

pressures. The diamond window is by far the most valuable for high pressure studies. It is the hardest material known and is transmissive throughout most of the electromagnetic regions. Generally, two types of diamonds are used — type I and type II. However, there may be variations from diamond to diamond, as has been indicated [53,72,75]. Type I shows absorption at ca. 3, ca. 4–5.5, ca. 7–10 μm while type II absorbs at ca. 3 and ca. 4–5.5 μm . Sapphires may be used in the IR region from 2–5 μm , although pressures are limited to about 12 kbar. Sapphire is promising for Raman pressure studies, since it may be used from $\Delta\nu$ of 500–2000 cm^{-1} , before fluorescence becomes a problem. However, pressure limits are low with sapphire windows.

Other measurements have been made with pressure, but these are beyond the scope of this review. For example, electrical conductivities [55,90,91], magnetic susceptibilities [92–100], the Mössbauer effect [101–104], magnetic resonance [105–113], nuclear quadrupole resonance [114–117], X-ray [118–124], and viscosity [125] have all been studied under pressure. However not all these studies have been made with the DAC.

C. PRESSURE CALIBRATION

It has been mentioned that a pressure gradient exists in the DAC. Duecker and Lippincott [58] have demonstrated that the pressure gradient face is parabolic, with pressures in the center reaching 1–1/2 times those on the edges. Any pressure in the contact area of the diamond is in reality only an average pressure, unless a gasket and a pressure-transmitting fluid is used.

Calibration of the DAC and for that matter other anvil-type cells can be made by several methods. Unfortunately, a number of these methods involve internal calibration incorporating a foreign substance, and the problem of a matrix effect is omnipresent. The methods are listed as follows: (1) The compression of the spring is measured by a Dillon force gauge. The contact area of the diamond is determined by means of microphotographs. One can thus obtain force per unit area of pressure. (2) Solids which undergo phase transitions at known pressure may be used to calibrate the cells. For example, KBr shows a phase transition at 18 kbar; KCl at 20 kbar; NaNO_2 at 14 kbar; HgI_2 at 13 kbar. These phase transformations can be followed with pressure using a microscope as well as being followed spectroscopically. (3) Calibration may be made by following the change in nickel dimethylglyoxime (NDMG) in the visible absorption region [58,126]. These changes have been related to pressures by the National Bureau of Standards. However, NDMG tends to lose intensity with pressure and the band being monitored is eventually too weak to follow. Other nickel complexes have been suggested [127,128]. (4) Scientists at the National Bureau of Standards [54,55,129–131] suggested calibration of the DAC by following the R_1R_2 doublet fluorescence lines at 694.2 and 692.8 nm with a pressure increase. Figure 8 shows the pressure calibration of the ruby R_1 fluorescence line. The freezing points of several liquids (e.g., CCl_4 , H_2O , $n\text{-C}_7\text{H}_{16}$, and $\text{C}_2\text{H}_5\text{Br}$) and two solids, which have character-

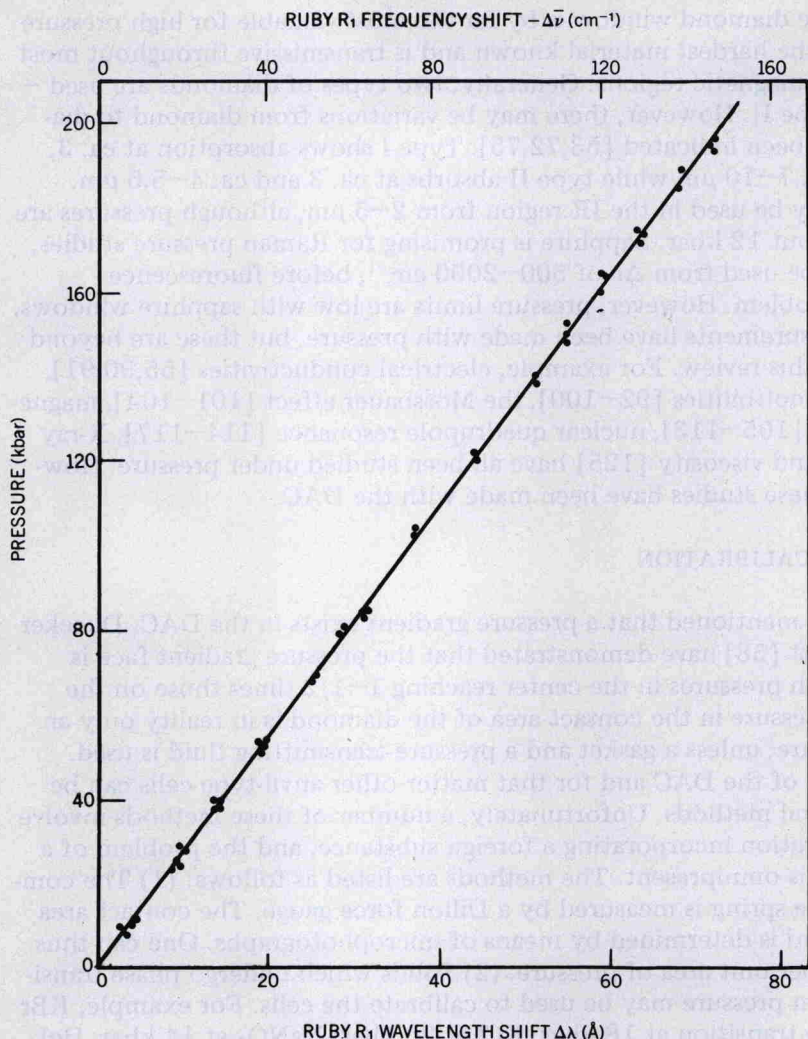


Fig. 8. Pressure calibration of ruby R_1 fluorescence line to ca. 160 kbar [55,129–131]. (Figure reproduced through the courtesy of the authors and the American Institute of Physics, New York.)

ized pressure transitions, were used in establishing the pressure response with cm^{-1} . It was suggested that the method can be used to high pressures (mbar region) since no significant departure from linearity in the curve occurs, and further that the method is useful to ca. 973 K.

The use of the ruby R_1 fluorescence line as a function of pressure has now been extended into the megabar region [90,132–135]. This was done by simultaneously measuring the specific volume of Cu, Mo, Ag and Pb, and