predicting the geometry of compression in many solids.

The results of high-temperature studies have been combined (15) to yield an expression for polyhedral expansivity, α , given by

$$\alpha = 4.0(4) \times 10^{-6}\underline{n}/(\underline{s}^2\underline{z}_c\underline{z}_a) \quad {}^{\circ}C^{-1} \qquad (2)$$

where $\underline{n}$ is the coordination number. The expansivity versus Pauling bond strength hyperbola (Fig. 5) shows close agreement between predicted and observed expansivities for weak bonds, but overestimates the expansivity of bonds of greater strength.

The structures of many complex solids can be described in terms of subunits, or modules, such as have been defined for silicates (16) and spinelloids (17,18). The modules are arranged in different sequences to form a number of closely related phases. Hazen and Finger (19) proposed that certain modular arrangements may be stable, in part, because of the fit or misfit of adjacent modules. As external or internal conditions change, the relative dimensions of the modules will be affected; thus limits to specific arrangements will be functions of pressure, temperature and composition.

CONCLUSIONS

Apparatus now exists to study single crystals in situ under pressure and temperature conditions that correspond to those of the crust of the earth. Results obtained with this equipment have been used to construct empirical relationships describing the polyhedral compression and thermal expansion in terms of simple parameters. With enhanced operating

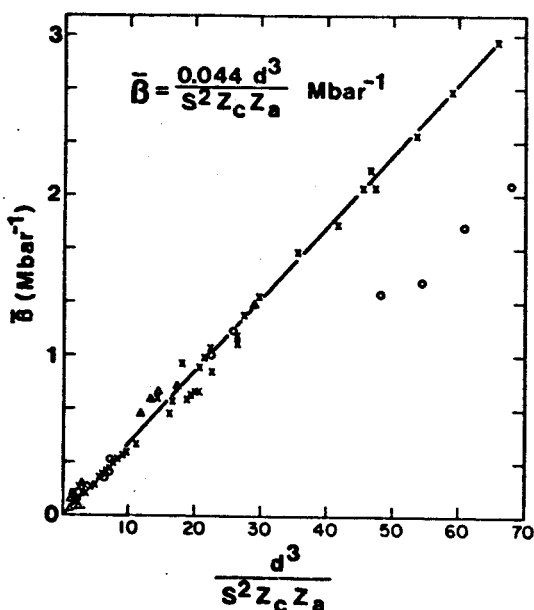$$\bar{\beta} = \frac{0.044\ d^3}{S^2 Z_c Z_a}\ \text{Mbar}^{-1}$$

Fig. 4 - Bulk-modulus relationship for polyhedra in a variety of materials. Triangles represent 4-fold; crosses, 6-fold; and circles, 8-fold or greater coordination. The line is a weighted linear regression fit of all data except CsCl-type structures (see text for explanation), constrained to pass through the origin. See Hazen and Finger (14) for table of data used to construct the figure
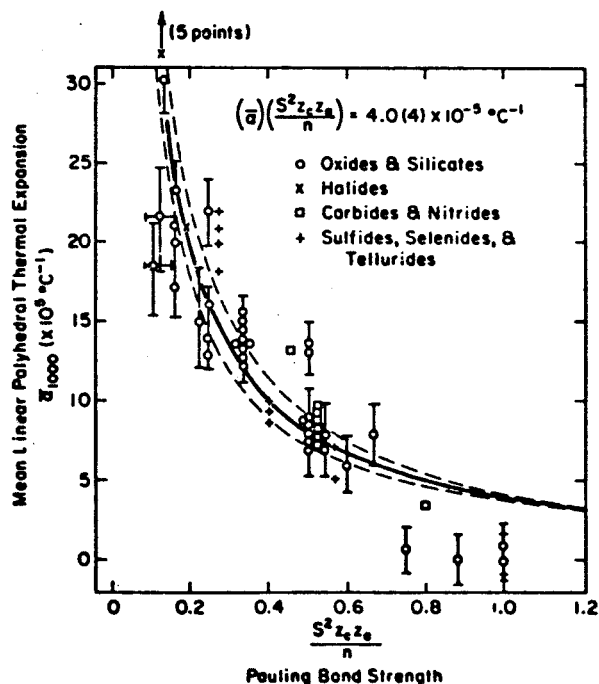

Fig. 5 - Polyhedral thermal expansivity relationship for a variety of materials. See Hazen and Finger (15) for table of data used to construct the figure

range for the equipment now planned, conditions deeper within the earth will be simulated. The new data will be used to improve the empirical relationships. Soon it may be possible to predict crystal-structure properties in pressure-temperature regions that cannot be reproduced in the laboratory. In addition, it should be possible to predict the stability regions in pressure, temperature, and composition for particular arrangements of subunits in families of modular structures, and to predict phase diagrams for these systems.

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