

The Diamond Anvil Pressure Cell

Two intimately related scientific and technological achievements occurred in the field of high pressure research at the NBS laboratory during the second-half of the 20th century: the invention of the diamond anvil high pressure cell [1] in 1958 and the development of the optical ruby fluorescence method of pressure measurement [2] in 1972. These two developments together stimulated the profound advances in high pressure research that evolved in the latter part of the 20th century.

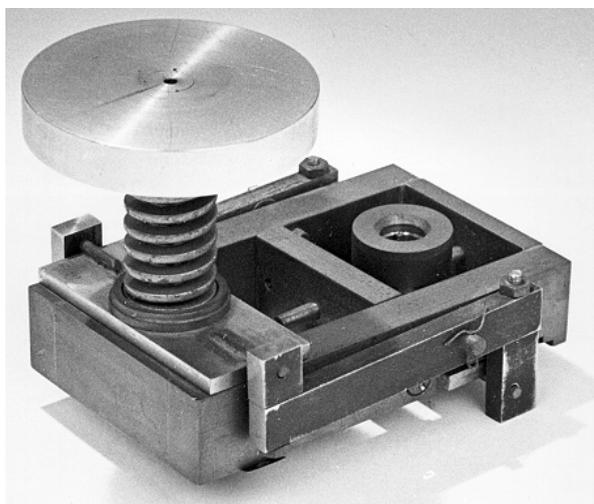


Fig. 1. The original DAC, on display in the NIST Museum.

The invention of the diamond anvil high pressure cell (DAC) took place in the Constitution and Microstructure Section (then headed by H. F. McMurdie) of the Mineral Products Division (Irl C. Schoonover, Chief) in the late 1950s at the NBS laboratories in Washington. It was the product of the joint effort of four individuals, Charles E. Weir, Alvin Van Valkenburg, Ellis R. Lippincott, and E. N. Bunting. Each of these scientists contributed a separate and distinct expertise which, when combined with the others, provided the impetus necessary for the development of the new pressure cell. Weir had developed an intense interest and appreciation for the effect of high pressure on the properties and structure of materials through his construction of a device to study porosity of leather and the compressibility of teflon and other materials. For this work, he received the Department of

Commerce Silver Medal in 1954. Van Valkenburg had designed a high-temperature furnace for the synthesis and growth of mica, but he also utilized a tetrahedral anvil press for the synthesis of diamonds. Bunting studied phase equilibria and electrical properties of ceramic oxide systems. Lippincott, a guest scientist from the University of Maryland, collaborated with these individuals on measurement of infrared spectra of inorganic materials. He had a special interest in short-range interatomic forces and the perturbing effects of neighboring atoms on each other—effects that would be amplified by the change in lattice spacing produced by high pressures. The presence of all four of these individuals in the same laboratory space enabled a fruitful exchange of ideas that eventually led to the concept of a miniature high pressure device with an optical access permitting the measurement of infrared absorption spectra.

The DAC conceived in this setting [1] was a lever-arm type device with a 180° optical transmission path which permitted, for the first time, the infrared spectroscopic measurements on powders squeezed between two opposed diamond anvils. Among the first materials studied were NaNO_3 , KNO_3 , AgNO_3 , ferrocene, ice, and CaCO_3 . These initial studies demonstrated that pressure-dependent shifts in frequency and changes in intensity of infrared absorption bands could be measured, and also led to the observation of large changes in spectra as a result of pressure-induced phase transitions. This NBS instrument was the prototype for all subsequent opposed-anvil diamond cells with 180° optical transmission.

The first cell was handmade by Charles E. Weir, who fabricated it utilizing only a lathe, drill press, hack saw, soldering gun, threading tools, files, and a high speed grinding wheel to polish down the culets of the diamonds to form anvil faces. The gem diamonds were obtained by Alvin Van Valkenburg from the General Services Administration, which, at that time, served as the custodian for contraband diamonds confiscated from smugglers by government agents. In those days, such diamonds were free for use by other government agencies, provided that their purpose could be justified. It is of interest to note that without the availability of these gratis gem diamonds, it is probable that the DAC would not have been developed as rapidly as it was, because during the early stages of its development many diamond anvils were destroyed in the testing process.



Fig. 2. Charles Weir, ca. 1960.

To replace them would have been prohibitively expensive. The original instrument, small enough to fit in the palm of one's hand, can be seen today on display in the NIST Museum.

By 1971, the DAC had undergone several stages of refinement and had been adapted to other measurement techniques by NBS and various other laboratories in the United States. Still, it was not fully appreciated as a scientific instrument because there remained a very significant problem. There was no convenient, precise method for determining the pressure being exerted on the sample in the diamond anvil cell. Pressures had either to be calculated (force per unit area) or measured from compression data (utilizing an equation of state, e.g., of sodium chloride) obtained by an x-ray powder diffraction method. However, the former procedure was very inaccurate, and the latter, although more accurate, was tedious and time consuming, often requiring as much as fifteen hours to make one pressure determination. Consequently, in 1970, acceptance of the DAC as a tool in high pressure research was somewhat limited. It was used primarily in laboratories engaged in research of geological interest where very high pressures simulating the earth's interior were desired, while the accuracy in the value of the pressure was not yet of primary importance.



Fig. 3. A. Van Valkenburg, 1962.

In 1971, this situation changed dramatically. The high pressure group at NBS was under the ever-present prodding of management to develop a better method for measuring pressures in the DAC. The problem was discussed one day in the NBS cafeteria among John (Jack) B. Wachtman, Jr., Chief of the Inorganic Materials Division, Stanley Block, Chief of the Crystallography Section, and Dean Barnett, a guest scientist at NBS on sabbatical leave from Brigham Young University. While they were having lunch together, the table conversation turned to possible techniques for measuring pressure. Wachtman suggested various methods, all of which had been considered already and found to be unsuitable. Finally, Wachtman asked the pivotal question, "Have you considered fluorescence spectroscopy?" As it happened, they had not, but replied that they would look into it. Encouraged by this meeting, Stanley Block, Dean Barnett, Gasper Piermarini, and Richard Forman began to study the pressure-dependence of several fluorescing materials. Some of these materials happened to be on the shelves in Forman's spectroscopy laboratory, while others were obtained from H. S. Parker and W. S. Brower of the Solid State Chemistry Section. Those materials included ruby (Al_2O_3), YAIO_3 , YAG, MgO , and a few others. While several materials had a readily observable pressure dependence, ruby exhibited

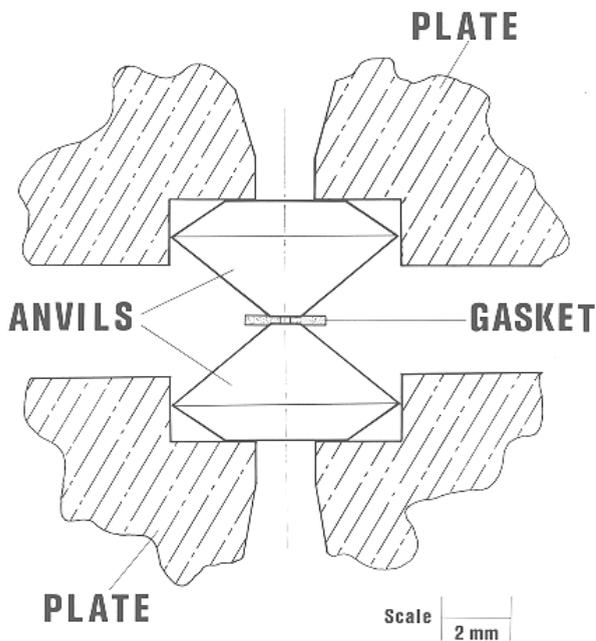


Fig. 4. A schematic diagram of the opposed diamond anvil assembly to illustrate the 180° optical transmission characteristics and the concept of Bridgman opposed anvils. A thin metal gasket containing a 250 μm diameter hole for encapsulating a sample (liquid or solid or both) is squeezed between the two anvils.

by far the most promising results. Ruby's main fluorescence lines (the R-line doublet lines) were intense and sharp, and the lines shifted toward the red end of the spectrum with increasing pressure. Significantly, pressure could be detected *in situ* using only a very small amount of ruby crystal (comprising only 1% of the available volume) as the internal pressure sensor. Further, because ruby is chemically inert, it could be present in the sample chamber to detect pressure without interfering with any other experimental specimen in the chamber.

Recognizing the significance of these observations, it was of paramount importance to calibrate the R-line shift against reliable pressure values. This calibration was accomplished at NBS [3] using an x-ray powder diffraction method to measure the compression of NaCl and relating this to the measured shift in the wavelength of the ruby R₁-line. The corresponding pressure was calculated from the compression data utilizing an established equation of state for NaCl. The R₁-line shift was found to be linear with pressure (2.740 ± 0.016 kbar \AA^{-1}) up to about 19.5 GPa. In subsequent work [4], the linearity was confirmed to about 29 GPa. The success of this calibration quickly established the ruby scale as a secondary pressure standard, and it became the *de facto* standard for measuring pressures in a DAC.

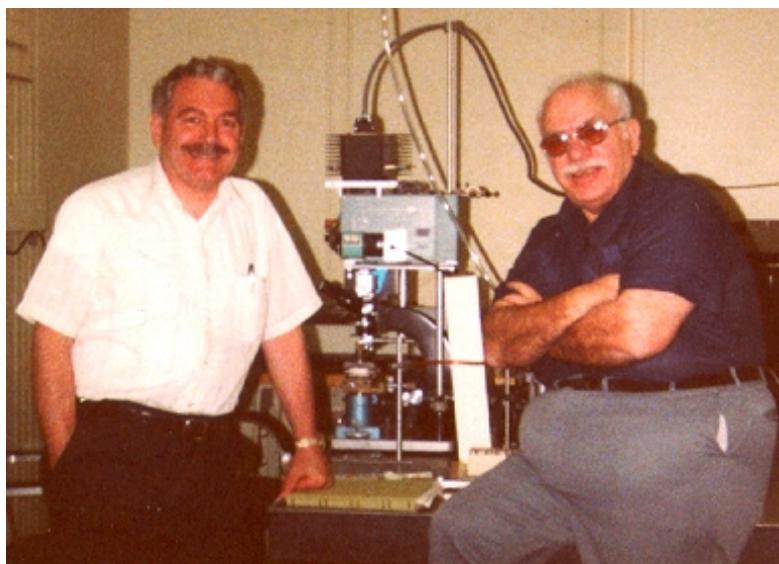


Fig. 5. Gaspar Piermarini and Stanley Block by the ruby fluorescence apparatus used with the DAC, ca. 1984.

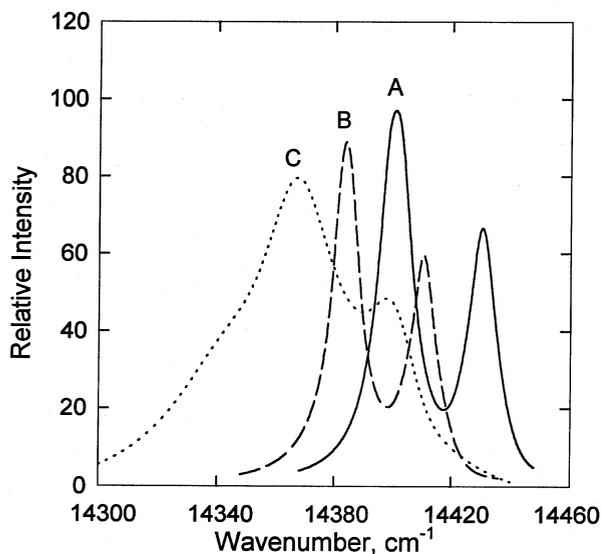


Fig. 6. The R-line luminescence spectrum of ruby in the DAC: curve A, ruby at ambient atmospheric pressure; curve B, ruby in a mixture of ices VI and VII at about 2.2 GPa; curve C, ruby in a nonhydrostatic mixture of CCl_4 III and IV at about 4 GPa.

In the years following the introduction of the DAC and the ruby pressure standard, numerous breakthroughs in high pressure research and technology were achieved at the NIST/NBS laboratory. Milestones or “firsts” were achieved in several areas, including the generation of ultrahigh pressures through improvements in the design of the original NBS DAC [4]; the development of a camera for obtaining x-ray powder diffraction data at high pressure [5]; the measurement of hydrostatic limits in pressure-transmitting media utilizing the ruby method [6]; the introduction of a metal gasket to encapsulate liquids and other materials under pressure between the diamond anvils [7]; the development of the methodology for determining crystal structures at high pressure in the DAC from single crystal x-ray diffraction intensity data (first application: growth and structure of a single crystal of ice VI) [8]; the application of the DAC to Raman spectroscopy [9]; and the measurement of the viscosity of liquids at ultrahigh pressures in the DAC by the classical Stokes method [10].

In 1974, Block and Piermarini were awarded the Department of Commerce Gold Medal for their work on the design, construction, and application of the high pressure system, including the diagonal pressure cell, the ruby fluorescent method of pressure measurement, and associated characterization techniques. These achievements ignited and fueled an explosion of activity in high pressure research by laboratories throughout the world, a profuse activity that continues unabated today.

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