

**MAGNETIC-ELECTRONIC PRESSURE RESPONSE OF
ILMENITE (FeTiO₃)**

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Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

(Wisdom Nkosilathi Sibanda)

----- Day of ----- 2010

Abstract

Polycrystalline powders of synthetic and natural Ilmenite (FeTiO_3) assemblages pressurized in a diamond anvil cell have been studied at room temperature using ^{57}Fe Mössbauer spectroscopy to elucidate the magnetic-electronic properties of different ilmenite samples. Natural ilmenite samples used included an untreated sample derived from the Hillindale mining area in KwaZulu-Natal, South Africa and a heat treated sample of the Hillindale sample (labeled SLS). Careful attention has been paid to the source-DAC-detector arrangement to obtain satisfactory count rates for a good signal-to-noise ratio. This has been achieved by using the 80° wide aperture of a Boehler-Almax diamond anvil cell as the entrance aperture for the 14.4 keV resonant γ -rays.

The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the natural sample (SLS) shows a gradual increase from 0 GPa to 14 GPa the highest pressure reached for that sample. The ratio increases gradually from 0.28 to 0.38 at 14 GPa. The phase abundance of the ferric component, in the synthetic sample as deduced from the theoretical fits from the data increases from 0% to 15% at 18.5 GPa, then decreases at higher pressure. A perovskite high pressure phase initiates at ≈ 18 GPa corresponding to Fe^{2+} in dodecahedral coordination, and over a wide pressure range coexists in ever increasing abundance with the corundum-type low-pressure phase. The relative content of Fe^{2+} in the perovskite phase increases at the expense of Fe^{2+} in the low-pressure ilmenite phase. The transition to the perovskite phase is sluggish at room temperature. The trend observed in the abundances of the ferric and ferrous components in the untreated sample is similar to what is seen in the synthetic and SLS sample, in that there is an increase in the abundance of the ferric component and a corresponding decrease in the abundance of the ferrous component. In the

relatively low pressure region (up to 4 GPa), the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the untreated natural sample significantly increases and continues to slowly increase in a “plateau” region. The ratio is ≈ 0.10 at 0 GPa and ≈ 0.30 at 15 GPa, the highest pressure reached for the sample.

Appreciable asymmetry in the Mössbauer lineshape profile is initiated at low pressure and persists to the highest pressure in all samples. This is more evident in the synthetic sample which has a symmetric doublet at ambient pressure. The asymmetry is perhaps attributed to Fe^{3+} emerging (i.e. pressure-induced oxidation). Metal-metal charge transfer along the *c*-axis of the unit cell between face sharing octahedra of Fe^{2+} and Ti^{4+} cations may be one, albeit, contentious explanation for this. ^{57}Fe Mössbauer experiments using a pelleted sample of synthetic ilmenite show that the asymmetry features due to pelleting (texturing) and development of Fe^{3+} (in a diamond anvil cell) in the sample are different as evidenced by the Mössbauer line profile of the spectra.

Dedication

To my Family;

My Dad and Mum

Pha, Phathi, Sne, and Co.

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Chapter 1

INTRODUCTION

1.1 Preamble and Background

The knowledge of the structure and properties of minerals in the pressure and temperature conditions that exists in the Earth's interior play a crucial role in understanding and interpreting geological and geophysical observations. For earth-science studies, high-pressure and/or high-temperature experiments are the only possible ways to investigate minerals under conditions equivalent to the Earth's interior providing information on phenomena occurring at these depths. Experiments that investigate the behaviour of minerals under extreme conditions link the behaviour of electrons and nuclei with the global processes that affect planetary bodies in the solar system. The material properties arise directly from the behaviour of electrons and nuclei. The materials are studied with respect to their fundamental properties, such as their crystal chemistry, equation of state, bonding and magnetism. At elevated pressures (0 – 20 GPa), the chemical and physical properties are altered with changes in ionic radii, electronic structure and bonding characteristics.

At high pressure-temperature conditions, representative of the Earth's interior, magnetic-electronic transformations may occur in Fe-containing solid-solutions of minerals like magnetite-ulvöspinel and ilmenite-hematite. These solid-solutions have an important role as the possible cause of magnetic anomalies observed in the Earth's deep crust and on other planets (Pentcheva and Nabi, 2008; Robinson et al., 2002). Laboratory based high-pressure and/or high-temperature experiments offer

the only means to probe directly (in-situ) the chemical and physical changes which occur in such solid solutions that comprise the interiors of planets. These measurements are carried out using experimental set-ups with diamond anvil cells (DAC), in which a tiny specimen is compressed between two culets of two gem quality diamonds. Since the surface areas of the culets are very small (200 μm – 500 μm), pressures greater than 100 GPa may be reached.

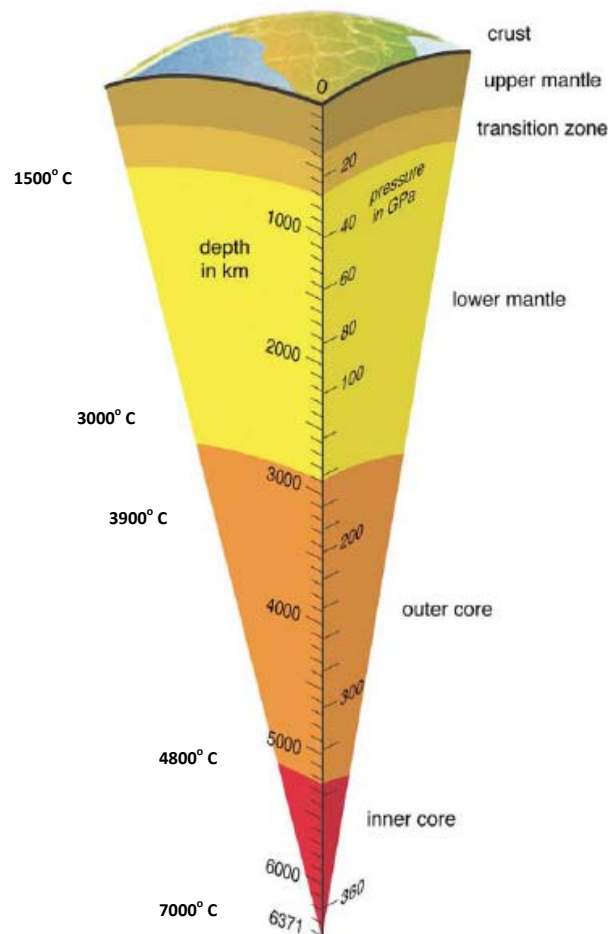


Figure 1.1: Pressure and temperature depth conditions in the Earth's interior (Boehler, 2005).

The principal effect of high pressure is a reduction in volume, which results in the shortening of the mean inter-atomic distances and intra-atomic distances (Bedassa, 2000). These structural changes introduce physical and chemical changes

in the sample materials, which may result in new properties of materials. Selected examples of pressure-induced properties are: metallization of insulating materials and pressure amorphization. There may also be structural-crystallographic transitions to new phases with physical properties that are different to that at ambient conditions (Hearne, 1999).

The development and implementation of the DAC as a high pressure research tool has revolutionised high pressure research in condensed matter physics (Jayaraman, 1986; Boehler, 2005). The feasibility of carrying out simulated laboratory experiments on minerals containing iron under the pressures and temperatures representative of the Earth's core has provided a wealth of information on physical processes that affect the earth. Some of the processes in the Earth's interior include heat transfer through the mantle and seismic velocity discontinuities (Amthauer, 1982). Much of today's knowledge of the behaviour of solids at elevated pressures of tens of GPa can be attributed to the DAC. Since its invention five decades ago the DAC has been developed for various experimental investigations, such as the pressure-temperature behaviour of materials (see Jayaraman, 1986), resistance and electrical conductivity measurements of samples.

Mössbauer spectroscopy (MS) used with the DAC in high pressure studies is an effective technique in analysing Fe-bearing compounds derived from the Earth's interior. Iron is the most abundant transition element and minerals that contain iron belong to the main constituents of the crust and mantle. Mössbauer spectroscopy serves as a non-destructive technique that can be used to obtain information on the magnetic-electronic and crystal-chemical properties of iron solid solutions as a function of various thermodynamic conditions of pressure and temperature. Mössbauer spectroscopy is the only technique that is readily available for the

investigation of magnetic phenomena at high pressures (Hearne et al., 1994; Pasternak et al., 2006).

Mössbauer spectroscopy has also received renewed publicity in the geosciences community as a result of the inclusion of two miniaturised Mössbauer spectrometers on the NASA Mars Exploration Rovers (Schröder et al., 2006; Dyar et al., 2006). Goethite, an iron oxide-hydroxide and jarosite, an iron hydroxide sulphate were identified by the Mössbauer spectroscopy on a crater, providing in situ evidence of an aqueous history on Mars (Schröder et al., 2006). Hematite was also identified providing further evidence of an aqueous history on Mars.

Mössbauer spectroscopy identifies Fe oxidation states, electronic configuration (high-spin or low spin Fe cations), magnetic ordering, quantifies the distribution of Fe between mineralogical phases, and provides information about the crystallinity and particle sizes of minerals (Schröder et al., 2006). For the mineralogist and the petrologist investigation of site occupancies in minerals is of paramount importance. The common techniques used for determining site occupancies are X-ray and neutron diffraction measurements (Bedassa, 2000). In the case of iron-bearing minerals, Mössbauer spectroscopy is a cheap alternative (Bedassa, 2000).

The assignment of the oxidation state in minerals is from the Mössbauer hyperfine interaction parameters, isomer shift and quadrupole splitting and hyperfine magnetic field. The knowledge of the oxidation state of Fe in mineral compounds and the ratio of its two mineralogical important cations Fe^{2+} and Fe^{3+} help explain phenomena such as colour, oxidation and weathering of minerals (Bedassa, 2000). Distortions in the symmetry of the bonding environment and the local structure around the Mössbauer active atom are reflected in the quadrupole splitting of the Mössbauer spectrum. An increase in the co-ordination number for both Fe^{2+} and Fe^{3+} gives a variation in the isomer shift enabling the detection of minute amounts of Fe in individual sites.

In this study, we use high-pressure ^{57}Fe Mössbauer spectroscopy at room temperature to investigate the magnetic-electronic properties of the selected mineral, ilmenite. Ilmenite (FeTiO_3) is one of mixed valence transition metal bearing minerals derived from the Earth's interior, in which Fe is expected to have the oxidation state Fe^{2+} and Ti is Ti^{4+} (Zhang et al., 2006). There may also be some oxidation of Fe^{2+} to Fe^{3+} with increasing pressure.

Ilmenite is commonly found as an inclusion in kimberlites, a type of igneous rock (Wilson et al., 2005). The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in mineral assemblages is considered to be an important indicator of temperature and oxygen fugacity at the time of the pressure-temperature equilibration of the assemblage. The knowledge of the oxidation state of ilmenite under various pressure-temperature conditions would potentially render it as a useful geobarometer/thermometer for ilmenite bearing rocks and an indicator of the crystal-chemical conditions of the mantle under which diamond formation has occurred (Bedassa, 2000).

The unique magnetic properties of ilmenite-hematite ($\text{FeTiO}_3\text{-Fe}_2\text{O}_3$) solid solutions has received interest in the earth and planetary sciences research fields as a possible cause of magnetic anomalies in the Earth's deep crust and on other planets

(Pentcheva and Nabi, 2008). Hematite (Fe_2O_3) is a canted antiferromagnet and ilmenite (FeTiO_3) is a room temperature (RT) paramagnet, but the solid solution of hematite and ilmenite is ferrimagnetic. According to McEnroe et al., (2005), the ilmenite-hematite ($\text{FeTiO}_3\text{-Fe}_2\text{O}_3$) system has been shown to carry a strong and stable remanent magnetization, which can account for the magnetic anomalies in the Earth's deep crust and on other planets, which do not have an internal magnetic field. Large magnetic anomalies were mapped by the Mars Global Surveyor (NASA, USA) program on ancient crusted areas on Mars. The presence of magnetization in the absence of an internal magnetic field indicated that the measured magnetization was due to a memory of an ancient magnetic field i.e. a remanent magnetization. It was found that, where the measured magnetization was strongest, the rocks were comprised of the ilmenite-hematite ($\text{FeTiO}_3\text{-Fe}_2\text{O}_3$) solid solution series.

Magnetic properties of the ilmenite-hematite ($\text{FeTiO}_3\text{-Fe}_2\text{O}_3$) and solid solutions ($\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$) have also received considerable attention because of their potential in the fabrication of spintronic devices (Takada et al., 2007; Fujii et al., 2008). According to Takada et al., (2007) the intermediate compositions ranging from $0.5 < x < 0.85$ are semiconducting and ferromagnetic, and theoretical calculations predict that these solid solutions should be magnetic semiconductors with a high Curie Temperature (T_C). The challenge therefore is to design ferromagnetic semiconductors of the likes of ilmenite-hematite ($\text{FeTiO}_3\text{-Fe}_2\text{O}_3$) or dilute magnetic semiconductors, which operate at room temperature (RT) for spintronic devices (Pentcheva and Nabi, 2008; Chambers et al., 2006).

1.2 Aim and Objective

There has been previous investigations of the pressure response of ilmenite (Seda and Hearne, 2004; Vaughan and Drickamer, 1967; Boekema et al., 1976). Seda and Hearne (2004) reported that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in a natural sample showed a rapid increase from ambient pressure up to a pressure of approximately 2 GPa, as deduced from the Mössbauer pressure studies. The ratio which was initially 0.2 at ambient pressure, saturated to 0.65 beyond 2-4 GPa to the highest pressure of 14 GPa used in the study. This corresponded to an increase in Fe^{3+} content of 13% at 0 GPa to 30% at 14 GPa (see Figure 1.2).

Some authors have studied the high pressure response of synthetic ilmenite at room temperature (Wu et al., 2009; Ming et al., 2006; Yamanaka et al., 2007; Zhang et al., 2006). Using high pressure ^{57}Fe Mössbauer spectroscopy, Wu et al., (2009), found that the Fe^{3+} content in their sample showed an increase of 13% around 16 GPa. An increase in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio has been attributed to intervalence charge transfer (Seda and Hearne, 2004). The charge transfer is of the form $\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow \text{Ti}^{3+} + \text{Fe}^{3+}$, with an increase in the abundance of the ferric component (Fe^{3+}) and a corresponding decrease in the ferrous component (Fe^{2+}). This is still a contentious explanation for this dramatic change in Fe oxidation state.

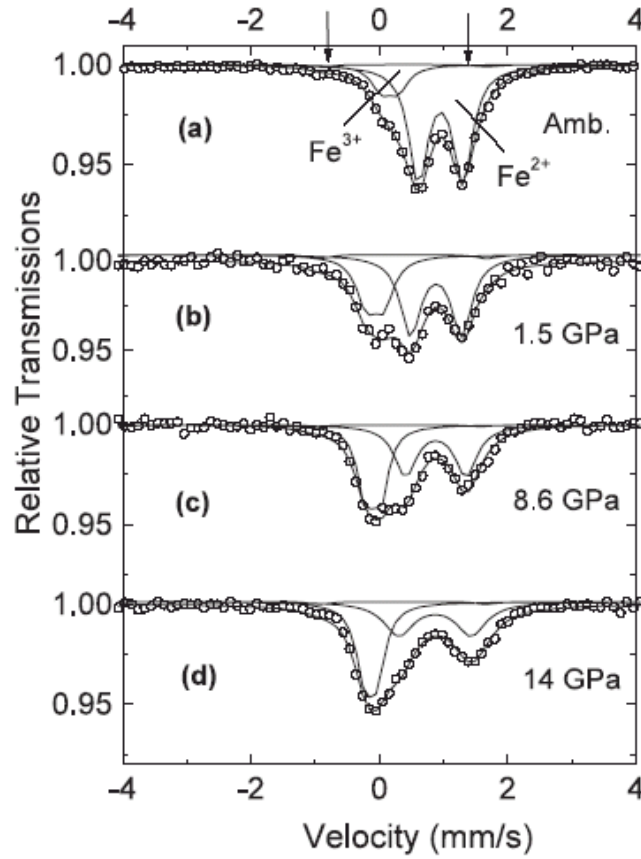


Figure 1.2: The dramatic pressure evolution of ^{57}Fe Mössbauer spectra of an untreated FeTiO_3 sample at room temperature observed by Seda and Hearne (2004). The spectra showed a pronounced increase in the relative intensity of the ferric Fe^{3+} component with pressure. This behaviour was also observed for a heat-treated sample of ilmenite.

Other studies (Zhang et al., 2006) explained the increase in electrical conductivity of ilmenite at high pressures (8-16 GPa) and temperatures (300-600 K) as due to hopping of small polarons due to charge transfer $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$. Agui et al., (2009) used resonant inelastic soft x-ray scattering (RIXS) and attributed energy losses in Ti 2p RIXS spectra of FeTiO_3 as being due to intermetallic charge transfer. According to Agui et al., (2009), because the oxygen octahedra are face sharing, intermetallic orbital overlap can occur directly thus charge transfer between Fe and Ti can occur during excitation with phonons. Yamanaka et al., (2007) using maximum entropy method (MEM) analysis of single-crystal XRD intensities attributes the charge

transfer mechanism to be between Fe and Ti via O^{2-} anions. Yamanaka et al., (2007) and Wu et al., (2009) note that there is an increase in charge density between Fe-O and Ti-O in ilmenite with pressure due to the decrease in bond length. The resulting charge transfer is then via the orbitals of the O^{2-} anion. The same results show that there is a decrease in charge density between the Fe-Ti connection hence making charge transfer between this path unlikely. This puts charge transfer between Fe and Ti via O^{2-} on par with the intervalence charge transfer proposed by Seda and Hearne (2004), Zhang et al., (2006) and Agui et al., (2009).

The primary goal of the study is to monitor the magnetic-electronic state of Fe in various ilmenite ($FeTiO_3$) samples under in-situ pressure conditions in the diamond-anvil cell. As a corollary of this goal, we study the pressure evolution of the Fe^{3+}/Fe^{2+} ratio in ilmenite (natural and synthetic) samples sourced from different locations. This will be a recheck of the previous measurements of Seda and Hearne (2004) using different experimental conditions (e.g. pressure medium and spectrometer) but identical natural sample which originates from a specific location in South Africa. We monitor the magnetic-electronic behaviour of a separate synthetic ilmenite sample to elevated pressures of 30-40 GPa. The pressure response of a separate natural ilmenite sample is also monitored.

The main body of this dissertation is as follows; Chapter 2 presents a theoretical background on the Mössbauer Effect. Chapter 3 details the high-pressure methodology with particular emphasis on the Merrill-Basset DAC which was used for all high pressure ^{57}Fe Mössbauer measurements in this work. The electronic, magnetic and structural properties of ilmenite are reviewed in Chapter 4. The experimental details are outlined in Chapter 5 where DAC preparation and the high-pressure ^{57}Fe Mössbauer facility are described. In Chapter 6 the experimental results and their analysis, followed by the discussions and conclusions are given.

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Chapter 2

THEORY OF THE MÖSSBAUER EFFECT

2.1 Introduction

The Mössbauer effect is the resonant emission and absorption of γ -ray photons by nuclei of atoms. The recoilless γ -ray distribution has a natural line width (Γ), of the order of 10^{-8} eV, which is extremely small compared to the γ -ray energy of $\approx 10^4$ eV. The use of recoilless γ -rays with a well-defined energy in Mössbauer spectroscopy allows for the detection of minute nuclear energy level differences between nuclei in the source and absorber. As a corollary of this it is possible to detect the extremely small effect of hyperfine interactions between the nucleus and its local environment. These hyperfine interactions lead to shifts and splitting of the nuclear energy levels of the order of $\approx 10^{-7}$ eV (Dyar et al., 2006; Greenwood and Gibbs, 1971) and reflect the changes in the electronic, magnetic, geometric, or defect structure as well as in the lattice vibrations.

2.2 Resonant emission and absorption of γ -rays

A nucleus with Z protons and N neutrons in an excited state of energy E_e decays to the ground state of energy E_g by emitting a γ photon of energy $E_e - E_g$. The γ photon may be absorbed by a nucleus of the same kind (same Z and N) in the ground state, and transition to the excited state E_e takes place (resonant

absorption). The subsequent emission to the ground state produces a conversion electron or γ photon (resonant fluorescence), see Figure 2.1.

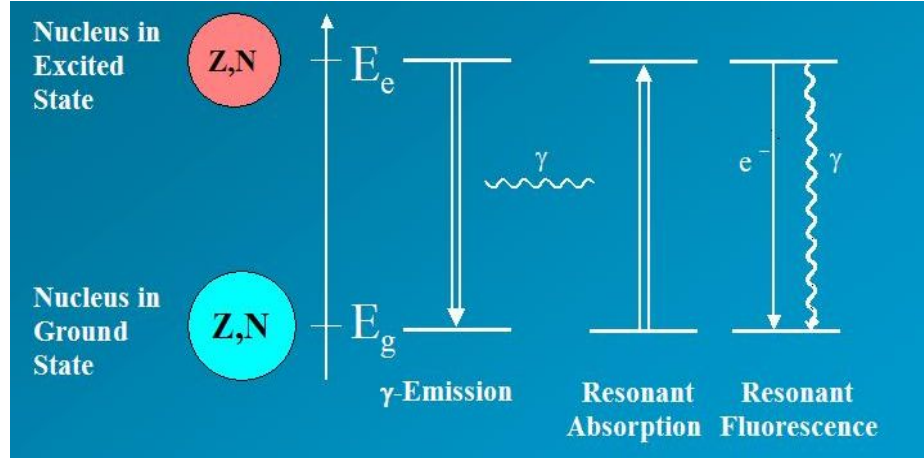


Figure 2.1: Mössbauer effect, recoilless nuclear resonance absorption and fluorescence of γ -radiation (Gutlich, 2005).

A free nucleus experiences recoil when it emits or absorbs a γ -ray due to conservation of momentum (see Gonser, 1975; May, 1971). The nucleus recoils with energy:

$$E_R = \frac{E_e^2}{2Mc^2} \quad (2.1)$$

where M is the rest mass of the atom, and c is the speed of light, see Figure 2.2. For a free ^{57}Fe nucleus, $E_R = 1.9 \times 10^{-3}$ eV (May, 1971).

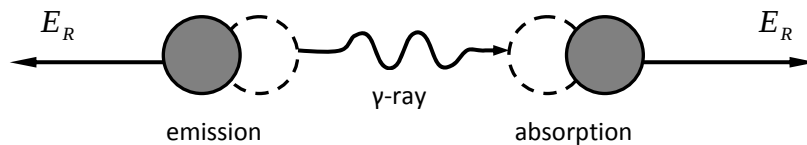


Figure 2.2: Recoil energy E_R received by an isolated nucleus up on γ -ray emission or absorption.

The emitted γ -ray has energy, $E_\gamma = E_e - E_R$ hence its energy is less than the transition energy. For the γ -ray to be resonantly absorbed, $E_\gamma \geq 2E_R$. This can be achieved by fixing the nucleus in a lattice, thus increasing M and suppressing E_R . Mössbauer discovered that when the atoms are within a solid matrix, the effective recoil of the nucleus is very small (Mössbauer, 1961). The recoiling mass is now effectively the mass of the whole system making E_R very small. If the γ -ray energy is small enough, the recoil of the nucleus is too low to be transmitted as a vibration (phonon mode) in the crystal lattice and so the whole system recoils, making the recoil energy practically zero and a recoil free event.

2.3 Recoil-free fraction, (or the Mössbauer-Lamb Factor)

The probability of a recoil-free transition increases when the atom is placed in solid lattice as detailed in the section before. Not all nuclei undergo recoil-free transitions because the energy of the γ -ray may cause excitation of a lattice vibrational mode, hence decreasing the energy of the emitted particle. The Mössbauer emission therefore corresponds to events where no phonon excitation occurs. The fraction of this emission event with zero phonon excitation is known as the recoil free fraction, f , or the Mössbauer-Lamb factor. The Mössbauer factor is therefore a measure of the probability of recoil-free resonance fluorescence of γ -photons. It is defined as the number of recoil-free γ events (emission or absorption) divided by the total number of γ events.

The probability that a zero-phonon transition occurs, in which there is no energy lost to the lattice is given by (Kuzmann et al., 2003; Dyar et al., 2006):

the recoil-free probability, $f = 1 - E_R / (\hbar\omega)$, where f is finite and $E_R = \hbar\omega$, and

$$f \propto \exp\left[\frac{-E_\gamma^2 \langle x^2 \rangle}{(\hbar c)^2}\right]. \quad (2.2)$$

The quantity $\langle x^2 \rangle$ is the mean square vibrational amplitude of the emitter or absorber nucleus in the direction of the γ -ray. The probability of a recoil free transition therefore decreases exponentially with the square of the γ -ray. It is evident from equation 2.2, that f depends on the temperature. Higher temperatures lead to larger $\langle x^2 \rangle$ values; hence smaller values of f . Temperature and binding energies control the magnitude of $\langle x^2 \rangle$, hence lowering of temperature and increase in ionicity cause an increase in the value of f .

The Mössbauer factor can also be represented by the equation (Dickson and Berry, 1986):

$$f = \exp(-k_\gamma^2 \langle x^2 \rangle) = \exp(-2W) \quad (2.3)$$

where $\vec{k}_\gamma$ is the wave vector of the γ -ray and $\langle x^2 \rangle$ is the mean square displacement of the Mössbauer nucleus in the direction of the γ -ray propagation, $2W$ is the Debye-Waller factor. For a Debye model approximation which is valid for cubic monatomic crystals, f is given by:

$$f = \exp\left\{-\frac{6E_R}{k_B \Theta_D} \left[\frac{1}{4} + \left(\frac{T}{\Theta_D} \right)^2 \int_0^{\frac{\Theta_D}{T}} \frac{x}{e^x - 1} dx \right] \right\} \quad (2.4)$$

where k_B is Boltzmann constant, T is the temperature in Kelvin and Θ_D is the Debye temperature. For higher temperatures ($T \geq \frac{\Theta_D}{2}$), f is approximated to:

$$f = \exp\left\{-\frac{6E_R T}{k_B \Theta_D^2}\right\} \quad (2.5)$$

In the low temperature limit ($T \ll \Theta_D$), f is approximated to:

$$f = \exp\left\{-\frac{E_R}{k_B \Theta_D} \left(\frac{3}{2} + \frac{\pi^2 T^2}{\Theta_D^2}\right)\right\} \quad (2.6)$$

A satisfactory Mössbauer resonance can be expected if the value of the dimensionless quantity, the effective absorber thickness $t_a = f_a n_a \sigma_o$ is high enough (Bedassa, 2000; Maddock, 1987). In this product f_a is the Mössbauer fraction, n_a is the number of atoms per unit volume able to give rise to resonance and σ_o the cross-section for Mössbauer absorption. The cross-section of the resonant absorption centered at E_o , for a Lorentzian line form is given by:

$$\sigma = \sigma_o \frac{\Gamma^2}{\Gamma^2 + 4(E - E_o)^2} \quad (2.7)$$

where, σ_o is the maximum cross section and Γ is the full width of the resonance at half maximum (FWHM) absorption. From equations 2.5 and 2.6 the recoil free fraction is high when E_R is small. E_R is small when the resonant γ -ray energy is small hence this makes it difficult to observe the Mössbauer resonance effect for high energy γ -rays. Also, the resonance effect is hardly observed for γ -rays with low energies below 10 KeV. To observe the Mössbauer effect the γ -ray energy must be in the range 10-100 KeV. These conditions are fulfilled for the 14.4 keV γ -ray for the ^{57}Fe Mössbauer transition.

The decay scheme is shown in Figure 2.3 below:

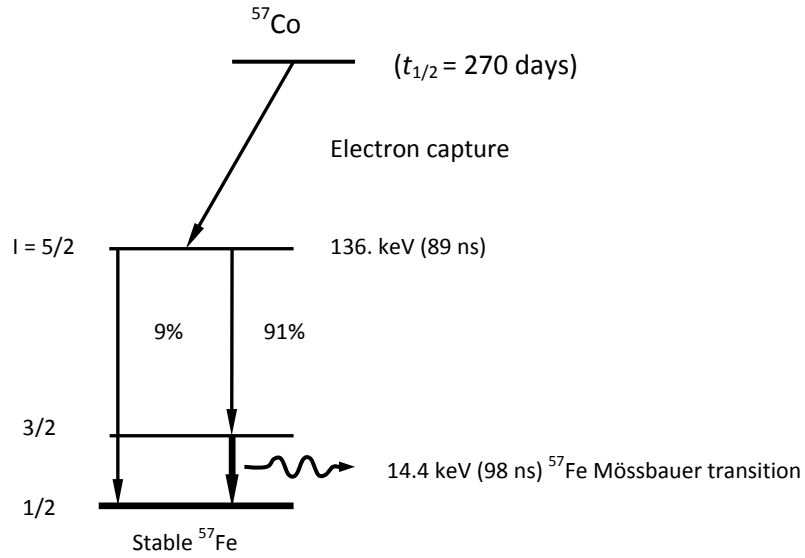


Figure 2.3: The decay of ^{57}Co by electron capture to ^{57}Fe , from which transitions take place involving emission of resonant gamma rays. I is the nuclear spin.

2.4 Hyperfine Interactions

The shifts and splitting of nuclear states caused by the electronic or magnetic couplings of the nucleus with electromagnetic fields are important to materials scientists. They are related to the local environment of the nucleus. In the absence of hyperfine interactions, the spectral line will always be centered at zero energy (velocity) without being shifted or split. The recoilless γ -rays have an extremely well defined energy, limited by the Heisenberg's Uncertainty Principle, according to the equation,

$$\Gamma = \frac{\hbar}{\tau} \quad (2.8)$$

where Γ is the line width and τ is the mean life of the excited state.

The line width (energy) is of the order of 10^{-8} eV, while the ^{57}Fe Mössbauer resonant γ -ray has energy of the order of 10^4 eV. Resonant absorption will occur if the energy level at the emitter site matches that at the absorber nuclear site to within a resolution of 1 part in 10^{12} . Any differences in the energy levels of the nuclei between the source and absorber (shifts and splitting of the nuclear levels) that exceeds this line width can therefore be resolved.

Mössbauer's discovery of the recoilless emission and absorption of γ -rays allows the possibility of detecting changes in nuclear energy levels of the order of 1 part 10^{12} (Kolk, 1985;1987). The hyperfine interactions lead to shifts and splitting of the order of 100 neV. The high resolution of recoil-free emission and absorption of 14.4 keV γ -rays allows such small perturbations to be detected. This allows the possibility to monitor the hyperfine interactions of the nucleus with its environment, which in turn yield information regarding the magnetic state and electronic structure of the resonant atom in question. A description of these hyperfine interactions is presented in the following sections.

Due to the shifts and splitting of nuclear energy levels there is a mismatch in the energy needed for resonance to occur between the absorber and source. In order to have a matching energy, a γ -ray with variable energy (within the limit of the shift and splitting of levels) is required. To achieve this, the energy of the emitted γ -ray is changed in the direction of propagation by use of the Doppler effect. The energy of the recoilless γ -ray using the Doppler effect is given by,

$$E_{\gamma} = E_o \left(1 + \frac{v}{c}\right) \quad (2.9)$$

where v is the velocity of the source relative to the absorber and c is the speed of light.

The γ -ray emitted by the source and passing through the absorber is detected as a function of the velocity of the source. The arrangement for observing the Mössbauer effect using the Doppler effect is shown in Figure 2.4 for horizontal transmission geometry.

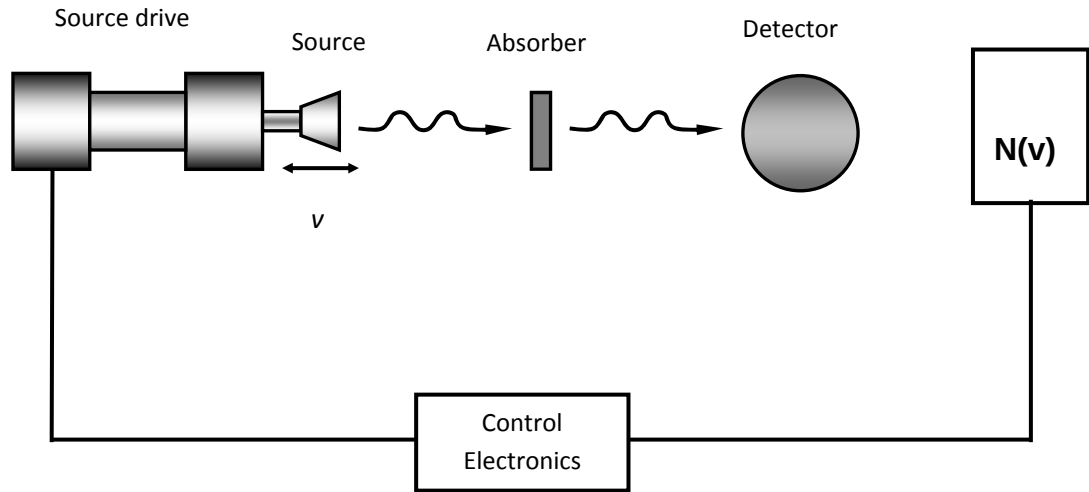


Figure 2.4: Typical Mössbauer spectroscopy arrangement in horizontal transmission geometry mode, using the Doppler Effect.

2.4.1 Electric Monopole Interaction (Isomer Shift)

Isomer shifts are caused by an electric monopole interaction, which is the interaction between the electrons of the atom and the nuclear charge of finite extent (finite radius). The local environments around Fe atoms in the source and absorber are different, hence there is a mismatch in transition energies and resonant absorption does not occur (see Figure 2.5).

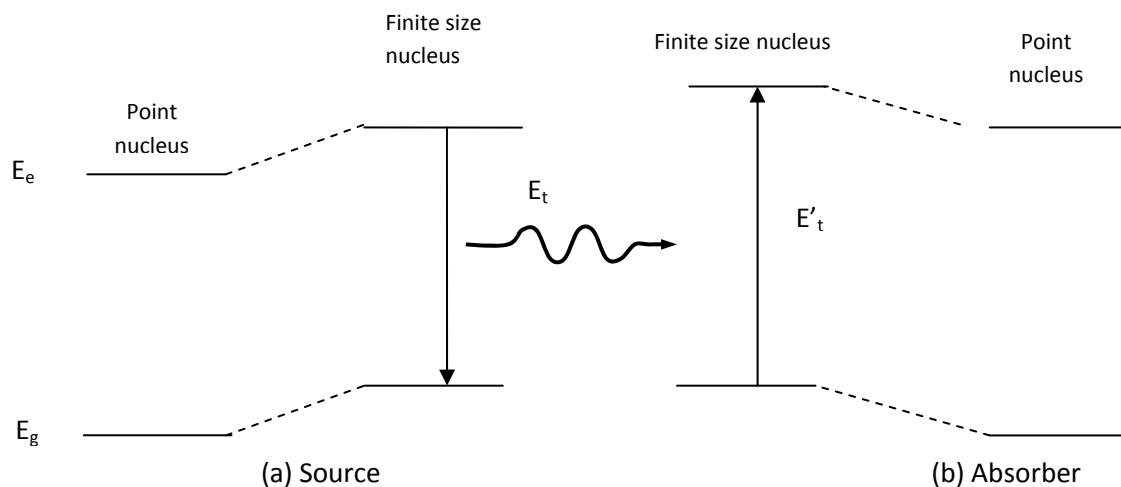


Figure 2.5: (a) Resonance absorption does not occur because there is no match in transition energies between absorber and source (b) no resonance absorption occurs because of mismatch in transition energies. $E_t - E'_t$ is the isomer shift.

The difference in energies is denoted by the isomer shift of the spectrum and results in the absorption spectrum not being centered on zero relative energy but being offset from zero velocity (see Figure 2.6).

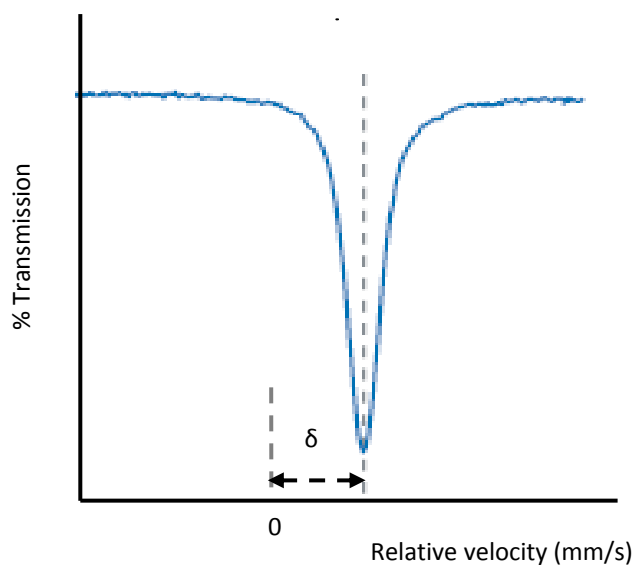


Figure 2.6: Isomer shift, δ , the peak minimum shifts from zero velocity reference.

The isomer shift is a function of the s -electron density at the nuclear site of both the absorber and source. The transition energy of a photon in a nucleus is, given by (Eriksson and Svane, 1989; Kolk, 1985):

$$E^o = E_o^o + \alpha\rho(0) \quad (2.10)$$

E_o^o , is the transition energy from a bare nucleus, $\alpha\rho(0)$ is the contribution to the transition energy due to electrostatic interaction between the nucleus and the electrons at the nuclear site. The term $\rho(0)$ is the contact density of the s -electrons at the nuclear site. $\alpha\rho(0)$ is proportional to the probability of finding s -electrons at the nuclear site, because only s -electrons affect $\rho(0)$. The quantity $\alpha\rho(0)$ will therefore change when an s -electron is added or removed. The s -electron density at the nuclear site is dependent on its interactions with the p , d and f electrons in their respective orbitals. These electrons are able to shield or screen the outer s -electrons from the nucleus hence affecting the spatial distribution of the s -electrons around the nucleus.

The isomer shift as determined in a Mössbauer experiment is given by,

$$\delta = \frac{2\pi}{5} Ze^2 \left\{ |\Psi_{(o)}|_a^2 - |\Psi_{(o)}|_r^2 \right\} (R_e^2 - R_g^2) \quad (2.11)$$

Z is the atomic number, e is the electronic charge, $|\Psi_{(o)}|_a^2$ and $|\Psi_{(o)}|_r^2$ are the s -electron densities at the absorber and source (emitter) nucleus respectively. R_e and R_g are the radii of the excited and ground state respectively. Furthermore the term $(R_e^2 - R_g^2)$ is negative. The isomer shift is therefore also a result of the finite size of the nucleus. In 3- d transition metal ions, an increase in the number of 3- d electrons, effectively decreases $|\Psi_{(o)}|_a^2$, and leads to an increased (less negative) isomer shift, because of the negative factor involving the nuclear radii.

An illustration of this is provided by the two mineralogically important cations $\text{Fe}^{2+} (\text{d}^6)$ and $\text{Fe}^{3+} (\text{d}^5)$. The $\text{Fe}^{2+} (\text{d}^6)$ ions have more electrons in the 3-*d* orbital than the $\text{Fe}^{3+} (\text{d}^5)$ ions, and therefore $\text{Fe}^{2+} (\text{d}^6)$ has a greater screening of the *s*-electrons. This greater screening leads to a decrease in $|\Psi_{(o)}|_a^2$, the *s*-electron density at the absorber nucleus. The resulting change in the isomer shift is positive because $R_e^2 - R_g^2$ is negative. The change is more positive for $\text{Fe}^{2+} (\text{d}^6)$ ions compared to $\text{Fe}^{3+} (\text{d}^5)$ ions and hence $\text{Fe}^{2+} (\text{d}^6)$ has a larger isomer shift compared to $\text{Fe}^{3+} (\text{d}^5)$. Therefore an increase in the 3-*d* electron density (more screening of the *s*-electrons) increases the isomer shift, an increase in 4*s* electron density decreases the isomer shift.

The isomer shift values obtained from the fitting of spectra give information on the oxidation state of Fe in a compound, coordination number, bonding properties of ligands, and the spin state (high-spin or low-spin). At room temperature Fe^{3+} in crystalline lattices gives isomer shift values between 0.20 – 0.50 mm/s and in minerals 0.30 – 0.50 mm/s (octahedral coordination). Tetrahedral coordinated Fe^{3+} in minerals has values of the isomer shift between 0.17 – 0.30 mm/s (Dyar et al., 2006).

2.4.2 Electric Quadrupole Interaction (Quadrupole Splitting)

The shape of a nucleus is not always spherical. If the nucleus has a non-uniform charge density (ellipsoid shaped), then it possesses a nuclear quadrupole moment eQ . This is the case when the nuclear spin is ($I \geq 1$). In such a case, the quadrupole moment, eQ may interact with the non-cubic electric field gradients (EFG). In the presence of a non-spherically symmetrical electrical field the excited state having non-spherical charge distribution may assume different orientations (quantized

energies) in relation to the EFG and the energy levels split (see Figure 2.7). For Fe with $I = \frac{3}{2}$, the excited state splits into two substates, $m_I = \pm \frac{1}{2}$ and $m_I = \pm \frac{3}{2}$. The difference in transition energy between the two states is the quadrupole splitting, ΔE_Q .

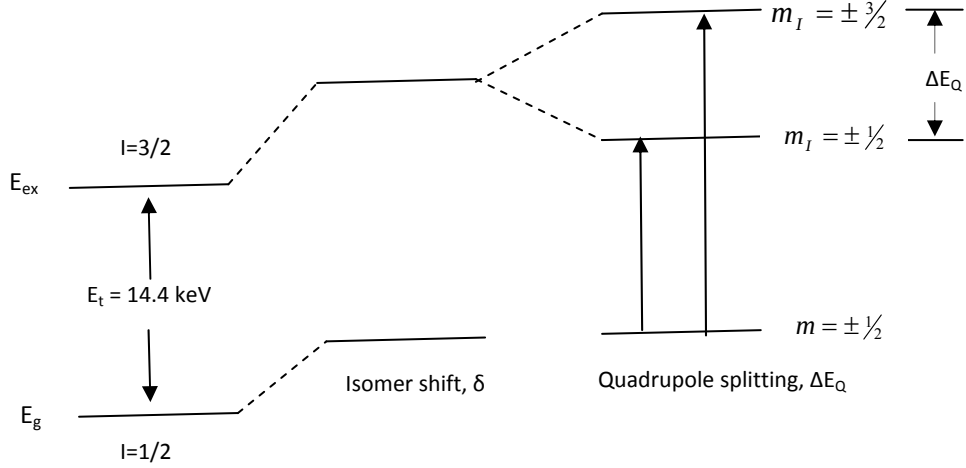


Figure 2.7: Interaction of the nuclear quadrupole moment with the electric field gradient leads to a splitting of the nuclear energy levels. Transitions from the ground state cause the transmission spectrum to split into a doublet (two resonance dips), the velocity separation of which is a measure of ΔE_Q .

The magnitude of the splitting, the quadrupole splitting (ΔE_Q), is proportional to $\frac{1}{2}e^2qQ$. ΔE_Q is therefore,

$$\Delta E_Q = \frac{1}{2}e^2qQ \left(1 + \frac{\eta^2}{3}\right)^{1/2} \quad (2.12)$$

The quantity, Q is the nuclear quadrupole moment, e is the charge on a proton, eq is the z -component of the electric field gradient tensor (V_{zz}) in the principal axes system and η is the asymmetry parameter, $\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$ ($0 \leq \eta \leq 1$). The quantity eq is the gradient of electric field at the nucleus and has a contribution of terms from the valence electrons and the surrounding charge distribution from the crystal

lattice. $q = (1 - \gamma_\infty)q_{latt} + (1 - R)q_{val}$ where γ_∞ and R are the Sternheimer anti-shielding and shielding factors respectively (Goodman, 1982). The quantities q_{latt} and q_{val} are contributions from the crystal lattice (nearest neighbor charge) and valence electrons respectively. In a cubic environment ΔE_Q is zero.

The resulting Mössbauer spectrum from ΔE_Q is shown in Figure 2.8 below:

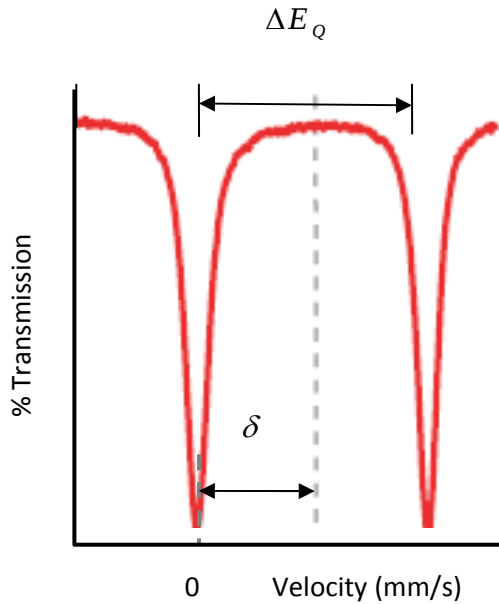


Figure 2.8: Quadrupole splitting, ΔE_Q in a Mössbauer spectrum and the associated isomer shift. The resulting spectrum is a doublet, of which the velocity separation of the two peaks gives the quadrupole splitting.

The quadrupole splitting reflects the symmetry of the bonding environment and that of the local environment near the Mössbauer active atom (Dyar et al., 2006). The quadrupole splitting also depends on the oxidation state and spin state, hence it can provide information on the ligand structure, electronic population of orbitals and isomerism phenomena of materials. A large value of the quadrupole splitting for Fe^{3+} indicates a strong distortion, that is, a departure from ideal local symmetry in the neighborhood of the ion (Putnis, 1992). In Fe^{2+} the electric field gradient is affected

by the distortion of the $3d^6$ electron cloud. This distortion changes the contribution of the electrons and the surrounding structure to the total electric field gradient leading to an increase in quadrupole splitting and then decreases (Putnis, 1992). Figure 2.9 shows typical values of isomer shifts and quadrupole splitting found in minerals.

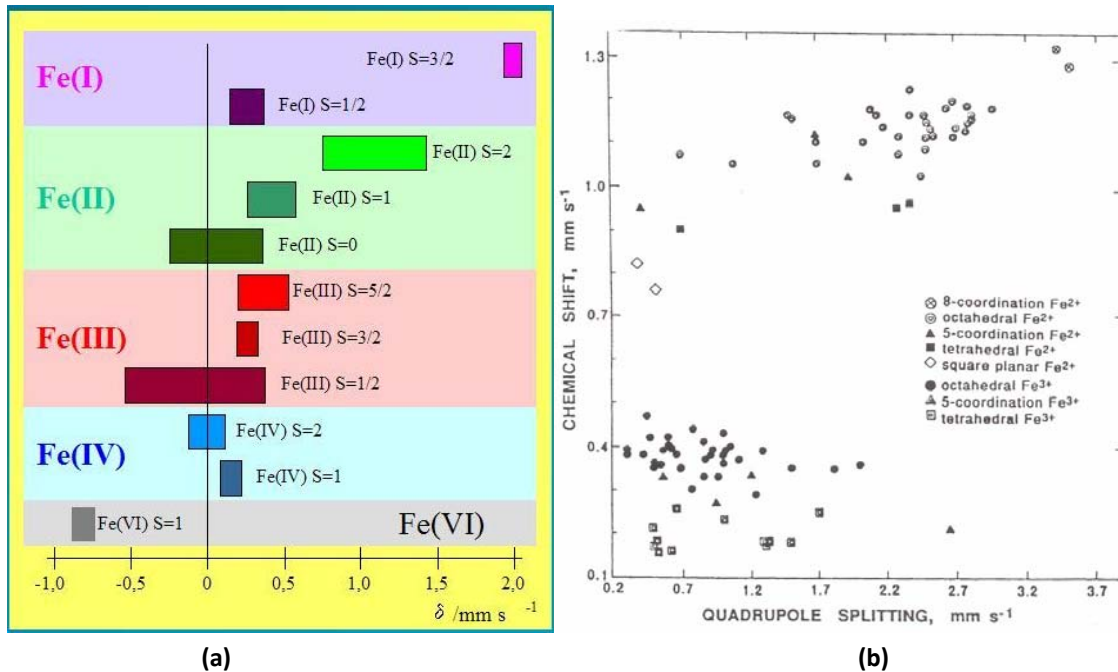


Figure 2.9: (a) Isomer shifts of different iron compounds (b) Correlations of chemical shift versus quadrupole splitting for Fe^{2+} and Fe^{3+} ions in a variety of coordination environments in different silicate and oxide minerals, Burns (1994).

2.4.3 Magnetic dipole interaction (Magnetic hyperfine field)

When a nucleus possesses a magnetic moment its degenerate energy levels can be perturbed if a magnetic field is present. This is the case for magnetically ordered material such as magnetite (Fe_3O_4) and iron. A nucleus with an angular momentum quantum number $I > 0$ has a magnetic dipole moment $\vec{\mu}$. The dipole moment may

interact with an external or local magnetic field $\vec{B}$ at the nucleus. This results in a splitting (nuclear Zeeman effect) of the degenerate nuclear state with I into $(2I + 1)$ non-degenerate substates. The magnetic interaction is given by (Greenwood and Gibb, 1971):

$$H_m = -\vec{\mu} \cdot \vec{B} = -g_N \mu_m \vec{I} \cdot \vec{B} \quad (2.13)$$

where g_N , is the nuclear Landé or gyromagnetic factor, and μ_m is the nuclear magneton. The effect of the magnetic field is to split the degenerate nuclear energy levels, thus removing degeneracy. In this case of ^{57}Fe , the $I = \frac{1}{2}$ level splits into two substates and the $I = \frac{3}{2}$ level splits into four substates, see Figure 2.10 (a). Six nuclear resonance transitions occur conforming to the selection rule $\Delta m_I = 0, \pm 1$.

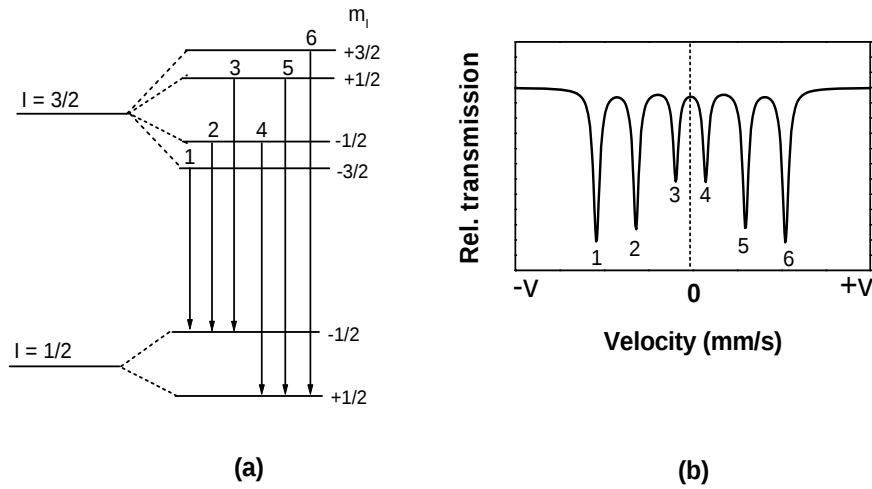


Figure 2.10: (a) Nuclear Zeeman splitting of the excited ($I = \frac{3}{2}$) and ground ($I = \frac{1}{2}$) nuclear levels and transitions between these levels in ^{57}Fe . (b) The resulting Mössbauer spectrum. The line widths of the spectrum are the same, but the intensities differ.

The resulting Mössbauer spectrum of ^{57}Fe for magnetic Zeeman splitting is shown in Figure 2.10 (b). The line widths of the resulting spectra are equal, but their intensities are different. The spectral splitting is directly proportional to the

magnetic field at the nucleus. Mössbauer spectroscopy gives an effective way of measuring this field. The effective hyperfine field at the nucleus is a vector sum of the magnetic hyperfine field and any external applied magnetic field, that is, $B_{eff} = (B_{contact} + B_{orbital} + B_{dipolar}) + B_{applied}$.

The bracketed term gives the total magnetic hyperfine field contribution and arises because of the unpaired spin of the atom's own electrons. $B_{contact}$ is due to the polarized spin density at the nucleus ; $B_{orbital}$ is due to the orbital momentum of the electrons ; $B_{dipolar}$ is the dipole-dipole interaction caused by the spin of the electrons. The term $B_{applied}$ is the externally applied magnetic field.

The information obtained from the magnetic hyperfine interaction helps in identifying the type of magnetic ordering in a material, the size of magnetic moment on atoms and the nature of the magnetic interaction. Many rock-forming minerals, especially oxides of Fe exhibit magnetic ordering, for example a magnetically split spectra of α -Fe gives a hyperfine field (B_{hf}) of 33 T, it is 51.7 T for α -Fe₂O₃ and 45.1 T for Fe (OH)₂ at standard room temperature and pressure (Dyar et al., 2006; Greenwood and Gibbs, 1971).

The combination of isomer shift, quadrupole splitting and magnetic hyperfine field (for magnetically ordered materials) manifested in a spectrum is used to identify the valence state, site occupancy of Fe in a given site and the actual mineral itself.

2.5 Instrumentation

The experimental arrangement necessary for the observation of the Mössbauer Effect is shown in the Figure 2.11, below:

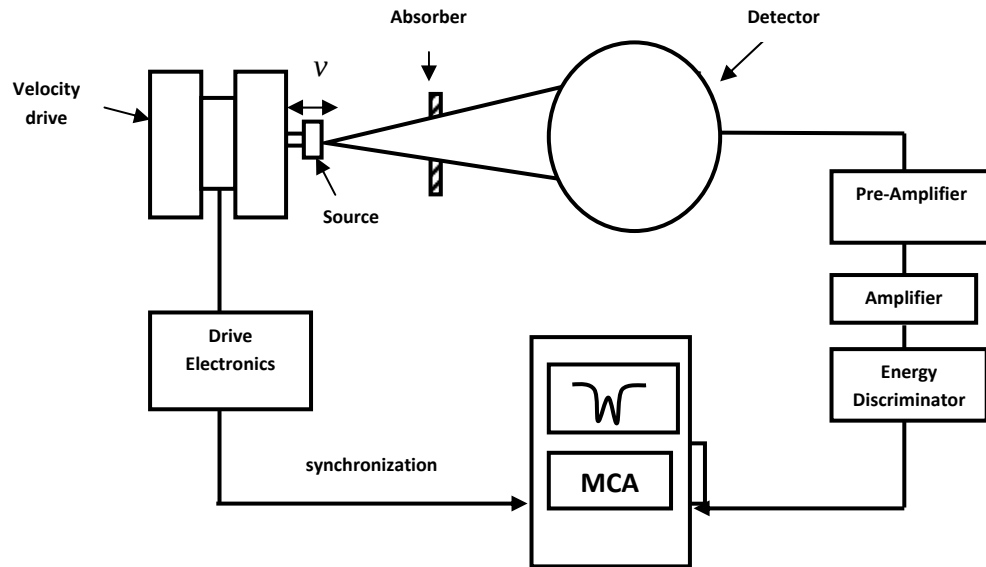


Figure 2.11: Typical Mössbauer spectroscopy setup in transmission geometry mode.

The Mössbauer spectroscopy setup in transmission geometry consists of the following, a source of radiation, an absorber (the sample being investigated), a radiation detector (gas proportional counter) and a mechanism to provide a relative motion between the source and the absorber.

The absorber is placed between the source and the proportional counter. The source is then mounted on a vibrator, which moves back and forth at a velocity that is a periodic saw tooth function of time. This motion of the vibrator results in a Doppler shift of the energy of the recoilless γ -rays according to which,

$E_{\gamma} = E_0 \left(1 + \frac{v}{c} \right)$, where v is the velocity of the source relative to the absorber and c is the speed of light. By convention v is taken to be positive when the source is

moving towards the absorber (this increases the γ -ray energy) and negative when the source is moving away from the absorber (decreases the γ -ray energy). This allows the well defined energy E_0 to be scanned over an energy range that includes, the shifts and splitting of the nuclear energy levels in the absorber. For materials that have doublets only, velocities of ± 3 to ± 5 mm/s are adequate to scan the necessary energy range to record the hyperfine interactions typical of Fe^{2+} and Fe^{3+} compounds. Magnetically split spectra usually need velocity ranges of ± 7 to ± 12 mm/s to observe the magnetic hyperfine interaction.

The gas proportional counter contains primarily krypton or argon plus a small amount of methane quench gas. A γ -ray photon entering the chamber through the Beryllium window (used for low energy γ -ray absorption) of the detector will ionise some of the Kr atoms, thus creating ion-electron pairs. The positive ions drift to the outer-walls and electrons will be attracted to the centre wire. The accelerating electrons ionise more atoms (avalanche effect), thus increasing the effective gas gain. The methane suppresses the random motion of the electrons, thus shortening the travel time to the centre wire and the rise time of the signal pulse.

The γ -ray photons strike the counter with different energies. Only the 14.4 keV γ -ray photon can be absorbed by ^{57}Fe . A pulse height discriminator (Single Channel Analyser, SCA) is used to remove most of the background radiation, like the 122 keV and 136 keV photons and unwanted X-ray lines. The charge pulse from the counter is amplified and differentiated by the preamp and then further amplification of the pulse is done by the main amplifier. The overall charge pulse is then fed into the MCA (Multi-Channel Analyser). In the memory channel of the MCA, the charge pulse is counted with the address (corresponding to a certain Doppler velocity, v) given by the corresponding number in the clock counter.

Each channel of the MCA contains a number of counts proportional to the number of photons that impinged the absorber with a range of energies corresponding to

the range of vibrator velocities of that channel address. If there is absorption of a γ -ray photon of particular energy (i.e. at a particular velocity), there will be a reduction in the counting rate in that channel.

2.6 Absorber (Sample) Preparation

Mössbauer spectroscopy has the advantage that it is a non-destructive method of investigation for sample materials. Two important considerations in preparing Mössbauer samples are to use a thickness close to the optimum and to avoid the presence of any texture. In choosing the optimum thickness two basic principles are followed. These are:

- a) Sufficient resonant nuclei are needed to obtain a reasonable dip. If the sample is too thick with resonant nuclei, appreciable line broadening is observed in the spectra. A rule of thumb that is often used is to use 5 – 10 mg/cm^2 of natural Fe in a sample (Rancourt et al., 1993) per resonance line. The natural abundance of Fe is 2.17%, which corresponds to 0.7 mg/cm^2 of natural Fe. A mineral containing 10 wt. % iron should have 7 mg of ^{57}Fe per cm^2 . This calculation is confirmed by workers such as Dyar (1984), Hawthorne (1989) and Greenwood and Gibb (1971). Thus for a single resonance line we would need approximately 5 mg/cm^2 of Fe.
- b) If the sample is too thick with non-resonant nuclei, then electronic absorption will reduce the count rate to unacceptably low levels. The attenuation of the γ radiation by the absorber may be obtained from the transmission function:

$$\frac{I}{I_0} = \exp(-\mu_e \rho x), \quad (2.14)$$

where I_0 is the intensity of the incident radiation and I is the intensity of the admitted radiation, μ_e is the mass absorption coefficient (cm^2/g) for the 14.4 keV γ -radiation, ρ is the density and x is the thickness dimension of the sample in cm. A computed value in the range 30% - 40% is considered adequate.

The intensity pattern of the lines in a Mössbauer spectrum depends on the preferred orientation (texture) of the crystals in the absorber (Pfannes and Gonser, 1972; Chandra and Ericsson, 1979). To circumvent texture, single crystal absorbers or randomly orientated small crystals in a powder are used. Powdered samples are crushed using a pestle and mortar and spread uniformly across the absorber holder (see Figure 2.12) to present a uniform cross-section for the γ -ray beam. If the sample is small ($< 50 - 100 \text{ mg}/\text{cm}^2$), the absorber is mixed with an extender to achieve uniform loading across the absorber holder. Materials that are free of Fe can be used as an extender, e.g. white sugar.

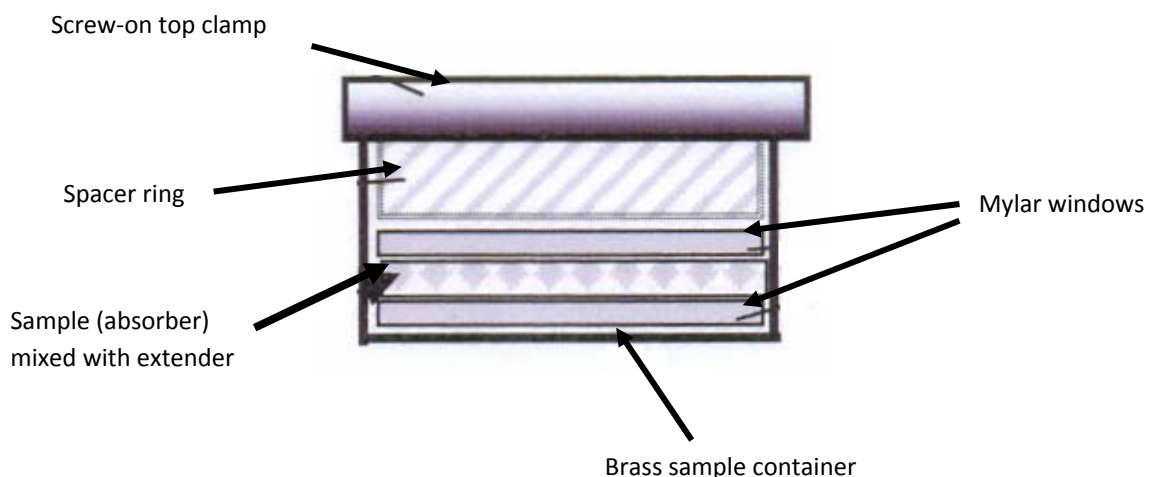


Figure 2.12: Sample holder made of brass ($\Phi=1.7 \text{ cm}$) used to load powdered samples (absorber). The holder can be used for room temperature and low temperature (90 K) ^{57}Fe Mössbauer measurements. ^{57}Fe Mössbauer spectra of ilmenite obtained using this holder are shown in Appendix A.

2.7 Analysis of Mössbauer Spectra

The simplest method for fitting Mössbauer spectra is to assume that the absorption lines are the sum of a number of Lorentzian lines shapes and to fit the parameters using a non-linear least squares technique. The Lorentzian line shape is the expected form for a thin homogenous absorber and has the form given by the equation below:

$$I(E) = \frac{\left(\frac{\Gamma}{2}\right)^2}{(E - E_o)^2 + \left(\frac{\Gamma}{2}\right)^2} \quad (2.15)$$

The minimum value of the line width is given by the Heisenberg Uncertainty Principle:

$$\Gamma = \frac{(\hbar \ln 2)}{T_{1/2}} \quad (2.16)$$

where $T_{1/2}$ is the half-life of the excited nuclear state of the isotope being used. For quadrupole split doublets it is common to assume that the two lines have identical intensities and line widths.

For magnetically split sextet with a small quadrupole interaction, it is common to assume that equivalent pairs of lines (1, 6), (2, 5) and (3, 4) have the same intensities and line widths and also that the splitting have to satisfy the Hamiltonian associated with the hyperfine interaction. Thus instead of having six independent line positions, their positions (energy) are each defined by the combination of isomer shift, quadrupole shift and magnetic hyperfine field (Murad and Cashion, 2004).

The initial stage of the fitting operation commences with the operator putting in a set of values for all, or most, of the desired parameters. The program then usually

proceeds by determining the gradient of the goodness-of-fit function (χ^2 parameter) with respect to each of the parameters and heading downhill to the minimum function. This technique relies on the operator's initial values being closer to the global minimum in the function than to any subsidiary, local minimum.

Most data fitting programs use minimization of the sum of squares of the difference between the fitted and experimental spectrum as the criterion for finding the best fit. The function χ^2 is commonly used as a goodness of fit parameter.

χ^2 is defined by (Murad and Cashion, 2004):

$$\chi^2 = \frac{1}{N - n} \sum_{i=1}^N \left[\frac{Y_{C_i} - Y_{D_i}}{\sigma_i} \right]^2 \quad (2.17)$$

where we have Y_{C_i} and Y_{D_i} are the calculated and data values at each of the N channels, labeled i , σ_i is the variance, and n is the number of parameters to be fitted. A χ^2 value of 1 is the optimum.

In this study all the Mössbauer spectrum were analyzed using the WinNormos-for-Igor Mössbauer spectra fitting software¹ that consists of two least-squares fitting programs, namely SITE for a series of different subspectra, each representing different environments and DIST for a distribution of hyperfine parameters. The hyperfine interaction parameters are obtained by fitting theoretical subspectral curves to experimental data with Lorentzian line shapes to deconvolute Fe phases in the spectrum.

¹ Written by R A Brand, Universität-GH-Duisburg and distributed by Wissel GmbH (Würmstrasse 8, D-82319, Starnberg, Germany)

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Chapter 3

HIGH PRESSURE METHODOLOGY

3.1 Introduction

Pressure is one of the thermodynamic parameters that can be used to alter the properties of a material. For most materials, pressure induces an overlap in the atomic orbitals, which in turn influence the magnetic and electronic properties of the material. This can be achieved by the application of several tens of GPa². The diamond anvil cell (DAC) has revolutionized high pressure research in the pressure range above 1 GPa (Dunstan and Spain 1989). Since its application by Bridgman in the 1950's the DAC and its application incorporating various characterization techniques such as Mössbauer spectroscopy, X-ray diffraction and neutron forward scattering has provided substantial information on the properties of materials.

The basic principle of the cell is that a force applied over a small area results in a high stress, according to the equation:

$$P = \frac{F}{A}$$

where P , is the pressure, F the force applied to an area A . Thus, to increase pressure one can either increase the force being applied or one can decrease the area. The most effective method in diamond anvil cells is to reduce the effective area between the flat anvils and thus achieving higher pressures than to increase

² 1 GPa = 10 kbar = 10 000 atm

the force on the anvils, see Figure 3.1. Increasing the applied force can exceed the compressive strength of the anvils and lead to failure of the anvils.

Bridgman (1952) showed that the maximum pressure achieved with anvils increases with the anvil angle, but he did not use diamonds - the hardest material known in science. Although diamond anvil cells were being used during the Bridgman era (see, Jayaraman, 1983), the main use for diamond anvils was as windows to provide optical access to the sample under pressure. The invention of the diamond anvil cell by Weir et al., (1959) paved the way for the wide use of diamond anvils to generate and contain high pressure. The pressure limit is determined by the type of anvils, the hardness of the material used to make the cell body and backing (support) plates, alignment of anvils and the pressure transmitting media.

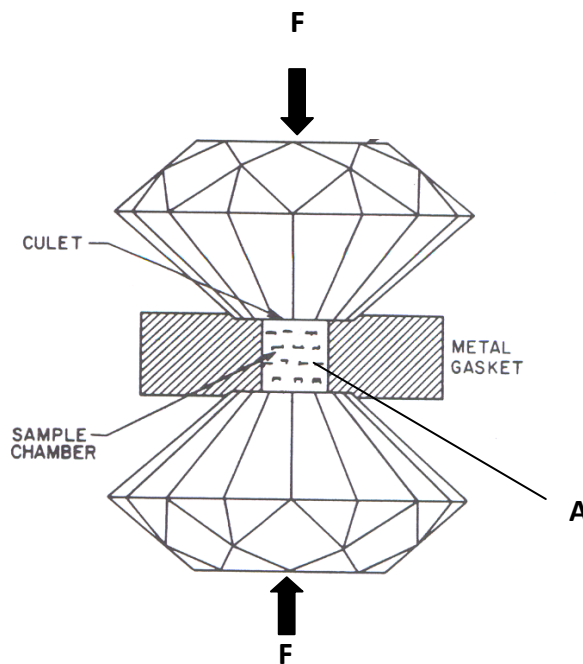


Figure 3.1: Schematic of the principle of pressure generation in the opposed diamond anvil cell.

3.2 Anvils

Diamonds used as anvils are selected from brilliant-cut gem stones see Figure 3.2 (a). Diamond is used as the anvil material because it is the hardest substance known and transparent to electromagnetic radiation over a wide spectral range, including gamma rays, X-rays, visible light, and much of the infrared and ultraviolet region where other anvils containing high-Z elements (quartz, sapphire and cubic zirconia) absorb strongly in certain regions of the electromagnetic spectrum. The use of a material as an anvil depends on the size, price, strength, transparency to radiation and other physical properties. Quartz, sapphire and cubic zirconia can also be used depending on the type of DAC and the nature of the investigation. Figure 3.2(c) is a version of a piston cylinder DAC designed by Mao et al., (1978) with beveled culets for ultra high-pressure generation above 100 GPa. This cell has been used for Mössbauer studies at variable cryogenic temperatures and pressures greater than 140 GPa (Machavariani et al., 1998). The culet is polished parallel to the table face, (see Figure 3.2(a)) and then beveled to further reduce the size for ultra high-pressure generation and to optimize the support of the culets by the gasket, see Figure 3.2 (b).

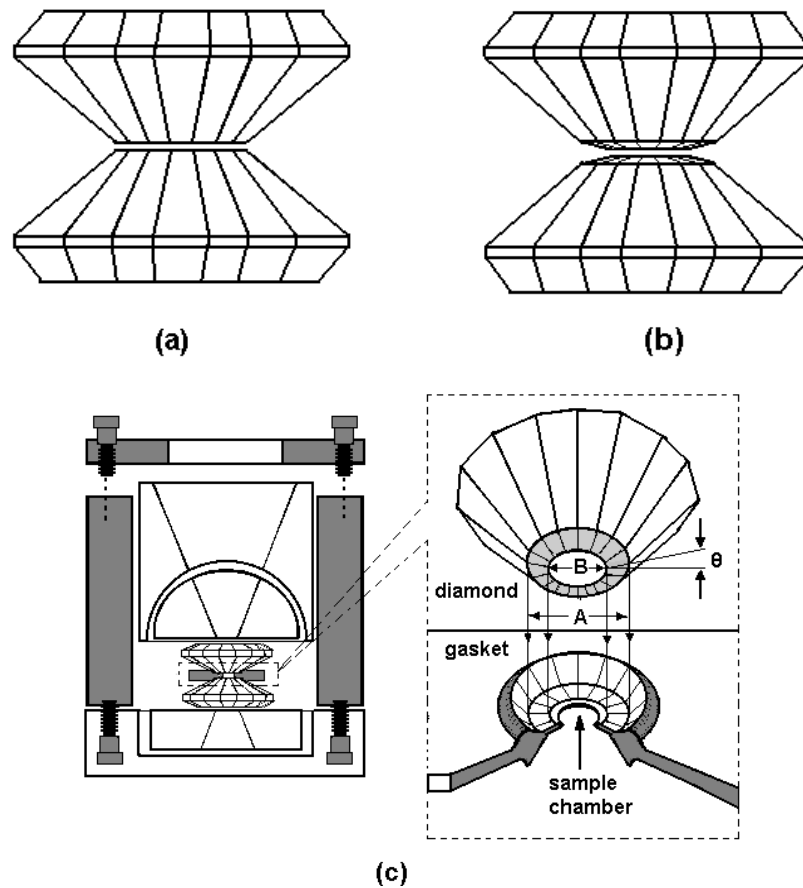


Figure 3.2:(a) Brilliant-cut gemstone opposed diamond anvils; (b) sharp edges of the anvils in (a) are beveled to reduce the flat face for ultrahigh-pressure and (c) left: the anvils in (b) are assembled in a miniature high-pressure cell (see Machavariani et al., 1998). The two important parameters; the beveled final flat face (B) and the bevel angle (θ) for ultrahigh-pressure generation are also shown together with the original brilliant-cut flat face (A) in the exploded cross-sectional view on the right.

The force on the backing (supporting) plates of the DAC is determined by the diameter of the table of the anvil in use, and thus determines the pressure attained on the pressure bearing culet. The culet of the anvil should be much smaller than the table of the anvil to intensify the low-pressure applied to the table for high pressure generation at the culet.

Earlier high pressure experiments used brilliant cut diamonds with anvil culets, as shown in Figure 3.3 (a). Recently the 8-sided Drukker standard cut

(see Figure 3.3 (b)) has been introduced for DAC applications (Dunstan and Spain, 1989). In the Drukker cut the table area is increased over that of the brilliant-cut diamond for the same weight, and the increased anvil angle and waist of this design allow it to be used at higher pressures (above 10 GPa).

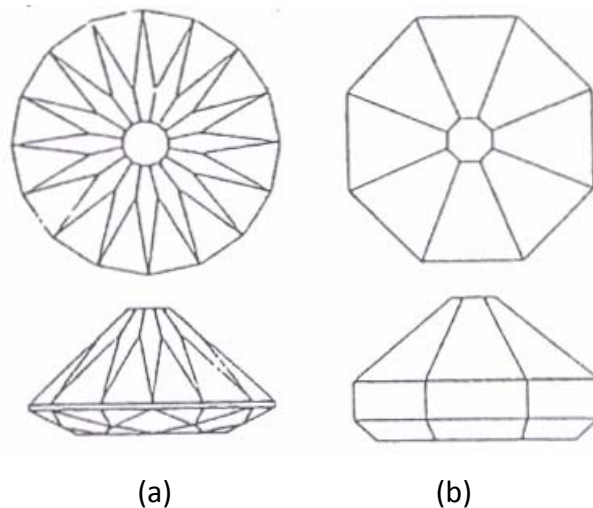


Figure 3.3: Diamond anvils (a) the brilliant cut and (b) the Drukker cut.

The design of the anvils as well as the structure of backing (support) plates determines the maximum pressure a diamond anvil cell can achieve. Diamonds with large culets (for example, 600 μm culets will allow 30-40 GPa) are mainly used for lower pressure and those with small culet diameters (200 μm or less) are generally used for high pressure (i.e. megabar pressures). For work at the megabar regime the diamond culets are usually beveled (see Figure 3.4). Using anvils with culets of diameter 550 μm pressures of 30-40 GPa can be reached and with 750 μm culet diameter 10 GPa can be reached routinely (Dunstan and Spain, 1989).

Also, the shape of the diamond influences the pressure reached. Those with 16 sides withstand higher stresses than those with 8 sides (Dunstan and Spain, 1989). Apart from the size of the culets, the dimension of the sample chamber also determines the maximum pressure that can be reached in high pressure experiments. For

example, 5 GPa, can be reached with a sample chamber of 300 μm diameter x 300 μm thickness and for 300 GPa, it is 20 μm x 3 μm thickness (Mao and Hemley, 1998).

A new design of diamond anvils has been introduced in high pressure research (Boehler and de Hantsetters, 2004), see Figure 3.5. Compared to conventional anvil (brilliant or modified brilliant cut) design the new Boehler-Almax design offers conical support for the anvil (see Figure 3.5 (c)), a large aperture of up to 90° on the backing plate. The design is also cost effective because anvils with smaller diameters are used.

The principle of the design is shown in Figure 3.4. For the same culet diameter and pressure range, conventional anvils typically have a diameter of 3-4 mm while the Boehler-Almax anvils have 2-2.5 mm diameter and heights of 1.5-2 mm. The large table diameters of the conventional anvils require 0.25-0.35 carat diamonds and for the Boehler-Almax design the weight by carat is 0.05-0.15. The smaller weight of the Boehler-Almax design makes the anvils cheaper since the cost of a diamond is proportional to its weight. However there is some expense involved in acquiring the backing plates.

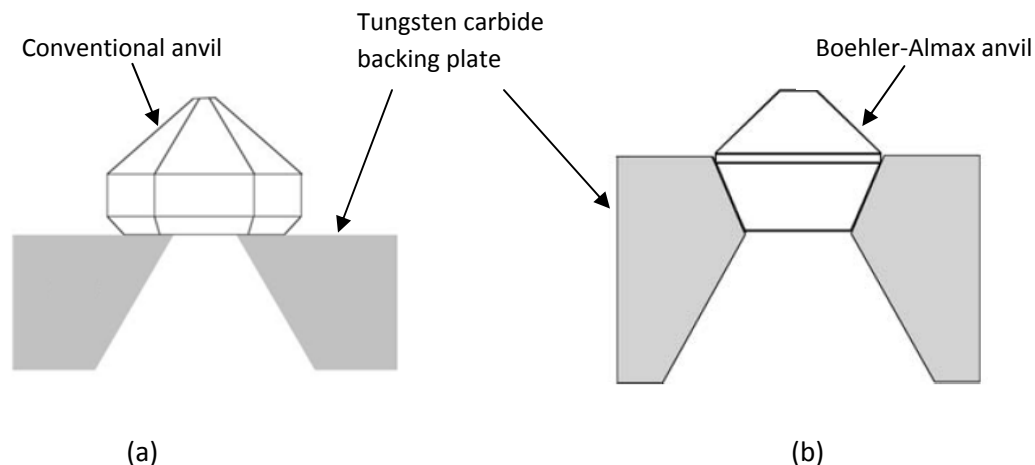


Figure 3.4: (a) Conventional design. The tungsten carbide backing plate with a central conical aperture supports the large flat table (b) Boehler-Almax design with conical support.

An additional advantage of the new design arrangement is that when the diamond fails the backing plate is not damaged. In the conventional design when anvil failure occurs, there is complete destruction of the anvil. The anvil fragments embed into the material of the backing plate and damage the plate beyond repair. In the Bohler-Almax design, the cracks do not propagate throughout the entire anvil but are stopped where the diamond is supported radially by the backing plate.

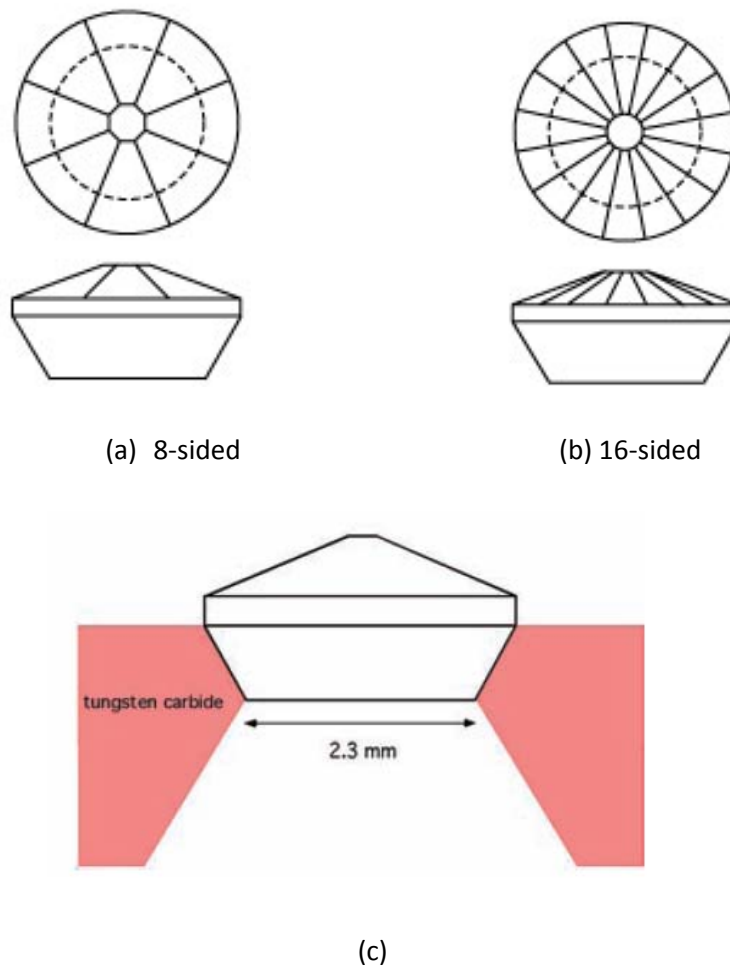


Figure 3.5: (a) 8 sided Bohler-Almax design (b) 16 sided Bohler-Almax design (c) A Bohler-Almax anvil with conical anvil support provided by a tungsten carbide backing plate. The backing plate has a very large aperture of 75°.

The conical design allows for a significantly larger aperture for the backing plate which results in a reduced anvil thickness that can be used. This reduced anvil thickness, results in reduced anvil absorption of radiation by the diamonds. A factor that is important in ^{57}Fe Mössbauer spectroscopy where there is $\approx 75\%$ absorption of the 14.4 keV resonant γ -ray radiation using conventional designs for a total of 4 mm thickness of diamond (Takele and Hearne, 2001; Seda and Hearne, 2004).

3.3 The cell and backing plates

The material supporting the diamonds is the next most important factor after the diamonds that limits the maximum useful pressure attained in DAC. Hard materials are therefore used for construction of DAC's. Most hard materials are brittle at low temperatures and contain Fe and therefore are not useful for construction of DAC's for low temperature ^{57}Fe Mössbauer measurements. Fe containing materials are not ideal because they may produce an interfering Mössbauer spectrum on the absorber spectra.

Materials with useful properties are precipitation hardened alloys for constructing the body of the DAC, e.g. copper-beryllium (CuBe) and Inconel. Copper-beryllium is a precipitation hardened material, formed by dissolving beryllium in copper at high temperature ($\approx 900^\circ\text{C}$) and then quenching. At 300°C heat treatment, beryllium precipitates, and the alloy hardens to hardness values of 400 HV (Vickers hardness test). Inconel is a nickel based precipitation hardened alloy. Nickel precipitates at 500°C and the resulting hardness of the alloy is 470 HV. When the stress in the backing plate exceeds that needed for plastic deformation, the diamond alignment can be upset and diamond breakage can result. The limiting stress of the backing plate hence provides a limit to the maximum pressure attained by the DAC.

Tungsten carbide (WC), containing small traces of cobalt (Co) as a binder is the material of choice for the backing plate.

The access hole in the backing plate should have a diameter equal to about one-third the diameter of the table of the diamond. The diameter should not be too large otherwise the removal of more material weakens the backing plate. Access holes are made with a cone angle of 50° - 60° (Dunstan and Spain, 1989; Merrill and Bassett, 1974) for large optical access for low pressure measurements. For high pressure measurements cone angles of 20° are made use of. Using such small angles for the access hole allows the hole to be made with dimensions smaller than one third the diameter of the anvil table. The hole should be always larger than the culet to allow viewing of the culet during alignment of the two anvils with respect to each other.

3.4 Gaskets

The introduction of the metal gasket for the containment of pressure was the key to hydrostatic pressure generation in the DAC (Jayaraman, 1986). The gasketed diamond anvil cell opened the way for the DAC to be used as a quantitative tool in high pressure research. This was first demonstrated by Van Valkenburg (Pasternak and Taylor, 2006).

The main use of the gasket is as a pressure containment chamber. Another useful function the gasket serves is that the gasket acts as a support ring around the anvil faces, when extruding around the diamonds. In this case, the gasket provides lateral support to the anvils, hence minimizing chipping at the edges and corners of the anvils. Figure 3.6 shows a gasket compressed between two anvils.

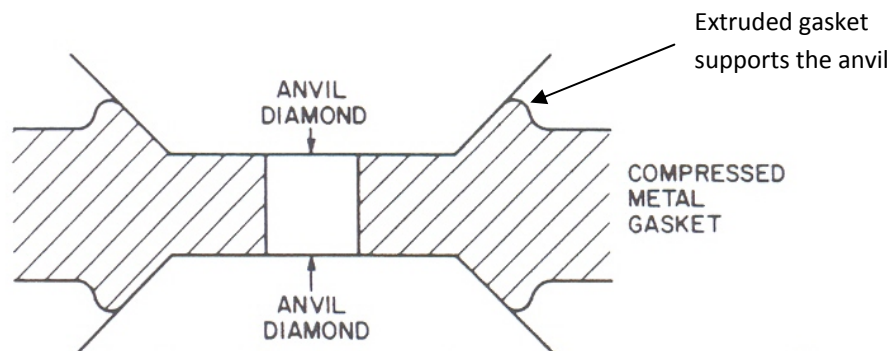


Figure 3.6: Gasket for sample confinement and lateral support of anvils. Typical dimensions of the cavity are, thickness 30-40 μm and diameter 100-200 μm .

Typical materials used for making gaskets are tempered stainless steel, tungsten and rhenium (Miletich et al., 1996; Jayaraman, 1986). Alloys such as Inconel and beryllium copper are also used (Dunstain and Spain, 1989). For high pressure Mössbauer spectroscopy, high atomic number alloys such as $\text{Ta}_{90}\text{W}_{10}$ and rhenium (Re) serve as effective collimators for γ -photons of energy less than 35 keV (Pasternak and Taylor, 2006). For pressures above 50 GPa, Re can be used because of its added hardness and strength.

The gaskets are made from starting material that is typically 250 μm thick, then pre-indented by compressing between two diamonds to the desired thickness. A sample chamber of required diameter, chosen to suit the culet size is then drilled at the centre of the indented area. The pressure the gasket can withstand (hence the sample chamber) without deforming is dependent upon the diameter of the sample chamber, the thickness of the gasket and also the shear strength of the gasket material (Dunstan and Spain, 1989).

When a gasket has a large thickness for the pressure being applied, the metal extrudes outwards, in all directions. The gasket hole enlarges as the pressure increases and hence is unstable leading to failure of the diamond anvils. An ideal situation is when the metal extrudes inwards towards the sample hole as the

temperature is increased. In this case the sample hole decreases in size as the pressure is increased. This situation is possible if a sufficiently thin gasket is used. The ratio of the thickness to the culet diameter should be $\approx 1:5$ (Dunstan and Spain, 1989) for excessive distortion of the gasket not to occur.

3.5 Pressure Media

In high pressure experiments involving the DAC, it is crucial to ensure that the pressure applied on the sample is hydrostatic, that is, it should be homogenous and free of any differential stress or shear strain. The solid sample should therefore be totally immersed in a hydrostatic medium that shows hydrostatic behaviour such as a liquid or gas.

Various fluids have been used as hydrostatic pressure transmitting media (see Jayaraman, 1983). An alcohol methanol-ethanol mixture in the ratio 4:1 was found to be hydrostatic up to a pressure of 10 GPa (Piermarini et al., 1975) at room temperature. The addition of water in the ratio 16:3:1, methanol-ethanol-water increases the hydrostatic pressure range of the alcohol mixture to 14.5 GPa (Jayaraman, 1986; 1983). Above 20 GPa this mixture becomes a soft solid and becomes non-hydrostatic. Condensed rare gases such as Ne, Xe, Ar, He and also H_2 have been found to be excellent pressure transmitting media up to the megabar regime (Jayaraman, 1983, 1986; Dunstan and Spain, 1989). These gases provide a quasi-hydrostatic environment at high pressures and low temperatures because they retain low shear strength at these conditions (Towle, 1967; Mao and Bell, 1979). In the use of these condensed gases, the gasket hole is either filled by cryogenic filling (Liebernberg, 1979) or high pressure gas loading (Millis et al., 1980). In these gas filling methods, the sample material and a ruby chip are placed in the diamond anvil cell before the gas is introduced. When the gas is trapped in the

gasket hole, the DAC is closed. The DAC is then taken out for further pressurization. The most convenient gas for loading is argon. Argon is easily liquefied and does not have the problem of remote sealing (Bedassa, 2000; Dunstain and Spain, 1989).

In this work, the filling of the gasket hole is at ambient conditions using pressure transmitting media such as fluourinet (a fluouro-carbon) and silicone oil (diffusion pump oil). Loading of liquids as pressure transmitting media in ambient conditions requires simple apparatus. The easiest and quickest way to load a pressure transmitting media is with a syringe. The transmitting media is injected into a semi-assembled DAC near to where the culet edge contacts the gasket, which already has some ruby chips and sample material in the gasket hole. By closing the cell (pressing the diamonds together), the sample material and transmitting media are trapped in the gasket hole, and the sample chamber is sealed. The DAC is now ready for further pressurization. Use of a syringe is particularly useful for loading the ethanol-methanol mixture, as the volatile methanol is prevented from evaporating.

3.6 Mounting and alignment of anvils

The diamond anvils must be secured correctly in place on the backing plates before the DAC is assembled for any high pressure experiments. The culets must be centered with respect to the access hole of the backing plate before any glue or epoxy resin can be applied. Centering can be checked using a compound microscope with upper and lower illumination. Once the culets are centered correctly, a slow-set epoxy resin or glue can be used to secure the diamonds. The epoxy or glue is used to secure the diamonds to avoid loss of alignment during cleaning and the actual carrying out of the experiments at extreme conditions.

The backing plates are the mounting surfaces in a DAC and are simple flats with holes for optical access. The two backing plates have to be aligned laterally and absolutely parallel to each other to prevent severe gasket deformation during indenting and to attain the maximum pressure for the given experiment. For this study a Merrill-Bassett DAC is used, see Figure 3.7. Alignment is achieved through a series of steps to get the two culets concentric and parallel to each other. To obtain concentricity, lateral adjustment of the anvils with respect to each other is done by moving the backing plate using appropriate built-in screws for fine adjustment. Absolute parallelism is achieved by adjusting thrust screws of the M3 type. Absolute parallelism of the culets is indicated by the disappearance of Newton's fringes (Sterer, et al., 1990).

The Merrill-Bassett DAC is compact, light weight and easily loaded into most sample probes used in cryostats with small bores or furnaces. Figure 3.7 shows a typical Merrill-Bassett and its constituent elements before assembling.

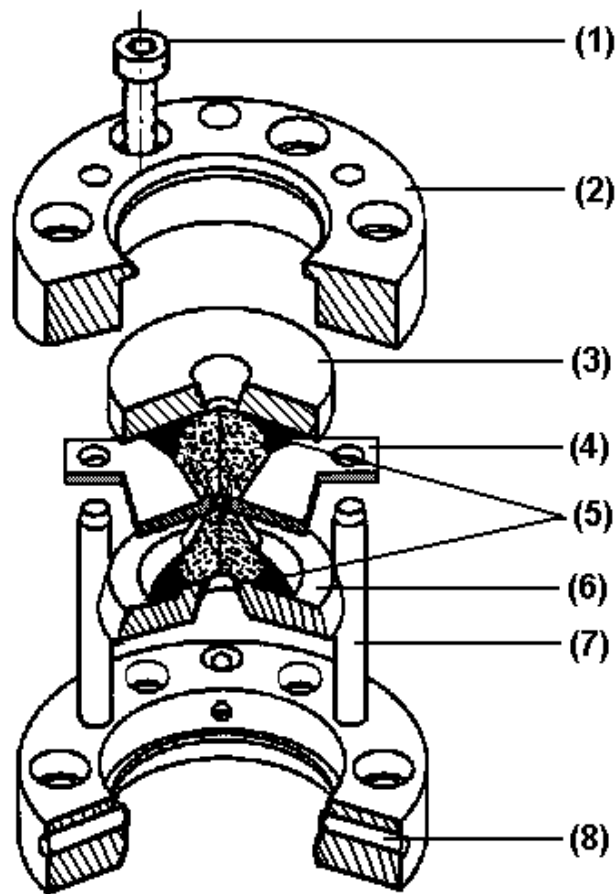


Figure 3.7: Exploded view of the modified miniature Merrill-Bassett DAC for high-pressure Mössbauer spectroscopy at cryogenic temperatures (Sterer et al., 1990): (1) Six Allen thrust screws for pressure generation, (2) platens, (3) upper backing plate, (4) gasket, (5) diamond anvils affixed to the backing-plates, (6) lower laterally adjustable backing-plate, (7) positioning and gasket locating pins, (8) lower backing-plate lateral adjusting screws.

Three M3 type thrust screws pull the two platens together when tightened, and hence the diamond anvils are pulled closer together. The guiding pins are used to hold the gasket and also for the top platen to slide on when tightening the M3 type screws. The upper platen is usually designed to tightly enclose the backing-plate while the lower backing-plate is laterally adjustable with respect to the upper

backing-plate using the lateral adjusting screws. In this study a DAC with a fixed lower backing plate and an adjustable top backing plate is used.

3.7 Pressure calibration

Accuracy in pressure determination is of great importance in high pressure experiments. A direct calculation of pressure using the equation of force divided by cross-sectional area is not possible because the distribution of the load over the anvil culets cannot be known (Miletich et al., 1996). To overcome these limitations, pressure determination is done using materials whose physical properties and their characteristic relative changes with pressure are known. One such material is ruby, which is 5% Cr^{3+} doped Al_2O_3 .

Forman et al., (1972) first showed that the R lines (R_1 and R_2) of ruby shift linearly with pressure up to 30 GPa. Forman et al., (1972) found that ruby fluorescence under a green-blue laser is characterised by a doublet due to electronic transitions of Cr^{3+} in a distorted octahedral crystal field. The band components are centered at 14402 cm^{-1} (R_1 at 694.2 nm) and 14432 cm^{-1} (R_2 at 692.8 nm) at a pressure of 1 bar. Forman et al., (1972) also showed that when the environment in the sample chamber is non-hydrostatic the R lines of ruby broaden. The ruby fluorescence shift method is now the standard in determining pressure in the DAC for up to 30 GPa. Small ruby chips are placed in the sample chamber and the R_1 and R_2 lines of the ruby are excited by green light of an argon ion laser or with the blue light of a Cd-He laser (see Figure 3.9a).

The two R lines, fluorescence sharply at 694.2 nm and 692.7 nm respectively at ambient conditions. The pressure dependence of the wavelengths is linear up to 30 GPa (Piermarini et al., 1975),

$$P(\text{GPa}) = 2.746\Delta\lambda(\text{nm}) \quad (3.1)$$

Where $\Delta\lambda$ is the change in the wavelength of a ruby R line measured using a spectrometer. A typical and widely used system for pressure calibration is depicted in Figure 3.8, Taylor and Pasternak (1990).

For pressure calibration above 30 GPa and less than 1 Mbar, the following relation holds (Mao et al., 1978),

$$P(\text{GPa}) = 380.8 \left[\left(\frac{\Delta\lambda}{\lambda_0} + 1 \right)^5 - 1 \right] \quad (3.2)$$

The plots for the two equations by Piermarini et al., (1975) equation 3.1 and Mao et al., (1978) equation 3.2, are shown in Figure 3.9(b). The dashed line is from equation 3.1 and the solid line by equation 3.2. Below 30 GPa there is linearity, above correction is necessary. The error is estimated to be $\approx 3\%$ (Jayaraman, 1983) when using equation 3.1 for determining pressure above 30 GPa.

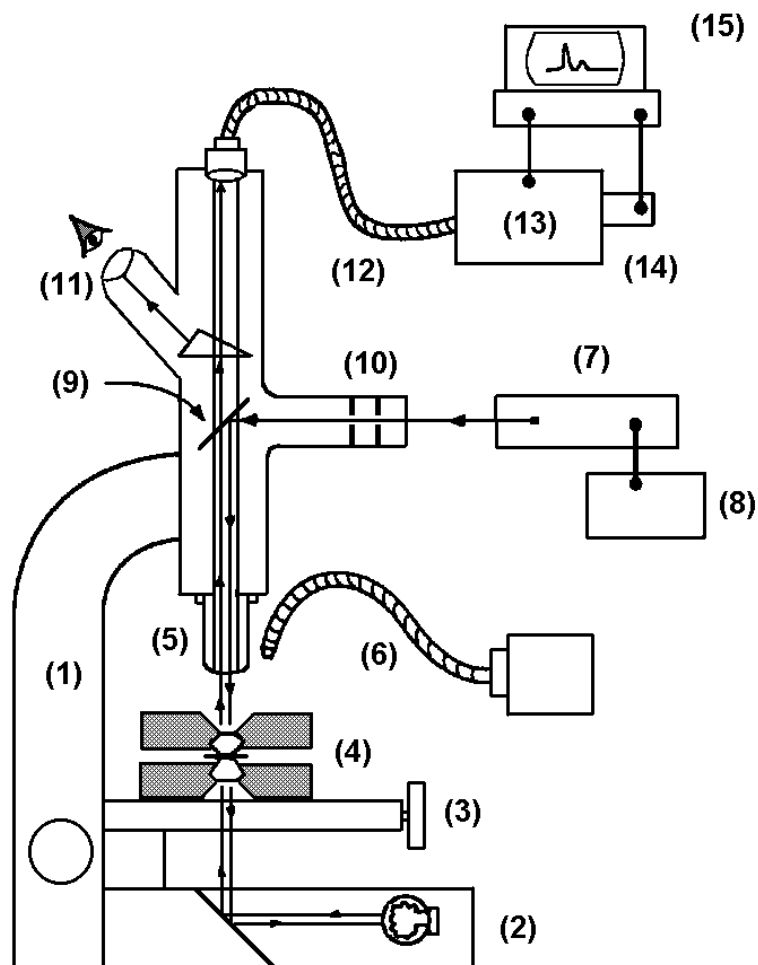


Figure 3.8: Block diagram of the laser microscopic system for pressure calibration. (1) Olympus microscope (2) bottom illuminator, (3) x-y stage, (4) DAC, (5) an extra long-working-length 20 × objective, (6) top illuminator (7) 20 – 160 mW variable power a argon-ion laser, (8) laser power controller, (9) a dichroic mirror, passive to red and reflecting for blue/green light, (10) filters: a combination of filters and the blue or green options of the dichroic filter (9) allow the use of the blue plus green, blue or green modes of the laser, (11) ocular, (12) fiber optic bundle with a circular cross-section at the microscope exit and a rectangular section matching the entry slit of the monochromator, (13) monochromator with a computer-controlled stepping motor, (14) 12-mm diameter photomultiplier, (15) PC for controlling the monochromator and for collecting and analysing the data from the spectrometer (modified from Taylor and Pasternak (1990)).

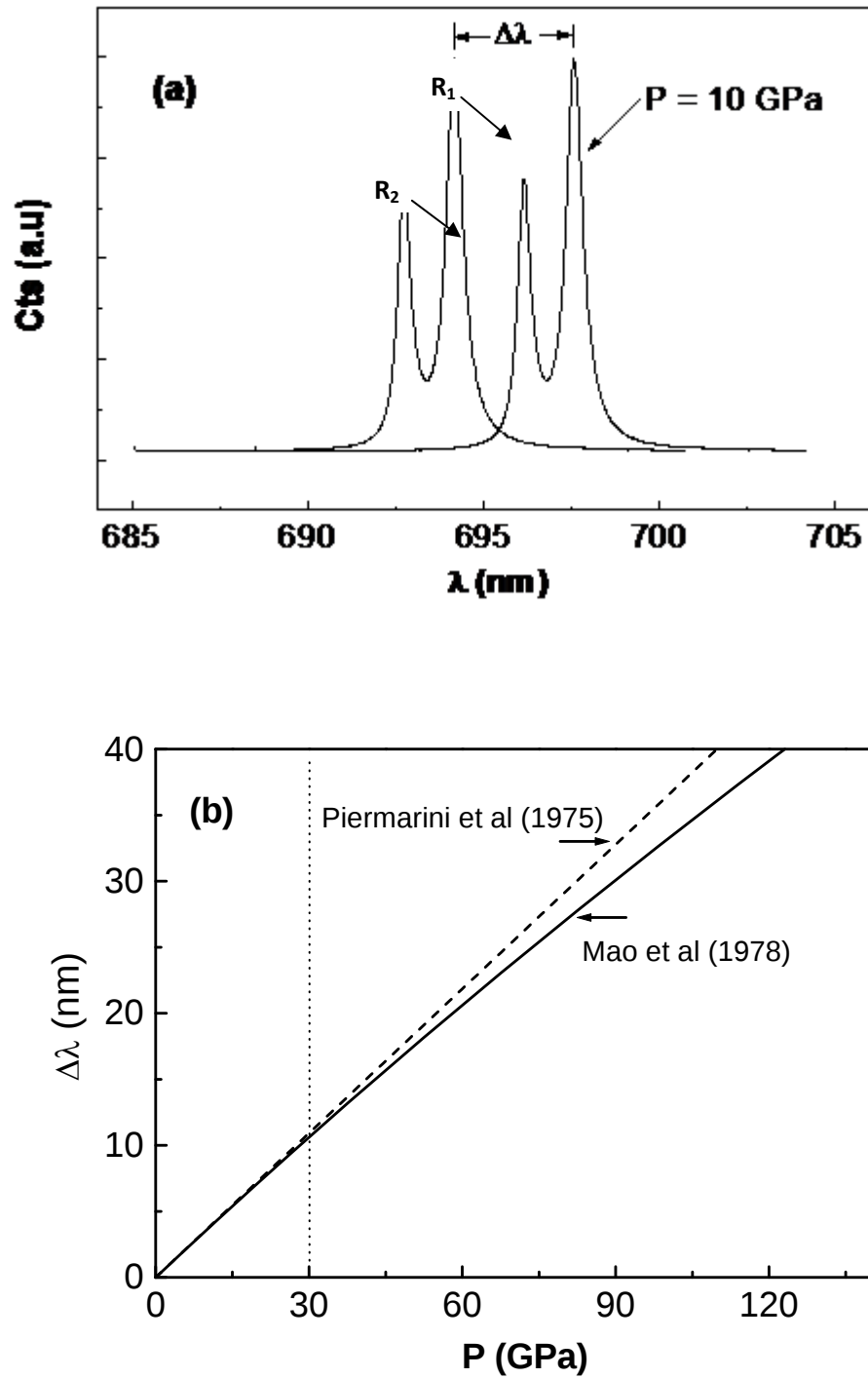


Figure 3.9: (a) Example of the ruby fluorescence spectra at two different pressures (ambient and 10 GPa) and (b) the shift in the wavelength $\Delta\lambda$ (nm) with pressure P (GPa) of the ruby line R_1 . Dashed line is the linear relation (after Piermarini et al., 1975) and solid line is the modified relation (after Mao et al., 1978).

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Chapter 4

ILMENITE (FeTiO_3)

4.1 Introduction and Background

Ilmenite is commonly found as an inclusion mineral in diamond bearing kimberlites and in volcanic rocks (Wilson et al., 2005) derived from the upper mantle and regions of the lower mantle thus corresponding to depths of 400-700 km and pressures of 12-13 GPa (Zhang et al., 2006). Deposits of natural ilmenite are also obtained from beach sands which are a result of the weathering of volcanic material (Gibb and Greenwood, 1969). The Fe oxidation state in FeTiO_3 can provide information on the weathering history of deposited minerals especially kimberlites, which are diamond bearing minerals formed from the extrusion of magma from the earth's mantle. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in mineral assemblages is considered to be an important indicator of temperature and oxygen fugacity at the time of P-T equilibration of the assemblage.

The ilmenite-hematite ($\text{FeTiO}_3\text{-Fe}_2\text{O}_3$) solid solution series is the second most abundant iron-titanium oxide after the ulvöspinel-magnetite ($\text{Fe}_2\text{TiO}_4\text{-Fe}_3\text{O}_4$) series (McEnroe et al., 2005). The solid solutions are ferrimagnetic and are the most important carriers of remanent magnetization in rocks after magnetite (McEnroe et al., 2005). From a petrology and mineralogy study the solid solutions provide information as a geo-thermometer and oxygen-barometer of the Earth's mantle when they are in equilibrium with ulvöspinel-magnetite minerals (Bedassa, 2000).

4.2 Structural Properties of ilmenite

The crystal structure of ilmenite (FeTiO_3 , space group: $R\bar{3}$, see Appendice B) is closely related to that of hematite. In ilmenite the Ti^{4+} ions replace half the Fe^{3+} cations in hematite, forming alternating layers of Fe^{2+} and Ti^{4+} ions. The rhombohedral unit cell is based on a hexagonally-close packed oxygen lattice, with alternating layers of facing-sharing Fe and Ti octahedra stacked along the c-axis. The ordering is of the form Ti-Fe-V-Fe-Ti where V represents the vacant sites which occupy one third of the crystal lattice and the cations two thirds. Hematite ($\alpha\text{-Fe}_2\text{O}_3$, space group: $R\bar{3}c$) has the corundum (Al_2O_3) structure with an approximately hexagonal close-packed array of oxygen anions. Fe^{3+} ions occupy two thirds of available octahedral sites between O^{2-} ions. Each FeO_6 octahedron shares a face with another in the layer above or below. Fe atoms lie on planes spaced approximately one third and two thirds of the distance between oxygen layers (see Figure 4.1).

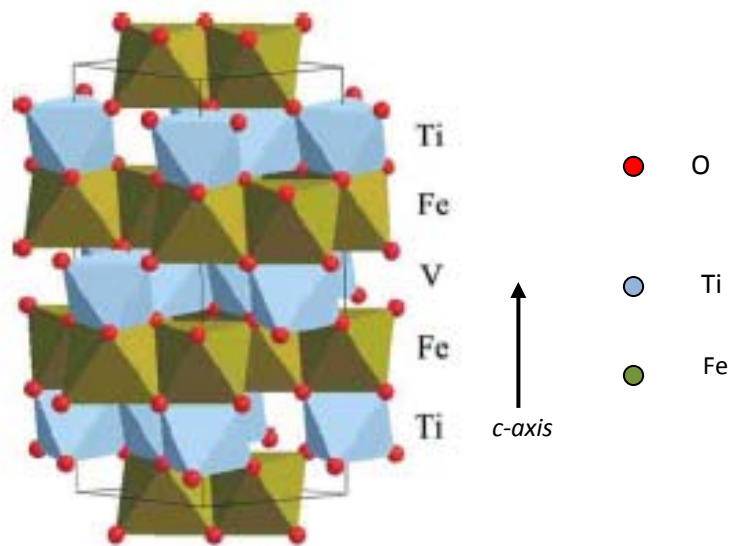


Figure 4.1: Crystal structure of ilmenite showing face sharing FeO_6 and TiO_6 octahedra (Wu et al., 2009).

Two other polymorphs of FeTiO_3 are known, namely lithium niobate (LiNbO_3)

structure and perovskite structures. The perovskite structure is a stable phase at high P-T conditions, with the ilmenite phase being favoured at low P-T conditions (Wilson et al., 2005). The lithium niobate (LiNbO_3) structure is a quench product of the perovskite phase, that is, it is formed during the decompression of the high-pressure perovskite phase at room temperature (Wilson et al., 2005; Ming et al., 2006). The lithium niobate (LiNbO_3) phase is only stable at pressures greater than 16 GPa (see Figure 4.2). Its structure is similar to that of ilmenite, but cations order along the c-axis meaning that the FeO_6 and TiO_6 octahedra share faces and edges (see Figure 4.3).

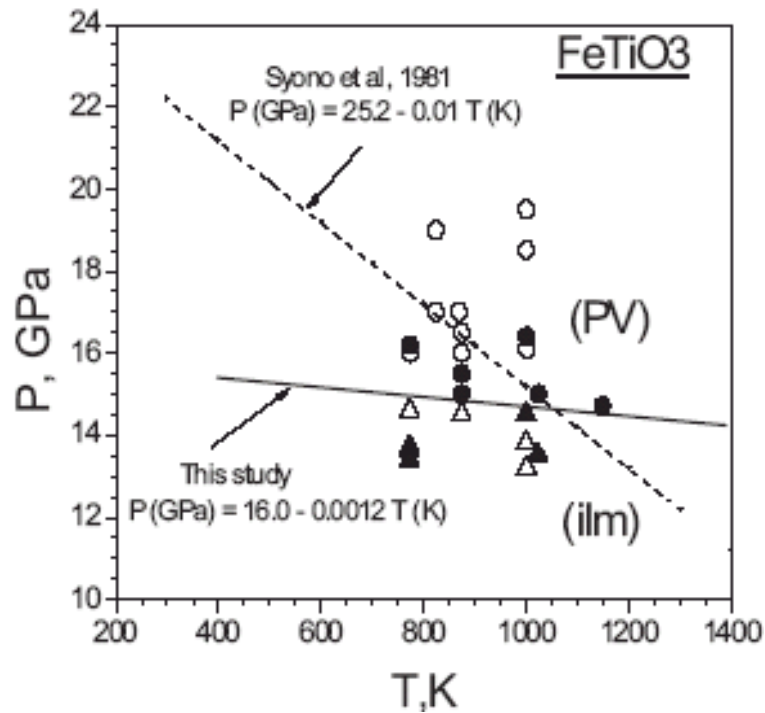


Figure 4.2: The phase boundary of the Ilmenite perovskite transformation determined by Ming et al., (2006) and Syono et al., 1980. Open and solid symbols show decompression and compression cycles, respectively. Circles and triangles represent the perovskite and ilmenite phases, respectively (Ming et al., 2006).

At high pressure Ti-O and Fe-O bond lengths decrease (Wu et al., 2009) and the corresponding bonding electron density increases at each bond (Yamanaka et al., 2007).

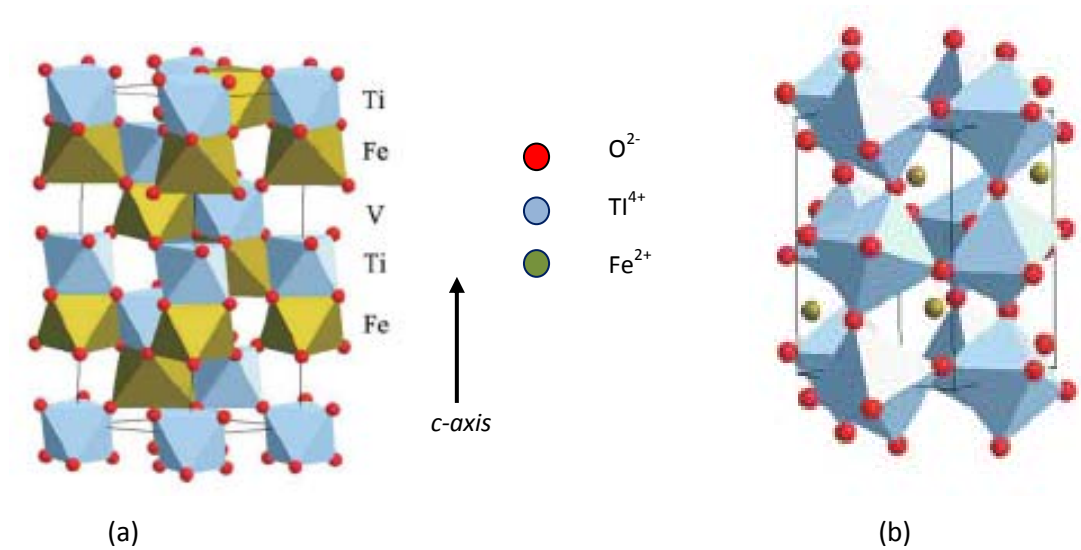


Figure 4.3: (a) The lithium niobate structure of ilmenite showing face and edge sharing FeO_6 and TiO_6 octahedra. The cations order along the c axis. (b) High-pressure polymorph of ilmenite, the perovskite phase. Ti coordinated oxygen octahedra are indicated in blue, Fe or Fe coordinated atoms are shown in brown (Wu et al., 2009).

4.3 Magnetic-electronic properties of ilmenite

$FeTiO_3$ is an antiferromagnetic insulator below its Néel temperature of 68 K. Fe magnetic moments are parallel in any given c -plane and antiparallel between adjacent planes. Hence magnetic sublattices with equal and opposite magnetic moments are formed. Antiferromagnetic coupling occurs between two layers separated by a layer of Ti atoms. Solid solutions of $FeTiO_3 - Fe_2O_3$ have been shown to exhibit both semiconducting and ferromagnetic properties (Hojo et al., 2007). It is because of these properties that the ilmenite-hematite solid solution has received great attention of late as a candidate for spintronic devices. The charge and spin of electrons are exploited in diluted magnetic oxide semiconductors with high Curie

temperature such as the ilmenite-hematite system to tailor-make multifunctional devices in spintronics. The conduction type in the system can be p or n type depending on the composition (Ishikawa, 1962). Bulk solid solutions with compositions where the solid solution is $x\text{FeTiO}_3 \cdot (1-x)\text{Fe}_2\text{O}_3$, show n-type conduction in the compositional range $0 < x < 1$ (Hajime et al., 2006). The compositional range $0 < x < 0.7$ shows p-type conduction. Solid solutions of the form $(1-x)\text{FeTiO}_3 \cdot x\text{Fe}_2\text{O}_3$ in a range of composition $0.1 < x < 0.6$ show strong ferrimagnetism (Ishikawa, 1962) and the presence of this ferrimagnetism was confirmed by Shirane et al., (1959).

Recently a new type of ferrimagnetic substructure, called lamellar magnetism in the ilmenite-hematite ($\text{FeTiO}_3\text{-Fe}_2\text{O}_3$) solid solutions has been proposed to explain magnetic anomalies observed in the deep Earth and on other planets that do not have a measurable magnetic field (Harrison et al., 2000, Pentcheva and Nabi, 2008), see Figure 4.4. In this theory mixed-valence contact layers of Fe^{2+} and Fe^{3+} form at the interfaces between fine precipitates of canted anti-ferromagnetic (CAF) hematite and paramagnetic (PM) ilmenite (exsolutions).

These layers are a combination of half Fe^{2+} ions from ilmenite and half Fe^{3+} from hematite. The charge neutrality at the interface is reduced and disrupted. The two contact layers have parallel magnetic moments to the left and are coupled antiferromagnetically to the hematite layer. Each contact layer has a weaker magnetic moment compared to the Fe^{3+} hematite layer, but the two contact layers combined have a greater magnetic moment than the hematite layer and produce a net magnetic moment per lamella of $4 \mu_B$ to the left.

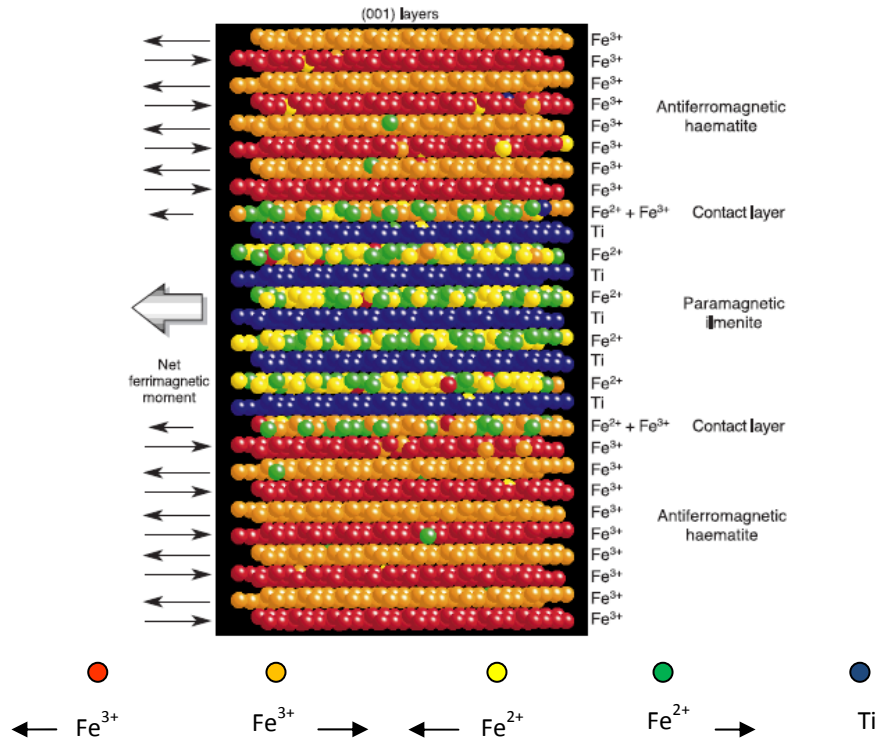


Figure 4.4: The bottom one-third of the system shows canted antiferromagnetic hematite and the upper second third paramagnetic ilmenite in which the cations are ordered. The ilmenite lamella is terminated at the ends by a layer of Ti and followed by a mixed layer of Fe^{3+} and Fe^{2+} called the contact layer and then a layer of Fe^{3+} . This symmetric termination creates an imbalance of left and right spins and leads to a stable net magnetic moment (Robinson et al., 2002; McEnroe et al., 2005).

The intensity of the lamellar magnetism is proportional to the density of lamellae and the surface area of contact layers (McEnroe et al., 2009). In this ferrimagnetic substructure parallel alignment of magnetic moments is favoured in the 001 plane parallel to the magnetizing field. Lamellar magnetism is very stable and extremely resistant to demagnetization. This makes it an ideal candidate for ancient crustal magnetization which is reported to be the cause of magnetic anomalies (Harrison et al., 2000, 2007; Robinson et al., 2002; McEnroe et al., 2005). The unusual properties of lamellar magnetism are also being investigated for technological applications. The unbalanced moments at the interface cannot be easily flipped at room temperature, hence lamellar magnetism can be used for tailor-making stable high density storage devices.

4.4 Previous ^{57}Fe Mössbauer high pressure studies of ilmenite

High pressure studies of ilmenite using ^{57}Fe Mössbauer spectroscopy at room temperature have been done by workers such as Seda and Hearne (2004) and Wu et al., 2009. Studies using a heat treated (to increase the ferric component) and an untreated sample of ilmenite (Seda and Hearne, 2004) show that the Mössbauer spectrum exhibits two paramagnetic doublets and a low abundance magnetically split component at ambient conditions. This stems from the fact that natural samples contain ilmenite in solid solution with hematite. Hematite is an antiferromagnetic below its Néel temperature ($T_N \approx 675^\circ\text{C}$) and hence produces a magnetically split spectrum at ambient conditions.

With increasing pressure the relative abundance of the ferric component increases as seen from Figure 4.5 and Figure 4.6. The increase is attributed to intervalence charge transfer between face-sharing octahedra of the Fe and Ti cations. A brief discussion of the phenomenon is found in Chapter One of this work and a detailed explanation of intervalence charge transfer is given by Seda and Hearne (2004).

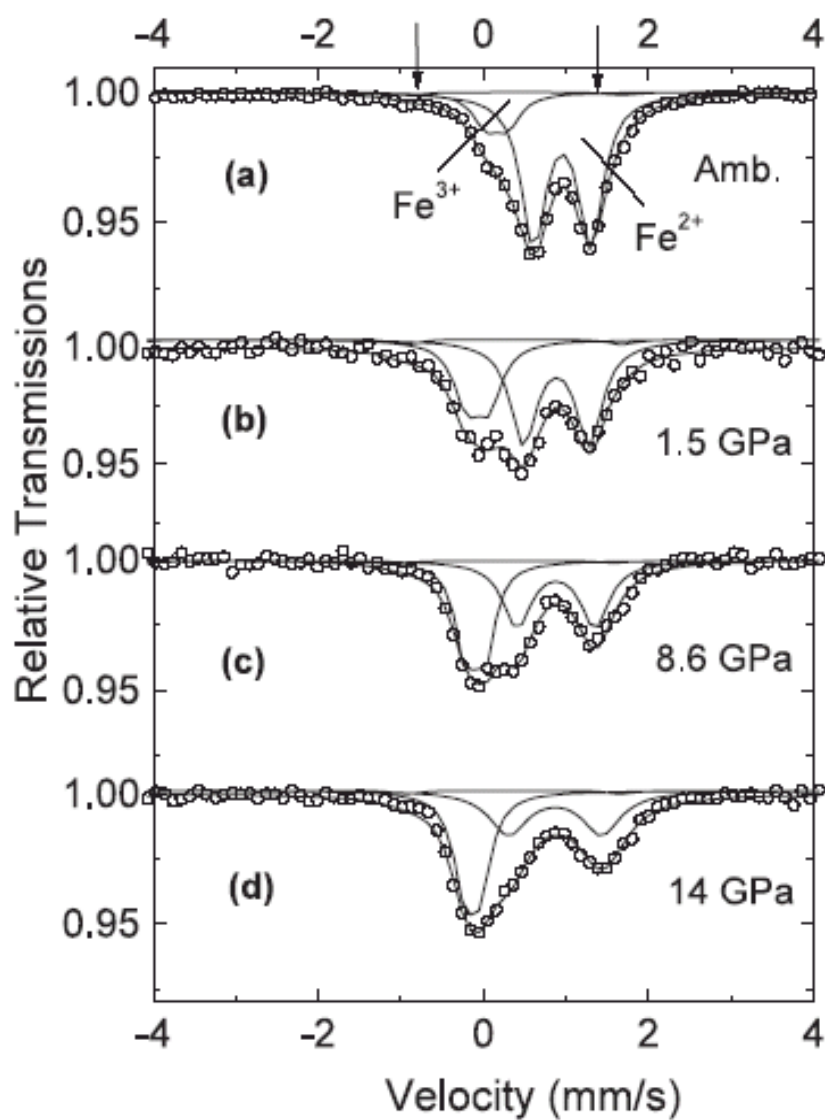


Figure 4.5: The dramatic pressure evolution of ^{57}Fe Mössbauer spectra of an untreated FeTiO_3 sample at room temperature observed by Seda and Hearne (2004). The spectra showed a pronounced increase in the relative intensity of the ferric Fe^{3+} component with pressure. This behavior was also observed for a heat-treated sample of ilmenite.

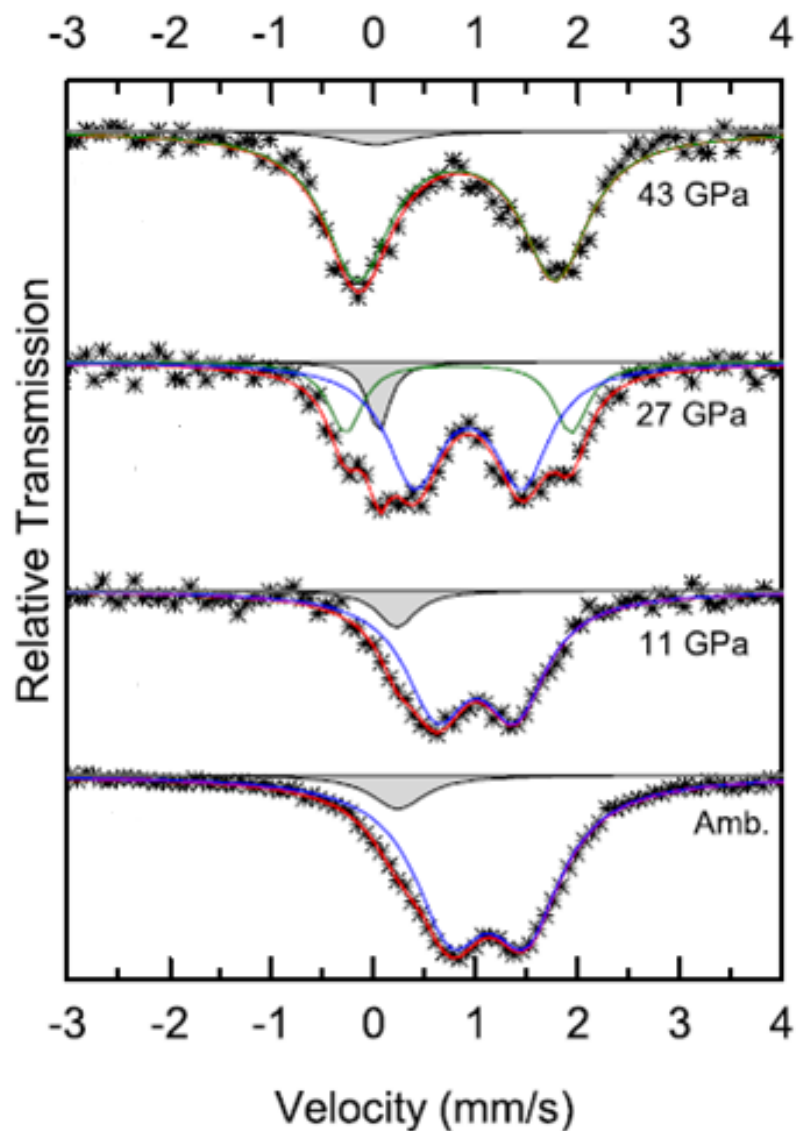


Figure 4.6: The pressure evolution of ^{57}Fe Mössbauer spectra of synthetic ilmenite as fitted by Wu et al., 2009. The spectra showed a pronounced increase in the relative intensity of the ferric Fe^{3+} component with pressure.

Seda and Hearne (2004) recorded an increase from 13% to 30% in the relative abundance of the ferric component on a natural sample up to 14 GPa. Wu et al., (2009) recorded a slight increase from 8% at ambient pressure to 13% at 13 GPa. The experimental results from Wu et al., (2009) on a synthetic ilmenite sample show that the perovskite phase of ilmenite, initiates at approximately 20 GPa. The two phases coexist up to 43 GPa, the highest pressure reached in that study, with the

perovskite phase having a greater abundance at high pressures.

The hyperfine interaction parameters obtained from the fitting of the Mössbauer spectra for the ferrous and ferric component show a similar trend in studies by Seda and Hearne (2004) and Wu et al., (2009). The isomer decreases as a function of pressure attributed to an increase in the s-electron density at the nuclear site and the quadrupole splitting increases with pressure. For a heated treated sample, the quadrupole splitting was found to decrease with pressure (Takele and Hearne, 2004). The isomer shift and quadrupole splitting of Fe^{2+} recorded on a natural sample of ilmenite is 1.06 mm/s and 0.69 mm/s respectively and for Fe^{3+} 0.27 mm/s and 0.32 mm/s respectively (Seda and Hearne, 2004). These values are consistent with those recorded in the literature (Wu et al., 2009; Vaughan and Drickamer, 1967; Annersten and Halenius, 1976; Dyar et al., 2006). The isomer shift values are quoted with respect to $\alpha\text{-Fe}$.

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Chapter 5

EXPERIMENTAL

5.1 Samples

In this study two natural samples of ilmenite (FeTiO_3) and a synthetic sample of ilmenite were used for all high pressure ^{57}Fe Mössbauer spectroscopy measurements. Natural assemblages of ilmenite were obtained from the Hillindale mining area of KwaZulu-Natal, South Africa (Nell and den Hoed, 1997). One of the samples was original untreated polycrystalline powder, which was ground into a powder under acetone for loading in a DAC. This sample originates from the same source as the one used by Seda and Hearne (2004). Mössbauer measurements up to a maximum pressure of 33 GPa have been applied to the synthetic sample and to 14 GPa for the natural samples.

5.2 High-pressure and room temperature ^{57}Fe Mössbauer facility

The high-pressure room temperature ^{57}Fe Mössbauer facility is designed for vertical conventional Mössbauer experiments. The block diagram for the facility used in this study for all high-pressure Mössbauer measurements is shown in Figure 5.1. All components of the facility inside the dashed rectangle are housed in a lead (Pb) enclosure to protect the user from γ -rays.

The source-DAC-detector arrangement is similar to the one described by Takele and Hearne (2001) (see Figure 5.2). Figure 5.3 shows the actual arrangement of the

source and DAC in transmission geometry for high-pressure Mössbauer measurements at room temperature. A detailed description of how the facility operates is found in section 5.3.3.

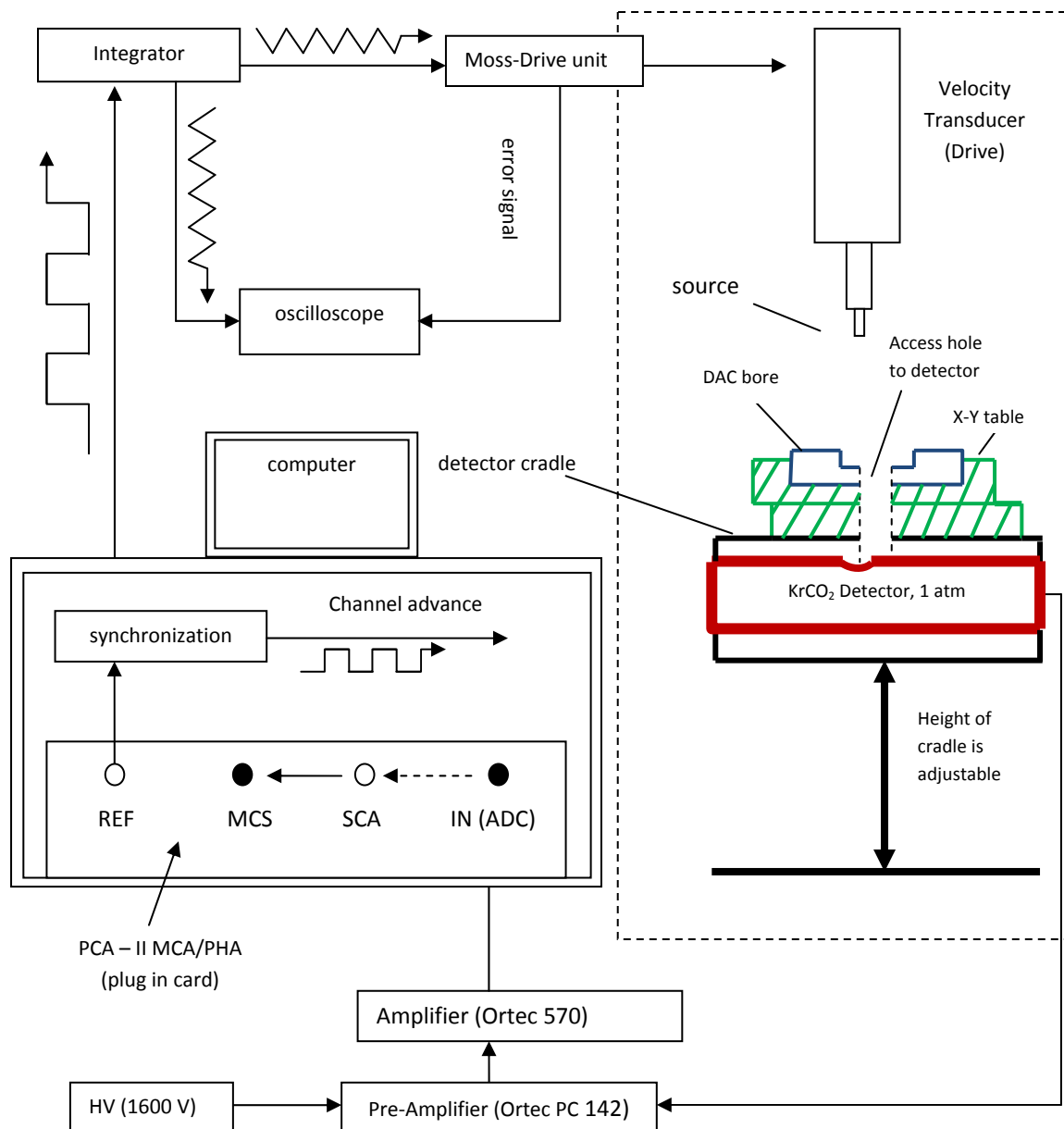


Figure 5.1: Block diagram of the high pressure ^{57}Fe Mössbauer facility for room temperature measurements. The source-DAC-detector arrangement is the same as the one described by Takele and Hearne (2001). The components enclosed by the dotted rectangle are housed in a lead (Pb) metal casing for safety from the γ -radiation emanating from the ^{57}Co (Rh) source (see also Figure 5.3).

5.2.1 γ -ray source

A custom-made ^{57}Co (Rh) point source with activity of 10 mCi (specific activity of 4000 mCi/cm²) has been used in close proximity to the DAC to concentrate the radiation flux on the sample cavity. It was produced by thermally diffusing ^{57}Co activity into a 12 μm thick rhodium foil and fixing an active area of 0.5 x 0.5 mm² into the tip of tapered aluminum holder. A conventional source on the other hand has an active diameter of 5 mm, making it totally inadequate to concentrate the radiation flux on small sample volumes used in DAC's. The source was determined by the manufacturer³ to have a maximum line-width of 0.132 mm/s and a recoilless fraction of 0.73 (at T=293 K). The output of 14.4 KeV γ -ray photons is $\approx$ 65%.

5.2.1 γ -ray detection

The constraints imposed by Mössbauer spectroscopy (MS) in a DAC make it beneficial to choose a detector with a high efficiency and resolution. A typical sample for MS in a DAC has an area of $\approx 10^{-3}$ cm² (sample size: 300 μm diameter x 50 μm thickness) compared to a sample size in conventional MS which has a typical area of 1.0 cm². In addition to the constraint of sample size, approximately 75% of the incident 14.4 keV resonant radiation is absorbed by the diamonds (Takele and Hearne, 2001). Figure 5.2 is a schematic diagram showing the source-DAC-detector geometry for high-pressure Mössbauer measurements at room temperature and Figure 5.3 shows the actual positioning of the source and DAC.

Pulse height spectra recorded on a synthetic ilmenite sample loaded on a DAC pressurized to 2.5 GPa and the same sample loaded on a conventional holder at

³ The point source is supplied by Cyclotron Co., Ltd (249033,Obninsk ,Russia)

ambient pressure are shown in Figures 5.4 (a) and 5.4 (b) respectively. It is clear that there is a considerable reduction in both the peak-to-background ratio and the count rate for the 14.4 keV resonance radiation in Fig.4 (a) when compared to Fig.4 (b). A detector with a high efficiency in the vicinity of the resonance radiation energy is therefore required to minimize unwanted background radiation.

Gas-filled proportional counters are appropriate for photons with energy less than 40 keV (Dickson and Berry, 1986). For ^{57}Fe Mössbauer spectroscopy gas-filled proportional counters are chosen because they combine high resolution for the 14.4 keV resonant γ -rays with an adequate efficiency and lower efficiency at higher energies which may originate from scattering events (X-ray emission) (Bedassa, 2000). Further scattering of this high energy X-ray emission events contributes to non-resonant background events in the 14.4 keV window.

The proportional counter in high-pressure Mössbauer spectroscopy must discriminate the 14.4 keV resonant γ -rays from other non-resonant high energy γ -rays and X-ray transitions originating from the source and scattering from surrounding materials. The non-resonant radiation arises from Compton scattering of the source radiation by the sample and surrounding materials and photoelectric scattering of the γ -rays and X-rays and scattering off the constituents of the DAC.

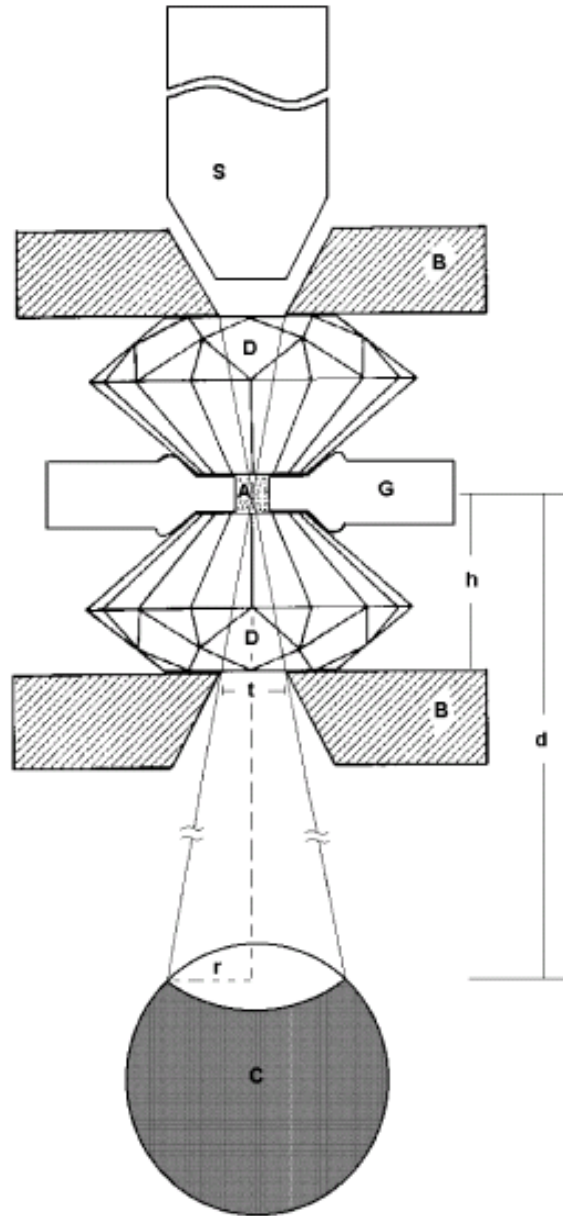


Figure 5.2: Schematic diagram of the vertical transmission geometry of the DAC for Mössbauer spectroscopy measurements. Label S refers to the point source, D denotes the diamonds (4.5 mm thickness), B denotes the backing plates ($\Phi = 3.3$ mm, with 80° exit aperture), G is the gasket, A is the pressurized absorber ($300\ \mu\text{m} \times 50\ \mu\text{m}$ thickness) and C is the detector. Typical values of $h=2$ mm and $d=65$ mm.

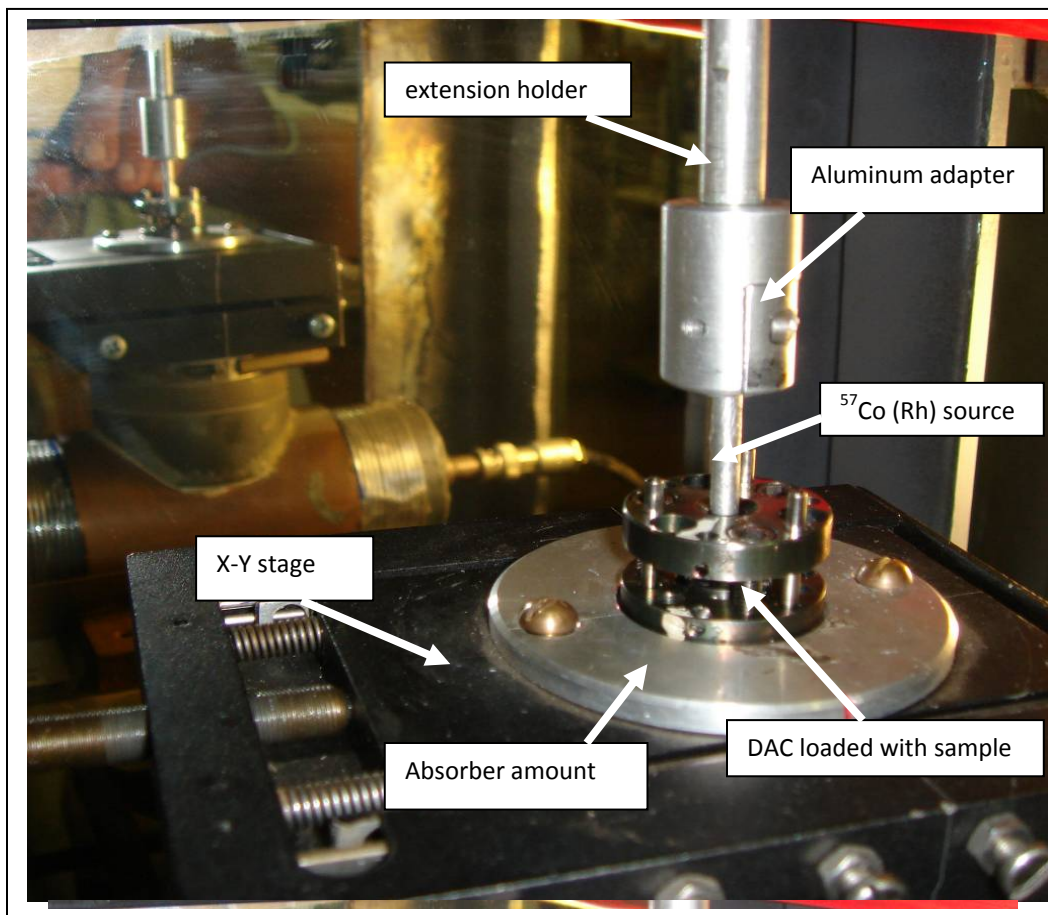


Figure 5.3: The actual positioning of a DAC with respect to the source in a Mössbauer spectrometer optimised for high-pressure room temperature measurements. The ^{57}Co (Rh) γ -ray source is placed in close proximity to the back of one of the diamonds in the DAC so as to concentrate the radiation flux on the sample chamber.

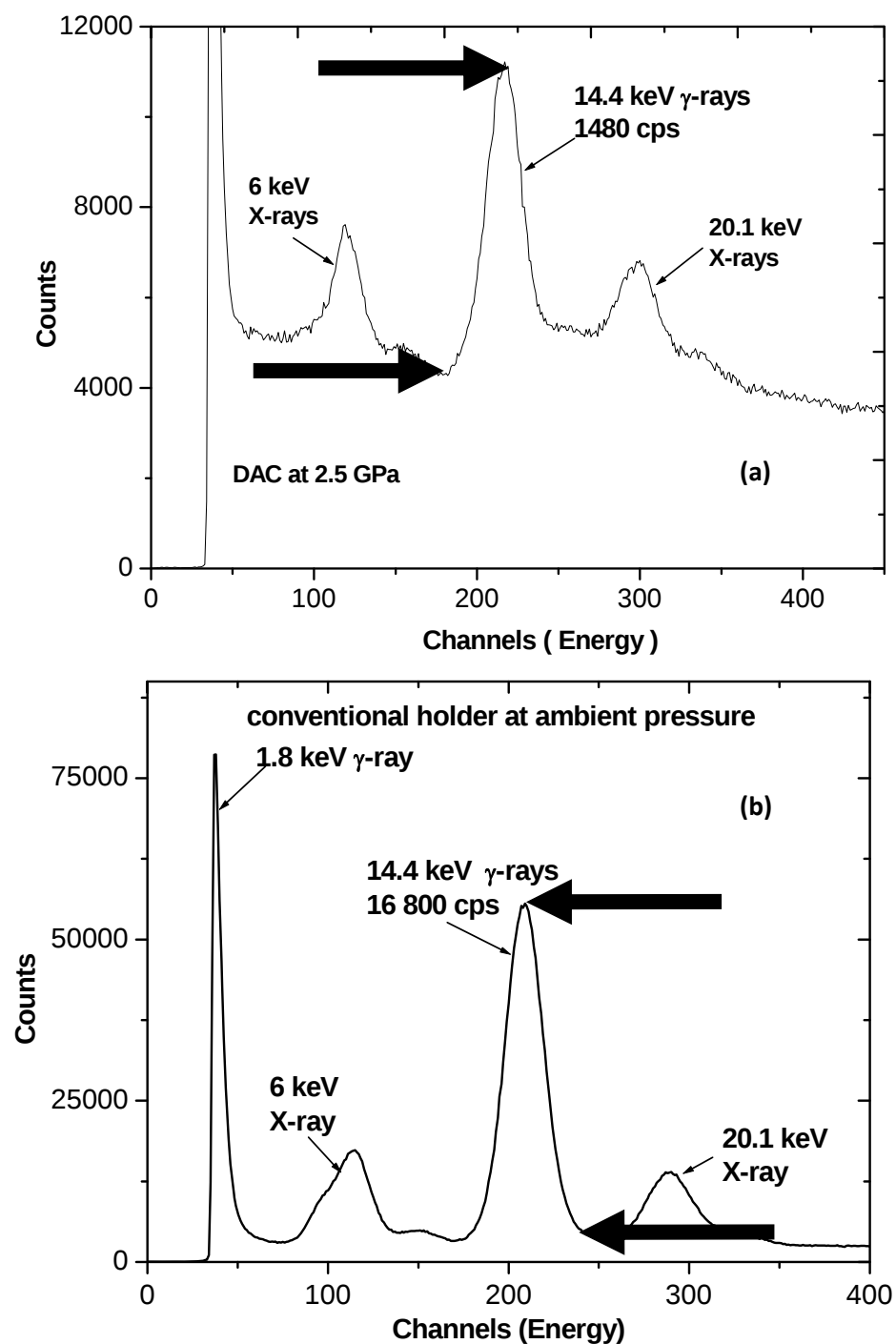


Figure 5.4: (a) Pulse height spectrum of the point source in combination with a synthetic ilmenite sample confined in a Re gasket (cavity, $\Phi = 250 \mu\text{m}$) of a DAC at 2.5 GPa. (b) Pulse height spectrum at ambient pressure for a point source in combination with synthetic ilmenite sample placed in a copper clamp holder ($\Phi = 1.5 \text{ cm}$). Note difference in the 14.4 keV peak/background ratio. The background is the total area below the bottom arrow, the distance between the arrows gives an indication of the height of the 14.4 keV peak.

In this study a commercial available Kr-CO₂ (1 atm) gas-filled proportional counter was used. The proportional counter has an efficiency of 12% for the 14.4 keV resonant radiation and a resolution of 60%. In addition to the 14.4 keV γ -ray, a 1.8 keV escape peak can be used to register the Mössbauer effect. The escape peak is produced from secondary processes in the detector and contributes $\approx$ 40% of the total count rate.

5.3 High-pressure ⁵⁷Fe Mössbauer measurements in DACs

The diamond anvil cell (DAC) is well recognised as being an important device for generating static, ultra high-pressure in the study of materials to investigate their physical properties as a function of the external high pressure. The Merrill-Bassett cell was used for all high-pressure experiments in this work. High pressures are generated in the sample cavity of a (metal foil) gasket sandwiched between two brilliant-cut, gem-quality diamonds, which serve as both pressure anvils, and as a window to the sample, as shown in Figure 5.2. The anvils consist of a pair of 0.3 carat 16-sided brilliant cut diamonds with bevelled culets (truncated tips) of 500 μ m diameter. The culets are polished parallel to the table faces. The bottom anvil is a Boehler-Almax anvil glued to a tungsten carbide backing plate with an 80° degree wide exit cone, see Figure 5.5 and the top anvil is a normal brilliant cut anvil glued to an Inconel backing plate.

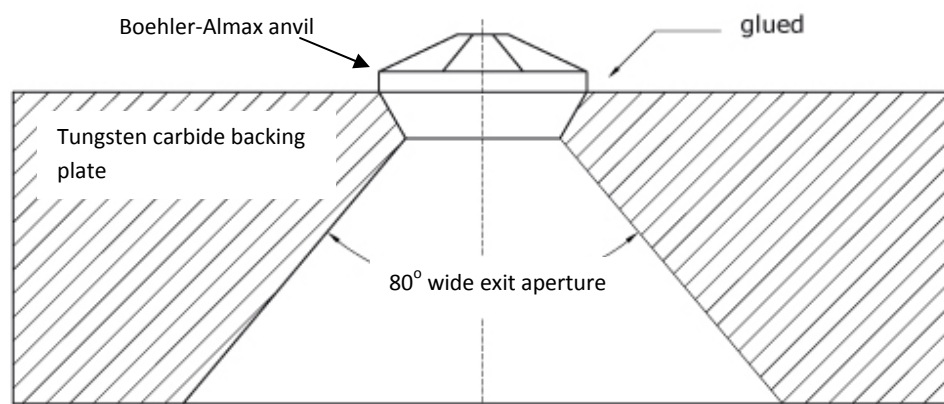


Figure 5.5: Boehler-Almax anvil with 80° exit aperture glued to a tungsten carbide backing plate.

The total thickness of the two opposed diamonds with a gasket in between is $\approx 4 - 4.5$ mm. A hole drilled as a sample cavity in pre-indented rhenium (gasket material chosen for synthetic ilmenite measurements) or $\text{Ta}_{90}\text{W}_{10}$ (gasket material chosen for the natural samples) serves as a sample cavity. High-Z (where Z is the atomic number) elements ensure that the gasket also serves as an effective collimator of the radiation (and there is negligible transmission through regions surrounding the cavity).

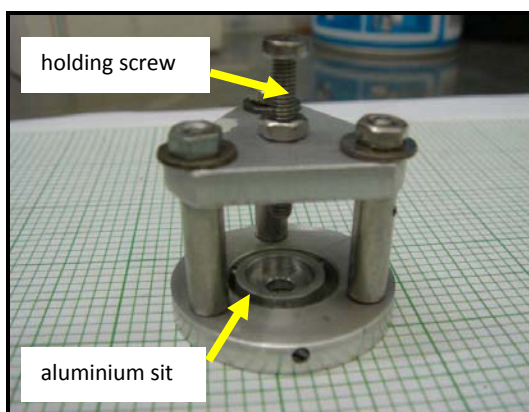
The diameter of the cavity is $250 - 300 \mu\text{m}$ and has a thickness of $30 \mu\text{m}$ at the initial stage of the measurements for each sample. The body of the Merrill-Bassett cell for all high-pressure measurements is made from Inconel-750 which has been hardened to ≈ 450 HV (Vickers hardness).

5.3.1 Diamond mounting and alignment

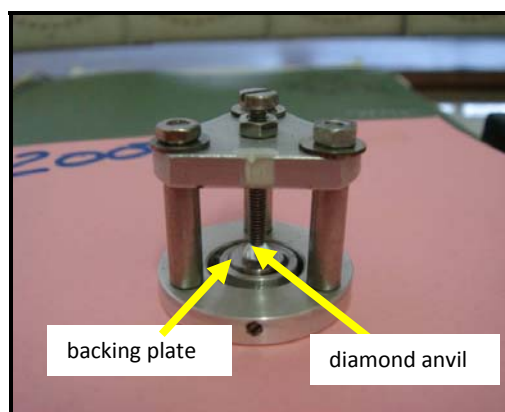
The first step in preparing the DAC for high pressure experiments is centering of the anvils with respect to the optical access hole and then subsequent mounting on the backing plates. The diamonds and the DAC were first cleaned of surface materials

and contaminations using alcohol before centering and mounting of the anvils could be undertaken. A small anvil holding jig was used in the place of the backing plate of the upper half of the cell to clamp one of the anvils down on the backing plate in the lower platen (see Figure 5.6 (a) and (b)). The anvil was then centered under an Olympus GX 71 inverted microscope by laterally moving the backing plate with three centering (lateral adjustment) screws, see Figure 3.7 (Section 3.6).

A small drop of quick set epoxy was put around the table of the anvil to fix it to the backing plate before the final epoxy for high pressure experiments could be applied. For high pressure applications a mixture of the epoxy Stycast 2850 FT and curing agent (catalyst) Catalyst 9 was used. These were thoroughly mixed by weight in the ratio 3.5% of catalyst per 100 parts of epoxy. The mixture was then gently spread around the anvil's table using a toothpick and inspecting with a X3 magnifying glass. For the final curing of the epoxy mixture, the jig was placed in an oven for two hours at a temperature of 65°C.



(a)



(b)

Figure 5.6: (a) A small anvil jig used for centering and fixing the diamond anvils. The laterally adjustable aluminum seats are used for centering the backing plates (b) A picture showing an anvil that has been centered on top of the backing plate and held by the upper screw.

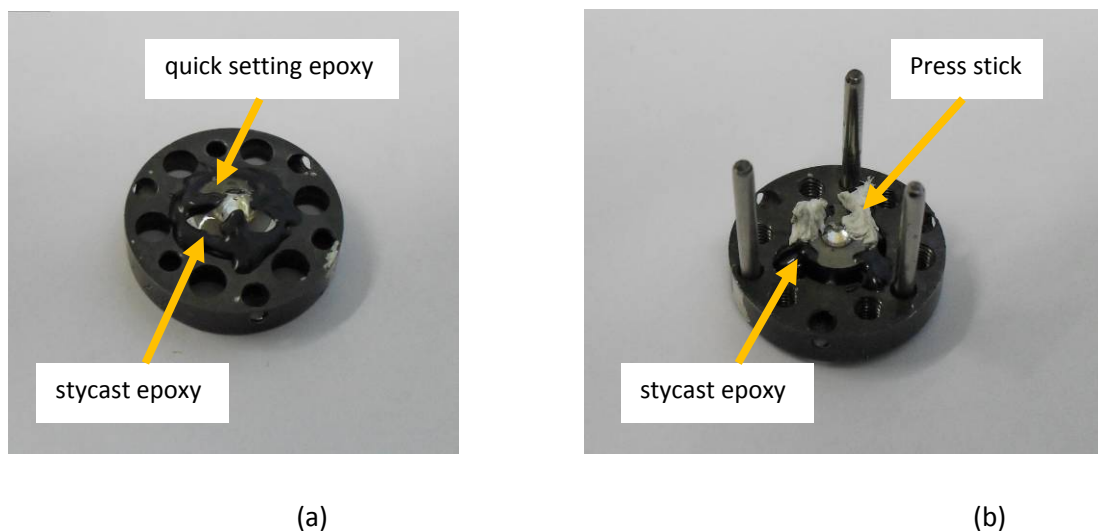


Figure 5.7: (a) The top anvil centered and glued to the Inconel backing plate. The epoxy is spread around the table of the anvil. (b) The bottom anvil, a Boehler-Almax anvil centered and glued on the tungsten-carbide backing plate. The press-stick is for holding the gasket firmly in place during loading of the sample.

Once the epoxy had cured, the next step in assembling the DAC was to adjust the lateral and parallel alignment of the anvils. The bottom anvil was a custom made Boehler-Almax anvil which was already fixed onto a backing plate. Before the DAC could be assembled for aligning the culet surfaces were again cleaned using alcohol. In aligning of the anvils care has to be taken that the anvils do not come into contact because diamond is hard but brittle and chips/damages easily when there is forceful contact. To circumvent this problem soft spacers are inserted in between the diamond anvils. In this work a glass-slide (microscope cover slip) of $\approx 100 \mu\text{m}$ was sandwiched between culet tips during all alignment procedures.

Alignment is achieved through a series of steps to get the two anvils perfectly lateral and parallel to each other. Lateral alignment is achieved by adjusting the culet faces with respect to each other by means of moving the backing plates with the centering screws. Parallelism of the culets is achieved by carefully and alternatively manipulating the Allen-type tension screws. Parallelism is confirmed by the

disappearance of the Newton's fringes formed from the air layer between the glass-slide and culets when the cell is viewed under a microscope.

Once lateral alignment and parallelism of the anvils has been achieved, the overall thickness (height) of the closed cell with the glass-slide in between is noted at three distinct circumferential positions (h_1 , h_2 , h_3) using a Mitutoyo digital micrometer. The heights were measured and the differences between the three points, [h_2-h_1] and [h_3-h_1] were recorded. The relative differences in the heights are maintained during indentation and pressurization in order to maintain parallelism of the culet faces (Sterer et al., 1990).

5.3.2 Gasket preparation and sample loading

In this work two gasket materials, rhenium (Re, hardness 70 RC) and $Ta_{90}W_{10}$ (hardness 40 RC) were used in preparing the gasket for high pressure measurements. Rhenium was used for the synthetic ilmenite measurements and $Ta_{90}W_{10}$ for natural ilmenite samples. In all cases the preparation and loading of the gasket is the same. To prepare the gasket, a small piece having an initial thickness of $\approx 200 \mu\text{m}$ was cut to the desired size from a sheet of the gasket material.

The first step in preparing the gasket for measurements is indentation between the two diamonds. For the indentation the gasket was placed on the bottom anvil and its position accurately marked on the backing plate and DAC. The cell was then assembled and the initial distance between the back of diamonds with the gasket in between was measured using a micrometer. To indent, a load was applied by progressively turning the screws using an Allen key in small steps. After each indenting step the screw-head positions were marked relative to the body and the

DAC allowed to relax (for plastic extrusion of the indented area to occur) for 1-2 hours before the gasket could be further indented.

Allowing the DAC to relax serves to relieve the stresses at the edges of the culets. The progress of each step was monitored using a stereo microscope to view the indented region while the DAC was closed. A symmetric profile of the indented region around the anvil meant that the indenting was progressing well. At each step the thickness of the gasket was estimated by measuring the new distance between the back of the diamonds and the relative heights using a micrometer. When the distance between the back of the diamonds had reached a particular value corresponding to a predetermined thickness of the gasket ($\approx 50 \mu\text{m}$) the DAC was opened to check the symmetry of the indented region and to measure the thickness of the indentation.

At this stage a $150 \mu\text{m}$ hole (approximately a third of the culet diameter) was drilled using a spark erosion facility. The facility is shown in Figure 5.8 and Figure 5.9, with the major components labeled. The position of where the cavity should be situated is first marked with a sharp needle in the centre of the indentation. This serves as a guide to the eye when drilling to ensure that the sparking electrode⁴ is positioned correctly with respect to centre of the indentation. Another added benefit is that the electrode is able to “key-in”, reducing the risk of breaking the fragile electrode (Miletich, 1996).

⁴ The tungsten electrode is supplied by American Probe & Technologies, Inc., 471 Montague Expressway, CA 95035-6800, USA

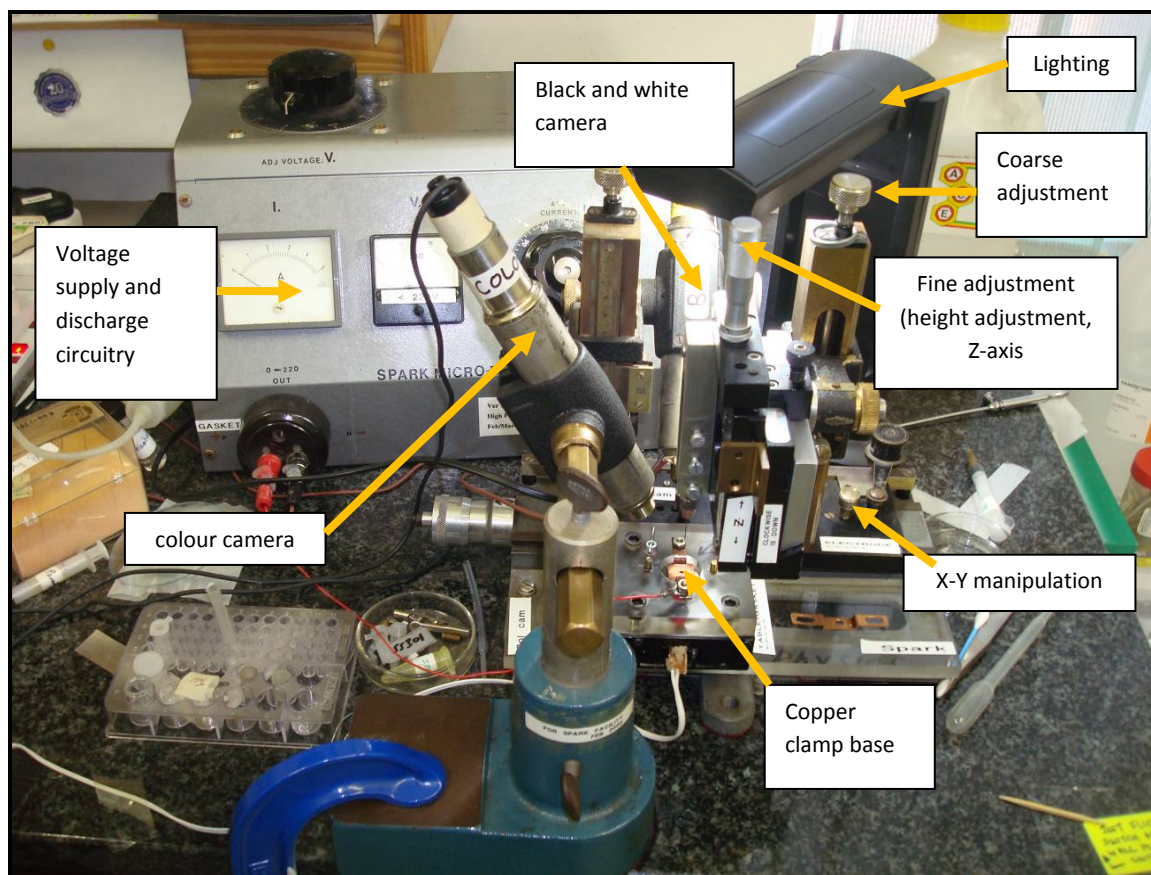


Figure 5.8: Spark erosion facility for drilling tiny holes (sample cavities) in hard metallic gaskets. The major components are highlighted. The black and white camera is used to view the position of the needle with respect to the gasket in the Y-direction. The color camera is used for viewing the position of the needle with respect to the gasket in the X-direction. Z-axis is perpendicular to the plane of the gasket (parallel to the electrode direction).

The tungsten electrode is visually positioned ≈ 1 cm above the copper clamp base and is centered with respect to the hole in the base. By tilting and moving the cameras accordingly the hole of the copper base is brought into focus on a color video monitor. The electrode is lowered towards the hole in the copper base and brought into focus. At this juncture the electrode and copper clamp base are visible on the centre of the screen. A gasket is then inserted on the copper base, with the indentation centered with respect to the hole in the copper base and then clamped. The indentation is then located on the screen by changing the focus, as well by

tilting or moving or moving the cameras. The electrode is lowered towards the spot marked on the indentation. Before spark drilling can commence care is taken to ensure the electrode is not in contact with the gasket (see Figure 5.9).

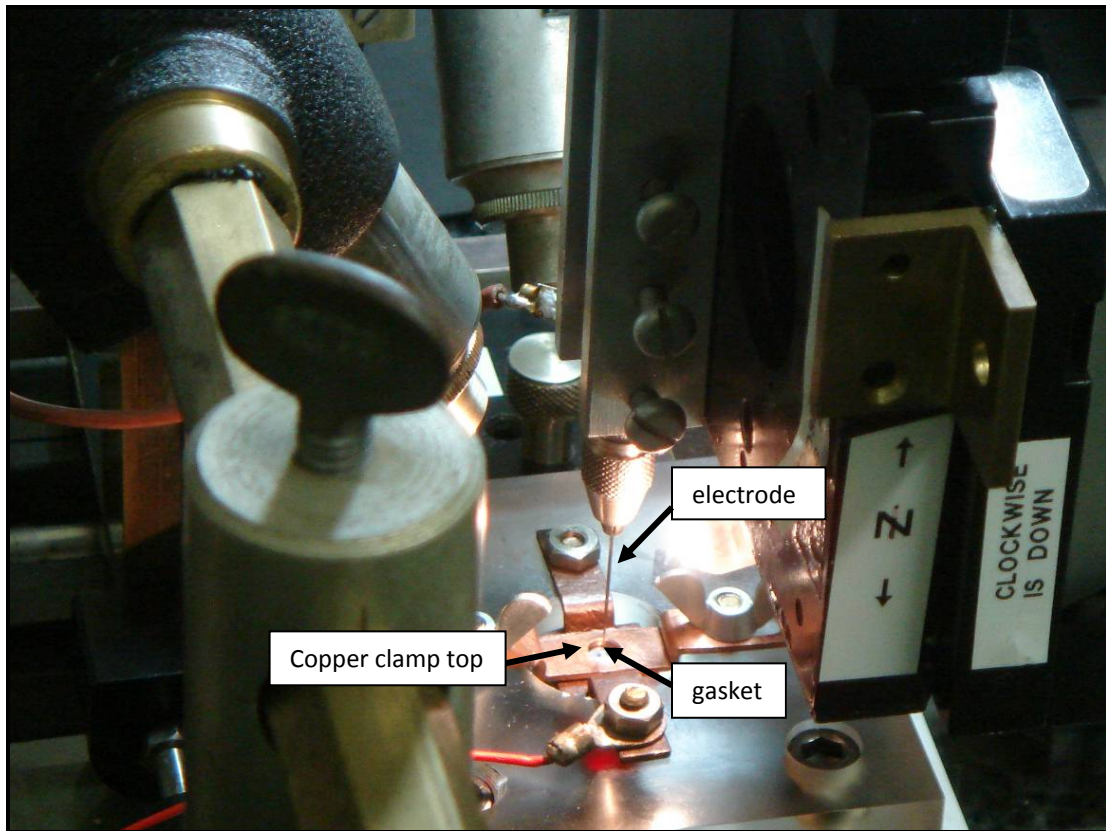


Figure 5.9: Close up of the spark erosion facility showing the electrode centered with respect to the gasket.

The removal of material from the gasket occurs by a series of rapidly recurring current discharges between the electrode and the gasket separated by a dielectric liquid and subject to an electric voltage. The electrode is lowered using the fine adjustment screw and comes into contact with the gasket. When the electrode is moved slightly away there is a current discharge shown by a bright spark. This can be explained in terms of the breakdown of the dielectric. The intensity of the electric field in the space between the electrode and the gasket increases as the distance

between the two is reduced. At a certain distance between the electrode and the gasket the breakdown voltage of the dielectric is reached and the dielectric breaks down allowing some current to flow between the electrode and the gasket. A beneficial effect that also results from this is a removal of the gasket material.

In this work a mixture of paraffin and alcohol was used as the dielectric liquid. Using electric voltages of less than 100 V, high quality circular erosion is obtained albeit taking a longer time. Voltages between 100-150 V produce low quality (irregularly shaped holes) and effective erosion. All the gaskets prepared for this study were spark drilled using voltages between 60-80 V.

The cavity is carefully cleaned using cotton buds dipped in alcohol and burs (rough edges on perimeter) are cleaned or cleared with micro-drill bits. After cleaning, the gasket is inserted back again on the DAC to be indented further to a final thickness of 30 μm . When the final thickness of $\approx 30 \mu\text{m}$ was reached, estimated by the distance between the back of the diamonds, the screw positions were marked relative to the body of the DAC and the relative heights for parallelism of the culets were measured for references. The cell was opened and the cavity was hand drilled to the final cavity diameter of $\approx 300 \mu\text{m}$ using a micro-drill bit (see Figure 5.10).

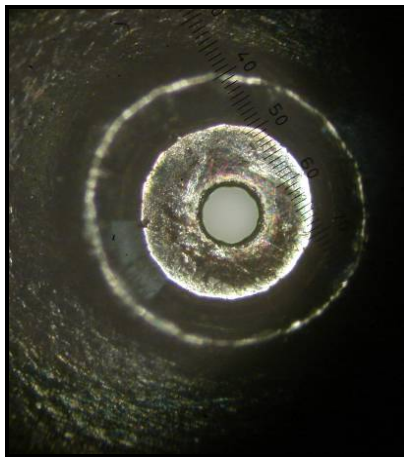


Figure 5.10: A 300 μm diameter cavity drilled in a pre-indentation using the spark erosion facility. The cavity is highly circular and is well centered.

5.3.3 Sample loading

The gasket was again mounted on the bottom anvil for the loading of the sample. The gasket is properly placed in its initial position indicated by the marks made on the bottom backing plate. Press-stick was used to secure the gasket firmly on the bottom anvil to prevent it moving during loading. Fine powder of the sample ground under acetone was placed on the edge of the indent in the gasket and carefully moved into the cavity using a 200 μm diameter needle. The remaining powder sample was cleared out of the indentation. The DAC was closed and the sample was compacted inside the cavity by shifting the top platen backwards and forwards until the sample was evenly distributed as viewed under a microscope.

A few ruby chips for pressure calibration were also added under a microscope. The top platen of the DAC was then mounted and the tension screws were tightened to the relative heights of parallelism of the DAC.

5.3.4 Pressure medium and calibration

Fluorinert⁵ mixture (1:1 combination of FC-70 and FC-77 fluorocarbons) was used as a pressure transmitting medium for high-pressure ⁵⁷Mössbauer measurements on the synthetic sample and silicone oil (diffusion pump oil, Angel et al., 2007) was used for the natural samples. The loading of the pressure media was at ambient conditions in all cases.

Figure 5.11 shows the simple arrangement needed to load the pressure medium at ambient conditions. The tension screws were loosened on the DAC and a small

⁵ Fluorinert supplied by Sigma-Aldrich (Pty) Ltd, South Africa

volume of pressure transmitting medium injected on one side of the top anvil. The medium adheres to the pavilion and culet edge of the anvil because of surface adhesion. When the top platen was shifted back and forth, the medium flows from the side of the anvil into the cavity, filling it. To check if the medium was inside the cavity the ruby balls were checked to see if they had changed positions and when tapping the top platen, motion of the fluid and sample was visible under a microscope.

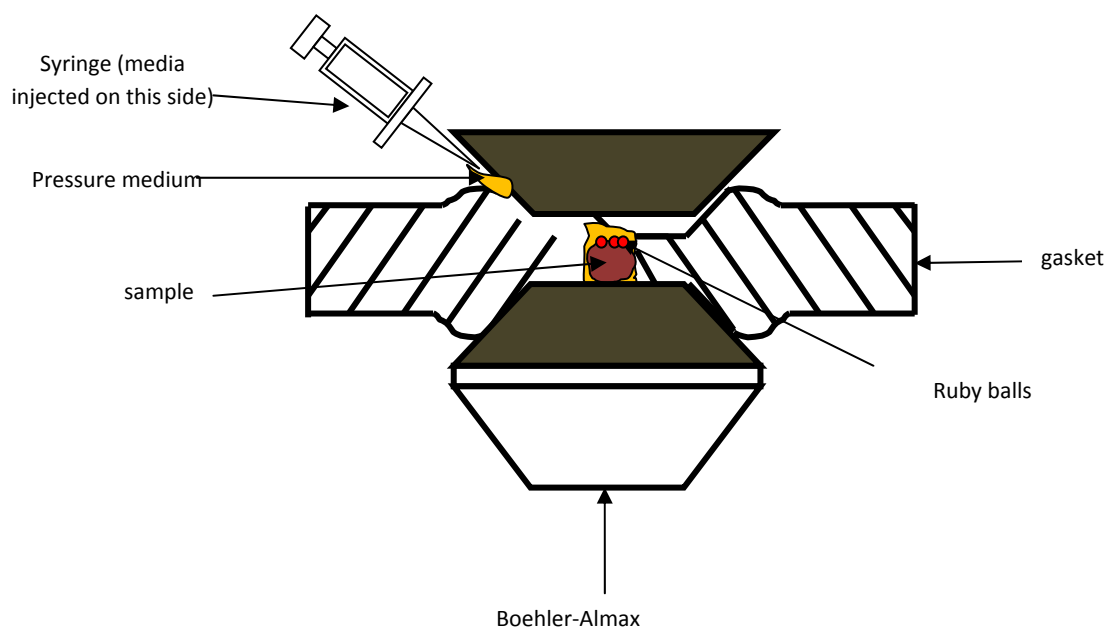


Figure 5.11: Arrangement for loading pressure transmitting media. The medium is injected on one side of the top anvil of a semi-assembled DAC. Small back and forth movements of the top anvil allows the fluid to flow into and fill the cavity.

5.3.5 Pressure calibration

The pressure calibration system used in this work is shown in Figure 5.14. An argon ion laser beam with a spot size of less than 5 μm and power output of 20 mW was used to excite the ruby fluorescence spectrum. The green line (514.53 nm) of the

laser light is focused onto the cell through an eyepiece (x20 magnification) of an Olympus Confocal Microscope (see Figure 5.14). An optical fiber (entrance aperture of 200–400 μm) coupled to a turret on top of the Olympus microscope collects and transmits the resulting radiation from the fluorescence to the HR 4000 spectrometer. The HR 4000 is a high resolution spectrometer for optical applications. It has a resolution of 0.025 nm (FWHM) and is responsive to wavelengths from 200–1100 nm. The spectrometer processes the signal from the optical fiber into a digital signal. The processed spectral information is then sent to an acquisition program through a USB 2.0 cable to a laptop. The data is acquired and displayed in real time by an application program called Spectra Suite. From the spectra displayed on the laptop values of wavelengths are easily read off.

The pressure in the cell was generated by turning the tension screws on the DAC using an Allen key (see Figure 5.12).

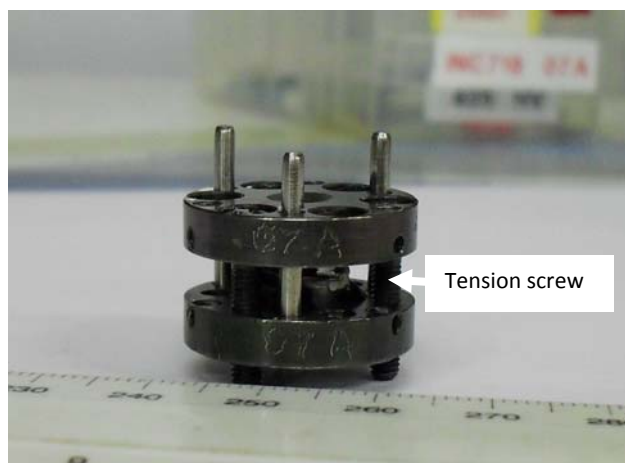


Figure 5.12: The assembled DAC ready for high pressure ^{57}Fe Mössbauer measurements.

The positions of the screws relative to the body were first marked. Turning all the three tension screws by a full thickness of a pen tip tick mark ($\approx \leq 5^\circ$) increased the

pressure by ≈ 3 GPa. The thickness of the tip mark was used as a guide for gauging the pressure that could be generated when the tension screws are turned as well for maintaining the relative parallelism height values at three circumferential positions on the platens.

Pressure calibration was performed following the relation:

$$P(\text{GPa}) = 2.746\Delta\lambda(\text{nm})$$

given in Chapter 3 (Piermarini et al., 1975; Mao et al., 1978). Shifts in the wavelength of the R_1 ruby fluorescence peaks from the ruby balls that were loaded in the cavity together with the sample have been used for pressure calibration. For the ambient calibration and DAC pressure measurements the spectral integration time was 100 ms using the Spectra Suite software. The laser light was focused on different ruby balls throughout the sample and pressures at a number of points calculated using pressure versus fluorescence wavelength (see Section 3.7). The average of the calculated pressure values was taken as the pressure of the sample. These values had an error of ± 0.5 GPa from the average value.

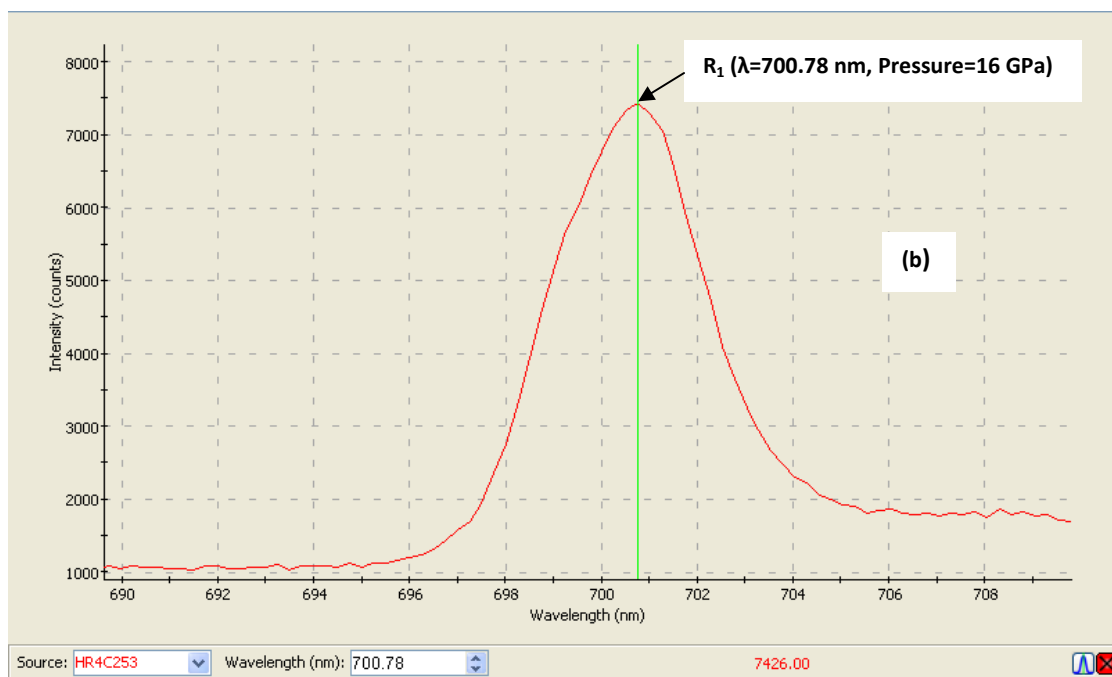
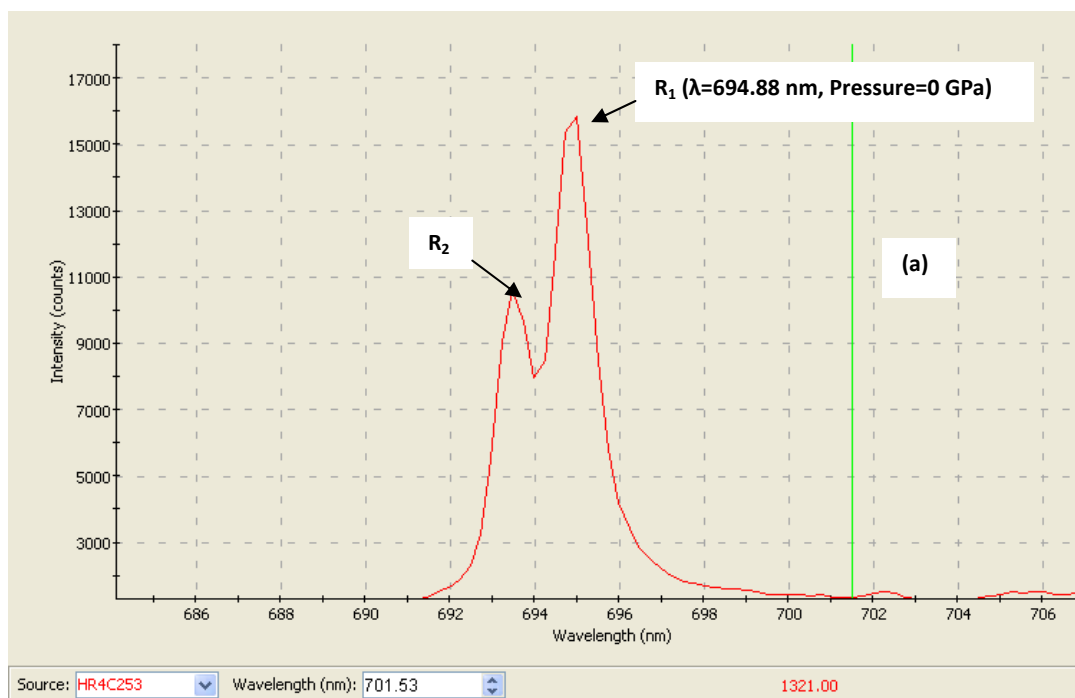


Figure 5.13: (a) Ruby fluorescence spectrum at ambient conditions captured using Spectra Suites software. The R_1 line has a wavelength of 694.88 nm. (b) A pressure of 16 GPa causes a shift of $\Delta\lambda = 5.9$ nm for the R_1 line from its ambient value. The ruby fluoresces at a wavelength of 700.78 nm. The pressure transmitting medium used is silicone oil. Note the broadening of the spectrum at 16 GPa, which indicates deviations from ideal hydrostatic behavior.

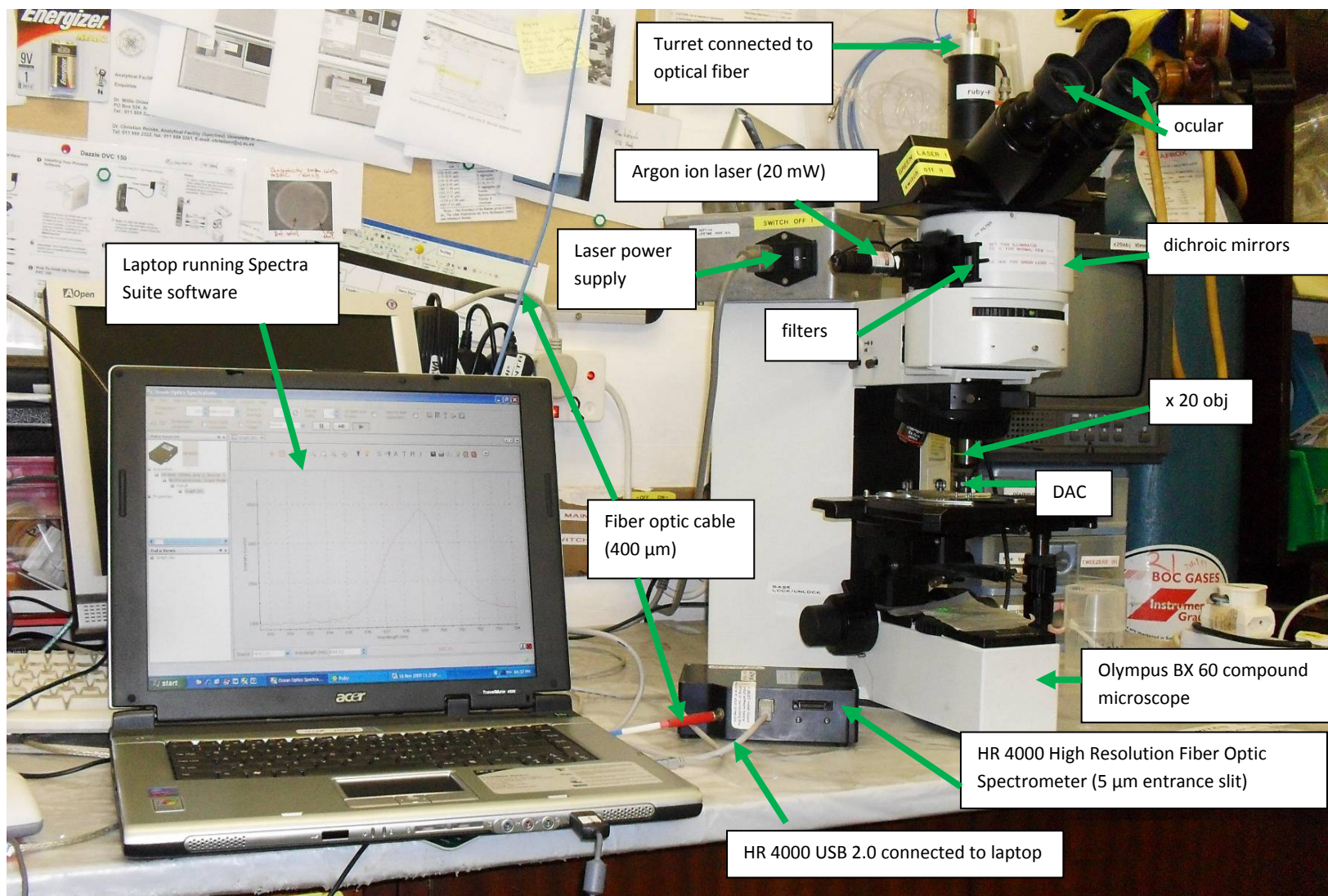


Figure 5.14: Pressure calibration set-up used in this study. Major components are labeled.

5.3.6 Spectral data acquisition

The point source was mounted in an aluminum holder on an aluminum adapter (see Figure 5.3). The aluminum extension holder is connected to the velocity transducer (Wissel model MVT-1000) to give the point source the velocity transferred from the Mössbauer Drive Unit (Wissel MR-260A) for the γ -ray energy modulation.

The compact features of the Merrill-Bassett DAC (2.2 cm diameter, 1.2 cm height) allows top-loading at the absorber mount. The DAC is placed at the absorber mount on top of the X-Y table, which is permanently fixed on top of a detector cradle. The position of the DAC is adjusted to ensure that the tapered tip of the source is centered and is lowered above one of diamond anvils (see Figure 5.3). In this work the point source was brought close to the back of a Boehler-Almax anvil (entrance aperture) and the conventional brilliant cut anvil on the Inconel backing plate was the exit aperture. This was done for two reasons, namely, the 80° wide aperture of the tungsten carbide backing plate where the Boehler-Almax anvil sits makes visual centering of the source with respect to the back of the diamond less tedious. The other reason is that the count rate for the 14.4 keV γ -rays is greater with this arrangement compared to using the narrower aperture of the Inconel backing plate where the conventional brilliant cut diamond anvil sits. A pulse height spectrum of the 14.4 keV resonant γ -ray and the 20.1 keV X-ray is recorded. The ratio of the pulse height counts of the two transitions is then calculated. A ratio of $\approx 2:1$ is taken to be near perfect alignment of the source and sample cavity. Once the optimal ratio has been obtained a single-channel analyzer is used to select the 14.4 keV window. Fine adjustments of the alignment of the source, DAC and detector window are made using the X-Y table in order to obtain the maximum integrated counts of the 14.4 keV transition in the discriminator window.

Transmission Mössbauer spectra were recorded in a vertical transmission mode with constant acceleration spectrometer in Multichannel Scaling mode (MCS). The velocity waveform was generated by using a commercial Personal Computer Analyser version (PCA II) controller card. This controller card is also used for MCS with a dwell time of 100 μ s per channel. A spectrum and its mirror image was collected in 1024 channels having two mirror images that were folded into 512 channels. This was folded into 512 channels and two adjacent channels combined so that statistical scattering was further reduced. In so doing the final processed spectrum comprised 256 channels ready for theoretical fitting.

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CHAPTER 6

RESULTS AND DISCUSSIONS

6.1 Experimental results and analysis

For all samples, high pressure ^{57}Fe Mössbauer measurements have been performed at room temperature in the facility described in Chapter 5. The Mössbauer spectra were recorded in the normal transmission geometry. A Wissel constant acceleration motor was used to scan the velocity range of interest (typically ± 5 mm/s) with a ^{57}Co (Rh) “point” source (≈ 10 mCi) at room temperature. A KrCO_2 (1 atm) proportional counter was used to detect the 14.4 keV resonance γ -radiation.

All the spectra were analysed using the WinNormos-for-Igor Mössbauer spectra fitting software⁶ that consists of two least-squares fitting programs, namely SITE for a series of different subspectra, each representing different environments and DIST for a distribution of hyperfine parameters. Spectral hyperfine parameters were obtained by fitting theoretical subspectral curves to experimental data with Lorentzian line shapes to deconvolute Fe phases in the spectrum. Prior to analysis each spectrum was folded with its mirror image and adjacent channels subsequently added. This serves to remove geometrical base-line distortions and reduces the statistical scatter in the final data set to be used for analysis.

The results from the fitting of the hyperfine parameters of the three samples of ilmenite are presented in the following sections.

⁶ Written by R A Brand, Universität-GH-Duisburg and distributed by Wissel GmbH (Würmstrasse 8, D-82319, Starnberg, Germany)

6.2 Pressure response of natural ilmenite sample (labeled SLS) up to 14 GPa

The natural ilmenite sample (labeled SLS) was obtained from heat-treating a natural sample of ilmenite obtained from the Hillindale area of KwaZulu-Natal, South Africa (Nell and den Hoed, 1997). A brief description of the untreated natural sample is given in Section 6.4. Mössbauer spectra recorded on a $\approx 10 \text{ mg/cm}^2$ sample show two paramagnetic doublets attributed to the ferrous component and ferric component (see Appendix A). The results are plotted on a restricted velocity scale.

6.2.1 Experimental results and analysis for the SLS ilmenite sample

Spectra of ^{57}Fe Mössbauer measurements at selected pressures are plotted in Figure 6.1 and Figure 6.2, for the SLS sample. The plots are shown on a small velocity scale, which shows clearly the pressure evolution of the various components at selected pressures. The hyperfine parameters of the ferrous and ferric components obtained from the fitting of the spectra are tabulated in Table 1 (a) and (b). Isomer Shift (δ) values are quoted with respect to $\alpha\text{-Fe}$ metal. It is clear from Table 1 (b) and Figure 6.1, that there is an increase in the abundance of the ferric component with pressure (more evident above 6 GPa) and a corresponding decrease in the abundance of the ferrous component. The abundance of each component is derived from the absorption areas in the theoretical fit to the data. The abundance of each component as a function of pressure is plotted in Figure 6.3.

Table 1: (a) Isomer shift (δ), Quadrupole Splitting (ΔE_Q), Line Width (Γ) values as derived from the fitting of the spectra of SLS ilmenite. The Isomer Shift (δ) values are quoted with respect to α -Fe metal.

Pressure	Fe^{3+} ilmn			Fe^{2+} ilmn		
(GPa)	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)
Ambient	0.273	0.250	0.363	1.059	0.754	0.508
0.7	0.264	0.275	0.379	1.056	0.769	0.497
1.4	0.239	0.277	0.373	1.049	0.770	0.459
4.0	0.225	0.278	0.419	1.042	0.781	0.534
6.5	0.221	0.299	0.392	1.023	0.791	0.500
10.8	0.215	0.304	0.378	1.017	0.805	0.520
14	0.211	0.315	0.384	1.013	0.820	0.520

(b): % Abundance of Fe oxidation states under pressure as derived from the fitting of the spectra.

	Abundance %*	
Pressure (GPa)	Fe^{3+} ilmn	Fe^{2+} ilmn
Ambient	22.1	77.9
0.7	23.3	76.7
1.4	24.1	75.9
4.0	24.9	75.1
6.5	25.6	74.4
10.8	26.1	73.9
14	27.5	72.5

* Typical error in abundance is $\approx 10\%$ of the quoted value, e.g. $22 \pm 2\%$ for Fe^{3+} and $78 \pm 7\%$ for Fe^{2+} at ambient pressure.

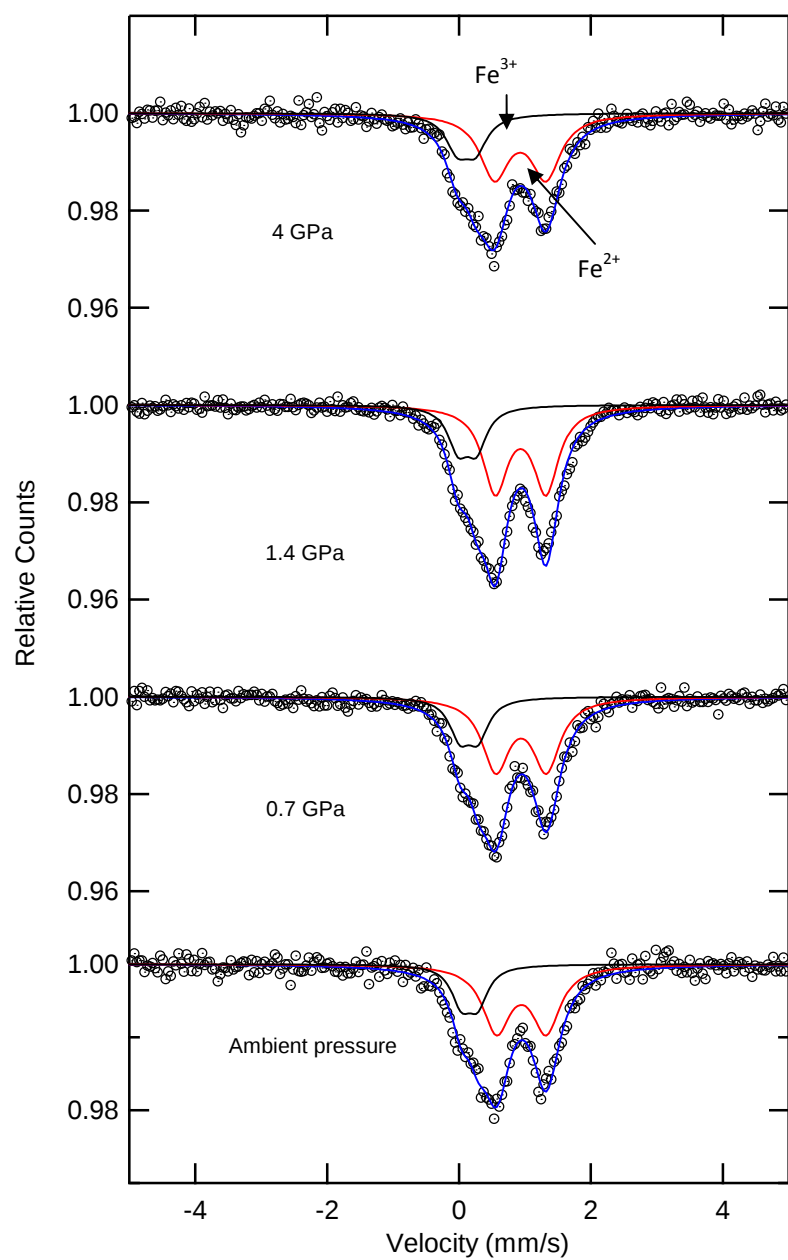


Figure 6.1: $^{57}\text{Mössbauer}$ spectra of the pressure response of SLS ilmenite at room temperature plotted on a restricted velocity scale. The increase in the abundance of the ferric component from ambient pressure to 4 GPa is not readily apparent. The spectra are fitted with two doublets, for the ferric component (in black) and ferrous component (in red). The intensities of the sub-spectra (Fe^{2+} and Fe^{3+}) are scaled by factor of half for clarity. The solid line through the data points is the overall fit to the data.

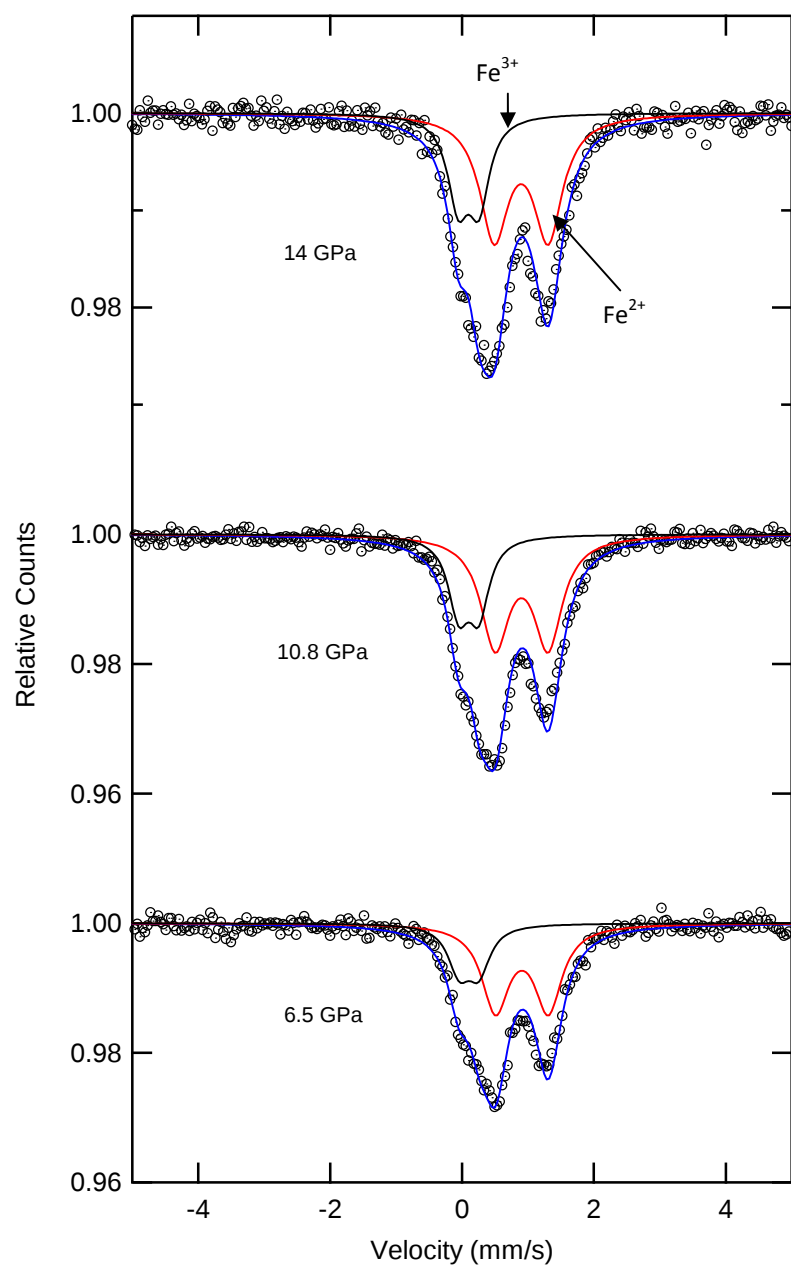


Figure 6.2: ^{57}Fe Mössbauer spectra of the pressure response of SLS ilmenite at room temperature plotted on a restricted velocity scale. The spectra show a more pronounced increase in the ferric component from 6.5 GPa to 14 GPa. The spectra are fitted with two doublets, for the ferric component (in purple) and ferrous component (in red). The intensities of the sub-spectra (Fe^{2+} and Fe^{3+}) are scaled by factor of half for clarity. The solid line through the data points is the overall fit to the data.

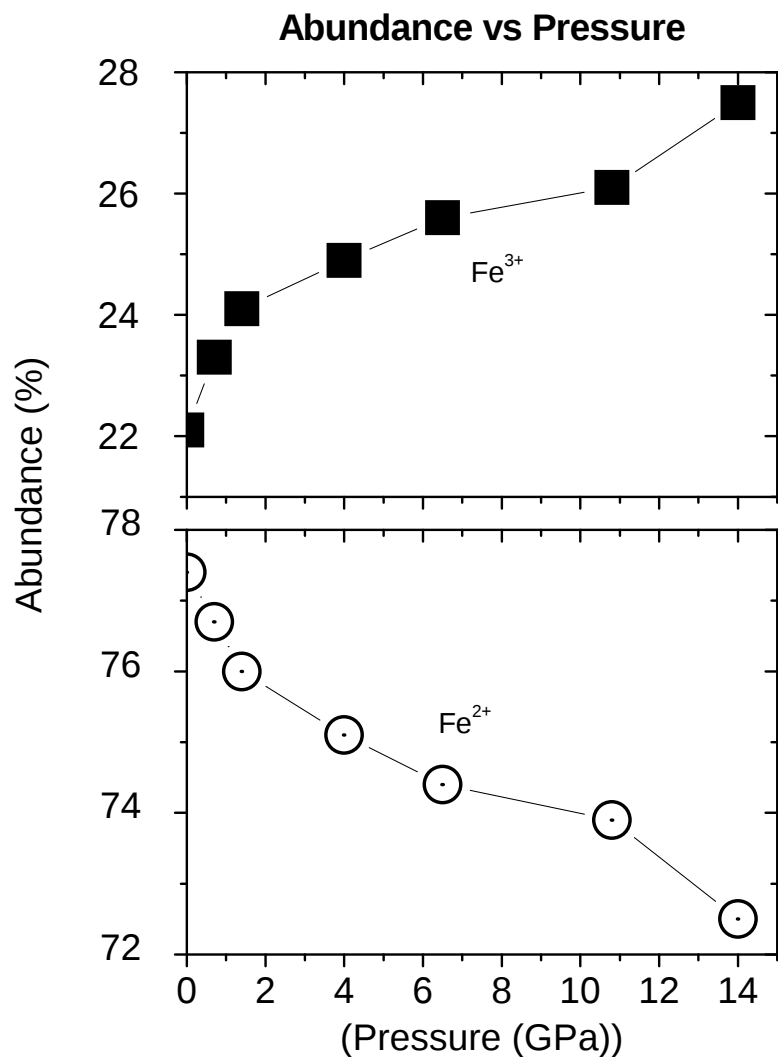


Figure 6.3: Variation of the abundance as a function of pressure for the ferrous and ferric components of SLS ilmenite. Open circles and black squares are data points. The solid lines through the data points are guides for the eye. As seen, the Fe^{3+} abundance increases with pressure, and the Fe^{2+} abundance decreases as a function of pressure.

The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio shows a gradual increase from ambient to the highest pressure of 14 GPa reached in this study, from an initial ratio of 0.28 to 0.38 (see Figure 6.4). This pressure response of the ratio in the SLS sample is not similar to that recorded by Seda and Hearne (2004). According to Seda and Hearne (2004), the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio

increases appreciably at lower pressures, reaching saturation above 4 GPa. In that work the ratio increases from 0.2 at ambient pressure to 0.65 at 14 GPa.

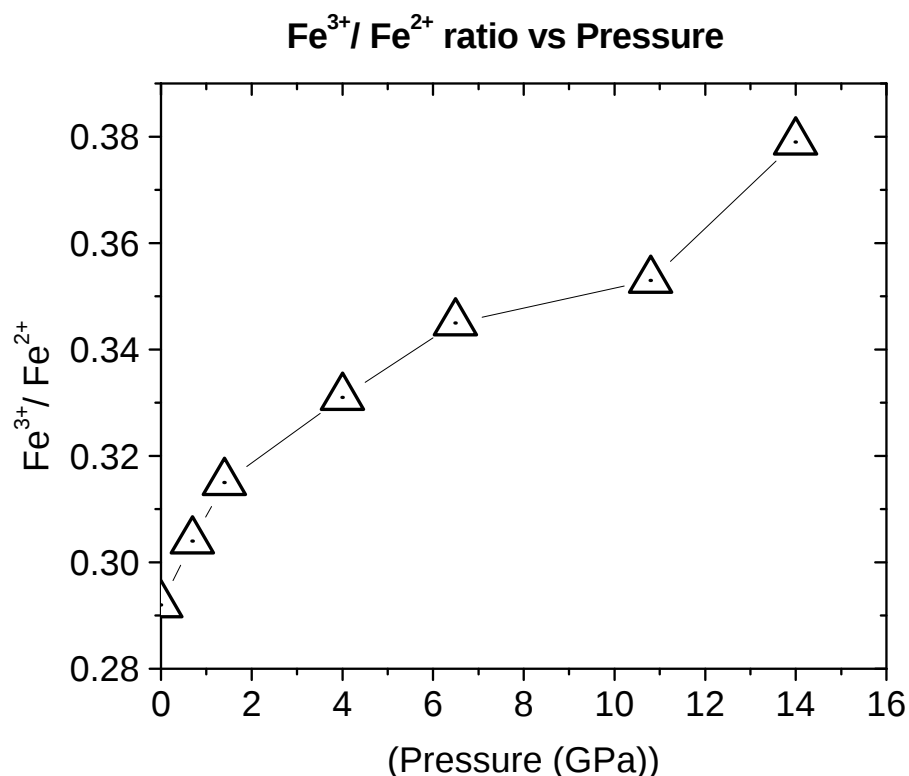


Figure 6.4: $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio variation with pressure for SLS ilmenite. Open triangles are data points. The solid lines through the data points are guides for the eye. The ratio increases with pressure up to highest pressure of 14 GPa, in this study.

The isomer shift values of the ferrous and ferric component relative to α -Fe as a function of pressure are plotted in Fig 6.5. The isomer shift shows similar behavior for both the ferrous and ferric component, in that; there is a decrease in the isomer with increasing pressure. This is attributed to the s-electron density increasing at the Fe nucleus (see equation, 2.10, Chapter 2). The pressure dependence changes

(decreases) as pressure rises beyond 4 GPa, likely related to the anisotropic compressibility of the unit cell (Seda and Hearne, 2004).

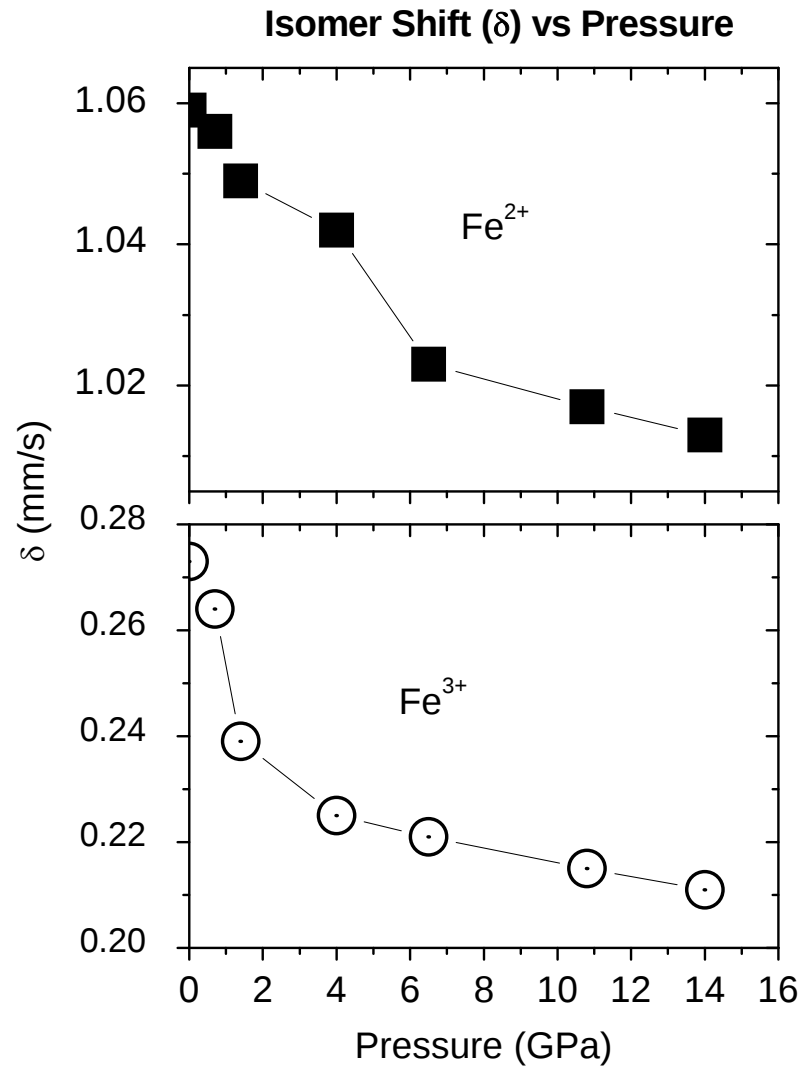


Figure 6.5: Isomer shift as a function of pressure for the ferrous and ferric components of SLS ilmenite. The values plotted are quoted with respect to α -Fe. Open circles and black squares are data points. The solid lines through the data points are guides for the eye.

The variation of the quadrupole splitting of both the ferrous and the ferric component as function of pressure are plotted in Figure 6.6.

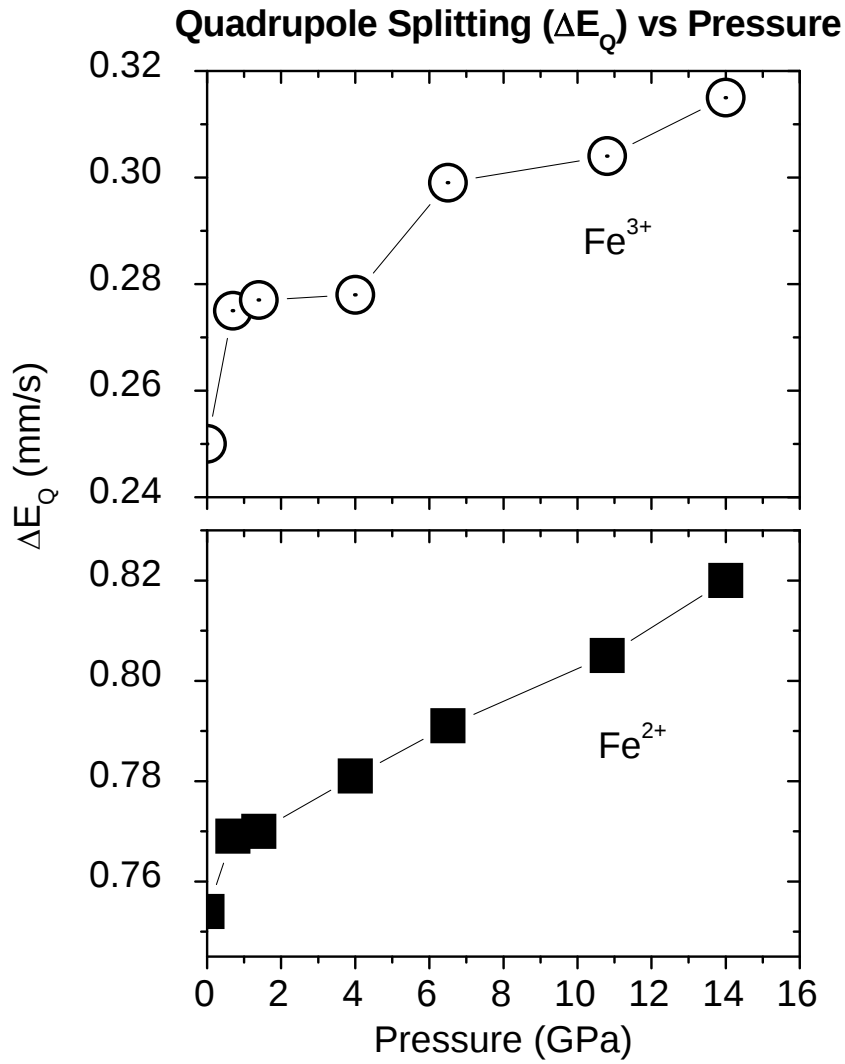


Figure 6.6: Variation of the electric quadrupole splitting as a function of pressure at room temperature for SLS ilmenite. Open circles and black squares are data points. The solid lines through the data points are guides for the eye.

The electric quadrupole splitting for both the ferrous and ferric component increases with pressure. This is in contrast to Seda and Hearne (2004) where the quadrupole splitting for the ferric component decreased with pressure. ΔE_Q reflects deviation from cubic symmetry. The increase in ΔE_Q is attributed to the increased

site distortion around the Fe ion when the pressure increases. The isomer shift and quadrupole splitting appear to follow the correct trends, increasing *s*-electron density and increasing site distortion respectively.

6.3 Pressure response of synthetic ilmenite sample to 35 GPa

Mössbauer spectra recorded on a $\approx 10 \text{ mg/cm}^2$ synthetic sample shows a single paramagnetic doublet attributed to the ferrous component (see Appendix A). The results are plotted on a restricted velocity scale.

6.3.1 Experimental results and analysis for the synthetic ilmenite sample

^{57}Fe Mössbauer measurements at selected pressures were done and the spectra are plotted in Figure 6.7 and Figure 6.8, for the sample. The plots are shown on a small velocity scale, which shows clearly the pressure evolution of the various components at selected pressures. The raw Mössbauer data was fitted using a Lorentzian line shape by the Mössbauer fitting program WinNormos-for-Igor. The fitting model used in this case is the model used by Wu et al., (2009) where the Fe^{3+} component is fitted using a singlet to represent an unresolved doublet because it has a low abundance and to ensure reliable fitting. This model has been adopted in the analyses of the Mössbauer spectra for the synthetic sample.

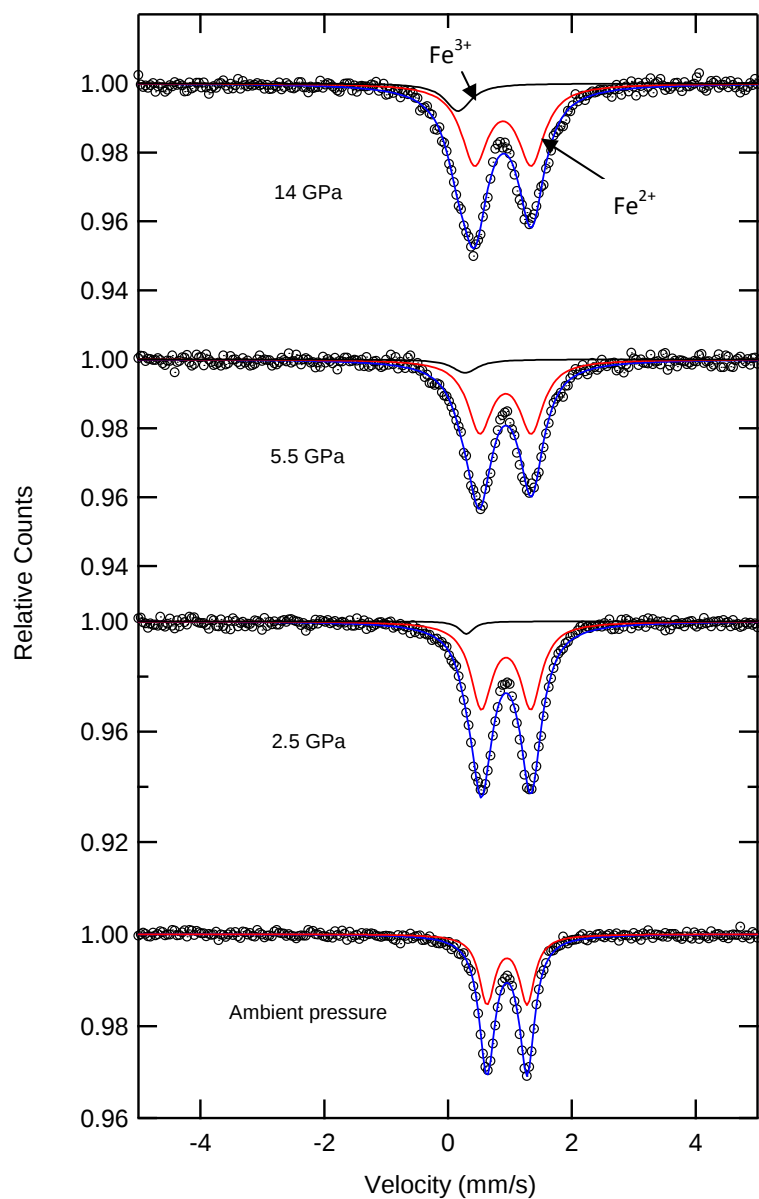


Figure 6.7: ^{57}Fe Mössbauer spectra of the pressure response of synthetic ilmenite at room temperature plotted on a restricted velocity scale. Note the increase in the intensity of the low-velocity line, attributed to an Fe^{3+} component. The ferric component initiates at ≈ 2 GPa. The ferric component is fitted using a broad doublet, i.e. the quadrupole splitting is 0 mm/s (Wu et al., 2009). All the spectra are fitted with a singlet for the ferric component (in black) and a doublet with the larger splitting for the ferrous component (in red). The intensities of the sub-spectra (Fe^{2+} and Fe^{3+}) are scaled by factor of half for clarity. The solid line through the data points is the overall fit to the data.

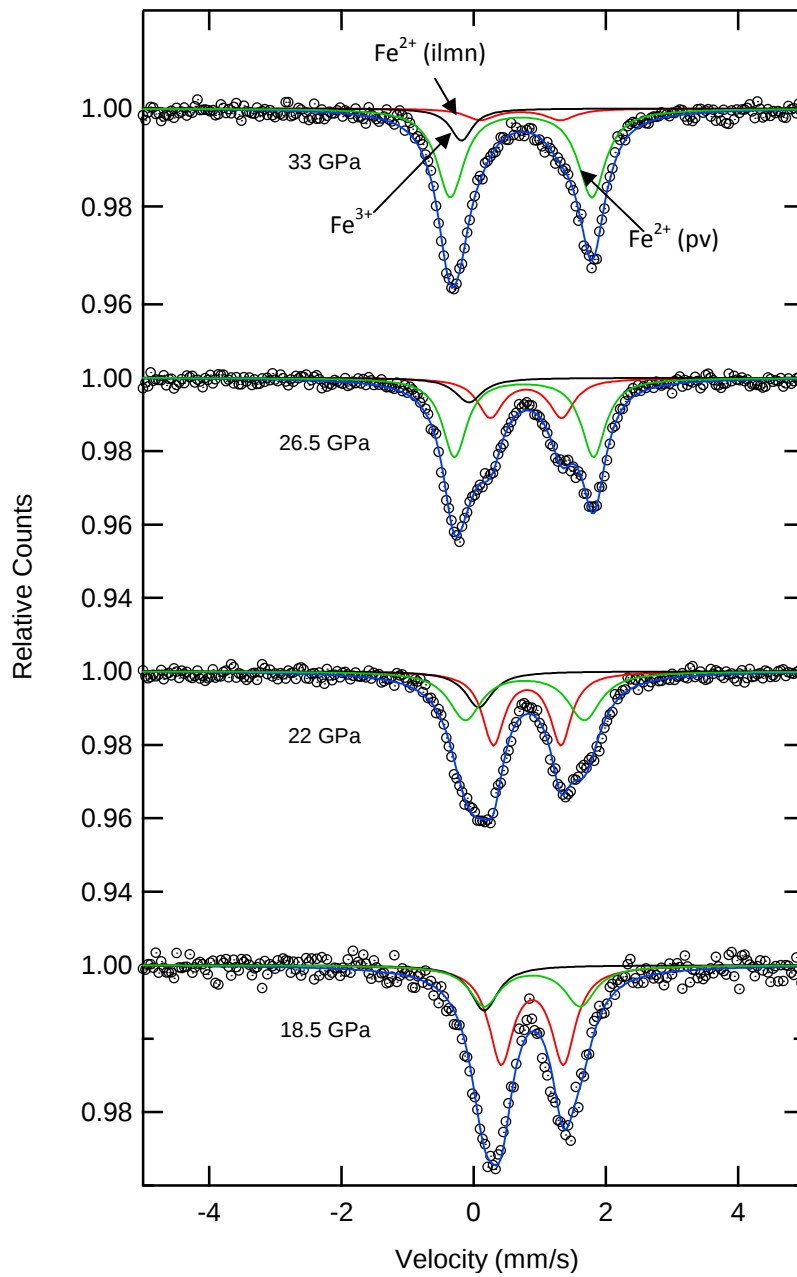


Figure 6.8: ^{57}Fe Mössbauer spectra of the pressure response of synthetic ilmenite at room temperature plotted on a restricted velocity scale. The perovskite phase initiates at ≈ 18 GPa, shown by the green line, this is the component the largest quadrupole splitting. The spectra are fitted with two doublets, for the perovskite component (in green, with the widest splitting) and ferrous component (in red). A singlet for the ferric component (in black) is also fitted. The intensities of the sub-spectra ($\text{Fe}^{2+}(\text{ilmn})$, Fe^{3+} , $\text{Fe}^{2+}(\text{pv})$) are scaled by factor of half for clarity. The solid line through the data points is the overall fit to the data.

At ambient pressure and room temperature the spectra shows a well resolved doublet attributed to a Fe^{2+} . At higher pressure, a new component appears, initiating at 2.5 GPa. This is a singlet attributed to the Fe^{3+} component. At ≈ 18 GPa, a new doublet appears, which is assigned to the dodecahedrally coordinated Fe^{2+} in the perovskite phase of ilmenite (Wu et al., (2009)). The hyperfine interaction parameters of the ferrous and ferric components obtained from fitting the spectra using the model of Wu et al., (2009) are tabulated in Table 2, below. Isomer Shift (δ) values are quoted with respect to α -Fe metal. It is clear from Table 2(a), that there is an increase in the abundance of the ferric component with pressure with a corresponding decrease in the abundance of the ferrous component. The abundance of each component is derived from the absorption areas in the theoretical fit to the data. The abundance of each component as a function of pressure is plotted in Figure 6.9. Also from Table 2(a), we note that the perovskite phase of ilmenite initiates at ≈ 18 GPa. The abundance of the perovskite phase (Fe^{2+} pv) continuously increases up to the highest pressure reached in this study.

Table 2: (a) Abundance of Fe oxidation states under pressure of synthetic ilmenite.

	Abundance %		
Pressure (GPa)	Fe^{3+} ilmn	Fe^{2+} ilmn*	Fe^{2+} pv*
Ambient		100	-
2.5	4	96	-
5.5	9	91	-
9.0	11	89	-
13.9	14	86	-
18.5	15	51	34
22	14	34	52
26.5	11	31	58
30	10	16	74
33	9	12	79

Table 2: (b) The isomer shifts are quoted with respect to α -Fe. The quadrupole splitting and line widths are also tabulated.

Pressure	Fe^{3+} ilmn			Fe^{2+} ilmn			Fe^{2+} pv		
(GPa)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)
ambient				1.607	0.647	0.303			
2.5	0.389	-	0.498	1.050	0.804	0.424			
5.5	0.364	-	0.507	1.046	0.832	0.478			
9	0.354	-	0.495	1.021	0.835	0.490			
13.9	0.279	-	0.502	1.002	0.919	0.524			
18.5	0.276	-	0.504	1.001	0.943	0.448	1.001	1.445	0.562
22	0.193	-	0.500	0.923	1.021	0.395	0.888	1.800	0.598
26.5	0.043	-	0.500	0.906	1.082	0.466	0.876	2.101	0.443
30	-0.053	-	0.500	0.854	1.097	0.433	0.854	2.120	0.500
33	-0.070	-	0.400	0.821	1.215	0.543	0.832	2.140	0.500

*Pv-perovskite structural phase

*Ilmn-ilmenite structural phase

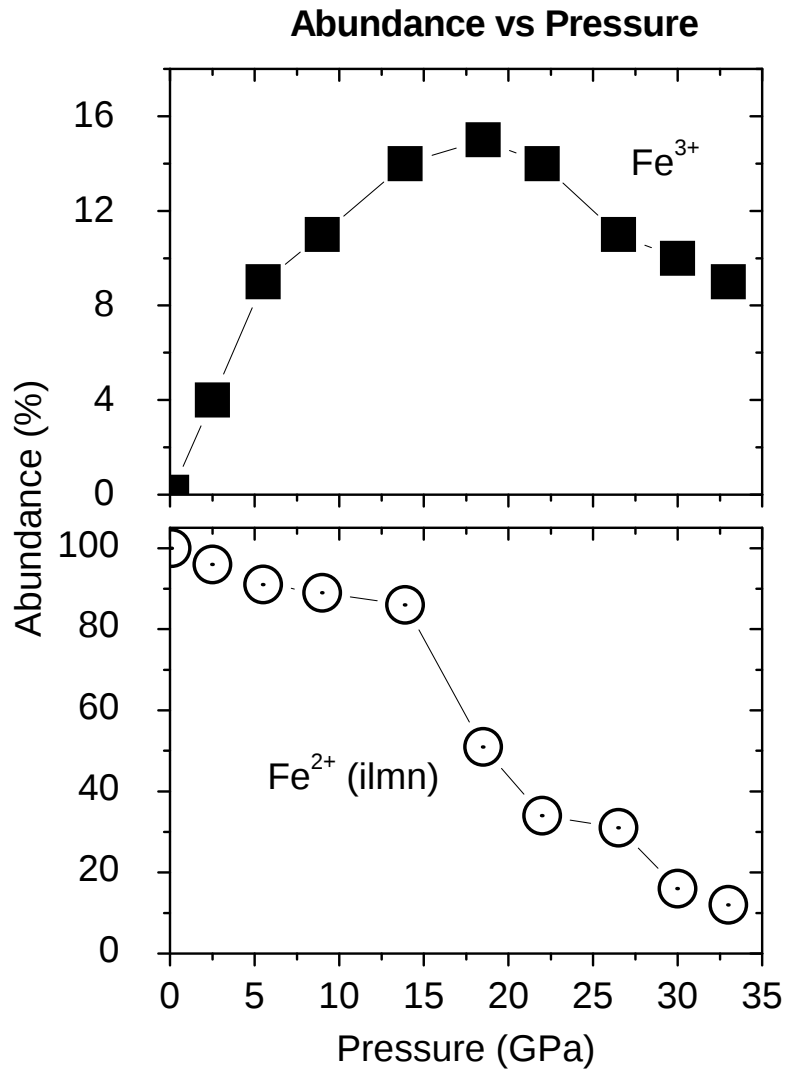


Figure 6.9: Variation of the abundance as a function of pressure for the ferrous and ferric component of synthetic ilmenite. Open circles and black squares are data points. The solid lines through the data points are guides for the eye. As seen, the Fe^{3+} abundance increases with pressure, and the Fe^{2+} abundance decreases as a function of pressure.

Table 2(a) and Figure 6.9, show that the abundance of Fe^{3+} increases from 0% at 0 GPa to 15% at 18.5 GPa, then decreases at high pressure. The relative Fe^{2+} (ilmn) content decreases with pressure at the expense of the new development of a high-pressure perovskite (pv) phase as shown by Table 2 and Figure 6.9. The $\text{Fe}^{3+}/\text{Fe}^{2+}$

(ilmn) ratio for the synthetic sample plotted as a function of pressure is shown in Figure 6.10. The abundance of the high pressure component of ilmenite as a function of pressure is plotted in Figure 6.11. At 33 GPa, the highest pressure reached in this study the Fe^{2+} in both octahedral and dodecahedral environments coexist, with the dodecahedral component having a higher abundance. Above 40 GPa, the spectra consists of Fe^{2+} in dodecahedral coordination and a singlet attributed to Fe^{3+} , Wu et al., (2009).

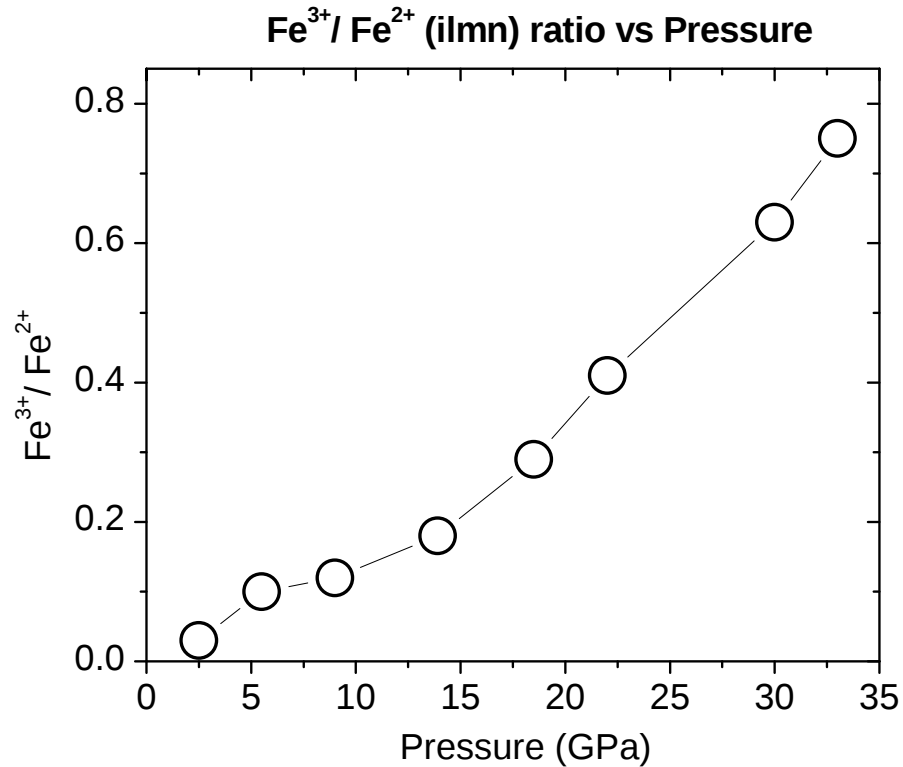


Figure 6.10: $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio variation with pressure of synthetic ilmenite. Open circles are data points. The solid lines through the data points are guides for the eye. The ratio increases with pressure up to highest pressure of 33 GPa, in this study.

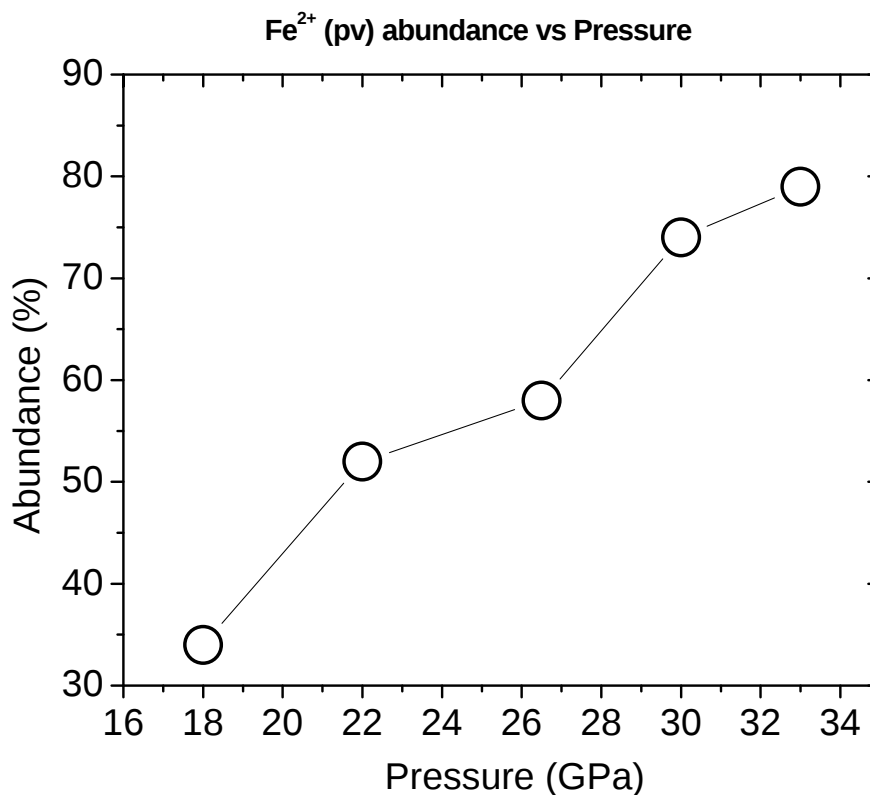


Figure 6.11: Pressure evolution of the abundance of the perovskite phase with pressure for synthetic ilmenite. The phase initiates at ≈ 18 GPa and reaches 82% at 33 GPa, the maximum pressure reached in this study before anvil failure at 35 GPa.

The isomer shift values of the ferrous (Fe^{2+} ilmn) and ferric component as a function of pressure are plotted in Figure 6.12. The isomer shift shows similar behavior for both the ferrous (Fe^{2+} ilmn) and ferric component, in that there is a decrease in the isomer shift with increasing pressure. This is attributed to the s -electron density increasing at the nuclear site.

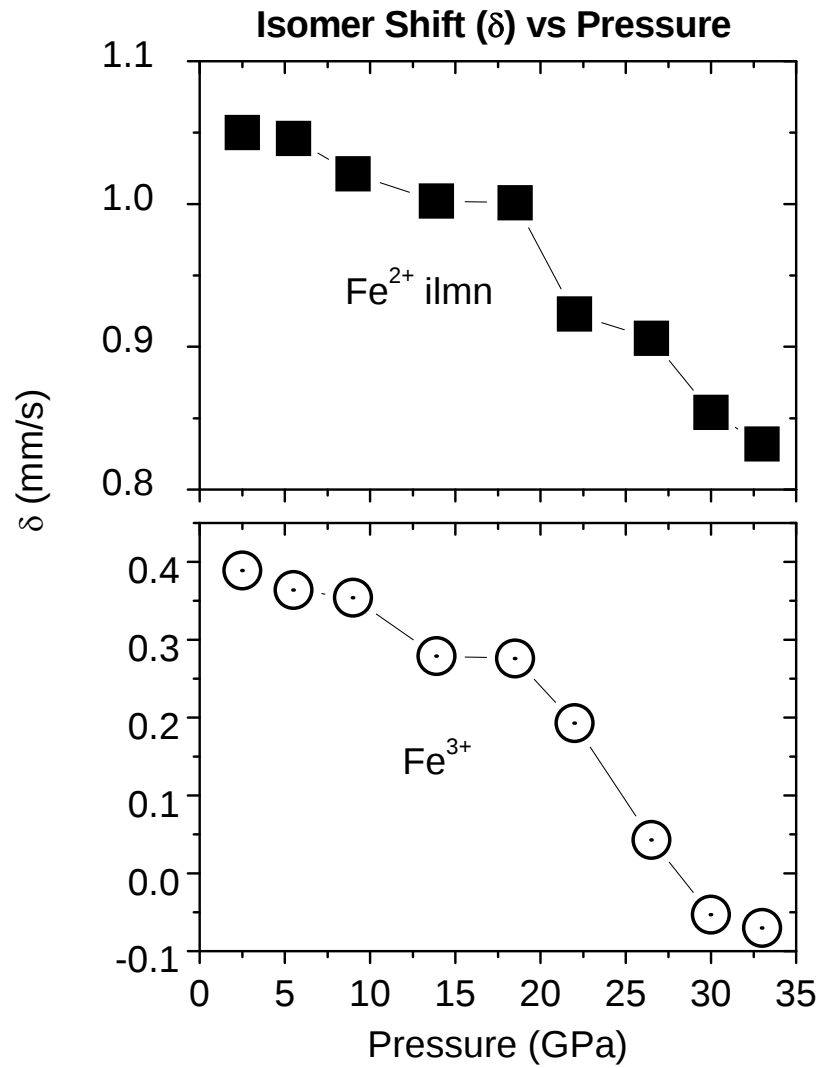


Figure 6.12: Isomer shift as a function of pressure for the ferrous and ferric components of synthetic ilmenite. The values plotted are quoted with respect to α -Fe. The isomer shift decreases for both the ferric and ferrous components with increasing pressure. This is attributed to the increase in the s -electron density at the nuclear site. Open circles and black squares are data points. The solid lines through the data points are guides for the eye.

The variation of the quadrupole splitting of the ferrous component (Fe^{2+} ilmn) as a function of pressure are plotted in Figure 6.13. The fitting model used is the Wu

fitting model (Wu et al., 2009), where the Fe^{3+} component is fitted using a broad doublet, with $\Delta E_Q = 0$ mm/s. As can be seen from Figure 6.13, the electric quadrupole splitting increases with pressure. The value of $\Delta E_Q = 1.22$ mm/s, is an agreement with previous measurements for Fe^{2+} ilmenite (Seda and Hearne, 2004; Wu et al., 2009), which corresponds to Fe in six fold coordination.

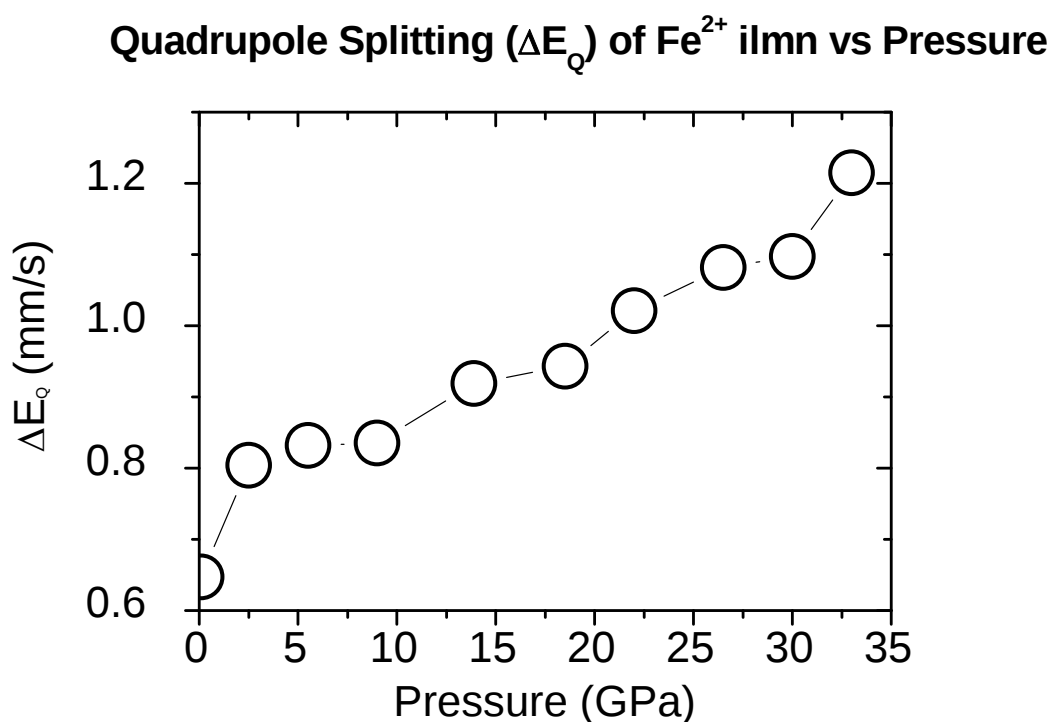


Figure 6.13: Variation of the electric quadrupole splitting as a function of pressure at room temperature for synthetic ilmenite. The quadrupole splitting increases with pressure for the ferrous component. Open circles are data points. The solid lines through the data points are guides for the eye.

6.3.2 Isomer Shift and Quadrupole Splitting for the perovskite phase

The pressure evolution of the isomer shifts and quadrupole splitting for the Fe^{2+} (pv) component are plotted in Figure 6.14. The value of $\delta = 0.83$ mm/s and $\Delta E_Q = 2.12$ mm/s obtained for the perovskite phase of ilmenite Fe^{2+} (pv), which is

assigned to Fe in a dodecahedrally coordination is consistent with values obtained by Wu et al., (2009). It is significant to note that ΔE_Q for the dodecahedrally coordinated Fe^{2+} in the perovskite phase is larger than of Fe^{2+} in ilmenite (see Table 2) for the same pressure. The isomer shift of Fe^{2+} in the perovskite phase is smaller than that of Fe^{2+} in six fold coordination for the same pressure (see Table 2).

Quadrupole Splitting (ΔE_Q), Isomer Shift (δ) of Fe^{2+} (pv) vs Pressure

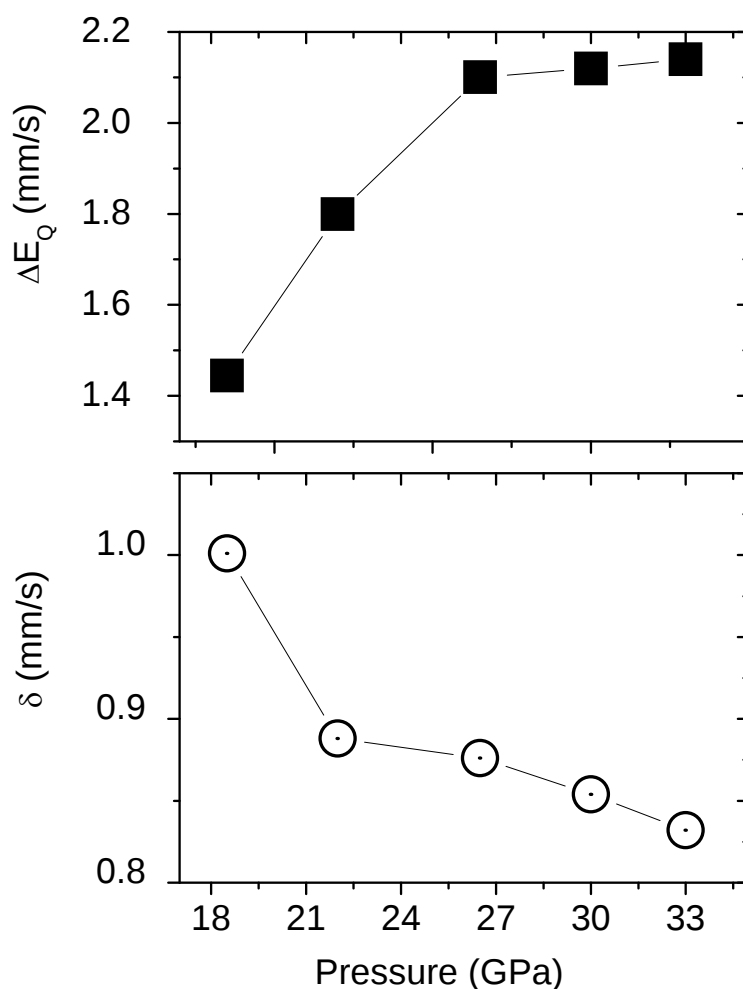


Figure 6.14: Isomer shift (δ) and quadrupole splitting (ΔE_Q) for the perovskite component of synthetic ilmenite Fe^{2+} plotted as a function of pressure. The Isomer shift (δ) values plotted are quoted with respect to α -Fe. The isomer shift decreases and the quadrupole splitting increases with pressure. Open circles and black squares are data points. The solid lines through the data points are guides for the eye.

6.3.3 Comparison of Wu and SLS fitting models

The Wu et al., (2009) model used in the fitting of the ilmenite spectra in this study attributes a broad doublet to the Fe^{3+} component emerging at 2.5 GPa with $\Delta E_Q = 0$ mm/s. Fitting in the SLS model imposes a definite quadrupole splitting and isomer shift for the Fe^{3+} component of ilmenite (see Section 6.2). ^{57}Fe Mössbauer spectra of synthetic ilmenite fitted using the SLS model are shown in Figure 6.15. The hyperfine parameters obtained by fitting using SLS model are tabulated in Table 3.

Table 3: Abundance of Fe oxidation states under pressure for SLS model fitted synthetic ilmenite spectra at three different pressure measurements. The isomer shifts are quoted with respect to $\alpha\text{-Fe}$. The quadrupole splitting, line widths are also tabulated.

Pressure (GPa)	Fe^{3+} ilmn				Fe^{2+} ilmn			
	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	Abundance (%)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	Abundance (%)
2.5	0.386	0.160	0.380	3.7	1.059	0.808	0.425	96.3
5.5	0.334	0.280	0.380	8.4	1.052	0.840	0.484	91.6
14	0.332	0.300	0.425	13.4	1.000	0.942	0.552	86.6

The comparison of fitting values obtained from the fitting of the spectra from the two models shows that the values of the hyperfine interaction parameters (isomer shift and abundance) are similar. Values of the hyperfine interactions for the SLS model fitted synthetic ilmenite spectra are tabulated in Table 3 (compare with the tabulated values in Table 2). We note that the values of the abundances for both the ferric and ferrous components are similar (or equal) when fitting with either model. This similarity (especially for the abundance), is therefore independent of how the

ferric component (Fe^{3+}) is fitted, that is, with a broadened singlet or a resolved doublet with quadrupole splitting.

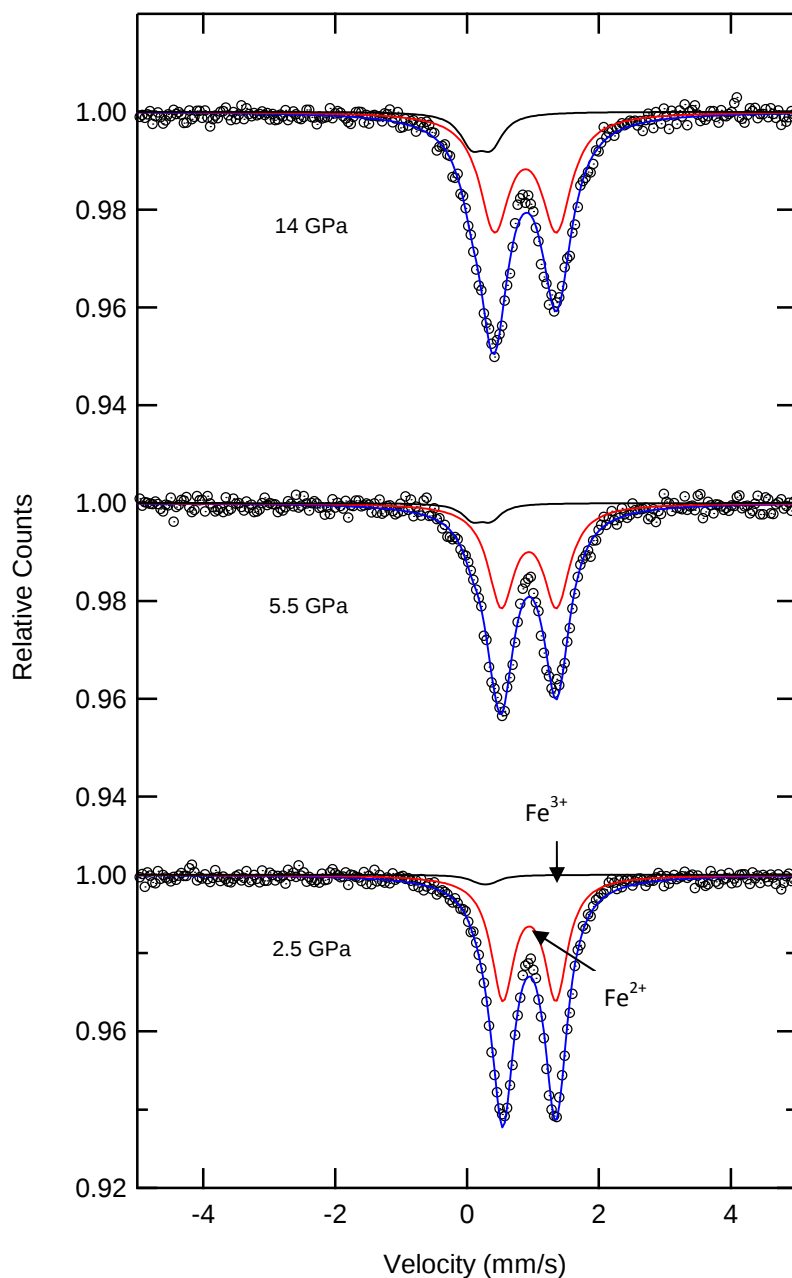


Figure 6.15: Synthetic ilmenite fitted with doublets for the ferric component at three different pressure runs. SLS model fitting of the ferric component where there is a definite quadrupole splitting. The ferric component (in black) and ferrous component (in red). The intensities of the sub-spectra (Fe^{2+} and Fe^{3+}) are scaled by factor of half for clarity. The solid line through the data points is the overall fit to the data.

6.4 Repeat pressure measurements of natural ilmenite (Hillindale Sample)

The natural sample used in this case was an untreated ilmenite sample obtained from the Hillindale mining area of KwaZulu-Natal, South Africa (Nell and den Hoed, 1997). X-ray diffractometry studies on the sample show the presence of hematite (α -Fe₂O₃) and rutile (TiO₂) as impurity phases (Nell and den Hoed). Ilmenite is the dominant phase. ⁵⁷Mössbauer spectra recorded on a $\approx 10 \text{ mg/cm}^2$ of the sample at ambient conditions gives two paramagnetic doublets attributed to ferrous and ferric components of iron and a third magnetically split component attributed to hematite (see Appendix A). The sample was original untreated polycrystalline powder, which was ground into a powder under acetone for loading in a DAC. This sample originates from the same source as the one used by Seda and Hearne (2004).

6.4.1 Experimental Results and Analysis for the natural sample

⁵⁷Fe Mössbauer measurements at selected pressures were done and the spectra are plotted in Figure 6.16 and Figure 6.17, for the sample. The plots are shown on a small velocity scale, which shows clearly the pressure evolution of the various components at selected pressures. The spectra were fitted with two paramagnetic components, corresponding to the ferrous and ferric component of iron. Due to the restricted velocity scale the inner lines of the magnetic sextet of hematite are not visible or easily discerned and the magnetic sextet was not included in the fitting of the spectra. The paramagnetic components are indicated in the spectrum by arrows and different color schemes on the plots.

The hyperfine interaction parameters for the ferrous and ferric components obtained from the analyses of the spectra are given in Table 4(a). The abundances

are given in Table 4(b). There is a pronounced increase in the intensity of the ferric component and a corresponding decrease in the intensity of the ferrous component with pressure as evidenced by the values in Table 4(b). This trend is similar to what is observed in the synthetic and SLS sample. The abundances of each component derived from the theoretical fits to the data are plotted in Figure 6.18. From observation of Figure 6.16 and Figure 6.17, it is clear that the absorption area of the ferric component increases appreciable (from 7.5 GPa to 15 GPa) and there is a corresponding decrease in the absorption area of the ferrous component. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio plotted as a function of pressure is shown in Figure 6.19. In the relatively low pressure region (up to 4 GPa) the ratio significantly increases and continues to slowly increase in a “plateau” region. The ratio increases from ≈ 0.10 at ambient pressure to ≈ 0.30 at 15 GPa.

Table 4: (a) Isomer shift (δ), Quadrupole Splitting (ΔE_Q), Line Width (Γ) values as derived from the fitting of the spectra of untreated Hillindale ilmenite. The Isomer Shift (δ) values are quoted with respect to α -Fe metal. (b) The percentage abundance of Fe oxidation states under pressure as derived from the fitting of the spectra for the natural ilmenite sample (Hillindale sample).

(a)

Pressure (GPa)	Fe^{3+} ilmn			Fe^{2+} ilmn		
	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)
Ambient	0.273	0.250	0.360	1.025	0.719	0.411
0.7	0.264	0.257	0.363	1.069	0.762	0.436
1.7	0.248	0.278	0.379	1.061	0.774	0.454
3.8	0.240	0.287	0.363	1.040	0.787	0.500
7.5	0.225	0.290	0.362	1.029	0.791	0.481
11.3	0.224	0.318	0.396	1.022	0.833	0.529
15.3	0.204	0.330	0.394	1.016	0.930	0.557

(b)

	Abundance %	
Pressure (GPa)	Fe ³⁺ ilmn	Fe ²⁺ ilmn
Ambient	9	91
0.7	10	90
1.7	12	88
3.8	16	84
7.5	17	83
11.3	20	80
15.3	22	78

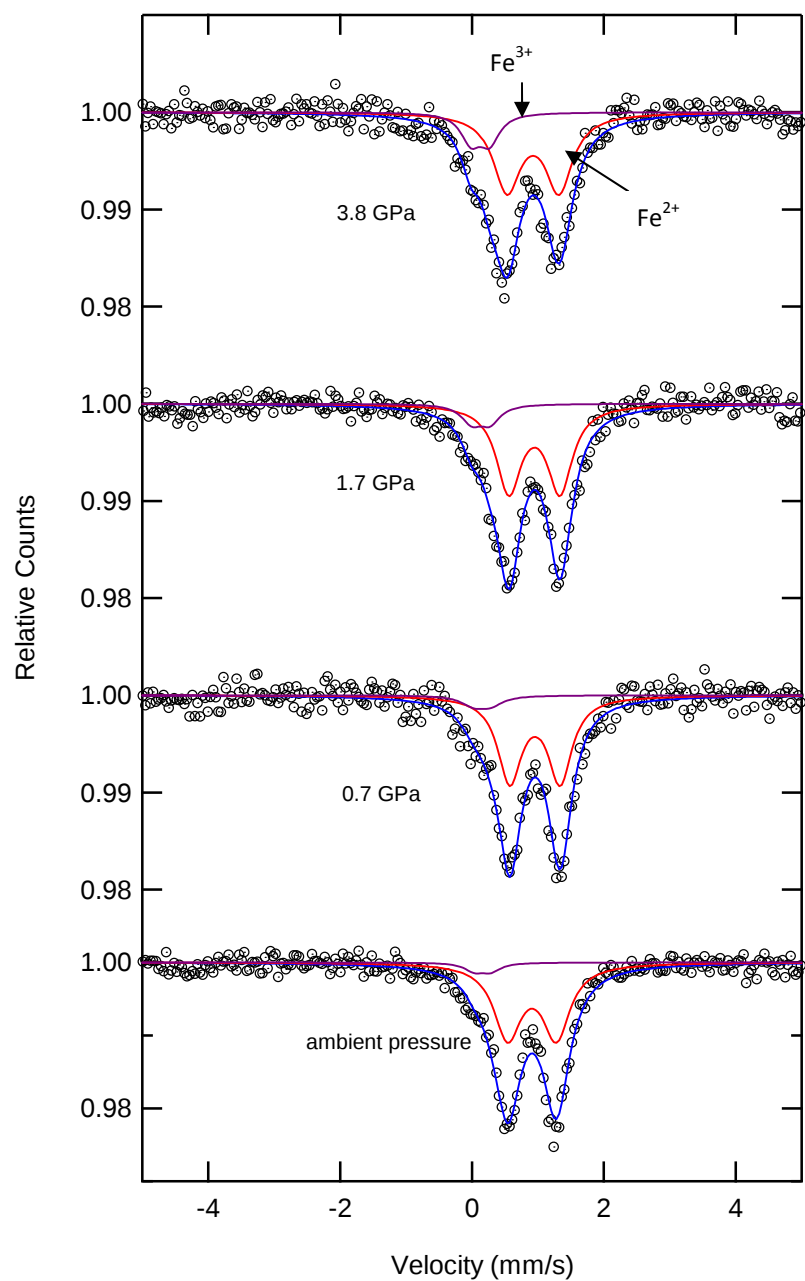


Figure 6.16: $^{57}\text{Mössbauer}$ spectra of the pressure response of untreated Hillindale ilmenite at room temperature plotted on a restricted velocity scale. The increase in the abundance of the ferric component from ambient pressure to 4 GPa is not apparent. The spectra are fitted with two doublets, for the ferric component (in purple) and ferrous component (in red). The intensities of the sub-spectra (Fe^{2+} and Fe^{3+}) are scaled by factor of half for clarity. The solid line through the data points is the overall fit to the data.

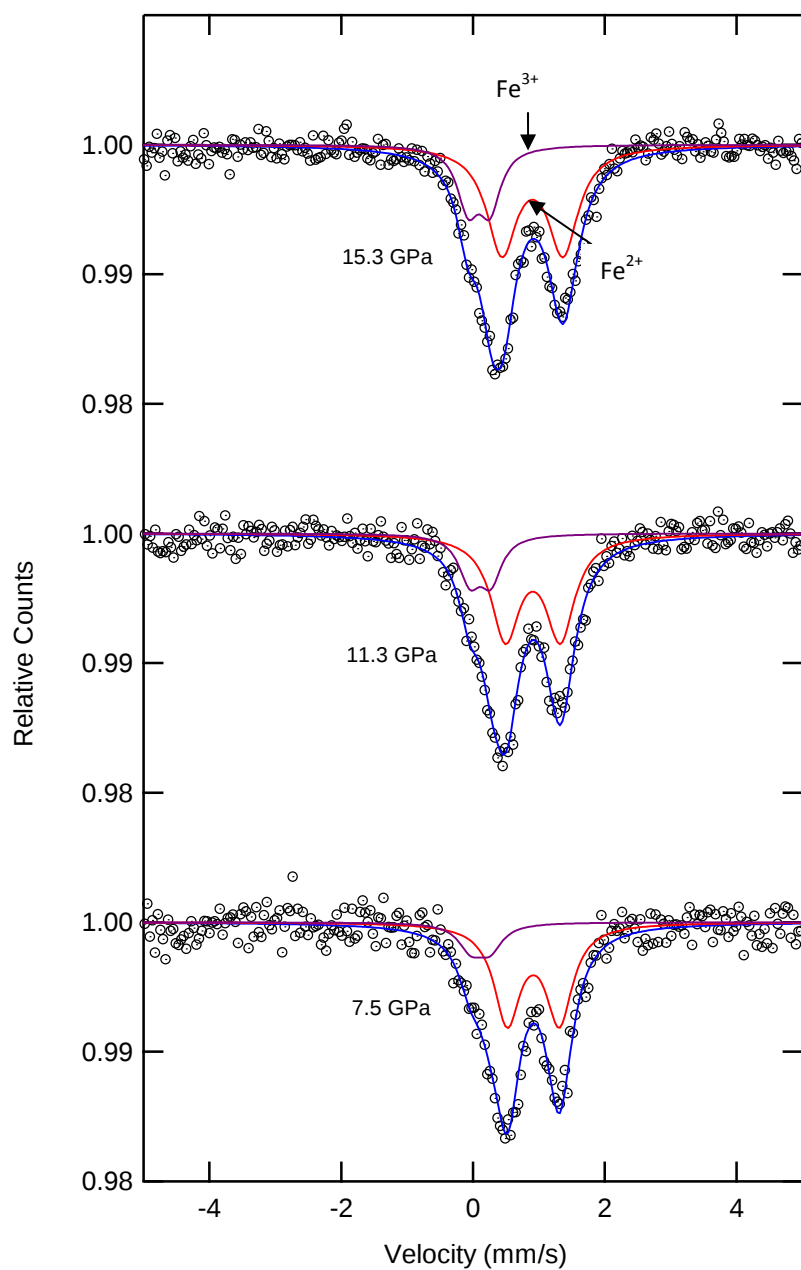


Figure 6.17: ^{57}Fe Mössbauer spectra of the pressure response of untreated ilmenite at room temperature plotted on a restricted velocity scale. The increase in the abundance of the ferric component from 7.5 GPa to 15 GPa is less pronounced than at lower pressures. The spectra are fitted with two doublets, for the ferric component (in purple) and ferrous component (in red). The intensities of the sub-spectra (Fe^{2+} and Fe^{3+}) are scaled by factor of half for clarity. The solid line through the data points is the overall fit to the data.

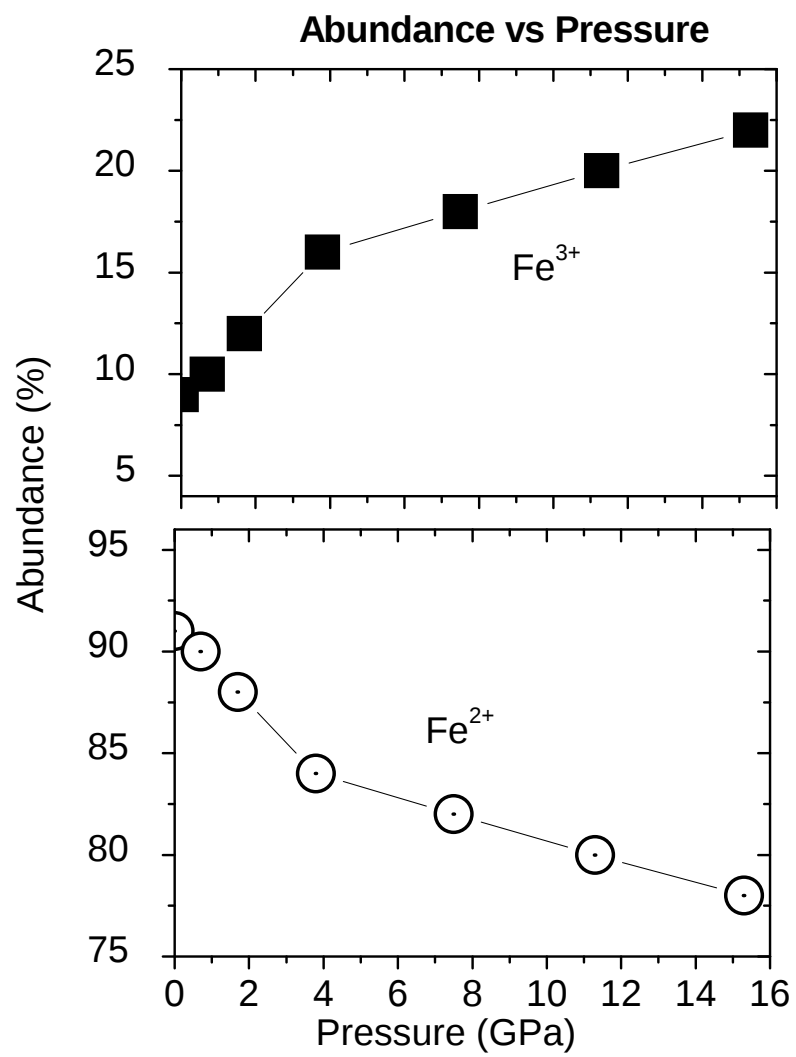


Figure 6.18: Variation of the abundance as a function of pressure for the ferrous and ferric components of untreated ilmenite. Open circles and black squares are data points. The solid lines through the data points are guides for the eye. As seen, the Fe^{3+} abundance increases with pressure, and the Fe^{2+} abundance decreases as a function of pressure.

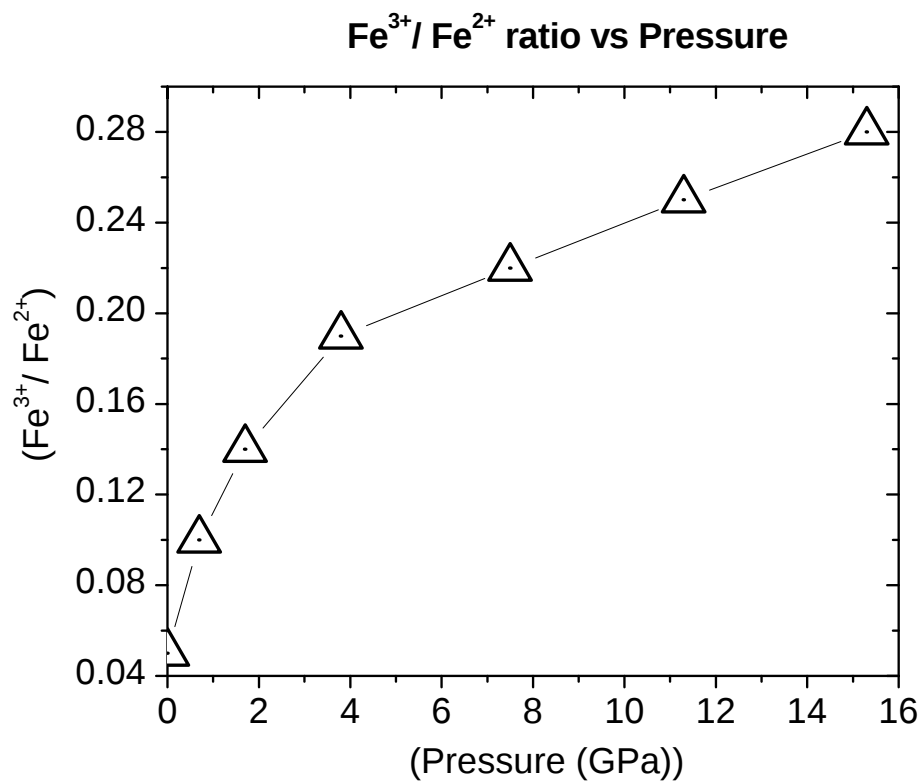


Figure 6.19: Fe³⁺/Fe²⁺ ratio variation with pressure for the untreated natural sample. Open circles are data points. The solid lines through the data points are guides for the eye.

The isomer shift values of the ferrous and ferric component relative to α -Fe extracted from the analysis of the data are plotted in Figure 6.20. The isomer shift for the two components decreases with pressure, indicating the s -electron density increases at the Fe nuclear site. The pressure dependence of δ , $\frac{d\delta}{dP}$ changes at ≈ 4 GPa and decreases as the pressure rises beyond ≈ 4 GPa.

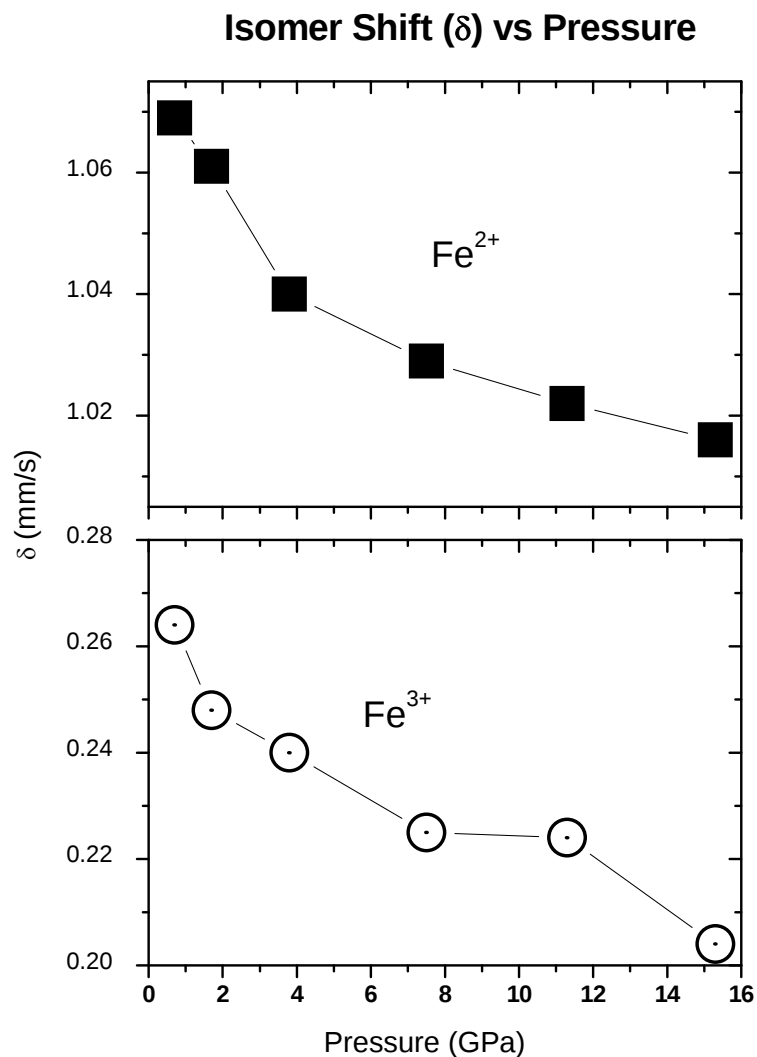


Figure 6.20: Isomer shift as a function of pressure for the ferrous and ferric components of untreated ilmenite. The values plotted are quoted with respect to α -Fe. The isomer shift decreases for both the ferric and ferrous components with increasing pressure. This is attributed to the increase in the s -electron density at the nuclear site. Open circles and black squares are data points. The solid lines through the data points are guides for the eye.

The quadrupole splitting for the two components increases with pressure. Below 7 GPa there is a gradual increase and above this pressure range there is a significant increase in the pressure dependence of the quadrupole splitting. This is in contrast to results obtained by Seda and Hearne (2004) where the quadrupole splitting of the

ferric component decreased with increasing pressure. The increase in the ΔE_Q can be attributed to site distortion around the Fe ion at high pressure.

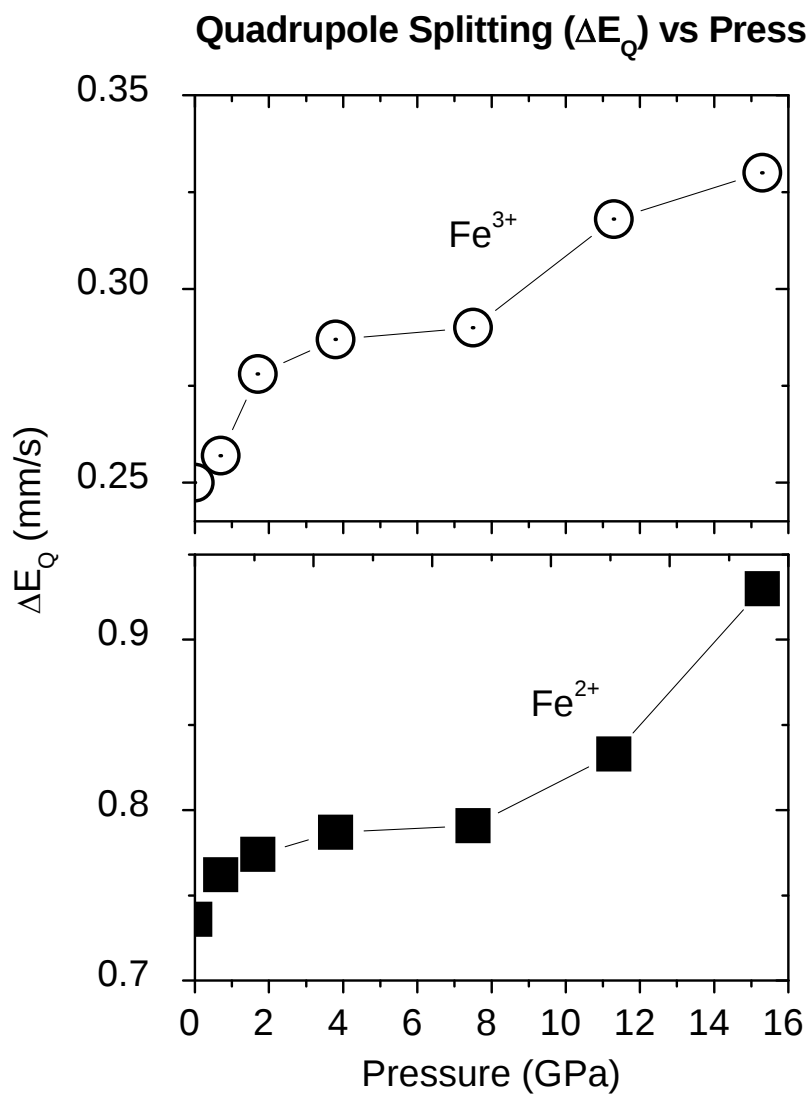


Figure 6.21: Variation of the electric quadrupole splitting as a function of pressure at room temperature of untreated ilmenite. The quadrupole splitting increases with pressure for the ferrous component. Open circles are data points. The solid lines through the data points are guides for the eye.

Comparison of the high pressure response of ilmenite and hematite

Hematite (α -Fe₂O₃, space group: *R-3c*) has the corundum (Al₂O₃) structure with an approximately hexagonal close-packed array of oxygen anions. Fe³⁺ ions occupy two thirds of octahedral sites between O³⁻ ions. Each FeO₆ octahedron shares a face with another in the layer above or below. Fe atoms lie on planes spaced approximately one third and two thirds the distance between oxygen layers. The crystal structure of ilmenite (FeTiO₃, space group: *R3*) is closely related to that of hematite (see section 4.2, to compare the two crystal structures).

In this section of the Chapter the high pressure response of hematite and ilmenite are compared by their hyperfine interaction parameters, the isomer shift and quadrupole splitting

Isomer Shift

The variation of the isomer shift as a function of pressure for the SLS ilmenite sample is similar to that of hematite. Experiments carried out by Syono et al. (1984) and Bruzzzone et al. (1983) using diamond anvil cells showed that the isomer shift decreases as a function of pressure when the pressure increases.

According to Syono et al. (1984), the isomer shift of hematite has a pressure coefficient of -0.0026 mms⁻¹/GPa. The estimated pressure coefficient in the lower pressure regime (0 to 4 GPa) for Fe³⁺ in the untreated ilmenite sample in our experiments is approximately 0.0087 mms⁻¹/GPa, for the high pressure regime the approximated pressure coefficient is 0.0027 mms⁻¹/GPa.

Quadrupole Splitting

The variation of the quadrupole splitting for hematite as a function of pressure differs from that of ilmenite. For the SLS sample used in this study the quadrupole splitting was found to increase with pressure. Syono et al., (1984) observed a discontinuity in the sign of the electric quadrupole interaction between 0 and 3.3 GPa, from positive to negative, in agreement with the results of Bruzzone et al., (1983).

Discussions

6.5 Comparison of the pressure response of the three samples

In all experiments it was noted that there is a significant asymmetry that develops in the doublet at low pressure (on the low velocity side of the spectrum) when the samples are pressurised in DAC. This is more evident in the synthetic sample which from experiments at ambient conditions has a symmetric doublet and no evidence of Fe^{3+} in the starting material (see Appendix A). Because the intensities of the lines in a Mössbauer spectrum can be influenced by the orientation of the crystals in the absorber (texturing effect), experiments were done to ascertain whether the asymmetry at low pressure was caused by the abundance of Fe^{3+} increasing or whether it was due to the texturing effect. To do this, a synthetic sample of ilmenite was pelleted by applying a force of 4 kN and Mössbauer measurements at room temperature recorded. Such pelleting action is anticipated to introduce texture, and it is of interest to see how this manifested in the spectrum (Pfannes and Gonser, 1972; Chandra and Ericsson, 1979). The results are shown in Figure 6.22.

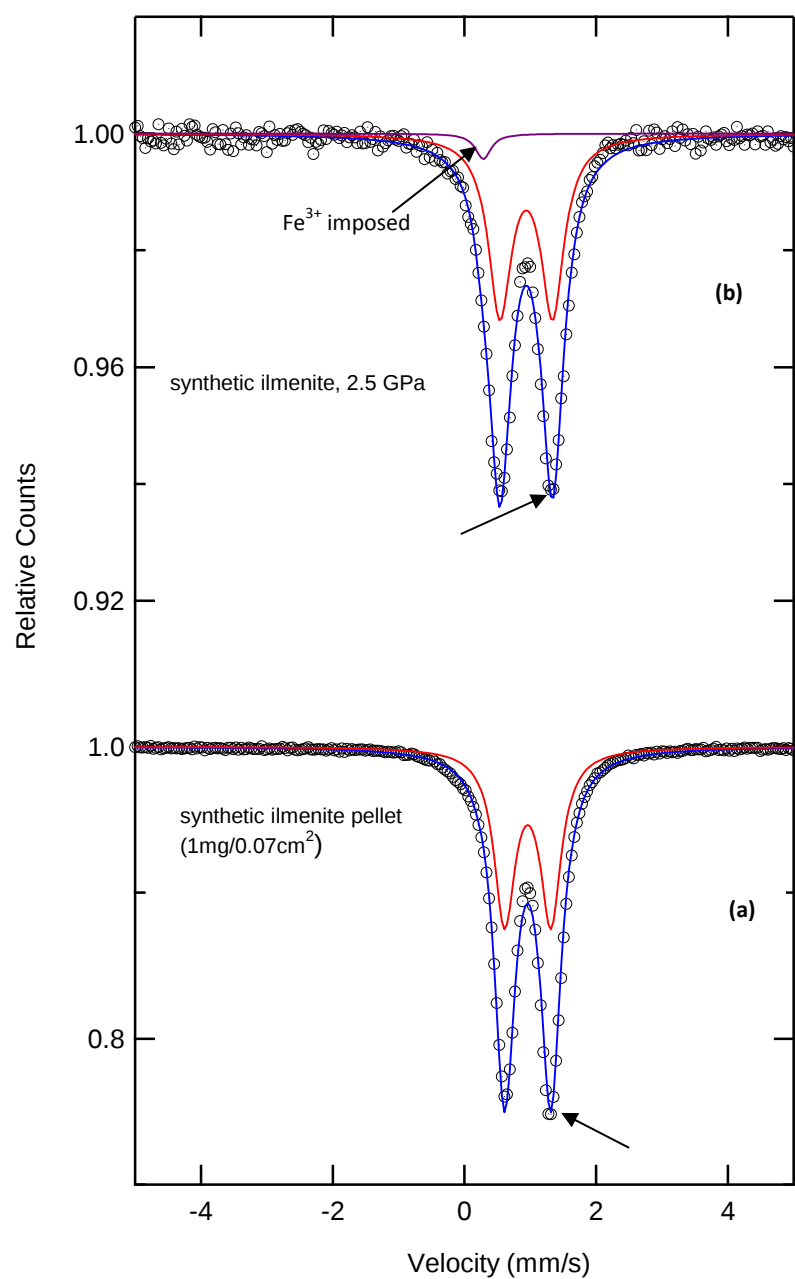
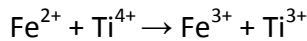


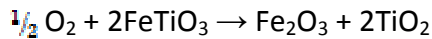
Figure 6.22: (a) Synthetic sample has been pelleted by applying a force of 4 kN, to check for effect of texturing. Pellet measured at ambient pressure. There is slight asymmetry, more intense on the high velocity side (indicated by the arrow). (b) Powder sample of synthetic ilmenite loaded into a Re gasket cavity (in a DAC) at 2.5 GPa. There is a slight asymmetry that develops which is more intense on the low velocity side of the spectrum (indicated by the arrow).

As seen from Figure 6.22, texturing leads to a different profile of the asymmetry as compared to external pressure in a DAC. We therefore concluded that the asymmetry of the doublet at low pressure is due to an additional component (Fe^{3+}) developing.

In all three samples there is an increase in the relative abundance of the ferric component, albeit the pressure response is different. An increase from 22% to 28% for the relative abundance of the ferric component was recorded for the SLS sample, 0% (ambient pressure) to 14% for the synthetic sample and 9% to 22% for untreated natural sample. This increase was attributed to intervalence charge transfer (Sherman, 1987; Seda and Hearne, 2004) between face-sharing octahedra of Fe and Ti cations according to the equation:



An alternative explanation is a pressure induced chemical reaction:



Seda and Hearne (2004) eliminated the possibility of the above reaction occurring by noting that there was no increase in TiO_2 content suggested by the reaction. Zhang et al., (2006) eliminated the above reaction occurring in their high pressure experiments on the electrical conductivity of ilmenite using multi-anvil high-pressure apparatus, by using two Fe disks to prevent oxygen reacting with FeTiO_3 and hence keeping the sample during the measurement.

The pressure response of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the natural samples is comparable. Below 8 GPa the pressure dependence is higher compared to higher pressures where it plateaus. The ratio reaches a maximum of ≈ 0.38 for the SLS sample and ≈ 0.30 for the natural untreated sample. At 14 GPa the ratio in the synthetic sample is ≈ 0.30 before the perovskite phase initiates and at 33 GPa the ratio is ≈ 0.75 . The

large value of the ratio at 33 GPa can be explained by noting that at higher pressure the ferric component has an abundance of 9% and the ferrous component of the ilmenite phase has an abundance of 12%.

Upon compression, the ΔE_Q increases for the ferric and ferrous components in all samples. The isomer shift decreases for all the ferrous and ferric components in all samples. The line width of the ferric component generally maintains a value of 0.36 – 0.38 mm/s in the natural samples regardless of the fitting procedure, i.e. letting the value of the other input parameters vary or be fixed. We note that for the synthetic sample the line width of the ferric component is quite broad compared to the other samples, having values ranging of 0.40 – 0.50 mm/s. In the case of the ferrous component the line width maintains a value between 0.40 - 0.55 mm/s regardless of the fitting procedure in all samples.

Results obtained for the synthetic sample verify that the perovskite phase initiates at ≈ 18 GPa. The Fe^{2+} component in octahedral coordination coexists with the Fe^{2+} perovskite phase in dodecahedral coordination up to 33 GPa, the highest pressure reached in that study. The pressure dependence of the isomer shift of Fe^{2+} (pv) is smaller than that of Fe^{2+} (ilmn) and the quadrupole splitting of Fe^{2+} (pv) is greater than that of Fe^{2+} (ilmn) for the same pressure. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio reaches a maximum at around 18 GPa of 15%. Experimental results verify that the perovskite phase is the more dominant phase at higher pressure.

6.6 Comparison with previous investigations of the Hillindale sample and recent work

Previous work by Seda and Hearne (2004) show that there is a dramatic increase in the abundance of the ferric component from 13% at ambient pressure to 26% at

14 GPa. This behaviour was also observed in our work. The abundance of the ferric component as obtained from theoretical fits to the data, was 5% at ambient pressure and reached 22% at 15 GPa. The absolute values of the abundances are not the same but we take note that the pressure dependence is the same. This also serves to confirm that the untreated sample of ilmenite has a high content of Fe^{3+} at high pressure compared to other samples.

The isomer shift values for Fe^{3+} obtained from the theoretical fits of the data of Seda and Hearne (2004) are small compared to the values obtained in this work. According to Seda and Hearne (2004) at ambient conditions the isomer shift of Fe^{3+} is ≈ 0.21 mm/s, it then decreases to -0.018 mm/s at 14 GPa. In our case the isomer shift is ≈ 0.27 mm/s at ambient conditions and decreases to 0.20 mm/s at 15 GPa, the highest pressure reached in the study. This anomaly could be due to the difference in the resolution of the experiments, that is, different velocity scales used in the collection of the data and the number of points (channels) used in the fitting of the spectra.

The effect of pressure on the quadrupole splitting of Fe^{3+} is significant in both studies. Seda and Hearne (2004) recorded a decrease in the quadrupole splitting, while in our experiments we note that it increases. In our experiments the increase is consistent in all experiments, and suggests that the mode of analysis is reliable.

6.7 Conclusion, Outlook and suggestions for follow-up studies

The oxidation state of iron in three different ilmenite samples has been studied as a function of pressure using ^{57}Fe Mössbauer Spectroscopy.

In the three samples we note appreciable asymmetry developing on the low velocity side of the doublet profile typical of Fe^{2+} ilmenite. This is attributed to additional

contribution of Fe^{3+} emerging which would also give rise to such asymmetric evolution of doublet intensities. In this work we have assumed that this behaviour is due to an increase in Fe^{3+} through some charge transfer process. This would need to be verified by means of XAS experiments.

Our high-pressure ^{57}Fe Mössbauer experiments show that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio increases appreciably at low pressures, corresponding to an increase in the abundance of Fe^{3+} . This pressure induced alteration of the abundance of Fe^{3+} can be explained in terms of the intervalence charge transfer of the form $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$, albeit this explanation is refuted by a number of workers such as Wu et al., (2009) and Wilson et al., (2005). Wu et al., (2009) suggests that there is some charge transfer via the O^{2-} anions (see Figure 6.23).

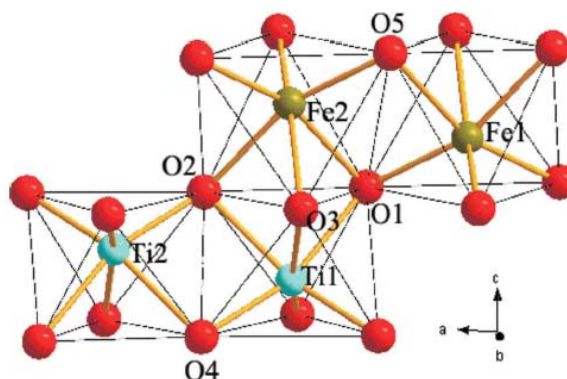


Figure 6.23: A fragment of the ilmenite structure. The bond lengths between Ti-O and Fe-O decrease under pressure. A charge transfer via Ti1-O-Fe1 is more likely than through the route Ti1-O1-Fe2, because the bond length between Fe1-O1 is shorter than between Fe2-O1, Wu et al., (2009).

Results obtained from the synthetic sample show that the perovskite phase of ilmenite initiates at ≈ 18 GPa and the perovskite and ilmenite phases of Fe^{2+} coexist at higher pressures, with the perovskite phase being the more dominant state of Fe.

Finally, we recommend that in-situ high-pressure and high-temperature ^{57}Fe Mössbauer studies of ilmenite are necessary to fully understand the behaviour of

ilmenite in conditions representative of the Earth's mantle. Apart from being able to explore the oxidation state of kimberlite assemblages and the genesis of diamond, this will also serve to explain the geomagnetic and geoelectric properties anomalies observed in the Earth's interior and other planets (Bedassa, 2000).

X-ray absorption spectroscopy (XAS) measurements

It would be highly desirable to perform XAS measurements at both the Fe and Ti K-edges in the DAC to elucidate the pressure evolution of Fe and Ti valences. This should be in consideration of the pressure-induced $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$, intervalence charge transfer proposed by Seda and Hearne (2004) using ^{57}Fe Mössbauer spectroscopy. XAS serves to probe in-situ, the Fe and Ti oxidation states under pressure. Wu et al., (2009) have performed the Fe K-edge measurements on synthetic ilmenite.

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Appendix A

A1: Room temperature Mössbauer spectra of ilmenite

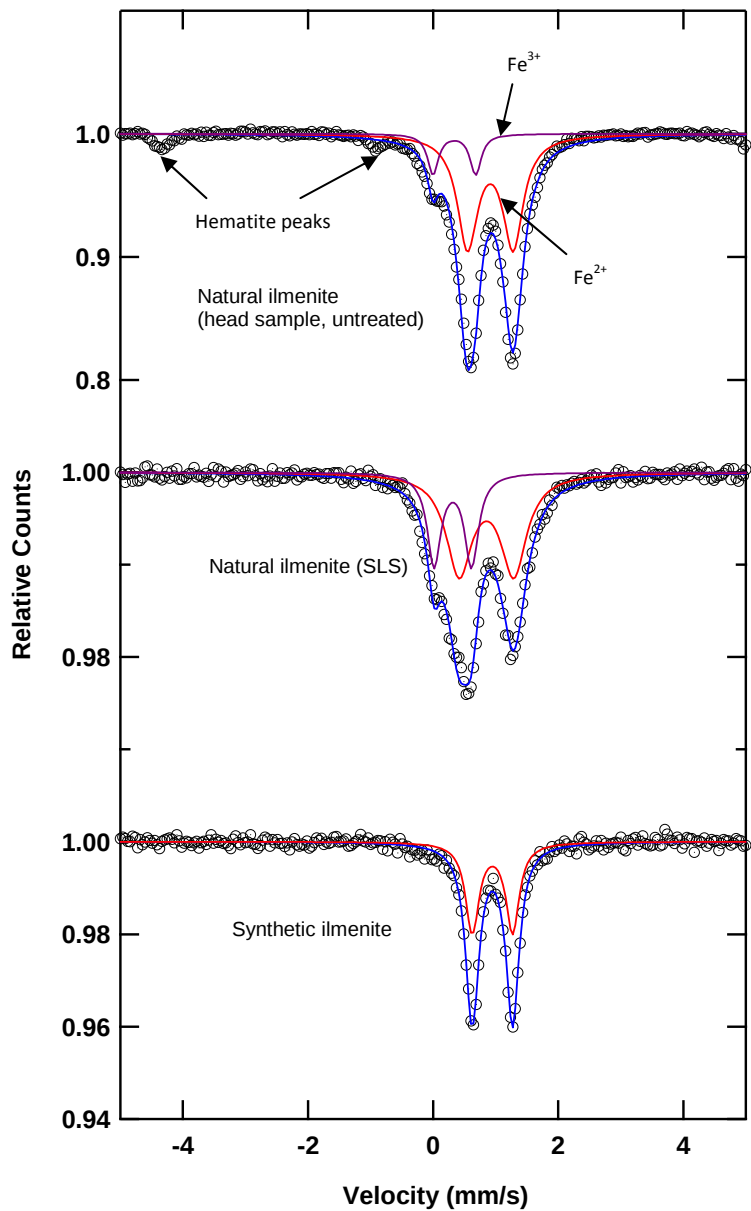


Figure A2: Room temperature Mössbauer spectra of ilmenite samples plotted on a restricted velocity scale. The samples were loaded in a conventional holder ($\phi = 1.5$ cm) and the mass of each sample was ≈ 10 mg/cm². A conventional source (50 mCi) was used in transmission geometry mode to collect the spectra. Solid lines are theoretical fits to the data. The intensities of the sub-spectra (Fe^{2+} and Fe^{3+}) are scaled by factor of half for clarity. The inner lines of the magnetic sextet component Fe_2O_3 in the head sample are discernable and their positions are shown by arrows.

A2: Low temperature (90 K) Mössbauer spectra of ilmenite

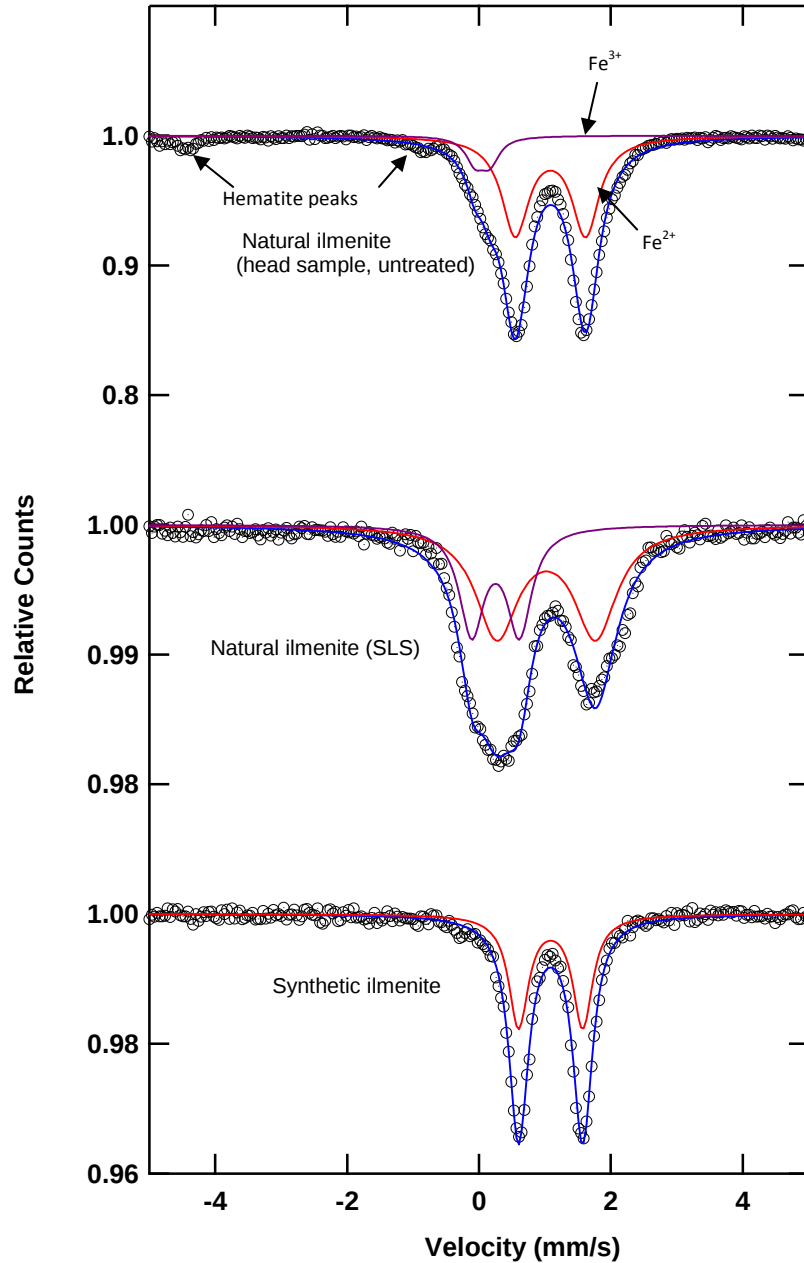


Figure A2: Low temperature (90 K) Mössbauer spectra of ilmenite samples plotted on a restricted velocity scale. The samples were loaded in a conventional holder ($\phi = 1.5$ cm) and the mass of each sample was ≈ 10 mg/cm². A conventional source (50 mCi) was used in transmission geometry mode to observe the Mössbauer resonance effect. Solid lines are theoretical fits to the data. The intensities of the sub-spectra (Fe²⁺ and Fe³⁺) are scaled by a factor of half for clarity. The inner lines of the magnetic sextet component Fe₂O₃ in the head sample are discernable and their positions are shown by arrows.

Appendix B

B: X-ray diffraction patterns of ilmenite samples

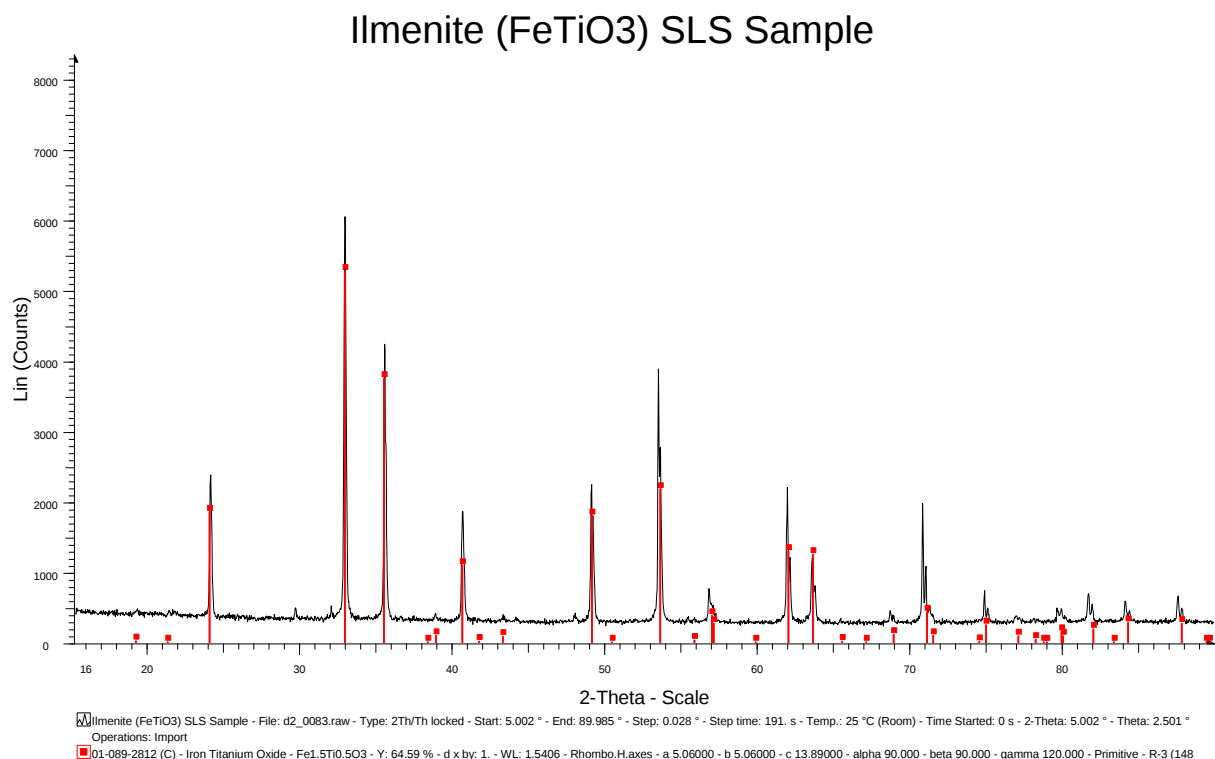


Figure B1: X-ray powder diffraction pattern of the SLS ilmenite taken at room temperature using a zero background holder. The solid black lines are the experimental data. The solid red lines and square boxes represent the calculated positions of peaks using Rietveld refinement analysis.

Ilmenite (FeTiO₃) Synthetic

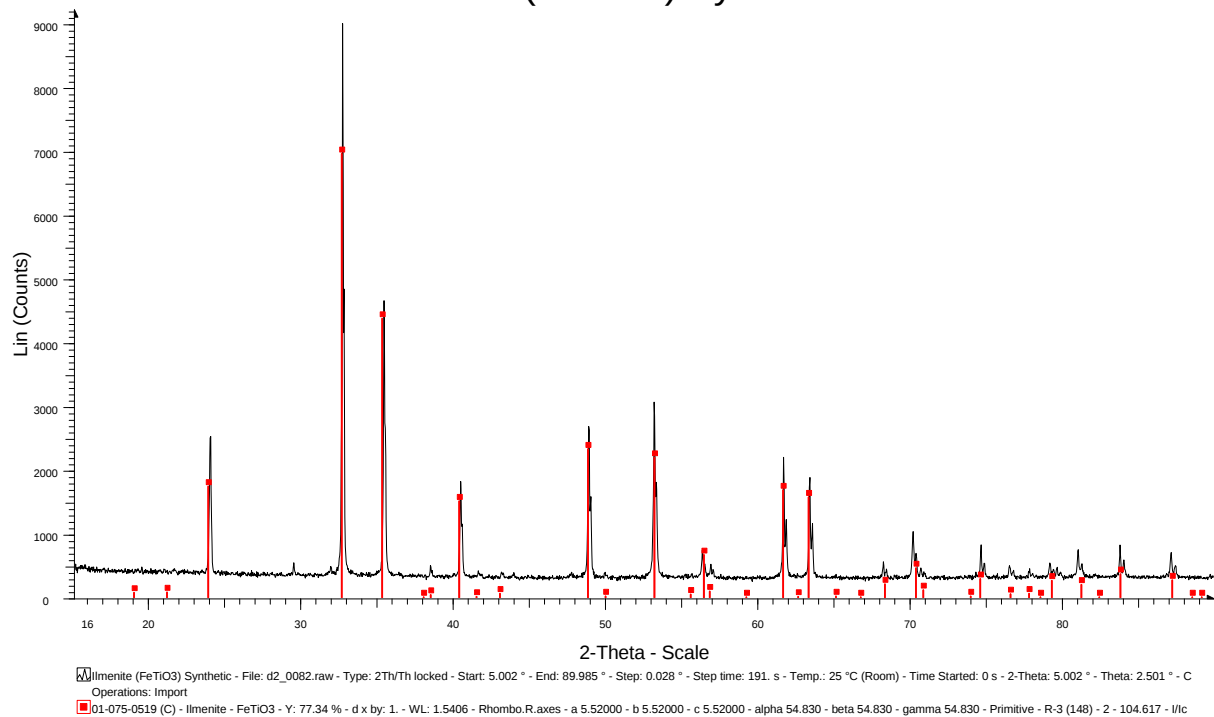


Figure B2: X-ray powder diffraction pattern of synthetic ilmenite taken at room temperature using a zero background holder. The solid black lines are the experimental data. The solid red lines and square boxes represent the calculated positions of peaks using Rietveld refinement analysis.

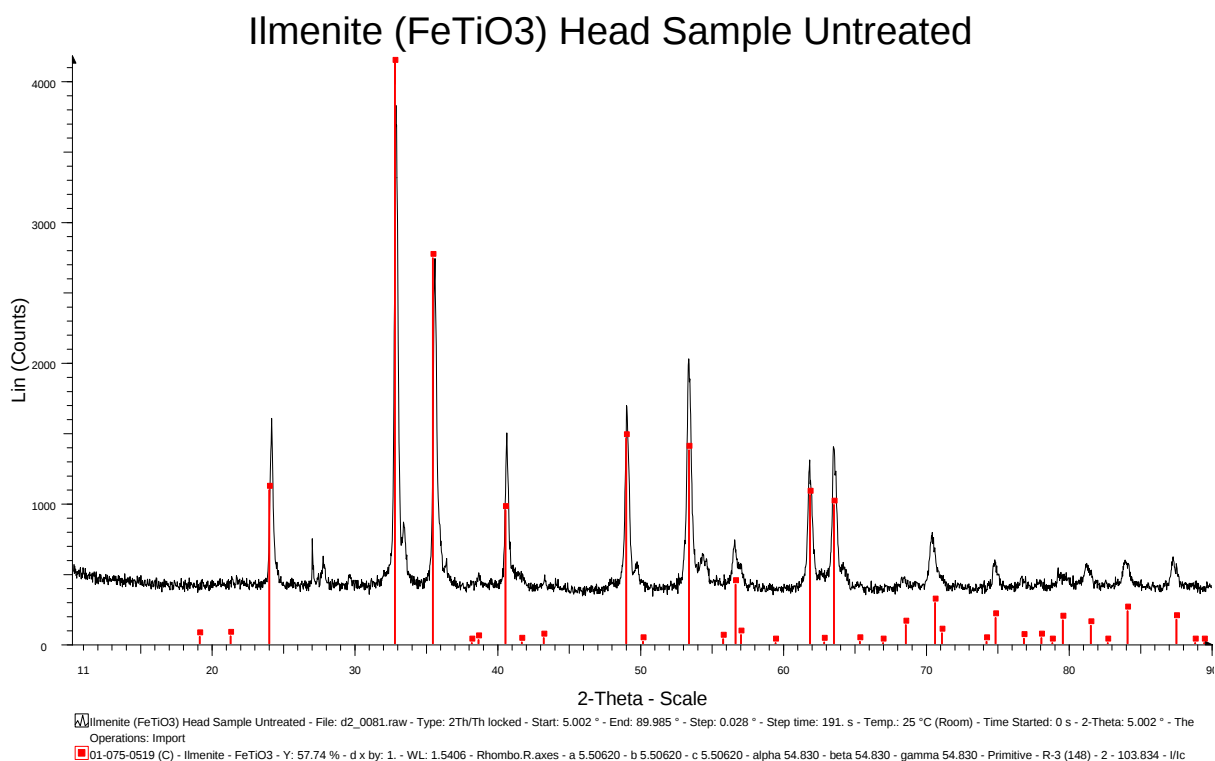


Figure B3: X-ray powder diffraction pattern of the untreated natural ilmenite taken at room temperature using a zero background holder. The solid black lines are the experimental data. The solid red lines and square boxes represent the calculated positions of peaks using Rietveld refinement analysis.

Table 5: Lattice Parameters of ilmenite samples obtained from Rietveld refinement analysis.

Sample Type	Lattice Parameteres		
	a	b	c
SLS ilmenite	5.06	5.06	13.89
Synthetic	5.52	5.52	5.52
Natural Ilmenite (Head Sample)	5.506	5.506	5.506