



DAC info

Document no.:DE08
Date:30.05.11

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High-Pressure apparatus

Prior to the invention of the diamond anvil cell, static high-pressure apparatus required large hydraulic presses which weighed several tons and required large specialized laboratories. The simplicity and compactness of the DAC meant that it could be accommodated in a wide variety of experiments. In addition to being hard, diamonds have the advantage of being transparent to a wide range of the electromagnetic spectrum from infrared to gamma rays, with the exception of the far ultraviolet and soft X-rays. This makes the DAC a perfect device for spectroscopic experiments and for crystallographic studies using hard X-rays.

The work done in compressing the system of interest to such high pressures is typically of a few electron volts, and is comparable to the chemical bond energies⁴. This can induce large changes in the behaviour of electronic orbitals and as a result increase the reactivity of the species under study. In addition, high or low temperature of the sample squeezed inside the DAC can provide the kinetics necessary to induce novel reactions between the reactant species by overcoming activation barriers that are otherwise impossible to do so at ambient conditions.

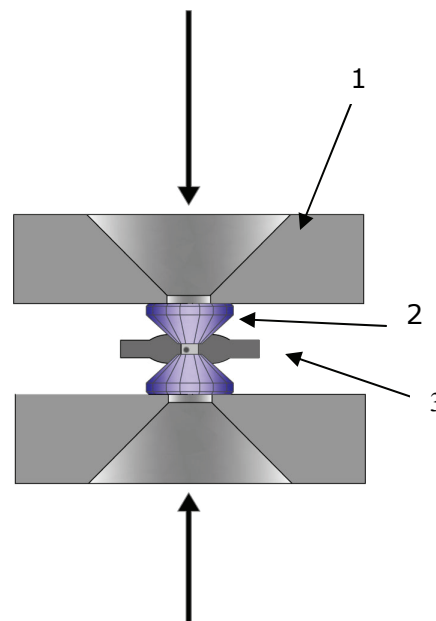
1-Diamond Anvil Cell

The Diamond Anvil Cell (DAC) is one of the fundamental devices employed to generate and exert high static pressures on solid, liquid or gas samples. It works by placing carved diamonds on the tips of piston cylinders so that the force of compression is concentrated over a very small area: the two specially cut diamonds are pressed upon each other so as to apply a large pressure on the medium between the two. DAC technology thus provides an inexpensive way to compress tiny samples of materials to ultra-high pressures in order to identify changes in their properties. Pressure is measured by observing the fluorescence properties of the investigated sample with a ruby laser.

The idea that high pressure may be attained through the application of a modest force on a microscopic area has to be ascribed to Drickamer, who in the early 50s performed high-precision measurements of electric resistivity, X-ray diffraction and optical absorption at pressures of up to tens of a Gpa^{1, 2}. In the following years, different and new types of diamond anvil cells were built, thus allowing the start of a new era, that of high pressures. In 1965 the metal gasket technique was employed in order to generate hydrostatic pressure³, thus allowing the pressurization of liquids and gases. The ruby-fluorescence technique for pressure calibration was introduced in 1973⁴.

The concept underlying the DAC system is very simple. The sample, held between two diamond anvils and confined by a gasket (fig. 1), is squeezed between the anvils' small faces. The maximum pressure value varies according to the dimensions of the small faces of the diamond anvil (*culets*), to the force exerted on the diamonds as well as to the dimensions of the hole in the gasket.

Figure 1. Schematic drawing of a diamonds anvil, showing the indented gasket and the sample chamber. 1) Diamond anvil seats. 2) Diamond anvils 3) Metal gasket.



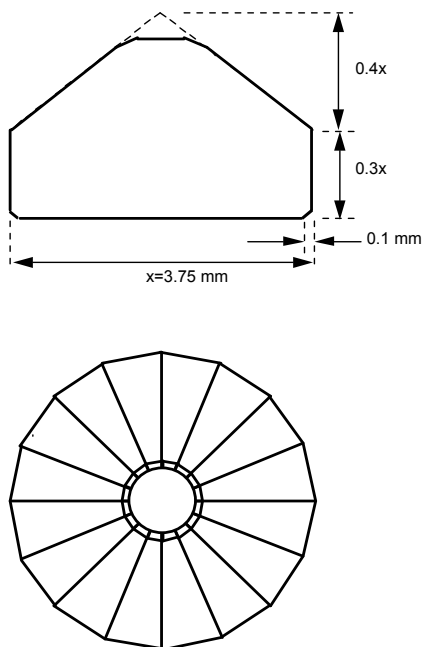
So far only natural diamonds have been employed in DAC technology. The main parameters determining the selection of diamonds are a very low birefringence (proof of a low-level strain) and a low photoluminescence, which is caused by impurities. Natural diamonds are classified on the basis of the impurities they contain. Type Ia diamonds representing the vast majority of natural diamonds - is the most frequently employed, while special applications require use of the more expensive Type-IIa diamonds, characterized by a lower impurity level. This determines a lower IR absorption and strongly reduces the photoluminescence observed in Raman spectra.

The culet of the diamond anvils is generally a 16-side polygon oriented along the crystal direction, with a diameter ranging from 100 to 600 μm . The large face has a diameter of about 4 mm. The cylindrical sample chamber - i.e., the hole in the gasket - typically has a 100 μm diameter and a 50 μm thickness, with a culet of 400 μm .

Diamond Anvil Cells can be classified according to the mechanism used to generate force. The precise movement of the two diamonds is usually achieved through a piston and a cylinder. Three main force production methods can be identified in DACs: a mechanical system based on levers, one based on screws, and a metal membrane system generating force when inflated with a gas at pressure < 200 bar.

The experiments DACs potentially

allow to perform the sample characteristics but this investigation is subjected to



16 pavilion facets
girdle diameter, $x = 3.75$ mm
table edge ground back 0.1 mm
single bevel on culet

Figure 2. The standard diamond dimensions

limitations due to the small dimensions of the sample as well as to the geometrical constraints imposed by the cell. The diamond windows is an excellent anvil in a very wide frequency range: from the UV to the infrared, including X-rays.

2-*LOTO-eng* DACs

LOTO-eng Diamond Anvil Cells are designed to fulfill the requirements of the most demanding applications in high-pressure research.

Cells can be operated at low temperature or be equipped with a miniature resistance heating element for the simultaneous application of high pressure and temperature up to 1000 K.

Three different drive systems are currently available for the transmission of force to the anvil mounts in order to achieve high pressures: the pressurized metallic membrane, the spring-loaded screw, and a screw system.

Figure 3. shows the completed setup of a *LOTO-eng* DAC provided with a membrane drive system: this type allows the attainment of ultra-high pressures. Force is applied to the diamonds by making helium pressure increase inside the membrane by means of a capillary. The force pushes the diamond mounted on a platform with four rectified pins; the platform is located against the bottom diamond on an optional mounting plate with four circular holes. The precise alignment of the two diamonds - set in the discs and surrounded by a thin copper ring - is ensured by the translation and tilting of the discs themselves, mounted on one disc and one hemispheres by tungsten carbide. These movements allow the alignment of the diamond anvils and thus the achievement of perfect parallelism between culets - a step that must necessarily be performed before any load application.

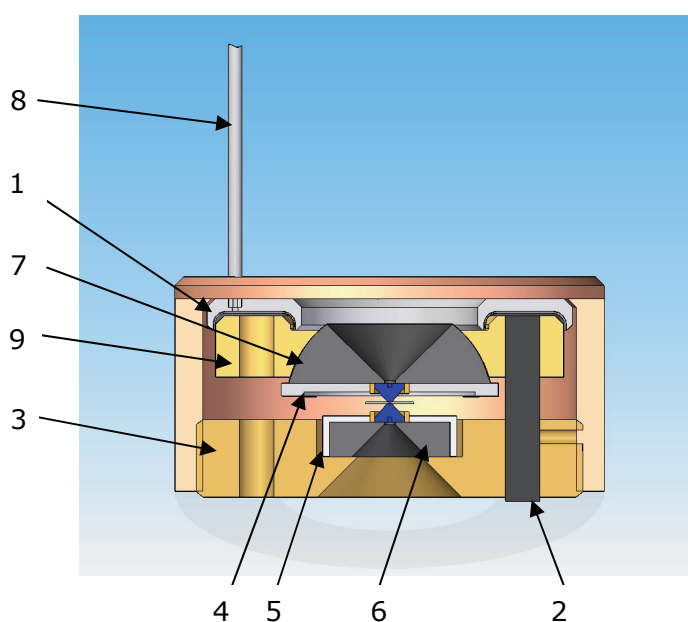


Figure 3. The view section of a *LOTO-eng* DAC with membrane for high pressure applications. Four rectified pins (2) penetrating the holes allow the precise movement of the platform (3). The precise alignment of the two diamonds is achieved through the translation by the disc (4-5), mounted on the disc (6) and hemisphere (7) a metallic membrane (1), which is inflated with pressurized helium through the capillary (8) that press the platform (9). Helium pressure is typically below 200 bar.

The tungsten carbide hemispheres are provided with an optical access to the anvils by means of cones. The optical aperture is about 70°.

The membrane system has the advantage of allowing a very fine pressure regulation; remote control provides additional operation comfort and proves essential when the cell is not directly accessible: for instance, during to loading procedure (cryogenic or gas loading), or when the cell is incorporated into a cryostat or, in general, in a vacuum vessel.

This DAC can be equipped with a microvalve allowing the closing of the capillary as well as the disconnection between the cell and the membrane pressure-control system; it also ensures the maintenance of high pressure within the membrane. The microvalve thus proves essential when the cell has to be placed in - or removed from - a closed vessel without varying the membrane pressure. The microvalve has the typical shape of a metallic mini cylinder, it has been tested up to 200 bar in the capillary at temperatures ranging from room temperature down to 77 K. The possibility of working at low temperature allows cryo loading with nitrogen, argon, etc. to be performed.

3-X-ray diffraction

X-ray diffraction measurements require the use of different hemispheres in order to increase the maximum diffraction angle. Three possible solutions are available: a beryllium hemisphere transparent to X-rays, which has the advantage of increasing the two-theta angle up to about 40 degrees, depending on the type of DAC, but reduces maximum pressure by ca. 30 % with respect to standard tungsten carbide hemispheres; furthermore, this solution has the disadvantage of producing additional weak diffraction rings due to diamond reflections passing through the beryllium hemisphere. The second solution is a tungsten carbide hemisphere with a big hole (2 mm in diameter) coupled with a small diamond (1.7 mm height instead of 2.6 mm): the result is a maximum two-theta angle of about 20° and a reduction of maximum pressure by ca. 30 % with respect to standard diamonds and hemispheres. The third solution consists in a boron carbide pellet placed inside a special tungsten carbide hemisphere. In this case, the maximum two-theta angle measures 30°.



Figure 4. DAC cell with screws

4-High temperature

Two systems are currently available for the achievement of high temperatures: for temperatures from to 600 K, an external resistive heating element can be applied to any type of *LOTO-eng* DAC, while temperatures above 600 K (up to 1000 K) require a special equipped with a miniature resistive heating element as well as with special heat-insulating devices which confine heat in the area surrounding the diamonds.

5-Routine procedures (Diamond setting)

This procedure has to be performed each time diamonds have to be replaced. The disc functioning as diamond-holder is provided with a hole in the center that is slightly bigger than the diamond itself. In order to perform the setting procedure, a special tool is required, whose function is to push and deform a thin copper ring placed around the anvil at the center of the disc in order to fix the diamond. Before the deformation of the copper ring takes place, the disc and the diamond have to be positioned upon the flat surface of a sapphire window placed inside the tool, which ensures perfect co planarity between the large face of the diamond anvil and the bottom surface of the disc. The copper ring is deformed by a piston whose movement is produced by the tool itself. The same tool can also be used to remove the diamond from the disc.

6-DAC alignment

The alignment of diamond anvils is a highly delicate procedure, decisive in order to avoid the premature failure of diamonds under high pressures. Its aim is to position the diamond faces parallel to each other. The method used to align *LOTO-eng* DACs is described below.

Looking with a microscope through one of the DAC diamonds, the operator moves the discs in which the diamonds are set to achieve a coarse translational alignment. Then, after a first rough parallelism achieved through a digital caliper, the flat faces of the anvils are delicately moved towards each other and put into contact. At this point, parallelism can be tested by looking at the interference fringes generated by white light coaxial illumination. If the light source is large and the distance between the diamonds small¹, fringes are visible also with non-monochromatic light. The fringes show the regions of the diamond faces which are separated by a distance multiple of $\lambda/2$.

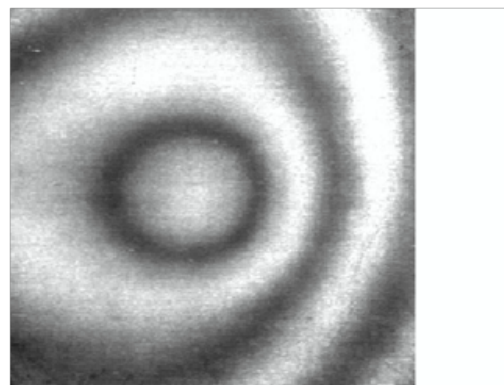


Figure 5. Culet's Interference fringes

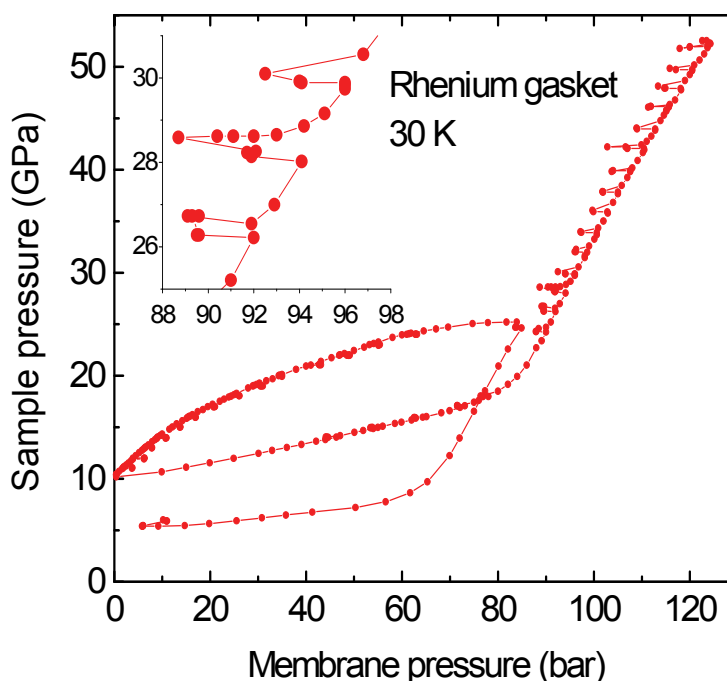
¹ M. Born and E. Wolf, “*Principles of Optics*”, Pergamon Press (1993)

If the two diamonds prove perfectly parallel, no interference fringe is present. In order to achieve this condition, the orientation of the hemispheres has to be adjusted with the aid of screws. The alignment is considered perfect when the fringe width is greater than the anvil flat diameter and no fringe is visible. Under these conditions, the maximum parallelism error between the two faces is: $d < \lambda_{\text{light}}/2 \approx 0.25 \mu\text{m}$.

For a culet of 500 μm in diameter, the wedge angle measures less than 1 mrad. At this point, the fine adjustment of the translation of the two discs holding the diamonds can be performed without compromising the tilting procedure, and the alignment procedure is at an end. The mechanical stability of the diamond anvils' alignment is maintained under pressure during all operation phases, including load application. The alignment of the anvils' working surfaces is central to the achievement of ultra-high pressures.

Figure 6.

The membrane is used to apply force evenly over the whole surface of the piston (the sketch of the cell shown in Figure 2.(9) in increments of 0.1bar, which allows very smooth control over the samples' pressure in the chamber. In Figure 6. we present a typical sample pressure as a function of the membrane pressure and the hysteresis loop. As expected with the decrease of the culet size higher pressures can be achieved with the same applied He pressure in the membrane



7-Preparation of the metal gasket

The purpose of placing a metal gasket between the two diamonds is to provide a chamber in which liquids and suspensions can be contained. Hydrostatic pressure is generated by squeezing the gasket between the diamonds in an adjustable clamp. The gasket is a metal foil, typically 200 μm thick, which provides great yield strength, a high friction coefficient on diamonds (necessary to hold the sample in its position) along with a certain degree of ductility. The materials typically employed are high-strength stainless steel

T301 or T304, but at ultrahigh pressures it is advisable to use rhenium, as it provides greater yield strength.

The following part describes the procedure for the preparation of the sample compression chamber, formed by the cylindrical hole in the gasket and by the diamonds' culets. First, the gasket has to be fixed over one of the two diamonds by means of two small dowel pins fitting into the gasket holes. Then, the cell is closed and force is applied on diamonds to create an indented region with the desired final thickness. The indented gasket can then be removed and a hole can be drilled in the center of the indented region. The gasket is then placed in its exact position using again the two pins, and a small ruby chip is inserted into the hole. The cell is now ready to be closed and loaded with gases, liquids or solids..

The gasket indentation produces deformation of the foil, which acquires the typical shape of a crater; the extruded material provides a lateral support, important for the attainment of high pressures.

The dimension of the circular hole drilled in the gasket, the gasket material, the original and final thickness of the indented region as well as the dimensions of the diamond culets are some of the most important factors determining the maximum reachable pressure in a DAC. Though a few empirical rules are followed, low values for all mentioned parameters are usually required when dealing with extreme pressures.

8-DAC loading

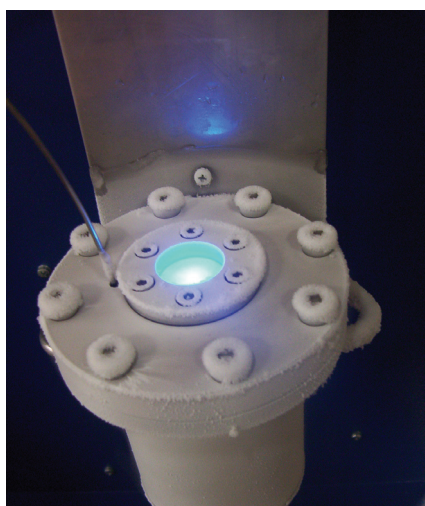


Figure 7. *Cryogenic gas-loading setup. A vacuum pump is used to clean the box before the gas inlet. The helium input is used to achieve room temperature after the loading procedure has taken place.*

DACs can be loaded with gaseous, liquid or solid samples. Load is applied using two hexagonal bolts, one of which has a left-handed thread.

The direct compression of a solid determines non-hydrostatic pressure even at low pressures. For this reason, it is recommended that solid samples be placed inside the gasket's hole and immersed in a gas or a liquid before compression. The pressure-transmitting medium - which provides a pressure as close as possible to perfect hydro staticity - is helium, but a methanol-ethanol-water mixture is also frequently used, as it allows an extremely simple loading: just a drop and the DAC can be closed. To load helium, DACs require a gas loading system allowing them to be immersed in the gas at a pressure range of 1000-3000 bar with a view to achieving a high initial density

as well as to minimizing volume reduction during compression. A compression of up to 5000-10000 bar is indeed necessary to avoid any leakage between diamonds and gasket. Only the type of DAC endowed with a membrane can be used during gas loading, as the remote-control system allows sample pressure to increase while the DAC is still immersed in gas at high pressure.

The pressure remote-control is also very useful during cryo-loading of the DAC at low temperatures (see figure 3). This technique allows DACs to be loaded with condensed gases such as nitrogen, argon, oxygen, etc. The advantage over gas loading is the higher initial density that determines a smaller volume reduction under compression.

9-Pressure calibration

The measurement of sample pressure is usually performed using the ruby-fluorescence technique. The intense fluorescence of the ruby's R lines (Al_2O_3 with impurities of Cr^{3+}) is sensitive to the change of interatomic distances resulting from the application of external pressure. Photoexcitation of R-lines luminescence is usually provided by a laser source: the 514.5 nm or the 488 nm intense lines of the argon laser prove suitable for this application. The fluorescence spectrum is composed by the R1 and R2 lines occurring respectively at about 694.25 nm and 692.7 nm at room pressure, and shifts towards longer wavelengths when pressure increases (see figure 5).

Pressure measurement is performed through different calibrations of the R1 line shift, established in different ways depending upon pressure conditions and ranges. The linear calibration of the ruby shift, introduced by Piermarini⁶ *et al.*, proves good up to 30 GPa for a quasi-hydrostatic environment. Mao and Bell⁷ extended the quasi hydrostatic calibration to 80 GPa and found a slight non linearity at high pressure, while - as for non-hydrostatic pressures - Bell *et al.*⁸ suggested a non-linear pressure calibration system ranging up to 180 GPa .

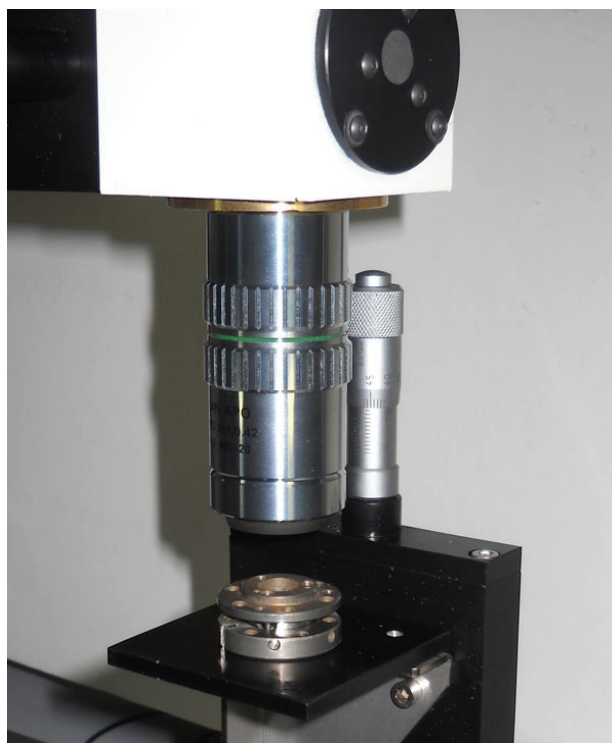


Figure 8. The LOTO-eng microscope designed to collect the ruby fluorescence

The *LOTO-eng* Microscope is designed for collecting the fluorescence emission of a small ruby chip placed inside the sample under pressure in the diamond anvil cell (DAC).

Photoexcitation is provided by a Laser source at 532nm. The intense line of the NdYag laser source is adjusted by a dedicated Fiber optic collimation system.

A long working distance microscope, objective 20X, ensures high fluorescence collection efficiency and good quality sample image. The fluorescence signal is sent through a dedicated optical fiber system to a compact spectrometer.

The side of the microscope has an optical entrance which allows, using the same microscope objective, to enlighten the sample for the visual observation. The light is carried to the microscope through a fiber bundle from an external LED source.

Through a Digital camera linked to computer monitor it is possible to see the gasket and the ruby crystal and it is possible to adjust the optic system over the ruby crystal by a X-Y-Z micropositioning system.

A typical spectrum of a ruby chip is presented in figure 9. The ruby is immersed in an argon crystal at room temperature and at a pressure of 40 GPa. The fact that the R1 and R2 lines are resolved reveals that the environment is quasi-hydrostatic.

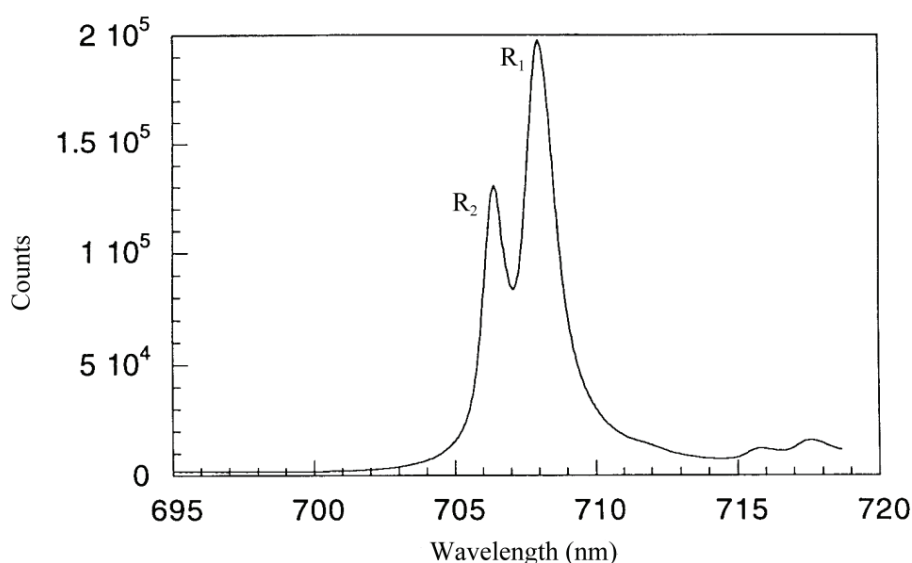


Figure 9. Fluorescence spectrum of the ruby immersed in argon at 40.2 GPa and 298 K.

The wavelength of the R1 line depends also on temperature. A correction value independent from pressure is usually assumed, so that the wavelength of the R1 line at given pressure and temperature results:

$$\lambda_{R_1}(P, T) = \lambda_{R_1}(P, T_0) + \Delta\lambda_{R_1}(T)$$

where T_0 is the reference temperature, 298 K. The temperature shift has been measured at 1 atm and fitted with a cubic law. The result is:

$$\Delta\lambda_{R_1}(T) = C_1 \cdot (T - T_0) + C_2 \cdot (T - T_0)^2 + C_3 \cdot (T - T_0)^3$$

where $C_1=0.0696$ nm/K, $C_2=7.6771(10^{-6})$ nm/K² and $C_3=-1.697(10^{-8})$ nm/K³. At the end, the quasi-hydrostatic calibration with temperature correction of the R1 line shift results:

$$P(\lambda_{R_1}) = \frac{1904(\text{GPa})}{7.665} \cdot \left(\left(\frac{\lambda_{R_1}(P, T) - \Delta\lambda_{R_1}(T)}{\lambda_{R_1}(0, T_0)} \right)^{7.665} - 1 \right)$$

The precision of pressure measurement - with respect to the ruby scale - can be as good as 0.01 GPa. However, pressure gradients in a sample are frequently higher, depending on the features of the sample. To mention an example, compressed helium is much more hydrostatic than nitrogen.

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