EXPERIMENTAL INVESTIGATION OF
MOLECULAR SOLIDS AND VANADIUM AT HIGH
PRESSURE AND TEMPERATURE

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Abstract

Understanding high pressure effects on simple molecular system is of great interest for condensed matter science and geophysics. Accessing the static pressure and temperature regions found in planetary interiors is made possible by the development of the Diamond Anvil Cell technique. We developed a double sided resistive heating method for the membrane DAC operating in low pressure (<0.5 mTorr) pressure environment requiring only 175 W input power to reach sample temperatures up to 1300 K. We applied this technique successfully to study molecular solids at high temperatures, such as H$_2$, N$_2$ and CO$_2$. We made an attempt to determine the melting line of hydrogen and present data up to 26 GPa in agreement with literature. Raman spectroscopy of Nitrogen indicates a high stability of the ε molecular phase, while θ phase is only accessible via certain P, T paths. Studies of solid CO$_2$ at high pressure and temperature lead to the discovery of a six-fold coordinated stishovite-like phase VI, obtained by isothermal compression of associated CO$_2$-II above 50 GPa at 530-650 K, or by isobaric heating of CO$_2$-III above 55 GPa. From our X-ray diffraction experiment on isothermally compressed H$_2$O we report a coexistence of ice VII and symmetric ice X from the start of the transition pressure 40GPa to just below 100 GPa and a volume change of 4% across the transition.

Vanadium, a transition metal undergoes a phase transition upon compression unlike other elements (Nb, Ta) from its group. We confirm the bcc phase transition to rhombohedral structure at 62 GPa under quasi hydrostatic compression in Ne pressure medium. Compression without pressure medium results in a much lower 30 GPa transition pressure at room temperature and 37 GPa at 425 K, pointing to a positive phase line between the bcc and rhombohedral crystalline phases.
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Publications

**Paper I:**
*High Temperature Experiments using a Resistively Heated Membrane driven Diamond Anvil Cell*
Zsolt Jenei, Ken Visbeck, Hyunchae Cynn, Choong-Shik Yoo, William Evans

**Paper II.**
*Six-fold coordinated carbon dioxide VI*
Valentin Iota, Choong-Shik Yoo, Jae-Hyun Klepeis, Zsolt Jenei, William Evans, Hyunchae Cynn

**Paper III.**
*Phase diagram of nitrogen: in situ Raman spectroscopy investigation*
Zsolt Jenei, Choong-Shik Yoo and William Evans
To be submitted to *Journal of Applied Physics* (2009)

**Paper IV.**
*High-Pressure/temperature Structural Phase Transition in Vanadium: Influence of Non-Hydrostatic Conditions*
Publications and positron annihilation spectroscopy work not discussed in the first part of this thesis:

My research on defect studies in low-k materials and semiconductors was used in my Licentiate of Philosophy thesis with the title: *Positron Annihilation Spectroscopy Analysis of Fluorine implanted silicon and porous low-k dielectrics.* (2004)

**Paper V.**

*Observation of fluorine vacancy complexes in silicon*
P.J. Simpson, Zsolt Jenei, P. Asoka-Kumar, R.R. Robinson and M. E. Law  

**Paper VI.**

*Role of intericosahedral chains on the hardness of sputtered boron carbide films*

**Paper VII.**

*Positron annihilation spectroscopy of sputtered boron carbide films*
L.G. Jacobsohn, M. Nastasi, L.L. Daemen, Zsolt Jenei, P. Asoka–Kumar  
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I. Introduction

High pressure physics is concerned with the effects of high pressure on properties of matter. Pressure is one of the thermodynamic variables with the widest range of variation in nature, from the near zero (~$10^{-35}$ Pa) intergalactic pressure to the over $10^{35}$ Pa in the center of a neutron star. In the laboratory only a small portion of this vast pressure range is accessible, from ultra high vacuum of ~$10^{-13}$ Pa to ~$10^{13}$ Pa in laser shocked experiments. In this study we explore the behavior of molecular solids and vanadium metal from ambient pressure to ~$10^{11}$ Pa region, pressures existent in planetary interiors or high energy explosions.

Along with temperature, pressure is the thermodynamic variable that experimentally is varied to study the response of the system in changing thermodynamic conditions. In the early days, due to the lack of high pressure generating tools, studies were mainly focused on the gas phases. With the development of high pressure generating devices high compression ratios for liquids and solids can be achieved, exceeding the effects that can be realized by temperature variation. In molecular materials for example volume compression in excess of an order of magnitude can be achieved compared to the volume at ambient pressure, corresponding to pressures of a few million times the normal atmospheric pressure (~400 GPa in diamond anvil cell). The pressure-volume (work) energy associated with this degree of compression can be as high as 10 eV or higher, exceeding even the strongest molecular binding energies. For comparison, one of the strongest molecular bonds in the diatomic nitrogen is 4.94 eV/atom (1). This large change in the free energy increases the kinetic energy of the electrons participating in the molecular bond, thus weakening it. Because of pressure induced changes in the chemical affinities, the reactivity of otherwise familiar elements are altered and entirely new class of materials can be formed. These phenomena have been extensively studied on molecular solids formed by elements with relatively low atomic number, such as N$_2$, O$_2$, H$_2$O, CO$_2$, and CH$_4$, simple homo-nuclear and hetero-nuclear molecules that are believed to be major constituents of giant planets and end products of many energetic processes in explosions. At low pressures and temperatures these molecules – low-Z molecules in general – form crystalline solid phases. Due to the rapid change in the intermolecular interaction with pressure and temperature many of these
phases have limited stability regions and some of them are metastable, kinetic phases, accessible only through certain P-T paths (2). This domain has been explored for many molecular solids in more or less detail, and phase diagrams or kinetic transformation diagrams have been published. Due to the metastable nature of some of these molecular phases, and different experimental conditions or different theoretical models used there are disagreements between different reports (see e.g. ref. (3) and (2)). Increasing the pressure and temperature the molecular bonds begin to weaken and the

![Figure I.1. General transitional phase diagram of low-Z molecular solids from ref (4)](image)

strength of the intermolecular interaction becomes comparable to the intra-molecular interaction. Under these conditions intermediate bonding states form, giving birth to a number of stable or metastable polymeric phases (ex: phases II, III, and IV in CO₂ (5)) At ultrahigh pressures and temperatures the molecular bonds are totally destroyed and a metallic or semiconducting atomic solid is expected to form. This general trend in the behavior of molecular solids as a function of pressure is presented in Figure I.1, and a specific case of the CO₂ phase diagram is shown in figure I.2, a phase diagrams of H₂, N₂, and H₂O are presented later in this study. As we can see CO₂ closely obeys the general rule in transitions with increasing pressure. More systematic behavior can be observed among isovalent molecules (example: CO₂ and SiO₂ (5)).
In this study we explore the p-T regions of simple molecular solids corresponding to phases I and II from figure I.1. To access these pressure regions we use diamond anvil cells designed at Lawrence Livermore National Laboratory and we apply external resistive heating technique to achieve temperatures up to 1200 K.

In the following chapter we present the experimental tools and techniques used in this study, beginning with the pressure generating device, sample loading devices and techniques. Followed by diagnostic tools adapted to diamond anvil cells, such as synchrotron x-ray diffraction, table top micro-Raman spectroscopy and conclude the chapter with the very important pressure calibration techniques – optical and x-ray methods.

![Figure I.2 Carbon dioxide phase diagram showing high pressure extended solid phases (similar to SiO₂) from ref (5)](image)

In Chapter III we describe a resistive heating technique for a diamond anvil cell developed as part of this study and applied to membrane driven diamond anvil cells. The technique consists of double sided heating in low pressure (0.5 mtorr) environment to prevent oxidation and unwanted heat loss. We describe the parameters of the setup and present p, T domain accessed by experiments with molecular solids (hydrogen, nitrogen and carbon dioxide)
Chapter IV is dedicated to the study of molecular solids at high pressures and temperatures. In this chapter we first look at the melting curve of hydrogen and present our experimental results obtained up to 26 GPa. Later, the changes in molecular bonding with increasing pressures are explored up to regimes in which the inter-molecular interaction strength becomes comparable to the intra-molecular bonding in nitrogen and carbon dioxide. We explore in some detail the phase diagram of nitrogen in the molecular region – with in-situ micro Raman spectroscopy – where we’ll present different p-T paths along which some molecular phases are accessible. We conclude this chapter by presenting our study on H$_2$O to a transition to the symmetric ice phase by compressing it at room temperature to 180 GPa.

In the last chapter (V) of this thesis we discuss the phase transitions in vanadium metal as it is detected by synchrotron x-ray diffraction when compressed from ambient pressure up to near 100 GPa. The transition pressure from the ambient bcc crystal structure to the rhombohedral phase shows dependence on the hydrostaticity of the pressure transmitting medium. A phase transition occurs as low as 30 GPa in samples compressed without pressure medium and at 62 GPa when compressed in Ne. Higher temperature compressions indicate a positive bcc/rhombohedral phase line in vanadium.
II. Experimental methods

II.1 Pressure generating devices

The most important among the experimental devices used in this study are those of generating the high pressure in the sample. Developments of new high pressure generating equipment in the history of the field always resulted in spectacular expansion of the knowledge base about material behavior under these conditions. Research in the first half of the 20th century was dominated by experiments limited to pressures up to 10 GPa reachable with the Bridgman anvil and piston cylinder devices (6) developed by Bridgman for electrical and compressibility measurements.

Diamonds were first used to generate high pressures in 1950 by Lawson and Tang (7) for X-ray diffraction studies and the first diamond anvil cell (DAC) was made by Weir et al. (8) for performing infrared spectroscopic measurements. Since then the DAC has remained the dominant device for exerting ultra-high static pressure. This pressure generating device has several advantages compared to the previously used ones: diamond is the strongest material available allowing achievement of the highest static pressures, at the same time its electronic properties makes it an ideal material for various optical spectroscopy and X-ray diffraction and spectroscopy experiments. Diamond is transparent (transmission curve shown in Figure II.1) from the UV (225 nm) to the far infrared. Only minor absorption bands exist resulting from two phonon absorption between 2.5 and 6.5 µm. Furthermore, its large bandgap (5.45 eV) prevents thermally generated charge carriers at elevated temperatures. Therefore diamond remains transparent even at very high temperatures. Beside these properties also its extreme thermal conductivity, wear and chemical resistance are of importance for various material studies.
The principle of the DAC apparatus is simple and in its essence has not changed since its invention. It uses a pair of brilliant or anvil cut diamonds facing each other symmetrically with the sample loaded in the sample chamber between their parallel tips as seen of figure II.2. Pressure in the chamber is generated by pushing the 2 anvils together. Chamber is delimited by the flat surfaces of diamonds and a – usually – metal gasket.

Figure II.1 Diamond transmission curve in red source: http://www.diamond-materials.de/bilder/transmission_en.jpg

Figure II.2 Diamond anvil configuration with a metal gasket for sample chamber ref. (9)
Based on the above mentioned simple principle different types of cells were developed and used. The main difference between them arises from the anvil alignment and force generating mechanism. The popularity of the DAC increased due to the many advantages compared to previous techniques, so by the mid 1980s there were about 6 generic types of DACs, some of which are in use even today along with newer designs. In this paper we present in some detail only the cell we used in our experiments.

Figure II.3 Diamond anvil tips: flat on the left, beveled on the right (9)

Diamonds used in the cells generating the pressure are selected from gem quality natural diamonds with low fluorescence – important for spectroscopic studies. The stones are brilliant cut and their size varies from 0.16 to 0.5 karats. Since the pressure applied to the sample is directly related to the force applied to the back of the diamond anvil and inversely related to the area of the diamond tip the achievable pressure in the sample chamber is inversely related to the size of the diamond tip. Issues arise when at ultra-high pressure the stress concentration at the edges of the culet becomes too high and the diamond breaks. In 1978 Mao and Bell (10) were the first to report successful achievement of 170GPa with the beveled geometry. Finite element stress analysis by Bruno and Dunn in 1984 (11) determined that the optimum beveled angle to achieve minimum stress is around 15°. Sketches of flat and beveled diamond tips are presented in Figure II.3. Sizes of the diamond tips vary depending on the targeted pressure interval. For relatively low pressure experiments diamonds with larger culets are used permitting higher amount of sample and finer control over the pressure. Typically a 300 μm flat culet will generate
a pressure of about 80 GPa, while a 200 µm culet can be used to generate pressure up to 100 GPa at room temperature. To achieve higher pressures beveled diamonds are used. The most common sizes for beveled diamonds range from 25 µm to 100 µm for the central flats on a 300µm (500µm in some cases) culet. With these diamonds pressures around 300 GPa can be achieved. The maximum pressure achievable depends on individual diamond anvil quality, alignment precision, sample properties relative to diamond and other factors.

Another very important component in the DAC assembly is the gasket that serves as a sample chamber. From historical point of view the introduction of the gasket made the DAC a quantitative tool permitting the use of pressure media allowing quasi-hydrostatic studies. The gasket is prepared by compressing a metal foil between the diamonds and drilling a hole in the center of the indentation created by the diamonds. Usually the sample chamber diameter is about 40-50% of the flat size. The most common gasket material in DAC is rhenium metal, it has the advantage of having a high yield strength and ductility allowing a plastic deformation during indentation and maintaining a reasonable thickness to high pressures. For most of the high temperature experiments presented in this work we used a W-Re alloy gasket that has advantage of maintaining its strength better than Re when heated to high temperatures than the pure rhenium metal gasket.

![Figure II.4 Membrane driven diamond anvil cell (mDAC) designed at LLNL](image-url)
As mentioned earlier many different types of DAC were developed since the first DAC.
The membrane DAC (mDAC) has its roots in the Mao-Bell piston cylinder cell, but it evolved through different development stages. The cells are made of hardened steel heat treated at 1100 C and consist of a piston cylinder assembly. Diamonds are mounted on tungsten carbide seats and held in place by 3 set-screws allowing excellent stability and easy alignment. A sketch of the membrane cell is presented in Figure II.4. The tight fit of the piston inside the cylinder provides the mechanical stability during compression, when the two parts are pressed against each other by the membrane. The membrane is placed inside a cap which is screwed onto the cylinder part of the cell, and by pressurizing the membrane with controlled amount of inert gas expands and the expanding membrane pushes the piston inside the cylinder with increased force. The use of a membrane has the advantage that the applied force is evenly distributed on the back of the piston, gives precise and systematic control over the pressure and allows remote operation. This is a major advantage not only for regular synchrotron experiments where the cell has to be enclosed inside a hutch while exposed to x-rays, but also for high temperature experiments. Advantages of this DAC in high temperature experiments will be discussed in more detail in the following chapter.
II.2 Sample preparation

The majority of materials covered in this study under ambient conditions are gases like Nitrogen, Hydrogen, Carbon Dioxide, others such as water is found in liquid form and finally Vanadium in crystalline form. Each of them is loaded differently, the gases that have a high enough boiling temperature are loaded cryogenically, in our specific case we used this method for loading CO\textsubscript{2} and N\textsubscript{2} (as well as when used as Ar as the pressure medium for one of the Vanadium experiments). The cryogenic loading consists in cooling the gas below the boiling temperature where the gas liquefies and fills the sample chamber. We use a specially manufactured chamber to match the size of our mDAC minimizing the dead volume that needs to be filled by liquefying the sample gas. The cell with the prepared gasket is inserted in the chamber, and then the cells closing screws are connected to the outside through Teflon sealed extensions. After purging the bomb the sample gas is kept at a constant 50-90 psi pressure while the bomb is being immersed in liquid nitrogen or argon for cooling purposes. The temperature is monitored by a thermocouple mounted at the sample level. The cryo-loading bomb is shown in Figure II.5.

Figure II.5 Cryogenic gas loader, LLNL design
Gases with much lower boiling point were loaded with a 30000 psi high pressure loader system. The gas from the supply cylinder is manually compressed over several cycles to 25-30000 psi and then captured in the sample chamber. We used this setup for our H₂ samples and for loading He and Ne pressure medium for the vanadium studies. See high pressure loader in Figure II.6
II.3 Diagnostic tools

As noted at the beginning of this chapter the choice of diamond as anvils has many advantages among them the possibility to use many diagnostic techniques for in situ sample characterization. Among the available optical spectroscopy techniques and synchrotron x-ray base techniques, in the following techniques used in experiments discussed in this thesis will be presented in some detail.

**Synchrotron based techniques:**¹

In very simple terms synchrotron techniques use the photons emitted by a charged particle as it is kept on curved trajectory by an acceleration perpendicular to its trajectory. Modern, ³rd generation synchrotrons were specifically built to be a source of various energy photons which can be used in material characterization. Electrons are accelerated in several stages to achieve relativistic energies in the GeV range. We performed our x-ray diffraction experiments at the Advanced Photon Source at Argonne national Laboratory. The electron energies cited here are characteristics of this synchrotron. In the first stage electrons from a hot cathode are accelerated in a linear accelerator by high voltage alternating fields to ~450 MeV. At this energy the electron is already traveling with relativistic speed and it is injected into the booster synchrotron where it gets accelerated to 7 GeV by radio frequency cavities, the orbital path is maintained by bending and focusing magnets that increase the field strength in synchronization with the accelerating radio frequency fields. The 7 GeV electrons then are injected into an 1104 m circumference storage ring consisting of several straight sections and bending magnets. In the straight sections of the ring insertion devices are producing high flux and brilliance x-ray beams. Insertion devices are periodic magnetic structures with specially calculated repetition of N and S poles that force the electrons in a sinusoidal path. The relativistic electrons moving through the periodic magnetic field experience transverse acceleration emitting radiation which is superimposed resulting in a much more intense x-ray beam than in case of a

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single bending magnet. There are 2 types of insertion devices; the wiggler which produces a wider range of energies and the undulator which has a much higher brilliance, meaning more photons per second in a narrow energy bandwidth per unit solid angle. The high intensity x-ray beam is transported in vacuum to the experimental station through a series of x-ray optics to obtain a highly collimated monochromatic beam for diffraction.

Since most of our powder diffraction experiments were done at 16IDB beam line of APS a schematic diagram of this sector's optical train is presented in Figure II.7. For x-ray diffraction first the x-ray beam is cut down by a pair of slits and then passed through a double diamond branching monochromator which splits the beam into a white beam and a parallel monochromatic beam. For x-ray diffraction, a Si (220) single crystal monochromator further monochromates the beam and a pair of Kirkpatrick-Baez (KB) mirrors focus the 500x500 μm monochromatic beam down to a less than 10x10 μm spot size at the sample. A pinhole just upstream from the sample cuts down tails on the x-ray beam which may contribute to unwanted

II.7. APS Sector 16 insertion device beamline optical train
scattering from the gasket. DAC experiments require hard x-rays with energies higher than 10 keV to penetrate through the diamonds.

X-ray diffraction (XRD) is an experimental technique used to explore the crystal structure of the material. The technique is based on the elastic scattering of x-rays from the electrons and it works only for wavelengths comparable to the size of the inter-atomic distances. W. L. Bragg in 1913 using a simple model found that constructive interference of the waves scattered from atoms from different planes occur when the following relation is satisfied:

\[ 2d \sin \theta = n\lambda \]  

(Equation II-1)

where \( d \) is the distance between reflecting planes, \( \theta \) is the angle of incidence and \( \lambda \) is the wavelength of the incident x-ray beam. (Equation II-1) is the original form of the Bragg law. Knowing the incident x-ray wavelength and the diffraction angle we can calculate the distance between the scattering planes, therefore the lattice parameters can be determined.

XRD performed on a powder sample in which the tiny crystallites are homogeneously oriented in every direction the diffraction results in concentric Debye-Sherrer rings. In Figure II.8 a typical diffraction pattern is shown for a body centered cubic structure, collected from a sample in a DAC with tungsten-carbide seat with a narrow slit. The diffraction peaks are visible at angle 2\( \theta \). The collected 2D images are processed with Fit2D, the result of the integration is a one dimensional intensity represented as a function of the 2\( \theta \) angle. The integrated patterns were analyzed by using XRDA (12) software.

Experimentally in the Angular Dispersive X ray Diffraction (ADXD) a monochromatic x-ray beam is used as the source that traverses the sample and the diffracted x-ray beams are
collected on an image plate or charge coupled device. Both the CCD and the image plate have their advantages: the CCD allows very fast readout in the detriment of the resolution, while the image plate has much higher resolution but the readout is very slow. At Sector 16 at APS where the x-ray diffraction data presented in this thesis were collected we had the choice of both CCD (MAR165) and image plate (MAR345). The experimental setup with the sample stage, detectors and the incoming x-ray collimator pinhole is shown in Figure II.9.

Figure II.9 Experimental setup at 16IDB at APS
Optical Spectroscopy

In our investigations we used Raman spectroscopy as our primary optical tool to detect the effect of pressure and high temperature on studied samples, it is based on the interaction between the incident photon and the vibrational, rotational and other low frequency modes in a periodic solid. The Raman spectroscopy is based on the inelastic scattering of a monochromatic beam on molecules or atoms in a crystal. When a sample is irradiated with a beam in the ultraviolet (UV)-visible region the scattered light consists of 1) a very high intensity (close to the incident beam intensity) elastically scattered beam with the same wavelength as the incoming radiation and 2) a small fraction (~$10^{-5}$) of the incident intensity that suffers inelastic scattering – Raman scattering. In Raman spectroscopy the shifts in the inelastically scattered photons wavelength is measured. During inelastic scattering the incident photon excites the molecule from the ground state to a virtual energy state, which is lower than the first unoccupied electronic excited states energy. The excitation is followed by relaxation to one of the vibrational energy levels through an emission of a photon that has lower energy than the incoming radiation. This is the Stokes Raman process. When the inelastic scattering occurs on a molecule already in one of the vibrational excited states and during relaxation from the virtual excited state the molecule goes into the ground state the emitted photons energy is higher that the incoming energy, this is the Anti Stokes Raman. A schematic diagram of the Raman process is shown in Figure II.10.

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Information from reference (63) used in this section
The intensity of the emitted photons is plotted as a function of the shift in the energy relative to the incident monochromatic beams energy. In spectroscopy the energy shift from the incoming line is plotted as a function of the wavenumber \( \bar{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \) [cm\(^{-1}\)] which is directly proportional to the energy. By knowing the wavelength of the incident photon and measuring the wavelength of the scattered photons the energy difference expressed in wavenumber can be calculated. \( \Delta E = h\bar{\nu} \)  

The wavenumber of each observed peak gives the energy of a particular vibration or rotation. We have to mention that not all vibrations are Raman active, selection rules apply: a vibration is Raman active if during the vibration the polarizability of the molecule is changed.

From experimentally collected Raman spectra it is not always possible to identify the origin of a particular phonon mode, but changes of the observed Raman peaks as a function of pressure can give positive indication of a phase transition. Since the vibrational energy levels in a molecule are influenced by the surrounding potential, with pressure the frequencies of these modes change as well.

In order to experimentally measure the Raman spectra of a sample in the DAC a high intensity monochromatic light source is needed. In our laboratory we used an Argon-ion laser which produces high intensity light over a wide range, but in our experiments we use the highest intensity 488 nm or 514 nm wavelengths. The laser beam is expanded, then focused to a small (<5 \( \mu \)m) spot on the sample. For our experiments we used Raman spectroscopy setups in 180\(^{\circ}\) and 135\(^{\circ}\) backscattering angles. In Figure II.9 (13) we present one of the Raman setups used in this study. As it can be seen in the figure we use a band pass filter to direct the monochromatic laser light to the sample and it allows the scattered light to pass through towards the spectrometer. The scattered light is passed through 2 holographic notch filters before entering the HR460 spectrometer, in which the light is spatially dispersed by a grating then collected with a liquid-N\(_2\) cooled CCD.
Figure II.11 a) schematic diagram of Raman spectrometer used in this study; b) holographic band pass filter in detail c) picture of the sample optical elements and the mDAC (from reference (13))
Pressure measurements

In the history of high pressure physics the development of accurate pressure measurement were almost as important as the invention of the DAC. In the early days pressure was estimated by force over area or in the x-ray studies by internal markers such as NaCl or Ag. Forman et al. showed first that the fluorescence lines of ruby shift linearly with the pressure in the 0.1-2.2 GPa interval. Later in 1975 Piermarini et al (14) tied the ruby scale to the Decker equation of state, and extended the pressure scale up to 19 GPa.

Ruby has the crystal structure of corundum (Al₂O₃) lattice with chromium ions Cr³⁺ substituting some of the aluminum ions. Corundum has a hexagonal-close-packed oxygen lattice with Al occupying 2/3 of the octahedral sites. These sites have cubic symmetry with slight trigonal distortion introduced by repulsive interaction between neighboring aluminum ions. In the strong cubic field approximation the field effect on d electrons is to split the single electron wave functions into 2 states, t₂g and e₉. Electronic degeneracies are further lifted by the trigonal distortion and spin-orbit coupling between the chromium ion and d electrons. (15) Using the notations from Eggert et al (16), the ruby R-line fluorescence can be described as follows; the ground state (g) of the chromium is optically pumped to a higher energy state (u). From this excited state through multi-phonon interaction decays very fast to a somewhat lower energy excited state (r). The r to g transition occurs by emission of a photon, which is the observed R-line of the ruby. Taking into account the spin-orbit coupling for the R-line we observe in reality a doublet (R₁ and R₂) for this transition. The energy levels of those states are very sensitive to the separation between the ions thus the position of the R₁ ruby line varies with pressure. The red-shift in the R₁ line position has been fitted to the empirical formula:

\[ P[GPa] = \frac{A[GPa]}{B} \left[ \left( \frac{\lambda[nm]}{\lambda₀[nm]} \right) - 1 \right] \quad (Equation \ II-2) \]

where \( \lambda \) is the ruby R₁ at pressure \( P \) and \( \lambda₀=694.28 \) nm at ambient pressure. For decades the parameters used to very high static pressures were A=1904 GPa and B=7.665 (17) however recent detailed experiments by Silvera et al (18) yield somewhat different values for these parameters: A=1876±6.7 GPa and B=10.71±0.14. Here we note that our pressures with ruby for consistency were calculated using the first set of parameters because most of the experiments were done before the publication of these latest refined parameters.
Ruby fluorescence is almost the universal pressure marker for spectroscopic studies, but above 100 GPa it becomes increasingly difficult to excite, and thus the fluorescence line intensity drops drastically. For high temperature experiments Sm:SrB$_4$O$_7$ can be used as pressure marker as it has a negligible shift with temperature (19). Beside the above mentioned two pressure markers, it has been demonstrated that the Raman shift of the diamond tip at the sample culet interface also can be used as pressure sensor at very high pressures. In a recent study B. Baer et al (20) published the fitting parameters and dependence on different culet shapes and sizes up to 180 GPa.

In XRD experiments usually a high symmetry crystal structure element with well established static EOS is loaded together with the sample. By determining the cell parameters of the marker material, the marker’s known EOS can be used to calculate the associated pressure. In our experiments we used as pressure markers Cu, Au, Pt and Ta. Beside their high symmetry – few diffraction peaks – these elements are also stable in their respective phases to very high pressures. When a pressure marker is chosen, care must be taken to limit diffraction peaks overlapping between the marker and the sample. The pressure marker often has higher x-ray scattering cross section than the sample due to higher atomic number; in this case the loaded marker amount has to be carefully measured not to overwhelm the sample intensity. The EOS that were used will be mentioned in the chapters where the respective pressure marker is used.
III. External resistive heating in DAC

High temperature experiments at high pressures in diamond anvil cell (DAC) are very important to explore materials in states that in nature exist only in planetary interiors or high energy explosions. To study the properties of the materials under these extreme conditions as a function of the pressure and temperature we need to achieve good control over these thermodynamic parameters even at extreme conditions for the extended periods of time needed to measure material properties with current diagnostic techniques. To achieve high temperatures there are two methods available: resistive heating and laser heating, both techniques have their advantages and disadvantages. While using laser heating one can achieve temperatures on the order of 5000K (21) it is required that the sample itself be able to absorb the IR photons heating itself or an absorber has to be loaded in the sample chamber that will heat the sample. When using an absorber, questions about chemical reactions always arise. The obvious advantage of this method is the high temperature and the local, very fast heating of the sample. However, it is difficult to maintain and measure the temperature below 1300 K using this method. To cover the lower part of the temperature scale an external heating technique has been used. Over the past few decades many different approaches have leads to increasingly higher working temperatures, but there are always limiting issues. In case of simple external heating experiments achieved either by wrapping a DAC body with a heating coil or placing a mini heater near the sample area, there are often issues of losing pressure as the temperature ramps up. One can attempt to mitigate the issue by manufacturing a DAC using special metals like Re and inconel (22). Although this approach sounds enticing, fabrication and material cost are too high. There have been many attempts to improve heating efficiency, heating stability, and extending pressure and temperature ranges simultaneously during heating experiments using a DAC. Table III.1. shows a comparison of various heating methods developed over the last twenty plus years. The maximum temperature reached seems to inversely correlate with the pressure limit of a particular DAC experiments. It is also true that P-T ranges of each experiment depend on the anvil design and gasket materials. The high temperature capability of the internal heating method using a Re strip inside a sample chamber (23) is severely limited due to chemical reaction of sample and pressure medium with
Re. The graphite heater can heat the sample very effectively, but the stability of the heating appears to be limited and often the gasket fails prematurely (24).

Table III.1 Comparison of heating methods using a diamond anvil cell.

<table>
<thead>
<tr>
<th>Year</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Heating</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>&lt;1000 °C</td>
<td>&lt;15 GPa</td>
<td>Fe wire</td>
<td>Fe (α-ε, α-γ), W</td>
</tr>
<tr>
<td>1987</td>
<td>~400-700 °C</td>
<td>5-13 GPa</td>
<td>HT oven-expensive (Re)</td>
<td>O₂</td>
</tr>
<tr>
<td>1993</td>
<td>-190–1200 °C</td>
<td>~2.5 GPa</td>
<td>Mo wire</td>
<td>H₂O, brucite, muscovite</td>
</tr>
<tr>
<td>1994</td>
<td>~700 °C</td>
<td>&lt;86 GPa</td>
<td>Mo wire, Inert gas flow</td>
<td>FeO</td>
</tr>
<tr>
<td>1998</td>
<td>~1200 °C</td>
<td>&lt;68 GPa</td>
<td>Graphite heater</td>
<td>Fe, Al₂O₃</td>
</tr>
<tr>
<td>1999</td>
<td>~1100 °C</td>
<td>&lt;4 GPa</td>
<td>Gasket heating (Re)</td>
<td>a-Si₃N₄, γ-Al₂O₃</td>
</tr>
<tr>
<td>2003</td>
<td>~2700 °C</td>
<td>&lt;10 GPa</td>
<td>Internal heating (Re)</td>
<td>SiO₂ (Raman: qtz-coe)</td>
</tr>
<tr>
<td>2003</td>
<td>~1000 °C</td>
<td>&lt;92GPa</td>
<td>Whole-cell – special alloy cell</td>
<td>Fe₀.₉₅Nι₀.₀₅, TiO₂</td>
</tr>
</tbody>
</table>

It is challenging to couple an externally heated DAC with angle-dispersive X-ray diffraction over Mbar pressure ranges. There are few examples dealing with the all the three issues collectively. We apply heating in vacuum to prevent oxidation of diamond and DAC metal body parts, and to sustain stable heating over 1300 K and we fill the space between the diamond anvils and the heating coil with a copper block lined with a thin ceramic ring or high thermal conductivity ceramic paste to improve the thermal contact for efficient heating. One of the greatest advantages of using a membrane driven DAC is the uniform delivery of force through the inflated membrane making contact with bottom of the DAC cylinder under constant He gas pressure during high temperature runs. This uniform loading and control helps tremendously to prevent uneven gasket thinning, which is one of the main cause of failure, often leading to a sudden anvil fracture.

**High temperature experimental setup:**

As mentioned in the previous chapter of this study for high pressure and temperature experiments we use membrane driven DAC (mDAC) that helps to minimize or completely eliminate the lateral force components applied to the table/bottom of the diamond anvil. This leads to a more even thinning of the gasket and with the selection of the right gasket material we
can reach pressures in excess of 100 GPa without uneven deformation of gasket chamber, which is a prerequisite for reaching high temperatures at these high pressures. The membrane can be used to apply force evenly over the whole surface of the piston (the sketch of the cell shown in Figure II.2.) in increments of 1 psi, which allows very smooth control over the samples’ pressure in the chamber. In Figure III.1 we present a typical sample pressure as a function of the membrane pressure. As expected with the decrease of the culet size higher pressures can be achieved with the same applied He pressure in the membrane. It is important to note that even in the case of 700K isotherm compression the sample pressure in the chamber is consistent with a room temperature compression, proving the excellent stability of our experimental approach at temperatures.

![Sample Pressure vs Membrane Pressure Graph](image)

**Figure III.1** Typical sample pressures as a function of He pressure in the membrane. Full black squares 100/300μm diamonds at 400C; open green triangles 100/300μm diamonds at room temperature and open red circles 300μm diamonds at 400C. Gasket material used W-Re alloy pre-indentet to 24GPa.
The basic part of the micro-heater is an Aluminum-oxide based ceramic ring – max working temperature 1650°C – with a diameter of 22mm and 4mm high to fit easily around the diamond anvils and between the seats on which the diamonds are glued on. The Pt-Rh alloy – melting temperature 1850°C – heating wire is spiraled inside of the ring as shown in Figure III.2 and covered with RESBOND 920 from Cotronics, a ceramic paste with thermal conductivity of 40 W/m K. The result is a heater with a resistivity of about 1Ω. This is one of 2 resistive heaters providing 60-70% of the power necessary for the sample heating and is mounted on the “bottom” part of the cell – cylinder, see Figure III.3.

The second heater is a smaller one and it is made using the same type of Pt-Rh alloy wire with smaller diameter. This is built around the “top” diamond – mounted on piston part of the cell – using the same RESBOND 920 both to glue and electrically insulate the wires from the seat. A thin, very low thermal conductivity layer is applied between the heater body and the seat to enhance the heating of the diamonds. This heater has an approximately 1.2Ω resistivity capable of delivering a maximum power of ~30W.

We use two K-type thermocouples mounted close to the tip of the diamond anvil to read the temperature. To ensure a firm contact between the thermocouple and the diamond, one of the thermocouples is mounted inside a copper disk that is pressed on the anvil or it is glued with high thermal conductivity ceramic that also serves as heat conductive medium between the diamond and the heater; this applied to the cylinder. On the piston side (smaller heater) the thermocouple is glued on the surface of the top diamond with thermally conductive ceramic paste.

Mounting the heaters is very simple and one of the advantages of these heaters is that they can be mounted in any type of DAC with an opening on the side for the electrical connectors. We have used 3 types of cells and the results regarding heating are virtually the same. However the membrane DAC has the best performance, enabling almost perfect isobaric
conditions for temperatures varying from 300 K to 1300 K. Therefore we present the cell assembly for mDAC.

![Diagram of the cell assembly for mDAC](image1)

Figure III.3 Heaters mounted into mDAC

![Picture of mDAC with ceramic covered electric contacts](image2)

Figure III.4 Picture of mDAC, ceramic covered electric contacts on the and right the heater for the 2 heaters. 2 parirs of thermocouple on the bottom

One of the heaters is mounted on the cylinder part of the DAC. To achieve the highest possible temperature, it is very important to make the best possible heat-coupling between the heater and the diamonds. We press 2mm thick copper disks on the diamond to ensure the best
thermal contact possible, at the same time it is important for the disks not to touch the seat for two reasons: avoiding the grounding of the thermocouple and creating a thin air (vacuum) layer between to avoid heat loss via Cu-seat contact. To further avoid heat loss, a thin insulating layer of mica is placed between the diamond seat and the cell, and between the heater ring and the seat (mica marked with red in Figure III.3). The heater is then glued with aluminum-nitride based glue to the copper ring, once again the criteria for choosing the glue is stability at high temperatures and high thermal conductivity. For practical purposes the copper disk can be replaced with high thermal conductivity ceramic paste, like the aluminum-nitride based one or even the Resbond 920, without noticeable decrease in the system performance up to 1000K.

Figure III.5 Sketch of the vacuum chamber with the mDAC mounted inside

To prevent the oxidation of the cell, gasket and graphitization of the diamond and to protect heating wires the cell is placed inside a vacuum chamber (figure 4.) and operated at a vacuum level of less than 0.5mtoorr. The cell mount in the chamber is made with the consideration to have very low thermal conductivity, preventing heat loss through conduction.
The pressure in the sample chamber is controlled by varying the pressure in the membrane through a thin feed-through capillary tubing connection. The chamber is a 3.85” long stainless steel tube with a 4” external diameter as can be seen on Figure III.5, in which the mDAC is mounted on the front flange of the chamber using thermally insulating mounts to minimize heat loss. The apertures in the chamber are such that it can be used for both Raman spectroscopy and X-Ray diffraction measurements. When cell is mounted in place the distance between the sample and the bottom of the chamber mount is 3.06”. To avoid overheating of the front flange, a cooling ring can be mounted between the front flange and the chamber body which would extend it to about 4”. For Raman spectroscopy experiments we used a glass window on the front flange, while for X Ray diffraction experiments kapton tape is the choice for the front window. At the back of the cell there is a small glass window in the insert that lets the X-Ray collimator pin-hole approach as close as possible to the sample. This window is critical only in X-ray diffraction experiments, though it is very useful for back lighting transparent samples for visual observation.

![Figure III.6 Heater efficiency](image)

The mica and vacuum thermal insulating layers, the compact design of the heaters and the enhanced thermal coupling between the elements of the setup lead to low maximum operating temperature of the mDAC, i.e. the sample is hot but the mDAC is “relatively” cold. At the sample temperature of 1200-1300K the temperature of the cell body at the membrane does
not exceeds 450-500°C, thus not requiring any special modification of the DAC. At the same time the efficiency of this double heater design is proven by the power reading too, it requires only 150W combined to achieve 1300K sample temperature. In Figure III.6 we present a plot of the maximum temperature as a function of the total power used by the heaters. Just for comparison we included the temperature power plot of a single heater configuration, used before the introduction of the 2nd heater. The difference in the power requirement is not that large, however the time required to achieve them is much longer and at high temperatures the temperature gradient across the sample (from culet to culet) is not negligible. The true advantage of this setup is the capability to sustain high P, T conditions for lengthy experiments. A few of the P-T paths are shown in Figure III.7.

Figure III.7 Typical P,T paths: full squares represent quasi-isobars at 95GPa for N2, the full circles are isobars of CO2 at 56 GPa, open triangles are isotherm compression of N2 at 700K.
IV. Molecular solids under high pressure and temperature

The molecular solids presented in this thesis are gases at ambient conditions, with the exception of water that is a liquid. Increasing pressure on any of these molecular systems be it a fluid or gas results in the shortening the average distance between the molecules, and attractive van der Vaals interaction leading to a molecular solid. Upon further compression the intermolecular distances become comparable with the inter-atomic distances within the molecule, leading to major changes in the bonding and ultimately to the breaking or reconfiguration of the molecular bond. These changes in the bonding and inter-molecular interaction induce phase transitions driving the crystal structure of the molecular solid to a close-packed structure, and eventually transforming it in an atomic solid after the pressure induced molecular dissociation.

Studies of high pressure behavior of H$_2$ as early as 1935 by E. Wigner and H. B. Huntington (30) predict a metallic solid as the final form of solid hydrogen under extreme pressure. Pressure induced molecular dissociation in different molecules occurs at very different pressures depending on the bond strength, but typically they occur at pressures well above 100 GPa. Before reaching the ultimate metallic state along the compression path many different molecular phases can be observed, some of them with unusual properties, such as polymeric nitrogen and carbon dioxide. There are large differences between molecular and non molecular phases in the bonding, intermolecular interactions, molecular configurations crystal structures and electronic structures. Therefore, phase transitions may follow very complex pathways whose explanations present fundamental challenges to condensed matter physics.

In the following we present some of the molecular solids and their known high pressure behavior and phases with our own experimental contributions.
IV.1 Melting of solid Hydrogen

Hydrogen being the simplest diatomic molecule and the most abundant material in the Solar system and the universe has been subject to extensive theoretical and experimental studies. As mentioned in the paragraph above, very early theoretical calculations pointed to metallic hydrogen forming from the insulating solid at sufficiently high pressures. Although it is the simplest element with only one proton and one electron, forming a simple molecule containing only 2 protons and 2 electrons, the understanding of its behavior under high pressure is has proven to be extremely challenging. Quantum effects are not negligible due to the relatively light nucleus formed, and they impact many of the physical properties of the fluid or solid formed by hydrogen molecules (31). Even though there is a consensus regarding the existence of a metallic phase, the transition pressure from insulator varies in different theoretical studies. Experimentally, the transition pressure has yet to be directly observed.

The quest for the predicted metallic hydrogen in both theoretical and experimental research has resulted in a wealth of new information at high pressures, but the majority of the experiments were performed at low temperature. Three molecular phases of solid hydrogen were identified and studied in detail (See figure IV.1), primarily at low T (4-77 K) rather than at ambient temperature. The known phases are: Phase I (symmetric phase), the high temperature-low pressure phase – exists up to 110GPa at low temperature; Phase II (broken symmetry phase) a low temperature high pressure phase, and Phase III a high pressure molecular phase above 150 GPa. These phases share a critical point near 165 GPa and 150K.

Optical studies of solid hydrogen up to 320 GPa at 100 K by Loubeyre et al (32) show no structural changes in the solid above 160 GPa and the persistence of the vibron signature of H2 up to 316 GPa. Based on their absorption edge measurement they predict a metallization pressure of 450 GPa. This later was confirmed in D2 by Coherent anti-Stokes Raman spectroscopy by Baer B. et al (33) by extrapolating the band gap closure pressure to 460 GPa. In the quest for the metallic hydrogen the phase diagram has been explored in detail by static high pressure experiments using DAC, at low temperature in the early stages and then later at higher temperatures.
Melting is an important first order phase transition, it separates the solid state from the liquid phase and it covers a wide range of the pressure and temperature domain. Changes of slope, cusps and maxima of the melting curve can reveal subtle changes in the interactions of the system or differences between the properties of the fluid and the solid.

Experimental studies of hydrogen in a DAC proved to be challenging, due to gasket and diamond failure caused by H₂. Achieving high pressures is even more challenging due to the high reactivity of the hydrogen. In addition, one of the most difficult tasks is the containment of the sample. As the temperature rises the hydrogen diffuses more and more into the gasket leading to loss of pressure and finally the loss of the sample. As described in Chapter II gaskets are made of metallic materials (Re and W-Re in our experiments) for their large yield strength and ductility, but in case of the hydrogen their use becomes problematic due to embrittlement by hydrogen. The embrittlement is pressure and temperature dependent, but all metals are expected to react with hydrogen at high pressure and temperatures. Datchi et al (34) in their study published in 2000 performed experiments using various metal gaskets and determined the melt line up to 15 GPa. By fitting the experimental data to the Simon-Glatzel (35) empirical equation they found
discrepancies well beyond the experimental uncertainty, at the same time they found a very good fit to the Kechin equation (36). The Simon-Glatzel equation is used to extrapolate the melting curve of a substance beyond the measured region. However, it can be applied only to materials with rising melting curves, it describes well the melting behavior of solids bonded by van der Waals forces, such as solid gases – not hydrogen as mentioned above. For materials with falling melting curves or curves with maxima it cannot be used. Instead the equation proposed by Kechin based on thermodynamic principles can be used. It is a generalized Simon-Glatzel equation and describes rising and falling melting curves as well as those with maxima. Based on the fit to the Kechin law, Datchi et al report a melting line with a maximum at 128 GPa and 1100 K as shown in Figure IV.2.

The appearance of a maximum melting temperature in hydrogen is in itself a manifestation of an unusual physical phenomenon. The few systems with a negative melt slope involve either open crystalline structures, such as water and graphite, or in the case of closed packed solids, a promotion of valence electrons to higher orbitals upon compression. In these latter cases the liquid is denser than the solid when they coexist, possibly because of structural or electronic transitions taking place continuously in the liquid, as a function of pressure, but only at discrete pressure intervals in the solid.

These experiments were followed up in 2003 by Gregoryanz et al (37) extending the experimental data up to 45 GPa, where the melting temperature is ~800K. They circumvented
the problems related to sample loss by using “composite gaskets made of compressed ceramic powder and Rhenium”. Melting was determined by following the shift in the H₂ Raman vibron as a function of temperature at the given pressure (isobaric heating). Fitting the additional data to the Kechin equation the results are similar to the one obtained by Datchi et al. with a shift in the melting curve maxima to ~100 GPa and 950 K.

Ab-initio calculations lead to similar conclusions, Bonev et al (38) predict that the melting curve of the hydrogen has a negative slope above 82 GPa. They explain the phenomenon by the softening of the intermolecular interactions, which occurs a faster rate in the liquid than in the solid, as a function of pressure. See Figure IV.6 with the ab-initio melting curve from Bonev et al.

Given the melting curve already established by theory and the extrapolations from literature the P, T domain where the maximum in the melt line would occur, it is easily accessible using our high temperature DAC system. The only issue with the experiment was the containment of the hydrogen at the extreme conditions for sufficiently long periods to detect the melt. It was obvious to us from the existing literature data that using a simple metallic gasket would not yield to the desired outcome. We first experimented with noble metal inserts serving as walls of the gasket chamber. In Figure IV.3 a picture of our gasket manufactured with gold is presented. We pre-indented a W-Re alloy gasket to moderate pressures, then a hole was drilled and filled with gold powder. After filling the hole we compressed the gasket with the gold to 20
and then drilled another hole, which served as sample chamber for our first melting experiments. Hydrogen was loaded with the high pressure gas loader presented in Chapter II.2. As known from the EOS, hydrogen is very compressible at low pressure and as shown in Figure IV.4 the sample diameter is less than half of the initial pressure chamber. With this type of gasket we were able to contain a hydrogen sample up to ~600 K at 23 GPa, which is just below the melting curve, but lost the sample before the melt could be determined. The last P,T point before losing the sample is shown in Figure IV.5. To detect the melting we used visual methods combined with measurement of the hydrogen vibron. The highest pressures at which the melt was determined with this method are presented in Figure IV.6 with full square symbols, at 15.1 GPa and 16.5 GPa.

Since it was obvious from our experiments and from previous reports that the limit of the Au gasket is below 20 GPa we tried to apply a different method. We kept the basic W-Re gasket in and tried different materials to insulate the metal from the hydrogen sample. Our efforts of coating the W-Re-Au chamber inner wall with paraffin yielded no better results that the simple gasket discussed earlier. To further extend the P,T range we tried coating the inner walls of the sample chamber with sputter deposited Al₂O₃. The results were considerably better than with the gold gasket, reaching close to 800 K at 26 GPa, allowing us to add another melting point to the melting curve (empty square in Figure IV.6)
Our results are in agreement with previous experiments, however we were not able to extend the experimental P,T range of the melting curve by externally heated DAC experiments. Since the conclusion of our experiments Deemyad and Silvera (39) applied a pulse laser heating technique and found a peak in the melting line at 64 GPa and 1055 K. Their results are shown in Figure IV.8. It is rather interesting to note the unexpected very sharp peak in the melt line. All other data points they report are in line with previous measurements and theoretical melt curve. They speculate that the unexpected sharpness of the melting line peak may be due to an as yet undetected solid-solid phase line intersecting the melt line; this might be an extension of a new phase recently detected in D$_2$ by Baer et al (33)

To conclude this chapter: there is reasonable agreement between experiments and theory that there is a maximum in the melting curve of the hydrogen and this maximum is somewhere between 50 GPa and 100 GPa and the temperature range between 900 K and 1000 K. Further
static high pressure experiments are required to determine the steepness of the decreasing part of the melting curve.

Figure IV.7 Melting data from Deemyad and Silvera (39)
IV.2 P-T path dependence in formation of high p, T molecular phases of Nitrogen

Nitrogen exhibits a very rich phase diagram in molecular solid and extended – non molecular phases. Being one of the simplest diatomic molecule, it has been the subject of extended studies at high pressure (both experiments and theory). From the static high pressure experiments point of view it is a much easier material to work with that the hydrogen described earlier, there are no diffusion and chemistry related issues. With its strong molecular bond and anisotropic repulsive intermolecular interaction, compression is initially achieved by more effective packing of essentially inert molecules. At low pressure and temperature the α-N₂ with completely ordered molecules is characterized by quadrupole-quadrupole interaction, and it is stable up to 36K at pressures lower than 0.4 GPa. Increasing the temperature further drives a transition to the β-N₂ phase, which has a hexagonal close packed structure with a high degree of molecular disorder. This phase remains stable up to the melting point, also it can be formed by compressing the gas at room temperature beyond 2 GPa. Increasing the pressure at low temperature beyond 0.4 GPa the γ-N₂ tetragonal phase is obtained. Further increasing the pressure at room temperature the quadrupolar interaction becomes less dominant with the formation of the cubic δ-N₂.

Figure IV.8 Schematic representation of phases observed in Nitrogen (from ref (40))
The delta phase is disordered with sphere- and disk-like molecules distributed between corners and faces of a cubic cell. With increasing pressure or decreasing temperature within the $\delta$ phase a second order phase transition takes place by partial ordering of molecules.
in the also cubic $\delta_{loc}$-N$_2$ phase. Further increasing the pressure the molecular ordering completes in $\epsilon$-N$_2$, a rhombohedral structure. Upon further compression at room temperature the $\epsilon$ phase transforms into the $\zeta$ molecular phase which has orthorhombic symmetry (1). For a long time $\zeta$ was believed to be the last molecular phase before the pressure induced dissociation. However, recently Gregoryanz et al. reported a new $\kappa$ molecular phase above 115 GPa and attribute a monoclinic structure to it (40). These phases – with the exception of $\kappa$ – have been extensively studied, their crystal structures have been established and characteristic Raman signatures are well known. Beside these molecular phases there are 2 more phases reported in literature that form at high pressure and temperature $\iota$ and $\theta$ (3) we will discuss later in this chapter. Increasing pressure beyond 150 GPa at room temperature the $\eta$ non molecular phase has been reported. It has been predicted theoretically (42) and already independently confirmed by different groups the formation of a single bonded high P,T phase of cubic gauche N$_2$ as well as other extended non molecular forms of nitrogen.

Figure IV.10 Raman spectra of $\epsilon$, $\theta$ and $\iota$ molecular phases
As is evident from the above paragraphs, nitrogen has a very rich phase diagram both in molecular solid and extended non molecular phases. Some of the phases and its boundaries are well established, for others like $\theta$ and $\iota$ the transformation $P, T$ are reported by only one group. Several studies use spectroscopy methods to trace changes with pressure and temperature in the nitrogen. As early as 1985 Reichlin (43) reports the Raman spectra of nitrogen compressed to 130 GPa, finding the transition pressures from $\varepsilon$ to $\zeta$ and from $\zeta$ to $\kappa$ without actually identifying these phases. Our own Raman measurements following their $P,T$ path yields the same results for transition pressures see Figure IV.11.

In our experiments we proposed to investigate the stability field of the new phases ($\iota$ and $\theta$) reported only by Gregoryanz et al. We used our high temperature expertise to obtain data in excess of 100 GPa at 900 K, as we report in our paper (2) we found only one of these phases and that only under special circumstances. The Raman spectra of $\theta$ and $\iota$ phases are very distinct easily differentiable from the $\varepsilon$ phase (see Figure IV.10). They have been reported to

![Figure IV.11 Nitrogen Raman vibrons as a function of pressure. Full squares epsilon phase, black at 300 K, red 700 K. Open black circles zeta phase at 300 K](image-url)
be thermodynamically stable high-pressure phases since they are formed irrespective of thermodynamic path (3). Based on these reports we were confident that by isobaric heating at 70 GPa from 300 to 900 K we would be able to find and later map out the stability field of η phase. We performed several experiments on the P,T paths shown with the grey arrows in Figure IV.12, and much to our surprise there were no traces of η phase. θ phase being reported to form at higher pressure but lower temperature (90–105 GPa at 600 K) we extended our experiments to pressures exceeding the 100 GPa range. Always preparing the cleanest possible samples shortly before the high P, T experiments we were not able to obtain any of the θ and η phases. After performing experiments on more than a dozen “fresh” samples we were able to confirm the phase boundaries between the ζ and ε phases both by isotherm compression and isobaric heating. Our findings are within the margin of error at low temperature and exactly on the previous line at higher pressure and temperature. Also during the isobaric compressions we extended the formation boundary line between the δ and ε phases (see Figure IV.12), which seems to be steeper than previously reported for example when compressing at 900 K the ε phase forms at 46 GPa. We intentionally remained below the melt line to avoid any unpleasant consequences that may arise from having a high pressure and temperature liquid sample.

![Figure IV.12 Phase diagram of nitrogen](image-url)
During our quest for the molecular phases we found an amorphous phase of “black nitrogen” when quenching the sample to room temp and 170 GPa, this phase has no Raman signature, nor x-ray diffraction peaks, and absorbs every line of the visible spectra. Unfortunately we could not make any conductivity measurements on this sample, but we assume that it is at least semiconducting as has been reported by others on samples in this pressure range. By heating the sample to 720 K we observe a slow opening of the bandgap with increase in the temperature and decrease in the pressure. However, no Raman signal could be detected in the 100 cm\(^{-1}\) to 4000 cm\(^{-1}\) region. Micro-photographs of this sample are presented in Figure. IV.12 in comparison to the ε phase of the nitrogen with both back and front of the sample illuminated.

Figure IV.13 Amorphous nitrogen transformation with increasing temperature and decreasing pressure

Figure IV.14 In-situ Raman spectra of θ phase at 920 K and 97 GPa
We report in our paper (2) the path to the θ phase; here we present (Figure IV.13) just a spectrum obtained in situ at 900 K and 97 GPa compared to a quench sample spectrum from the literature. Every single peak from in the low frequency modes has its corresponding one with a small pressure shift.

An important general conclusion of this work is that the definitive determination of the equilibrium phase relations of nitrogen is more complex than previously thought due the presence of substantial transformation barriers between different classes of structures. These structures include the well-known phases based on weakly interacting N₂ molecules, the recently observed non-molecular phase and the strongly interacting molecular phases are documented in this study.
IV.3 X-ray diffraction study of H₂O ice VII to ice X transition

Water is one of the most abundant molecules on Earth and in the outer solar system. Understanding its behavior over a broad range of thermodynamic conditions is of great importance to both Earth and planetary sciences and to fundamental physics and chemistry. In its solid form, water ice forms the polar caps and is a major constituent of a plethora of icy bodies in the solar system and is believed to be a major component of the intermediate ice layers in the interiors of giant planets. From this perspective it is a priority to build an accurate phase diagram of water. Just like the other molecular solids discussed in this study water has a very rich phase diagram especially in the low pressure region, due to the flexibility of hydrogen bonding.

It is accepted now that up to about 50 GPa in the observed phases, the H₂O molecule is preserved and the structures follow the ice rule: 1) molecular crystals composed of “gas phase like” water molecules, 2) each water molecule is oriented so that it participates in four hydrogen bonds with neighboring water molecules, and 3) at most one hydrogen atom is located between neighboring oxygen atoms (44). At higher pressures ice rules are no longer satisfied, with compression the distance between oxygen atoms become smaller and the H-O-H bond becomes symmetric. The structure with the symmetric bond is the ice X phase of water, its formation will be discussed later in this chapter.

Since our study focuses on the high pressure phase of ice at room temperature we will not discuss the low pressure phases that have already been documented and can be seen on the phase diagram presented on Figure IV.15. Water compressed at room temperature first transforms from liquid to a tetragonal crystal, ice VI at 0.9 GPa and upon further compression transforms to phase VII, in which the oxygen atoms sit in a bcc structure. The bcc oxygen sublattice seems to be stable up to 170 GPa (45). However, the above mentioned bonding change induces a transition to the symmetric ice X. Schematic representation of ice VII and ice X shown in figure IV.16.

Due to the hydrogen’s very low x-ray scattering cross section cross section the traditional X-ray diffraction technique yields information only about the oxygen sublattice. In the low pressure range – up to 20 GPa – crystallographic studies of the different water phases at low temperatures were done by neutron scattering, which allows the determination of the hydrogen
positions due to the high scattering cross sections. Unfortunately this technique is limited to the lower pressure range.

The transition to the theoretically predicted symmetric ice has been studied by spectroscopic means, as early as 1984 Polian and M. Grimsditch (46) performed Brillouin scattering study on ice and reported a phase transition to ice X around 44 GPa. Infrared studies at low temperature and room temperature provide evidence for the transition to ice X at 62 GPa (47) and 60 GPa (48) respectively. High pressure Raman spectroscopy (49) of H\textsubscript{2}O revealed major changes associated with the transition to the non-molecular, symmetric hydrogen-bonded state, the disappearance of the strongly pressure-dependent O-H symmetric stretching mode at 60 GPa indicating the transition.

Loubeyre et al. (45) used single crystal synchrotron x-ray diffraction to study high pressure behavior of H\textsubscript{2}O up to 170 GPa, based on the 111 reflection line – coming from hydrogen – normalized to the 222 line – reflection from oxygen – they report that bond

![Phase Diagram of H\textsubscript{2}O from Lin et al. 2005](image_url)
symmetrization occurs as low as 40 GPa and as high as 70 GPa and it remains symmetric up to 150 GPa. At this pressure they found changes in the intensity ratio indicating a new structural transition, which could be the predicted (50) bcc→hcp transition. Based on their study it seems that the transition from ice VII to ice X can be sluggish. Sugimura et al (51) report a slow transition from Ice VII to ice X based on x-ray diffraction and density functional theory calculations. According to their study the transition from ice VII starts at 40 GPa, when a dynamically disordered, very compressible ice VII' phase forms before the transition to a dynamically disordered ice X (ice X'), which persists up to 110 GPa, when the transition to ice X occurs.

![Schematic representation of ice VII (left) and ice X (right)](image)

Figure IV.16 Schematic representation of ice VII (left) and ice X (right)

In our study we investigated the ice VII/ice X transition as well as a possible new phase above 150 GPa. We collected all of the high quality diffraction patterns at 16IDB APS, and used the MAR350 image plate detectors. Patterns were integrated with Fit2D, and analyzed with XRDA (12) to obtain unit cell volumes for both water, the sample and the Ta pressure indicator. We calculated pressure with Birch-Murnagahan Equation of State (EOS) using the isotherm bulk modulus values and its derivative (K0=194.7 GPa and K0’=3.4) for Ta published by Cynn et al. (52).

We were able to collect diffraction patterns at room temperature up to 180GPa. On Figure IV.17 we present a few representative integrated patterns with the corresponding indexing. The first integrated pattern shown is one from the sample at low pressure in the ice VII phase, indexed to the previously described structure, where the observed intensities are coming from oxygen atoms sitting in a bcc lattice. Our unit cell volumes are in good agreement with the
latest available data from literature. Upon compression at 36 GPa we notice a sudden broadening of the bcc (110) peak that becomes more pronounced at higher pressures ultimately resulting in easily observable peak splitting – see integrated pattern at 63 GPa on Figure IV.17. Not only the (110) but the (211) peak also splits at the same time. At the lowest pressure where the split shows up, the new peaks can be indexed to another bcc lattice, which gives a smaller volume.

Following the intensity ratios of the “old” and “new” bcc (110) we observe that at the beginning when the new bcc (110) can be identified, its intensity is much weaker relative to the (110) belonging to ice VII. With the increase of pressure the intensity ratios of these peaks are changing, the intensity of the new (110) peak increasing at the expense of the ice VII (110), which was last observed at 100 GPa see figure IV.17.

Figure IV.17 Integrated X-Ray diffraction patterns collected at room temperatures. Data at 8 GPa from ice VII indexed to bcc, at 63 and 100 GPa coexisting bcc ice VII and X respectively.
The unit cell volumes obtained for the H$_2$O are presented in Figure IV.18 as a function of pressure with the Vinet equations of state (53) resulted from fitting to the experimental data.

\[
P = 3K_0 \left( \frac{V}{V_0} \right)^{-\frac{2}{3}} \left[ 1 - \left( \frac{V}{V_0} \right)^{\frac{1}{3}} \right] \exp \left[ \frac{3}{2} (K'_0 - 1) \left[ 1 - \left( \frac{V}{V_0} \right)^{\frac{1}{3}} \right] \right]
\]

We fit the pressure-volume data to the Vinet EOS separately for the 2 different phases ice VII and ice X. For ice VII we obtain $K_0$=2.96GPa (±0.3) for the bulk modulus and $K'_0$=8.75 (±0.29) for the derivative, these values are similar to the already published ones in the literature for ice VII, showing a very compressible solid. Fitting the data above the pressure where the discontinuous volume change occurs to the same Vinet EOS we get slightly different results, with bulk modulus value higher than for ice VII: $K_0$=4.89GPa (±1.3) and $K'_0$=8.19 (±0.75) indicating a less compressible solid in symmetric ice X phase. The start of the

![Figure IV.18](image1.png)

**Figure IV.18** The unit cell volume of H$_2$O in Å$^3$ as a function of pressure at 300K from 8 to 180GPa. Solid black squares ice VII, open circles ice X. Solid black line the fitted Vinet EOS for ice VII, dashed line extrapolation of it

![Figure IV.19](image2.png)

**Figure IV.19** Unit-cell volume change across the transition relative to the ice VII EOS plotted as a function of pressure. Black squares ice VII, red circle ice X.
110 and 211 peak splitting at 40 GPa is the indication of the phase transition to the symmetric ice X phase, this value is in good agreement previously reported single crystal X-ray diffraction (45) and Brillouin spectroscopy experiments (46). Infrared and Raman spectroscopy experiments (48), (49) indicate a higher pressure for the start of transition to ice X, 60 GPa and 70 GPa respectively, with the transition complete at 95 GPa. From our X-Ray diffraction experiment results we see the onset of the transition to the symmetric ice X at 40 GPa and the transition completes at 100 GPa.

![Graph showing unit cell volumes against pressure (GPa)](image)

**Figure IV.20** Unit cell volumes from our experiments – open squares and open circle – compared to Loubeyre et al (45) data – full circle and up triangles – plotted atop of ice VII EOS from Loubeyre et al (45)

At the beginning of the transition to ice X we observe a discontinuous volume change, which persists between the two coexisting phases. The plot of the volume change across the transition relative to the ice VII is presented in figure 3, the volume decreases by 4.25% at the beginning of the transition. More careful observation of the data published by Loubeyre et al in 1999 also indicates a steeper volume curve at the transition in one of their samples. Between 40
and 80 GPa the data from literature and from our experiment are almost perfectly overlapping, as we present them on figure IV.20.

Extending our experiments beyond the 150 GPa we do not observe any changes, the bcc structure remains stable up to the highest pressure of 180 GPa. We do not observe a transition to the predicted hcp structure.

By covering the pressure range between 8 GPa and 180 GPa we observe a slow transition from the ice VII to ice X phase, with a drop in the unit cell volume similar to Sugimura et al.
V. High pressure phase transition in Vanadium

Vanadium, a transition metal with 3 3d electrons in the valence band has been subject to several studies. Early theoretical work based on simple rigid-band models can explain the phase stability of non-magnetic transition metals with the number of d electrons in the valence band ($Z_d$) as the only variable parameter. In the transition metals $Z_d$ increased with the atomic number and, except from the late members of each series, also by the application of pressure (54). The variation of $Z_d$ with atomic number explains the canonical hcp-bcc-hcp-fcc sequence observed across the nonmagnetic transition metal (4d, 5d) series (see their crystal structures under ambient conditions in Table V.1). The increase of $Z_d$ with increasing pressure in vanadium (and transition metals in general) results from an $sp \rightarrow d$ transfer of valence electrons under compression. This is explained by the nature of the spatial distribution of s and p states that are more extended than the more localized d states, therefore they “feel” the effects of high pressure (decreasing distance between atoms) more strongly. Thus, the energy levels of corresponding s and p bands rise faster than do the d bands, transferring electrons from to the d like states. We note here that the increase in $Z_d$ with pressure is always less than one.

<table>
<thead>
<tr>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
</tr>
<tr>
<td>Lu</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
</tr>
</tbody>
</table>

Table V.1 Transition metal crystal structure under ambient conditions

J. Moriarty used the rigid-band model to predict behavior under pressure of several 3d, 4d and 5d elements, in figure V.1 we show his results from 1992. Based on the relative energy
differences of the different structures in a given group it correctly predicts the ambient structure and its relative stability with increasing pressure. As stated above, the increase in pressure increases the $Z_d$, in group V and VI the bcc structures seems to remain stable even at very high pressure, especially in group V where the increase in pressure should increase the stability of the bcc phase. The extreme stability of the bcc-Ta has been experimentally proven to 300 GPa by shock experiments and static compression experiments by H.C. Cynn and C.S. Yoo (52) to 174 GPa. Nb is also known to be stable up to 145 GPa in bcc structure (55). According to this model, as in case of the other 2 elements for the group, vanadium is supposed to be stable in the bcc phase to very high pressures. Experimental studies of Vanadium EOS by Takemura in 2000 (55) did not contradict this theoretical prediction.

Suzuki and Otani (56) in order to explore the possibility of a structural phase transition to another phase performed first principle calculations of the lattice dynamics of V in the pressure range up to 150 GPa. They found that the transverse acoustic phonon mode $\text{TA} [\xi_00]$ around $\xi=1/4$ shows dramatic softening with increasing pressure and becomes imaginary around

![Figure V.1 Schematic representation of bcc-fcc and hcp-fcc energy differences as a function of d-band occupation for the nonmagnetic 3d, 4d and 5d transition metal series at ambient conditions. (from ref (54))](image-url)
130 GPa, indicating a possibility of structural phase transition around this pressure. A. Landa et al. (57) have performed elastic constant calculation for vanadium using exact muffin-tin orbital and shown the trigonal shear elastic constant \( C_{44} \) softening around 200 GPa, preceded by a change in the increasing trend at ~60GPa. The pressure induced shear instability in vanadium is attributed to the intra-band nesting of the Fermi surface.

These theoretical calculations were followed by the experimental confirmation of a new rhombohedral phase of vanadium by Ding et al (59). They conducted high pressure experiments at ambient temperature on quasihydrostatic samples and found the phase transition pressure to be at 63 GPa, experiments on samples loaded without pressure medium transformed at 69 GPa, which they use as reference pressure for this transition.

B. Lee et al. (60) confirmed the experimentally found rhombohedral phase by electronic structure calculations, from which results not only one, but actually two different rhombohedral phases \( \beta, \gamma \). The difference between them is the angle between the rhombohedral basis vectors, the \( \beta \) phase that forms around 84 GPa has its \( \alpha=110.25^\circ \) and \( \gamma \) phase with \( \alpha=108.14^\circ \) and becomes the stable phase from 120 GPa according to the calculations. Increasing pressure beyond 280 GPa vanadium transforms back to bcc again which remains the stable at least up to 400 GPa. (61) According to B. Lee et al. calculations the volume change associated with the bcc

![Figure V.2 The volumetric strain \( V/V \) of the ground state of single-crystal vanadium at zero temperature with respect to that of the bcc structure. (after ref (58))](image-url)
to β transformation is small: 0.03% or less in magnitude. The magnitude of the volume change associated with the second transformation is larger: about 0.15% for the β to γ transformation at 120 GPa. The volume change would be about the same if bcc were retained to a pressure of 120 GPa and then transformed directly to γ. However, if the bcc or β phase persists to higher pressures, the volume change becomes progressively smaller and eventually changes sign, becoming a volume expansion near 200 GPa. The final transition back to bcc again has a change of over 0.1% in magnitude. (58). Volume changes and the relative stability of the different vanadium phases are shown in Figure V.2. As we see the theoretically calculated volume changes across the transition are very small, with current experimental technique they fall within the experimental error. However, the broadening of the 110 and 211 diffraction peak from the from the bcc vanadium are a good indicator for the beginning of the transition. The new phases are confirmed with Rietveld refinement as well, but the diffraction peaks relative full width at half maximum can be used as a good first indication for transition.

Figure V.3 XRD integrated patterns from isothermal compression of vanadium at room temperature (left/black) and 425 K (right/red)
From the experimental report of Ding et al. seemed very unusual that the transition pressure for quasi-hydrostatic sample is smaller than for sample compressed without pressure medium. We performed experiments both under hydrostatic conditions using various pressure media (Ar, Ne, He) and under non-hydrostatic condition (only sample loaded with Pt pressure marker). Experiments and samples described in our paper (62).

In Figure V.3 integrated patterns are shown at different pressure points from isothermal compression of vanadium at ambient and 425 K from ambient pressure to 70 GPa, the peaks are indexed to bcc, if we follow the 110 and 211 peaks width relative to the 200 peak we notice a broadening and at higher pressures the split is almost visible. From the broadening of these peaks plotted as a function of pressure (figure V.4) we see similar behavior and the only difference between the room temperature and high temperature compression is the pressure at which the broadening begins. From these experiments results a much lower bcc-rhombohedral transition than reported by Ding et al. However, the obtained rhombohedral phase is consistent with the theoretically predicted β phase, $\alpha=109.61^\circ$ (62) (the angle between the basis vectors) being larger than the $109.47^\circ$ corresponding to the perfect cubic. We found that at room temperature the transition begins at 30 GPa, which is much lower than the 69 GPa previously reported. At 425 K
the transition happens at 37 GPa indicating a positive phase line between bcc and \(\beta\) phases. Transition pressures were confirmed by Rietveld refinement included in ref (62).

Under quasi-hydrostatic conditions the peak broadening is not that evident. Only in case of Ar pressure medium the broadening can be used as an indicator of transition. When Ne is the pressure medium (much softer than Ar) no evident peak broadening is observed. However, plotting the difference between the actual peak position and ideal bcc position (Figure V.5) one can notice an evident discontinuous jump for the 110 and 211 peaks. From the pressure of discontinuity indexing the peaks to the rhombohedral structure yields a much better fit that the bcc fit. This transition pressure of 61 GPa is in excellent agreement with the ones previously reported in ref (59) and (61).

![Figure V.5 Difference between actual peak positions and ideal bcc positions in vanadium compressed in Ne pressure medium.](image)

In table V.2 we summarize our relevant experiments performed on vanadium with different pressure media and include the Vinet EOS parameters obtained by fitting the data from our experiments. A general observation regarding the transition pressure is that the “softer” the pressure medium the higher the transition pressure and more close to the one calculated under ideal perfect hydrostatic conditions. When the pressure medium used is He we did not observe
the transition up to 70 GPa this is not unexpected since as it results from theoretical calculations 
the bcc structure can exist as a metastable structure to 130 GPa (60)

<table>
<thead>
<tr>
<th>Temp</th>
<th>P.med</th>
<th>P.mark</th>
<th>Trans P</th>
<th>Vinet EOS param</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>Ar</td>
<td>Cu</td>
<td>57 GPa</td>
<td></td>
</tr>
<tr>
<td>300 K</td>
<td>Ne</td>
<td>Pt</td>
<td>61 Gpa</td>
<td>(V_0=13.909 \text{ Å}^3) (K_0=179.09(\pm8.37) \text{ GPa}) (K_0'=3.11(\pm1.23))</td>
</tr>
<tr>
<td>425 K</td>
<td>He</td>
<td>Pt</td>
<td>&gt;70GPa</td>
<td>(V_0=13.952 \text{ Å}^3) (K_0=175.46(\pm8.37) \text{ GPa}) (K_0'=3.39(\pm0.49))</td>
</tr>
<tr>
<td>300 K</td>
<td>No med</td>
<td>Pt</td>
<td>30 GPa</td>
<td></td>
</tr>
<tr>
<td>425 K</td>
<td>No med</td>
<td>Pt</td>
<td>37 GPa</td>
<td>(V_0=13.952 \text{ Å}^3) (K_0=202.2(\pm37.4) \text{ GPa}) (K_0'=1.71(\pm1.51))</td>
</tr>
</tbody>
</table>

Our experiments confirm the existence of previously reported rhombohedral phase of 
Vanadium at higher pressure. We report a dependence of the transition pressure as a function of 
the pressure media, the less hydrostatic the compression the lower the transition pressure, thus 
we find the bcc→rhombohedral phase transition occurring as low as 30GPa for compression 
without any pressure medium and as high as 61.5 GPa. Also we found a positive slope for the 
bcc→rhombohedral transition under non hydrostatic conditions.
VI. Conclusions

Understanding behavior of the matter under high pressure and temperature is important for basic science and planetary physics. Varying pressure and temperature in a controlled fashion at extreme condition is needed to collect meaningful information from samples, which in many cases require maintenance of high pressure and temperature for extended period of time. In this study we presented an external resistive heating setup that we designed for the LLNL membrane diamond anvil cell, but it can be easily adapted to any piston-cylinder type DAC with openings in the cylinder at the diamond level. With the mDAC placed in a vacuum jacket we were able to reach temperatures up to 1300 K with as little as 175 W total heating power, while keeping the cell body several hundred degrees cooler to avoid causing strength and oxidation damage to the cell due to high temperatures. We used the high temperature setup in the exploration of the CO$_2$ phase diagram (5), in-situ Raman spectroscopy study of N$_2$ (2) and melting studies of H$_2$.

As presented, in this thesis we began our work on molecular systems by investigating the melting of molecular hydrogen. We faced experimental challenges in containing the hydrogen sample in the sample chamber at high pressures and temperatures to cross the solid-liquid line in the p-T diagram. We were able to reproduce the existing melting curve up to 26 GPa, the second highest pressure at that time. However, finding the gasket material capable of holding the liquid hydrogen at temperatures in excess of 700 K for long enough time to measure pressure and detect the melting proved to be difficult. The right gasket material would allow us experimental verification of melting line well beyond the predicted maximum.

We performed in-situ Raman spectroscopy on solid molecular nitrogen at 900 K isotherm up to 105 GPa on several different occasions. The high temperature setup and our gasket choices proved their stability, by allowing experiments to be carried out for more than 12 hours for each sample, time long enough to obtain good quality Raman spectra from even the very thin, weak scattering samples. We found that ε molecular phase with rhombohedral symmetry has the largest stability field in the p-T domain. However, following certain p-T paths other molecular phases can be accessed at high pressure and temperature. We found that the θ phase of molecular nitrogen forms at 92 GPa only from quenched samples that crosses the ε-ζ boundary along the
isobar down and then up, followed by further isotherm compression at 900 K. By simple isotherm compression or isobaric heating to the p, T domain where θ was found proved only the stability of the ε phase.

Compressing H₂O ice to 180 GPa lead us to the conclusion that transition from the molecular ice VII phase to the symmetric ice X phase is a slow transition, and implies a volume change across the transition leading to a solid with higher bulk modulus. Up to the highest pressure we found no evidence for new ice phases.

Using synchrotron x-ray diffraction in studying vanadium at high pressures we confirm the transition from the bcc crystalline phase to a rhombohedral structure at 62 GPa when compressed under quasi-hydrostatic conditions in Ne pressure medium. However this transition pressure shows strong dependence on the pressure transmitting medium, the less hydrostatic the compression the lower the transition pressure. Without pressure medium we found the transition taking place at pressure as low as 30 GPa at room temperature. When sample compressed without pressure medium at 425 K the transition to the rhombohedral phase occurred at 37 GPa hinting to a positive phase line on the p-T diagram of vanadium between the low pressure bcc and the rhombohedral phases.
VII. Bibliography


55. *Equation of state if V and Nb under truly hydrostatic conditions.* Takemura, Kenichi. [ed.]


