Chapter 2

Experimental set up used for High Pressure and Low Temperature Raman Scattering Measurements
2.1 Raman Spectroscopy

2.1.1 Introduction

Raman spectroscopy records the highly specific vibrational fingerprint of a material by analysing inelastically scattered light. Raman spectroscopy is based on the Raman effect, which was named after the Indian physicist Chandrasekhara Venkata Raman, who found in 1928 “A new type of secondary radiation” [1]. Independently, the same observation was reported by Landside and Mandelbaum [2]. With the development of intense single mode lasers as powerful monochromatic light sources, the Raman effect became widely popular in science and engineering [3]. The non-destructive nature of the probe, flexibility in sampling arrangements, and a technical revolution in multi-channel detection and Rayleigh filters have opened up many new areas where Raman measurements have proven to be very informative [4].

2.1.2 The Raman Effect

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman effect.

The Raman effect is based on molecular deformations in electric field (E) determined by molecular polarizability (\( \alpha \)). The laser beam can be considered as an oscillating electromagnetic wave with electrical vector E. Upon interaction with the sample it induces electric dipole moment \( P = \alpha E \) which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency \( \nu_m \).

After interacting with a molecule, the scattered photons of light can either be of higher or lower energy than the incident photons, as previously mentioned. This, between the Raman line and the Rayleigh line difference in frequency (\( \Delta \nu \)) will correspond to
fundamental vibrational frequencies that are intrinsic to the scattering molecule. It is important to note that molecular vibrations can be of several different types including stretching, bending, torsion, and deformation. Although stretching molecular vibrations will produce stronger peaks than bending molecular vibrations, bending molecular vibrations are very useful in differentiating similar types of bonds. It is the correspondence between molecular vibrational frequency and the shift in incident light frequency that allows Raman spectroscopy the ability to gain specific molecular level insight of a sample.

For a spectroscopic application of the Raman effect, the incident light has to be monochromatic. More than 99% of scattered light still has the same wavelength after scattering, and only a small amount of photons ($10^{-6}\%$) are spectrally shifted with respect to the incident ones due to inelastic scattering. The Raman shift is given in (relative) wavenumbers with respect to the excitation. Despite blocking the unshifted photons, the spectra always show a peak representing the Rayleigh scattering together with the Raman shifted photons. For Raman-scattered photons, the matter is excited into a virtual intermediate state and then relaxes to a vibrational state above the ground state. The photon transfers a certain amount of energy to the material, losing energy (Stokes shift). If the matter is already in a vibrationally excited state, inelastically scattered photons may also gain energy. The incident photon excites the material to a virtual intermediate state, which then can relax to its ground state. The scattered photon gains the energy difference, having a higher energy than before the scattering event (anti-Stokes shift). These three Raman scattering processes can be understood in a classical picture as a collision between the incident photon with matter. The Jablonski energy diagram in Figure 2.1 shows the processes caused by incident photons. As in absorption spectroscopy (IR spectroscopy), the photon is absorbed and the system is excited to a higher state (Figure 2.1(a)). If there is no state available that can be populated by the system, scattering occurs. Three important scattering processes include [5–8]:

1. elastic scattering without energy transfer (Rayleigh scattering, 0.01%, Figure 2.1(b)), the scattered photon has the same energy as before ($\hbar\omega = \hbar\omega_R$);
2. inelastic scattering with energy loss (Stokes shift, $10^{-6}\%$, Figure 2.1(c)),
the scattered photon loses energy ($i > s$); and
3. inelastic scattering with energy gain (anti-Stokes shift, $10^{-6}\%$, figure 2.1(d)),
the scattered photon gains energy ($i < as$).

![Jablonski energy diagram of the scattering processes of light with Rayleigh scattering and Raman scattering (Stokes and anti-Stokes shifts). For comparison, an IR spectroscopy scattering scheme is shown on the left.](image)

Figure 2.1: Jablonski energy diagram of the scattering processes of light with Rayleigh scattering and Raman scattering (Stokes and anti-Stokes shifts). For comparison, an IR spectroscopy scattering scheme is shown on the left.

Thus, Raman spectroscopy measures the energy that is transferred due to inelastic scattering. The energy transfer between both collision partners is equal to the difference between the two involved energy levels, $j$. With the energy $j$ transferred during the scattering process and the energy $i$ before scattering, the scattered photon will have the energy

$$s/as = i \pm j \quad (2.1)$$

The plus and minus in equation (2.1) stand for the energy gain (anti-Stokes shift) or energy loss (Stokes) of the photon. The Stokes and anti-Stokes shifts are symmetric, determined by the difference of energy between the ground state and the vibrational state.
For scattering on molecules, the electric field of the photon affects the molecule's electrons, resulting in molecular distortion. The distorted molecule acquires a contribution to its dipole moment $\mu$ (even if initially non-polar):

$$\mu = \alpha E$$  \hspace{1cm} (2.2)

where $\alpha$ is a proportional constant of molecule's polarisability. The polarisability corresponds to the ease with which the electron cloud around a molecule can be distorted. The induced dipole can emit or scatter light at the optical frequency of the incident light wave. Vibrational Raman scattering occurs because a molecular vibration can change the polarisability. The change is described by the polarisability derivative, $\frac{\partial \alpha}{\partial Q}$, where $Q$ is the normal coordinate of the vibration. The polarisability is typically different if the field is applied parallel or perpendicular to the molecular axis or in different directions relative to the molecule. Nevertheless, for a small electric field, the polarisability is the same for the field oriented in opposite directions along the same axis ($\mu(-E) = -\mu(E)$).

Thus, the distortion induced in a molecule by an applied electric field depends on the relative orientation and returns to its initial value after a rotation of $180^\circ$. The selection rules for Raman-active vibrations are linked to molecular symmetry and identify vibrations that change a molecule's polarisability. For scattering on anisotropic crystals, with the propagating phonons dependent on the crystal axis, a similar dependence to the orientation of the light to the crystal axis is distinguishable. Raman peaks were observable within the spectra, depending on the scattering geometry. The features of one phonon contributing to Raman scattering, incipient next to the Rayleigh peak, were followed by higher order scattered peaks in the spectra, involving multiple phonons (in the second-ordered peaks, two phonons participate). The peak intensity decreases with increasing number of participating phonons. The population of present elementary oscillations gives the efficiency of the anti-Stokes process, proportional to the Boltzmann distribution. The stronger of the two processes is by far Stokes scattering because the population state is dominated by its vibrational state at room temperature. Most Raman techniques investigate the Stokes photons only, while ignoring the anti-Stokes photons [9–13].
2.1.3 Experimental set up

A Raman system typically consists of four major components:
1. Excitation source (Laser).
2. Sample illumination system and light collection optics.
3. Wavelength selector (Filter or Spectrophotometer).
4. Detector (Photodiode array, CCD or PMT).

The sources used in modern Raman spectroscopy are nearly always lasers because their high intensity is necessary to produce Raman scattering of sufficient intensity to be measured with a reasonable signal to-noise ratio. Five of the most common lasers along with their wavelength (nm) used for Raman spectroscopy are: Argon ion (488 or 514.5 nm), Krypton ion (530.9 or 647.1 nm), Helium / Neon (632.8 nm), Diode laser (782 or 830 nm) and Nd:YAG (1064 nm).

Since spontaneous Raman scattering is very weak the main difficulty of Raman spectroscopy is separating it from the intense Rayleigh scattering. More precisely, the
major problem here is not the Rayleigh scattering itself, but the fact that the intensity of stray light from the Rayleigh scattering may greatly exceed the intensity of the useful Raman signal in the close proximity to the laser wavelength. In many cases the problem is resolved by simply cutting off the spectral range close to the laser line where the stray light has the most prominent effect. People use commercially available interference (notch) filters which cut-off spectral range of $\pm 80–120 \text{ cm}^{-1}$ from the laser line. This method is efficient in stray light elimination but it does not allow detection of low-frequency Raman modes in the range below 100 cm$^{-1}$. Stray light is generated in the spectrometer mainly upon light dispersion on gratings and strongly depends on grating quality. Raman spectrometers typically use holographic gratings which normally have much less manufacturing defects in their structure then the ruled once. Stray light produced by holographic gratings is about an order of magnitude less intense then from ruled gratings of the same groove density. Using multiple dispersion stages is another way of stray light reduction. Double and triple spectrometers allow taking Raman spectra without use of notch filters. In such systems Raman-active modes with frequencies as low as 3–5 cm$^{-1}$ can be efficiently detected.

![Figure 2.3 Experimental setup of the Raman experiment](image-url)
Figure 2.3 shows the experimental setup of the Raman experiment. Two mirrors guide the light to a notch filter. Since the Raman light is orders of magnitude weaker than the elastically reflected laser light, a notch filter is used to cut off the laser line. A dielectric coating reflects the light of only this particular wavelength. Therefore, the notch filter can also be used as a mirror for this wavelength. It reflects the light towards a microscope objective. The objective focuses the light onto the sample. Therefore, this experimental setup is called a micro-Raman setup. The scattered light is collected by the objective and hits the notch filter at the same position as the incident beam if the setup is calibrated correctly. The notch filter then cuts off the laser light and only the inelastically scattered part hits the fiber behind the notch filter. The fiber guides the light into the spectrometer. The spectrometer consists of a fixed grating and a detector. The grating disperses the light onto the detector. Due to this process the spectral distribution of the light is converted into a spatial distribution and can be recorded by the detector. The data analysis is done by a computer program.

The equipment used to acquire Raman signal data has evolved over the past decades to accommodate the growing applications of Raman spectroscopy. Raman systems are designed with the necessary equipment to obtain fast, high signal to noise ratio (SNR) spectra, with high accuracy and efficiency. A typical micro-Raman system consists of a microscope and stage, excitation laser, filters, slit, diffraction grating, necessary optics, detector, and post-processing software [14, 15].
Specification of Micro Raman system from Jobin Yvon Horibra LABRAM-HR (as shown in figure 2.2)

- Raman spectra can be recorded from 50 cm\(^{-1}\) to 4000 cm\(^{-1}\) of Raman shift.

- Excitation Laser Sources - He-Ne 632.8 nm and Argon 488 nm

- Optics: high stability confocal Microscope for Micro Raman 10x, 50x, 100x objective lens. The laser can be focused on to a spot from ~1micron to 5 micron by choosing suitable objective lens.

- Polarization analysis of samples can be carried out.

- Automated XY sample stage for Raman mapping. Sample can be scanned with an accuracy of 1 micron in lateral direction i.e. Raman imaging of smooth surfaces is possible.

- A lateral resolution of 1 micron and an axial resolution of 2 micron can be achieved with confocal optics

- A white light with a video camera for viewing sample. Sample can be viewed optically using microscope and Raman spectra can be recorded on any desired portion of sample.

- Dispersive geometry

- 600 and 1800 lines/mm gratings - Detector : CCD detector

- Spectral Resolution of the order of 1 cm\(^{-1}\)

- Low temperature measurements up to 10 K
2.2 Low Temperature Raman Spectroscopy

For variable temperature measurements there is a Linkam THMS 600 heating and cooling microscope stage, which allows for the micro-Raman measurements to be performed within the 77 to 900 K temperature range as shown in figure 2.4.

![Figure 2.4 LINKAM THMS600 - System attached with Raman spectrometer](image)

Figure 2.4 (a) is the THMS600 one of the most popular heating and freezing stages used in many applications where high heating/freezing rates and 0.1°C accuracy and stability are needed. The LINKAM THMS600 heating/cooling stage is equipped with a CI94 temperature controller and a LNP94 Liquid Nitrogen Pump as shown in figure 2.5 (b) and (c) respectively.

Samples loaded onto a 0.17 mm thick cover slip are placed on a highly polished pure silver heating element to ensure excellent heat transfer and extremely sensitive temperature measurement. A platinum resistor sensor, accurate to 0.01°C provides far more accurate and stable temperature signal that can be achieved with a thermocouple. Sample position can be precisely controlled 15 mm in XY directions via the precision
ground gas sealed manipulators. Samples can be quickly characterized by heating to within a few degrees of the required temperature at a rate of up to 100°C/m in with no overshoot, then slowed down to a few tenths of a degrees per minute to closely examine sample changes. The entire experiment can be saved as an online plot or exported to a spreadsheet application. The stage body is fitted with quick-to-fit gas ports so that sample atmosphere can be controlled by gas flow and condensation eradicated by dry nitrogen gas purge supplied by the LNP95 cooling pump.

**Figure 2.5 (a)** LINKAM THMS 600 heating/cooling stage

(b) CI94 temperature controller

(c) LNP94 Liquid Nitrogen Pump
Technical data:

- Temperature range –196° to 600°C.
- Up to 130°C/min heating.
- Temperature stability < 0.1°C.
- 16 mm X,Y sample manipulation.
- Sample area 22 mm diameter.
- 100 W platinum resistor sensor.
- Light aperture - 2.4 mm.
- Silver heating block for high thermal conductivity.
- Direct injection of the coolant into the silver block.
- Single ultra thin lid window - 0.17 mm.
- Objective lens working distance - 0.1mm to 4.5 mm.
- Water cooled stage body for high temperature work (>300°C).
- Sample side loading without removing the stage lid.
- Can be used with all microscope techniques
- Controlled heating rates of 0.01°C to 130°C/min.
- Controlled cooling rates of 0.01°C to 100°C/min.
- Displays temperature to 0.01°C
- Hold time 0 – 9999 minutes
- RS232 interface to allow programming by Linksys software.
• A cooling system consists of the 2 liter dewar and a control unit housing the pump which can be controlled by selecting one of 5 manual pump speeds.

• Recycled dry nitrogen gas is used to purge the sample chamber and upper lid window surface of condensation.

• The precise control of liquid nitrogen flow allows for specific stages controlled cooling rates as fast as $130^\circ$C/min or as slow as $0.1^\circ$C/min.

Figure 2.6 Cooling Procedure

As shown in figure 2.6, the dewar should be 2/3 filled with liquid nitrogen. The lid must be placed so that the thin capillary tube is pointing upward. The thin silicon tube carries exhaust nitrogen gas and is used to prevent the blurring of the top of the window on the stage lid [16].
2.3 High Pressure Experimental Techniques

2.3.1 Introduction

Research in the field of high pressure is very much dependent upon techniques and every advancement has resulted in a phenomenal expansion in our knowledge concerning the behavior of matter at high pressure. The Bridgman era [17–25] (roughly from 1910 to 1950) was dominated by the so called Bridgman anvil and the piston-cylinder device, both of which were invented and developed by Bridgman for electrical resistance and compressibility measurements up to ~10 GPa. In the post-Bridgman era, Drickamer and his co-workers [26–28] developed the ultra-high-pressure supported anvil devices for resistance, Mössbauer, X-ray diffraction, and optical absorption studies and pioneered ultra-high-pressure research of the solid state. They extended the pressure range above Bridgman devices and discovered many new phenomena concerning the behavior of solids at high pressure. Concurrently, improved versions of the piston-cylinder device, the belt apparatus and the multiple-anvil devices became powerful tools in the hands of the high pressure researcher for the study of phase transitions and material synthesis at high pressure and high temperature. Also, the extension of high pressure techniques to very low temperature had considerably succeeded and scores of new superconductors (materials which become superconducting at high pressure) were added to the list of superconducting elements and compounds. Thus, while a lot of new results at high pressure were accumulating, a rather quiet revolution in high pressure generation techniques had taken place in this era, resulted in the development of the diamond anvil cell (DAC). The DAC straight away became the most powerful ultra-high-pressure tool, helping physicists and chemists in search of new states of matter and study of basic physics underlying ultra-high-pressure phenomena. The DAC had put the geophysicist nearer to the center of the Earth’s pressure, because it was now possible to combine laser heating of the material in the DAC to simulate pressure and temperature conditions prevailing deep down in the Earth's interior. Today a DAC capable of generating ~100 GPa pressure can fit into the palm of the hand and a variety of sophisticated measurements can be performed on materials of microscopic dimensions. For instance, optical absorption & reflectivity measurements, Raman & Brillouin scattering studies to
several hundred kilobar have become possible. Powder and single-crystal X–ray diffraction studies are becoming routine investigations with DAC.

2.3.2 Diamond Anvil Cell

Although it has been known that diamond is the hardest material known to man and is quite transparent to X–rays and light, its value for generation and containment of high pressure was not realized until 1950, when Lawson and Tang used a drilled three-carat single-crystal diamond (in a split-bomb configuration) with a miniature piston, for performing high-pressure X–ray diffraction studies [29]. After that two different versions of the DAC conceived independently, appeared on the scene; one for high-pressure X–ray powder diffraction study by Jamieson, Lawson, and Nachtrieb at the University of Chicago [30] and the other for infrared absorption measurement by Weir et al. [31] at the National Bureau of Standards (NBS). After this original 1959 NBS version, DAC experienced several advancements in its design such as development of the DAC for powder [32] and single crystal X–ray diffraction [33], the introduction of the metal gasket technique for hydrostatic pressure generation [34], the ruby fluorescence technique [35] for pressure calibration, the evolution of the pressure scale based on the R-line shift [36, 37], introduction of new pressure transmitting media for hydrostatic pressure to 100 kbar [38], generation of pressures of half a megabar in the gasketed anvil, and many innovative changes in the mechanical design [32–38]. All these advances have turned the DAC into a fine quantitative tool for modern physical research in the field of high pressure physics.

2.3.3 Construction of DAC

Basic principle of the DAC is very simple. A sample placed between the flat parallel faces of two opposed diamond anvils (see figure 2.7) is subjected to pressure when a force pushes the two opposed anvils together.

However, variations in the DAC arise from different ways in which the force-generating and the anvil-alignment mechanisms can be designed.
Accordingly, five types of DACs have evolved till the date.

- NBS cell
- Bassett cell
- Mao-Bell cell
- Syassen-Holzapfel cell
- Merrill-Bassett cell

The DAC designed at High Pressure Laboratory of the Department of Physics, Sardar Patel University is of Merrill-Bassett miniature type cell. Figure 2.8 shows such miniature DAC in which four screws push the two platens together when tightened, carrying the diamond anvils with them. This device is extremely compact and is widely used for single-crystal X-ray diffraction studies. Main advantage of this cell is that it can be mounted on any type of head. Suitably shaped anvil seats, press-fitted into the steel platens, provide wide-angle access to the incoming and transmitted optical beam.
Diamonds for the anvil are selected from brilliant-cut gem stones. The culet is removed by grinding a flat, octagonal surface with area of ~400 µm × 400 µm. Selection of diamonds and their size depend upon the type of DAC and the nature of the investigation. For instance, diamonds with very low luminescence have to be used in DAC for optical measurements and type-II diamonds usually satisfy this criterion [39, 40]. Figure 2.9 shows the DAC used for the present investigations.
### 2.3.4 Alignment of DAC

Alignment of DAC is very important procedure because of the brittleness of diamond. Working tips of both anvils must be 100% parallel and have equal coincident diameters. Two types of misalignments are possible in any DAC. Both of them are pictured in figure 2.10.

1. Lateral misalignment
2. Angular misalignment

In order to remove the lateral misalignment, outer diameter of anvil seats are kept smaller than inner diameter of platens. Due to this anvil seats remain floating inside platens. Four screws with micrometer threading are provided in the platens (as shown in figure 2.11) to adjust the lateral positions of anvils. Therefore the coincidence between both anvils can be easily achieved by adjustment of these four screws. The most difficult is angular alignment. There are different types of alignment mechanism as shown in figure 2.12. In the present cell four screws, which are used to generate pressure themselves allow the angular alignment.

![Figure 2.10 Misalignments in DAC: (a) Lateral misalignment, (b) Angular misalignment](image)
Figure 2.11  Arrangement (Fine threaded screws) for the adjustment of lateral position of anvils in the DAC.

Figure 2.12  Angular alignment mechanisms: (a) Sphere-plane, Piermarini-Block cell, (b) Crossed cylinders, (c) Rotating wedges (d) Merrill Bassett cell alignment.

In fact all the systems allow the anvils to be aligned perfectly. Testing is also easy to carry out by using the arrangement shown in figure 2.13. Interference fringes between the opposing diamond culets are observed until they are not exactly parallel. This is achieved by tilting of the anvils. Thus the necessary accuracy of parallelism is achieved. The Comparator (Goniometer) is used for the proper alignment of diamond anvils after
applying pressure for each step during experiment. Details of the alignment procedure are well described by Jephcoat et al. [41] in 1987 and Dunstan and Spain [42] in 1989.

### 2.3.5 Gasketing

The introduction of the gasket into the DAC is a very important development in the history of the DAC that makes the DAC a quantitative tool for the high-pressure research. Functionally, the gasket reduces the magnitude of pressure gradients and confines the sample, pressure calibrate, and pressure-transmitting medium. Over and above these functions, the gasket provides an additional support to the diamond anvils, thereby enhancing their pressure-sustaining capability. Generally, hardened stainless steel is used. However, for ultra high pressure work, high speed steel or rhenium or tungsten gaskets are used. Typically, the initial thickness of the gasket is 200 to 300 µm. A thick gasket is preferred because it gives a better lateral support, although this causes a part of the load to be consumed in the plastic deformation of the gasket.

**Figure 2.13** Before indentation

Gasket thickness = 200 µm

**After indentation Gasket**

Gasket thickness = 60 µm
For better performance and improved success of a DAC experiment, the preindented gasket is used for drilling. Initially the gasket is fixed on the lower anvil and is pressed between two anvils. Therefore indentations of anvils get formed on both the sides of gasket. This reduces the deformation of the hole during compression. Generally, the gasket is preindented up to ~65 µm. After preindentation, a hole is formed by drilling at the centre of indentation. This is done with a miniature drill bits of diameter 50 to 250 µm.

The gasket, apart from providing confinement for the pressure medium, extrudes around the diamonds and acts as a supporting ring, preventing failure of the anvils due to concentration of stresses at the edge of the anvil faces.

### 2.3.6 Sample Preparation and Loading

Preparation of samples for the DAC is a specific problem because of their small dimensions. There is no universal procedure. Usually the thickness of the gasket between the anvils is ~60 µm. Therefore the sample thickness must be less than this in order to prevent it being crushed between the anvils. Thus one problem is the preparation of samples with thickness of 1–10 µm and with sizes of 5–100 µm. The best procedure is to prepare a platelet with the desired thickness and to chop it under the microscope and then select suitable pieces. Frequently a sample for the DAC is selected from small single crystals contained in polycrystalline powder. Sometimes in order to avoid preferred orientation effect, fine powder particles of ~1 µm are loaded. A ruby chip of ~5 µm thickness is mounted on the diamond. 16:3:1 methanol-ethanol-water mixture used as a pressure transmitting medium. Handling of samples is a delicate procedure; however, samples of dimensions ~50–100 µm are easily handled with the help of sharply ground needles. It is better to use a tungsten needle (drill bits) with a tip of dimension ~1 µm. A sharp needle made up of a small tungsten carbide (WC) drill is also good. The samples stick to it well and are easily transferred to the anvil facet.
2.3.7 Generation and Measurement of Pressure

Generation of pressure in the loaded miniature DAC is easy. After getting the parallelness anvils were pressed against each other by tightening four screws in same manner. The pressure applied in this way was measured by the ruby fluorescence technique. Ruby has strong luminescence doublet of peaks R\textsubscript{1} and R\textsubscript{2} at 694.2 nm and 692.8 nm respectively [43].

Using well established freezing points of several liquids and some solid-solid transitions as fixed points, Forman et al. [44] first showed that the R lines of Cr\textsuperscript{3+} doped Al\textsubscript{2}O\textsubscript{3} (ruby lines) shift linearly with hydrostatic pressure in the range of 1–22 kbar, and that the R lines broaden if the ruby experiences nonhydrostatic stresses. Further work by Barnett, Block, and Piermarini [45] has made the ruby fluorescence technique a very rapid and convenient method for the measurement of pressure. Mao et al. [46-48] calibrated ruby against Cu as a standard quasi hydrostatic conditions in the argon medium and W in neon medium up to 110 GPa. Both calibrations showed that the ruby R line shifts with pressure obeying the equation (2.3) given below [43].

\[
P = \frac{A}{B} \left[ \left( \frac{\Delta \lambda}{\lambda_0} \right)^B - 1 \right] \quad \text{(GPa)}
\]  

(2.3)

where \( P \) is in GPa, \( \lambda_0 = 694.24 \text{ nm is the zero-pressure value at 298 K} \) (\( R_2 \) is at 692.81 nm) and \( \Delta \lambda \) is the ruby \( R_1 \) line shift in nm as shown in figure 2.14. Parameter \( A = 1904 \) and \( B = 7.665 \) for quasihydrostatic condition and \( B = 5 \) for non-hydrostatic condition.

Figure 2.14. Ruby R\textsubscript{1}-line shifting at high pressure
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