RAMAN MICROPROBE STUDIES OF MECHANICALLY STRESSED Si₃N₄ CERAMIC MATERIALS USING CCD ARRAY DETECTION,

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RAMAN MICROPROBE STUDIES OF MECHANICALLY STRESSED Si₃N₄ CERAMIC MATERIALS USING CHARGE-COUPLED DEVICE DETECTION

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ABSTRACT

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Modifications were made to a Raman microprobe system to permit in-situ studies of mechanically stressed Si₃N₄ ceramic to be conducted using CCD array detection. A four-point bend fixture was integrated into the system to allow Raman spectra to be collected of Si₃N₄ ceramic specimens while they were being mechanically stressed. Changes in the spectral features of the Raman data were used to obtain qualitative and quantitative information about stress/strain parameters in the material. A 576 by 384 element CCD array detector was also integrated into the system allowing spatially resolved Raman spectra to be acquired. Spatial resolution to 2.89 μm and spectral resolution to .335 cm⁻¹ were possible with the CCD detector. The image degradation effects of astigmatism due to the off-axis nature of the spectrometer system were corrected by using a cylindrical lens between the spectrometer and the CCD array. The system was modified to allow either photomultiplier tube (PMT) detection or charge-coupled device (CCD) detection. A comparison of the two
detection schemes, which included signal-to-noise ratio (SNR), data collection time, and sensitivity comparisons, was done. The effects of binning the CCD detector's pixels in the spatial and spectral directions were also studied. Changes in the Raman spectra of the mechanically stressed Si$_3$N$_4$ were studied and the results showed possible fatiguing effects in the bar for loading levels above 30 lbs for incremental loading. A cyclic-loading study showed a similar nonlinear behavior in the test specimen that can be explained by the presence of a residual strain in the material after the first loading sequence. The cyclic-loading study also showed a hysteresis type behavior.
I am most grateful to my thesis advisor, Dr. Perry P. Yaney, for his patient support and help during the past two years. I have learned a great deal from him, and hope to put this new knowledge and experience to good use in the years to come. I wish him all the best, and hard working students in the future. I am also very grateful to Dr. Norman L. Hecht, of the University of Dayton Research Institute (UDRI), Metals and Ceramics Division, for support and council on this thesis, and to Dr. J. Michael O’Hare, and the University of Dayton Department of Physics for additional financial support. I am thankful to my thesis committee, Dr. Perry P. Yaney, Dr. Norman L. Hecht, and Dr. Gordon Little, for their patient and timely reading of the thesis and for their most helpful comments. I would also like to thank Leon Chuck for designing the four-point bend fixture, and all of the members of the UDRI Metals and Ceramic Division for their help in my understanding of ceramics, mechanical loading and strain gages. I also owe tremendous thanks to my parents, family, friends, and my new wife Laura without whose support and encouragement I am sure this thesis would not have been possible. Through good times and bad they have always been by my side, helping me along the way. This thesis is dedicated to them.
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CHAPTER I

INTRODUCTION

Historical Background

In 1921 C. V. Raman began a series of experiments dealing with the scattering of light by transparent media. In the course of his studies, he observed a new kind of light scattering that was characterized by shifted frequencies with respect to the incident light.¹ After determining that the new light was not due to some anomaly in the incident radiation, he concluded that the new phenomenon was a fundamental characteristic of light scattering.

Raman first announced his new discovery on March 16, 1928, at a meeting of the South Indian Science Association at Bangalore.² At the meeting he presented experimental evidence of the new scattering phenomenon in liquid benzene and toluene. His work showed that the frequency shifts, their relative intensities, and their state of polarization, were independent of the exciting radiation. Raman’s work also suggested that the new phenomenon was a universal one, and that the new spectral lines were characteristic of the scattering medium. For his work on the scattering of light and for the discovery of the effect which bears his name,
Professor Raman was awarded the Nobel prize in physics on December 11, 1930.¹

The 'Raman effect' has since matured into a valuable and very capable material characterization tool that has been used in the microanalysis of gases, liquids, and solids. The effect involves an interaction of the incident light with the normal modes of vibration of the material, and it can be used to provide information on such fundamental atomic parameters as atom placements, bond lengths, bond angles, and bond strengths. These atomic parameters can, in turn, be used to understand the various microstructural properties of a material.

The Raman technique has grown in use and popularity and is complimentary to other microprobe techniques such as infrared (IR) absorption, electron microprobe (x-ray fluorescence and Auger emission), and x-ray diffraction (XRD). The Raman microprobe is often the microstructural characterization tool of choice in instances where spatial resolution, molecular specificity, and ambient probing conditions are important.² Relative to IR absorption measurements, for example, the spatial resolution capability of a Raman microprobe (≈1 μm) can be 10 times higher.³ Raman spectra are also usually sharper than corresponding IR spectra, and are not obscured by the presence of water. The spatial resolution capabilities of Raman microprobes also outperform that of XRD, where data acquisition on samples
smaller than 1 mm$^3$ is difficult. Most other microprobe techniques either require a vacuum for sample examination, or require some other type of sample preparation that may influence the material's character. Because of these advantages Raman spectroscopy has become a versatile and widely used technique for microstructural characterization of materials.

**Statement of Problem**

This thesis is the result of investigations using Raman spectroscopy for the study of advanced ceramic materials. Structural ceramics have long been used in many different high-temperature engineering applications, and in recent years have shown potential for use in advanced heat engine applications. Operating at 1,370°C, compared with the present maximum of about 1,050°C for nickel-chrome alloys, an all-ceramic engine could increase engine efficiencies by as much as 30%. This would result in a dramatic savings in fuel, lower engine production and operating costs, and reduced atmospheric pollution. In addition, ceramic engines would require less lubrication, and would provide a better power-to-weight ratio.

Structural ceramics are inherently brittle, however, and before they can become commercially viable, their structural integrity and reliability need to be established. There is, consequently, an expanding need for a better understanding of
the microstructure of these materials, and the interaction between their microstructure and mechanical behavior. Raman and other microprobe techniques are being employed in an effort to better understand these processes.

The Raman technique offers several advantages for studying the microstructure of advanced ceramics. First, the technique is usually nondestructive such that the material is not significantly disturbed while being probed. Generally, Raman measurements require little or no specimen preparation and can be carried out in air, in solution, at elevated or cryogenic temperatures, or in other environments such as found in gas-turbine engines. The diffraction-limited spatial resolution of a Raman microprobe (≈1 μm) is also comparable to the grain sizes in most advanced ceramics (0.1 - 10 μm), and this allows selective probing of individual grains. In-situ detection of microstructure characteristics is also possible under a variety of mechanical loading conditions. For example, external stresses placed on a ceramic bar, can result in shift, broadening, intensity or lineshape changes in Raman modes. These parameters can be monitored and can be used to obtain qualitative and quantitative information about the ceramic microstructure.

One of the major limitations of the Raman technique is the very weak signals that are typically observed. The scattered Raman intensity is typically only $<<10^{-7}$ (for scattering by solids) of the incident radiation. These low-
light-level conditions impose severe performance requirements on the various components of a Raman microprobe system, and often limit the applicability of the technique.

The very weak Raman signals require high irradiance levels on the sample and long integration times in order to achieve acceptable signal-to-noise ratios (SNRs). The use of lasers and microscope systems can provide these high irradiance levels, but this often leads to specimen heating effects which can affect the Raman spectrum. Long integration times can also be a problem because of the possibility of changing microstructural characteristics. Weak Raman signals also require very efficient collection methods for the scattered Raman light. This necessitates an optimization of the Raman microprobe's optical, signal collection, and signal detection systems.

Recent advances in multichannel detection systems have increased the collection efficiency and sensitivity of Raman systems, and have had a dramatic effect on Raman microprobe performance capabilities. One multichannel detector in particular, the charge-coupled device (CCD), has jumped to the forefront of low-light-level detection applications such as Raman spectroscopy. This is primarily because of its high signal-to-noise ratio (SNR), wide dynamic range, high quantum-level sensitivity, and excellent linearity.\textsuperscript{11}
Goals of the Thesis

The goals of this thesis were two-fold. First, Raman studies were carried out in order to characterize the microstructure of mechanically stressed Norton/TRW NT-154 Si₃N₄. A four-point bend fixture was integrated into the Raman microprobe’s stage assembly so that in-situ Raman studies could be performed on mechanically stressed Si₃N₄ bars. The bend fixture was calibrated and an assessment of its performance was made. The fixture was used to investigate the microstructure of Si₃N₄ under a variety of mechanical load conditions, where qualitative and quantitative measurements were obtained.

The second goal of this thesis was to integrate a CCD array detector into the microprobe. The CCD detector’s performance characteristics were evaluated, and a comparison of the photomultiplier tube (PMT) and CCD detection schemes was accomplished. Unique capabilities of the CCD detector were also investigated such as its charge binning and line-imaging capabilities. Limitations of the CCD were also examined. A study of the possible interference of material fluorescence on Raman spectra when using the CCD detector was also accomplished.

The remainder of this thesis concentrates on three major themes, namely 1) the Raman effect in crystalline solids, 2) the properties of Si₃N₄ ceramic, and 3) CCD array detection. Chapter II provides background information, and Chapter III
presents the basic theory necessary for the analysis presented in Chapter VI. Chapters IV and V review the microprobe design/modifications and experimental studies, respectively. Conclusions and recommendations are given in Chapter VII.
CHAPTER II

BACKGROUND

The Raman Effect

When a substance is irradiated with monochromatic radiation, the incident radiation is weakly scattered. This scattering is due to inhomogeneities in the medium (Tyndall scattering), and, to a lesser extent, to the polarizability of the medium (Rayleigh scattering). Both of these processes scatter radiation at the same frequency as that of the source. A third, much weaker scattering process also occurs in which the light is scattered at shifted frequencies with respect to the source frequency. This third process is known as Raman scattering or the Raman effect.

The observed Raman frequency shifts in a solid substance are due to an interaction of the incident light with the normal modes of vibration of the material. This interaction can be thought of as an inelastic collision process that satisfies the law of conservation of energy. An incident photon of energy $h\nu$ can, under the right circumstances, give up part of its energy to a normal vibration mode of the material. Conservation of energy requires that the energy given up to the molecule show up in the scattered photon
as a decrease in photon energy, or alternatively as a downward shift in frequency (referred to as a Stokes Raman shift). An incident photon can also accept energy from the material if the system is initially in an exited state and moves to a lower energy state. Conservation of energy in this case requires the scattered photon have an upward shift in frequency (referred to as an anti-Stokes Raman shift). These two inelastic Raman scattering processes, as well as the Rayleigh elastic scattering process, are illustrated in Figure 1.

![Diagram](image)

Figure 1. Diagram illustrating the vibrational Raman effect.

The scattering processes shown in Figure 1 can be regarded as the simultaneous annihilation of the incident photon and creation of the scattered photon. The interacting light quantum raises the medium or molecule to an
unstable virtual excited state which in most instances decays back to the original state with the re-emission of a photon of the same frequency. This is classical Rayleigh scattering. Occasionally the system returns to a different state at the conclusion of the scattering process, where there is a re-emission of a photon of lower or higher frequency. This is the Raman scattering process. A typical Raman spectrum resulting from these various processes is depicted in Figure 2.

![Figure 2](image_url)

**Figure 2.** The Raman spectrum of monoclinic ZrO$_2$ powder, showing the Stokes and anti-Stokes Raman lines, and the Rayleigh line.

At some temperature, all Raman transitions will appear
as pairs of symmetrically placed spectral lines centered about the exciting frequency. The Raman lines appear in pairs because every 'Raman active' normal mode of vibration of the material can both accept energy during the light scattering process, or can give energy up (if it is already in an excited state). Each normal mode of vibration of frequency $v_n$ can therefore give rise to one down-shifted ($v_S = v_0 - v_n$), and one up-shifted ($v_{AS} = v_0 + v_n$) Raman transition, each with the same relative frequency shift away from the exciting frequency $v_0$.

The intensity difference between the Stokes and anti-Stokes lines arises because of the population difference between the different vibrational energy levels of the molecule. At room temperature there are many more molecules in the ground vibrational state than in the higher vibrational states. The incoming light is, therefore, more likely to interact with a molecule in the ground state and excite it to a higher energy state (Stokes process) than it is to interact with a molecule in a higher energy state causing it to transfer to a lower state (anti-Stokes process). The Stokes lines are consequently of higher intensity than the anti-Stokes lines at room temperature.

For a vibrational mode of a material to be Raman active, there must be a change in the polarizability of the atomic
arrangement during the vibration. A change in polarizability can be identified with a change in the shape of the electron cloud surrounding the molecule. This can be understood by looking at the normal modes of vibration of the triatomic molecule illustrated in Figure 3. In this figure, the normal modes of vibration of a linear molecule with a center of symmetry and no permanent dipole moment are depicted.

![Figure 3. Normal modes of vibration of a linear triatomic molecule.]

The $v_3'$ and $v_3''$ modes are indistinguishable in space and are considered together as one "doubly degenerate" vibration. If it is assumed that the center atom has a slightly higher electron density than the outer two atoms, and the vibration amplitudes are small, then there will be no first order change in the polarizability of the molecule during vibrations $v_2$ and $v_3$, because the electron cloud around the
molecule does not change shape. These two vibrational modes are, therefore, not Raman active. In the symmetric stretching mode, \( \nu_1 \), however, the electron cloud around the molecule expands and contracts along the axis, changing its shape. This gives a change in polarizability, and the vibration is Raman active.

Measurable parameters provided by a typical Raman spectrum include the Raman frequency shifts, linewidths and lineshapes, polarization response, and relative intensities. Measurements of these and other parameters can provide both qualitative and quantitative information on the properties of a material. The Raman frequency shifts are expressed in wavenumbers (cm\(^{-1}\)), and are equal to the difference between the Raman wavenumber and the wavenumber of the exciting radiation. In solids, these shifts are functions of the interatomic forces in the material, the atomic placements and the symmetry. Raman frequency measurements can, therefore, provide useful information on the changes in the atomic arrangement and in the bonding forces present in a material's atomic/crystal structure.

**Silicon Nitride Ceramic**

The development of silicon nitride (Si\(_3\)N\(_4\)) ceramics for heat engine applications dates back to the late 1960's. The great interest in Si\(_3\)N\(_4\) is due to a large extent to its
high strength and good wear resistance. Si₃N₄ also has a high decomposition temperature, excellent oxidation resistance, good thermal-shock properties, a low coefficient of friction, and high resistance to corrosive environments. These and other attributes make it an excellent candidate for use in advanced heat engines and other high temperature, oxidizing environments.

Crystalline silicon nitride exists in two polymorphs, designated as α-Si₃N₄ and β-Si₃N₄. Norton/TRW (NT-154) Si₃N₄ was selected for this work. NT-154 is a Si₃N₄ with 4% Y₂O₃ and is a β-Si₃N₄ polymorph. A schematic representation of the β-Si₃N₄ structure found in NT-154 crystallites is shown in Figure 4.

![Figure 4. The crystal structure of β-Si₃N₄.](image-url)
As shown in Figure 4, the silicon and nitrogen atoms of $\beta$-$\text{Si}_3\text{N}_4$ are covalently bonded together with the crystal network built up of $\text{SiN}_4$-tetrahedra, where each nitrogen atom is common to three $\text{SiN}_4$-tetrahedra. The planes of atoms are linked along the [001] direction in a sequence of ABAB, ABAB, etc.

The $\beta$-$\text{Si}_3\text{N}_4$ unit cell has an overall hexagonal symmetry and contains 14 atoms and two formula units ($Z=2$). The lattice dimensions are $a = 7.606 \text{ Å}$ and $c = 2.909 \text{ Å}$, and its space group is $C_{6h}^2 (P6_3/m)$, with two nitrogen atoms in the $C_{3h}$ sites and the rest in $C_s$ sites.\(^{21}\)

Group theory and crystal symmetries can be used to calculate the theoretical selection rules for Raman active modes of a solid. A group theoretical analysis performed by Wada et al.\(^{22}\) yielded the following results for the $\beta$-$\text{Si}_3\text{N}_4$ Raman active modes:

\[
\begin{align*}
\Gamma_{\text{acoustic}} &= A_u + E_{1u} \\
\Gamma_{\text{optic}} &= 4A_g (R) + 3B_g + 2E_{1g} (R) + 5E_{2g} (R) \\
&+ 2A_u (IR) + 4B_u + 4E_{1u} (IR) + 2E_{2u}
\end{align*}
\]

where the terms designated with (R) are Raman active and the terms designated with (IR) are infrared active. The remaining modes are inactive or "silent modes". Wada's
analysis predicted 11 first order Raman lines for $\beta$-Si$_3$N$_4$, with four $A_g$ modes, five $E_a$ modes and two $E_{lg}$ modes.

A major focus of this thesis was to study the effect of an externally-applied stress on Si$_3$N$_4$ as manifested in changes in the vibrational Raman spectra. When a crystal is subjected to an external stress the following effects may occur in the Raman spectrum:

(i) Sufficient strain can develop in the crystal to disorder it or to change its symmetry. This can cause mixing between modes which can result in infrared or silent modes that were not allowed in the unstrained crystal becoming Raman active.

(ii) The fundamental Raman frequencies nearly always shift when an external stress is applied. This is primarily due to a change in the normal mode vibrations arising from anharmonic terms in the potential energy function of the crystal. This causes the fundamental Raman frequencies to depend on the crystal volume. An applied external stress will almost certainly change the crystal volume (the size of the unit cell), and this ultimately shows up in the Raman spectrum as shifts in the fundamental Raman frequencies. Frequency shifts are normally to higher frequencies for compressive forces and to lower frequencies for tensile forces. For anisotropic crystals, however, the shift depends on the particular mode.
(iii) The intensities of Raman bands may change due to changes in the induced dipole moment or polarizability brought about by the strain.

**Charge-Coupled Device Detection**

For many years, there were relatively few changes in the way that optical radiation was detected in low-light-level spectroscopic applications like Raman spectroscopy. Photomultiplier tubes (PMTs) were used almost exclusively because they offered very high and almost noiseless gain which is required for low-light-level applications. For this reason, solid state and other detector technologies have not been able to match PMT performance.

Recent advances in multichannel solid state detector technology, however, have made them very competitive with PMTs. One multichannel detector in particular, the charge-coupled device (CCD) detector, has shown particular promise. When compared on a detector-element-by-detector-element basis, it has sensitivity and dynamic range ($10^5 - 10^7$) comparable to the PMT.\(^{25}\)

CCD detectors are optical-array detectors based on silicon metal-oxide semiconductor technology. They are light integrating detectors that accumulate charge as light strikes them. This is in contrast to that of a photomultiplier tube, which produces an anode current proportional to the instantaneous photon flux incident on the photocathode.
The majority of CCD detectors are produced from silicon and are based on silicon technology. It is therefore useful to examine the properties of silicon and the way in which it interacts with light. In crystalline form, each atom of silicon is covalently bonded to its neighbors. The photon flux of incident electromagnetic radiation can break the silicon bonds and generate electron-hole pairs. It is this photo-electron generation process that allows silicon to be used as a light detector.

Silicon detectors are typically limited to detecting photons in the 400 - 1100 nm wavelength range. This is primarily due to the fact that there is a direct relationship between the wavelength of incoming light and the photon absorption depth; the shorter the wavelength, the smaller the penetration depth into the silicon. Silicon becomes transparent at approximately 1100 nm and becomes progressively more opaque to light as the wavelength shortens.

Besides photon excitation, silicon bonds can also be broken by high-energy particles, such as X-rays and cosmic rays, and by thermal agitation. High energy particles tend to break many thousands of bonds at a time, and excessive high energy exposure can cause damage to the crystal lattice. Bonds broken by thermal agitation are one of the primary sources of noise in CCD detectors. At room temperature, approximately 50 bonds/second/μm³ are broken and recombine on
a continuous basis due to thermal agitation. These "dark" electrons can have an adverse effect on the detection limits for photon-induced charge. The rate of electron-hole pair generation due to thermal energy is highly temperature dependent, and can usually be reduced to an acceptable level by cooling the detector.

In order to measure the electron charge produced by incident photons, it is necessary to collect the charge. CCD detectors use potential wells to accomplish this. Figure 5 shows a schematic of a typical silicon potential well used in CCD detectors. A thin layer of silicon dioxide is grown on a section of silicon and a conductive gate structure is applied to the oxide. When a positive electrical potential is applied to the gate, a depletion region is created where free electrons generated by the incoming photons can be stored.

![Figure 5. Silicon potential well.](image-url)
A potential well collects electronic charge until it is filled. Once filled, excess charge can spill into adjacent potential wells, and this affects the ability to quantify the stored charge in both the saturated potential well and the adjacent potential well. Practical potential well capacities are on the order of a million electrons for depletion depths ranging from a few micrometers to tens of micrometers. This is usually more than adequate for most low-light-level imaging applications.

A CCD detector uses a matrix arrangement of oxide and gate structures so that many thousands of potential wells are established over a large area of a silicon chip. The gate structure is arranged with multiple phases so that potential wells can be propagated through a silicon sheet, as illustrated in Figure 6. The application of an appropriate sequence of potentials causes the potential well to propagate from left to right. As shown in Figure 6, when isolated gates apply potentials (time-$t_1$), the charge is held by those isolated gates. When two adjacent gates apply potentials (time-$t_2$), the charge will migrate between the two gates. And when a gate turns off its potential (time-$t_3$), the charge will migrate to the next available potential down the line. A typical CCD can transfer charge packets hundreds of times without significant loss of charge.31
It is possible to extend the one-dimensional charge transfer concept to two dimensions as shown in Figure 7. Arrays of potential wells are arranged in columns, with the device geometry prohibiting charge from migrating between columns. Along the columns, the charge is contained in individual photosites by potentials that are applied to the multiphase gate structure. This arrangement makes it possible to support a two-dimensional array of independent potential wells. This two-dimensional array of potential wells is called the parallel register.
An image focused on the parallel register produces a pattern of charge in proportion to the total integrated flux incident on each photosite. The CCD array can integrate and collect charge over a prescribed period of time with the total charge collected at a photosite being proportional to the product of flux level and the integration time.

The serial register, shown at the top of Figure 7, is itself a one-dimensional CCD array and plays an important role during CCD readout. When the CCD detector is exposed to light, an electronic image accumulates as a pattern of charge in the parallel register (Figure 8a). The CCD is now ready
to be read out. All rows in the parallel register are shifted in parallel towards the serial register, where the top row is shifted into the serial register as shown in Figure 8a and 8b. Once in the serial register, pixels are individually shifted toward the output amplifier where a measurable signal proportional to the quantity of the charge in each charge packet is produced (Figures 8c and 8d). While the serial register is being read out, the parallel register remains stationary. After the serial register has read out all of the pixels in the top row, the next row in the parallel register can be shifted into the serial register (Figure 8e and 8f), and the whole process repeats until the entire parallel register is read out.

Figure 8. CCD detector charge readout sequence.
Multichannel detectors offer the advantage over single channel detectors of having the capability for selectively combining photogenerated charge from several detector elements into a single charge packet. This summation process can increase the sensitivity and dynamic range of spectroscopic measurements. It also allows control over the size and shape of the effective resolution elements of the array, and can provide a signal-to-noise ratio (SNR) improvement which can improve the quality of Raman spectra acquired with a CCD detector.

The combination or summing of charge packets can be accomplished either in digital or analog form. Digital summation is accomplished by individually reading out and digitizing each charge packet, followed by storing and summing the digitized intensities in a computer. Analog summation is performed by physically combining the photogenerated charge packets into a single charge packet in a process called 'binning'. Compared to digital summation, binning reduces the number of analog-to-digital operations needed to quantify the amount of charge associated with a group of charge packets and thereby reduces the total detector noise and increases the readout speed. In spectroscopic applications, binning is used to gather and noiselessly collect photogenerated charge packets from a spectral line illuminating many detector elements of a CCD detector typically along the length of the spectrometer slit.
The only limitation to binning is that the combined charge packet does not exceed the charge holding capacity of the output node or the on-chip amplifier.\textsuperscript{35} Exceeding the charge capacity of any potential well in a CCD can cause the excess charge to spill into adjacent potential wells, a condition known as 'blooming'.\textsuperscript{36} Blooming can be disastrous when charge from a strong spectral line spills into the charge packets from a weak spectral line and must be avoided when quantitative spectral measurements are being made.
CHAPTER III
THEORETICAL BACKGROUND

The Raman Effect

A simple classical treatment of the Raman effect and the associated Rayleigh effect (scattering without change of frequency) is based on the fact that an incident light wave can induce oscillating dipole moments in the polarizable molecular units of a substance. For isotropic media, this induced oscillating dipole moment is normally given by the expression

\[ p = \alpha E_0 \cos(2\pi v_0 t) \]  

(2)

where \( \alpha \) represents the molecular polarizability, which, in general, is a second order tensor, and \( E_0 \) and \( v_0 \) are the electric vector and frequency, respectively, of the incident light wave. The polarizability is a function of the vibrational or other motion of the nuclei, so that for a given normal mode of frequency, \( v_n \),

\[ \alpha = \alpha_0 + \alpha_n \cos(2\pi v_n t + \beta) \]  

(3)

where \( \beta \) is an arbitrary phase. Substituting this into Equation (2) gives an oscillating dipole moment of the form
\[ p = \left[ \alpha_0 + \alpha_n \cos \left( 2\pi v_0 t + \beta \right) \right] \left[ E_0 \cos \left( 2\pi v_0 t \right) \right] \]
\[ = \alpha_0 E_0 \cos \left( 2\pi v_0 t \right) + E_0 \alpha_n \cos \left( 2\pi v_0 t + \beta \right) \]
\[ = \alpha_0 E_0 \cos \left( 2\pi v_0 t \right) + \frac{1}{2} E_0 \alpha_n \left\{ \cos \left[ 2\pi \left( v_0 - v_n \right) t + \beta \right] + \cos \left[ 2\pi \left( v_0 + v_n \right) t + \beta \right] \right\} \]

From classical electromagnetic theory, the average power radiated by a dipole \( p \) over all directions is

\[ \langle p \rangle = \frac{16 \pi^4 v^4 \left| p \right|^2}{3c^3} \]

The induced electric dipole moment \( p \) can thus be regarded as the superposition of three periodically changing moments of frequencies \( v_0, (v_0 - v_n), \) and \( (v_0 + v_n) \), each of which radiates light of a corresponding frequency that constitute, respectively, the Rayleigh line, the Stokes Raman line and the anti-Stokes Raman line.

For solids, the polarizability, \( \alpha \), as mentioned earlier, is a second rank tensor. The components of the induced moment vector are then related to the electric vector as follows:

\[ p_x = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \]
\[ p_y = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \]
\[ p_z = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z \]

where the coefficients \( \alpha_{xx}, \alpha_{xy}, \) etc., are the components of
the polarizability tensor, and $\alpha_{xy} = \alpha_{yx}$, $\alpha_{xz} = \alpha_{zx}$, $\alpha_{yz} = \alpha_{zy}$.

A Raman transition is allowed, and an observed Raman line usually has an appreciable intensity, if one or more of the six components of the polarizability tensor $\alpha_{xx}$, $\alpha_{yy}$, etc. is non-zero.\(^4\)

If the polarization of the medium is not spherically symmetric, the induced dipole moment will depend on the orientation of the specimen. The tensor character of the polarizability can then be used to selectively excite different Raman modes or phonons, which can be used to selectively study different microstructural properties of a material.

**Strain Measurements Using the Raman Effect**

When a crystalline solid is subjected to load, several changes in the crystal's structure occur. If the external load is a homogeneous stress, $\sigma$, then there will be an elastic deformation of the crystal.\(^4\) This deformation is homogeneous and is best described by the strain, $\varepsilon$, which, in the elastic region and for tensile stress is related to the applied stress by the equation\(^4\)

$$\sigma = E \varepsilon$$  \hspace{1cm} (7)  

where the proportionality constant, $E$, is called the modulus.
of elasticity or Young's modulus. Both \( \sigma \) and \( \varepsilon \) are, in general, second-rank tensors. In view of the proportionality between stress and strain, it makes no difference whether stress- or strain-induced effects on the Raman spectrum are considered.

As mentioned in Chapter I, the application of a homogeneous stress to a material can have dramatic effects on the observed Raman spectrum. The most noticeable changes that occur in Raman spectra when an external force is exerted on a crystalline solid are Raman mode frequency shifts.\(^4^4\) These shifts result from a change in the shape or volume of the unit cell, which is due to changes in bond lengths. Because the Raman phonon frequencies are a function of the interatomic forces in the crystal (which are related to the bond lengths), the change of the bond length under stress gives rise to a shift of the Raman bands with respect to that in stress-free crystals.

A homogeneous, uniaxial stress can actually be broken up into two separate stress components.\(^4^5\) The first component is a shear stress, and this gives rise to phonon splittings in the Raman spectrum. This was not observed in any of our mechanical load studies so it will not be covered any further. Additional information on this phenomenon is given in References 45-48. The second component of uniaxial stress is a hydrostatic stress that changes the volume of the unit
cell in the material, which causes Raman phonon frequencies to shift.\textsuperscript{46} This was observed in our loading studies and our analysis will be based on this type of stress.

The strain can be calculated using the relation between the shift of the Raman line and the hydrostatic strain, provided that the observed shift is due to the hydrostatic component of the stress. This relation is given by\textsuperscript{47}

\[
\frac{\Delta \omega}{\omega_0} = K \frac{\Delta V}{V_0} = K \varepsilon
\]

(8)

where $\Delta \omega$ is the shift in phonon energy, $\omega_0$ is the unstressed phonon energy, $K$ is a proportionality constant that depends on crystal and strain parameters, $V_0$ is the unstressed unit cell volume, $\Delta V$ is the change in volume when the crystal is stressed, and $\varepsilon$ is the hydrostatic strain induced by the applied stress. Thus, from the theoretical viewpoint, Raman frequency shifts are linear with strain within a certain range of applied stress.\textsuperscript{48}

**CCD Array Detector Performance Characteristics**

The performance characteristics of the CCD array detector (hereafter referred to as simply “CCD detector”) important to Raman spectroscopy applications include spatial and spectral resolution, linearity, sensitivity, dynamic range, and noise considerations. The low-light-level
operating environment of Raman experiments places stringent demands on a detector system and requires that the CCD detector have a high responsivity, minimal read noise, and negligible dark current. Scientific-grade CCD “cameras” accomplish this by operating at low frame rates (e.g., several seconds), by employing cooling to reduce dark current, and by using very low noise amplifiers and signal conditioning circuits. Unique capabilities, such as the ability to nondestructively read the detector array and the ability to alter the effective detector element size by binning, also greatly enhance CCD detector performance.

Resolution

The resolution of a CCD detector is determined by the geometry of the specific device being used. A CCD resolution element, often called a picture element or pixel, typically varies in size from a few micrometers up to 30 μm. In full frame imagers, there is no dead space between pixels, so that charge generated by photons striking between pixels diffuses to the nearest potential well.

For spectroscopic imaging applications, the CCD detector is often used to record spatial information in one direction (parallel to the spectrometer slits), and spectral information in the other direction (perpendicular to the slits). The spatial resolution in the slit direction will depend on the optics used in the imaging system and will
ultimately be limited to the diffraction limit of these optics.\textsuperscript{51} The spectral resolution will depend on the reciprocal linear dispersion of the spectrometer which depends on the wavelength of the light, the grating constant and focal length of the spectrometer, the spectral order, and the size of the entrance slit as imaged on the CCD detector.\textsuperscript{52}

**Linearity**

Light incident on the CCD detector creates electronic charge. This is intrinsically a linear process, and charge so produced can be detected and measured at the output amplifier.\textsuperscript{53} With suitable electronics, the output signal can be amplified, processed, and digitized to yield a digital representation of the image which was focused on the CCD detector. Ideally, there should be a linear relationship between the light level and the digital number representing that level.

High-performance cameras have been designed to exploit the excellent linearity characteristics of the CCD detector. These cameras employ precision analog electronics and digitizers with high dynamic range to maintain the intrinsic linearity of the CCD detector. This high performance is achieved by cooling the detector and operating the readout electronics at significantly slower rates than those used in video cameras. Scientific-grade CCD detectors exhibit a linear signal transfer relationship within a few hundredths
of a percent over a dynamic range of $\sim 10^4$.

**Sensitivity**

High sensitivity is crucial for Raman and other forms of low-light-level spectroscopy. Sensitivity is the minimum detectable signal to which a CCD detector will give an observable response. The sensitivity of a CCD detector is determined by two factors. The first is quantum efficiency which is a measure of the sensor's efficiency to generate electronic charge from incident photons. Within the 400 to 1100 nm wavelength range, quantum efficiency typically ranges from 3% at 400 nm to a maximum of 40% at 700 nm and down to 1% at 1100 nm. Peak quantum efficiencies greater than 80% at 700 nm are achievable with detectors that utilize thinned, back-illuminated CCDs.

The second factor determining the sensitivity is the system noise level. At low light levels, CCD preamplifier noise begins to dominate, and sensitivity is degraded to the point where signals get lost in the preamplifier noise. For low-light-level applications, it is therefore necessary to reduce preamplifier and other types of system noise to a minimum.

The CCD detector is currently the most sensitive array detector available for low flux imaging applications. The factors responsible for this include high quantum efficiency,
the ability to integrate charge for hours, negligible dark current, and an extremely low detector read noise.

**Dynamic Range**

The dynamic range of a CCD detector is simply defined as the ratio of the device saturation charge to the system noise level, expressed in electrons. Saturation charge is limited by the well capacity of the CCD, which depends on the device architecture and pixel size. Small pixels have small potential wells, and low saturation charge levels. The saturation charge level scales more or less linearly with pixel area and is completely independent of the system noise level. A rough rule that can be used to estimate the device saturation charge is that in electrons it is about 1000 times the pixel area in square micrometers. An imager with 23 μm x 23 μm pixels has a 529 μm² area/pixel and a saturation level of about 529,000 electrons. System noise levels typically vary between a few electrons in a high-performance, slow-scan cooled cameras, up to many thousands of electrons for inexpensive video cameras. If the noise level is ~10 electrons for the above 23 μm x 23 μm pixel example, then the dynamic range would be ~10⁴. In some spectroscopic applications, dynamic ranges exceeding 7 orders of magnitude have been quantified.
CCD Detector Noise

CCD detector noise is composed of undesirable signal components that arise from various sources within an electronic imaging system. The three primary noise sources for CCD detectors are photon noise, preamplifier noise, and read noise. Dark current due to thermally generated electrons in the CCD structure also add to the noise when long signal integration times are used.

Photon noise, or photon shot noise, is a fundamental property of the quantum nature of light. Photon shot noise arises from the randomness in photon arrival rate at the CCD detector. This randomness results in an uncertainty when measurements of that rate are made in a finite length of time. The uncertainty is approximated by Poisson statistics, which gives a noise value equal to the square root of the signal electron count level. Photon shot noise is unavoidable and is always present in imaging systems. When the level of photon shot noise exceeds all other forms of system noise, the data is said to be photon-shot-noise limited.

Preamplifier noise sets the detection limits of a CCD detector. The noise is generated by an on-chip preamplifier and in scientific-grade CCD detectors it can be reduced to a few electrons. Under low light conditions, the CCD signals are normally preamplifier noise limited. Once the signal level is high enough so that the photon statistics
are the dominant source of noise, preamplifier noise is usually not relevant.

When the anode of a fast (~2 ns) PMT is terminated in a low resistance, typically 50 Ω, then the signal from the anode will be in the form of short pulses corresponding to single photoelectrons emitted by the photocathode. Because of this, very little noise is associated with the actual readout of PMT detectors. For integrating detectors, however, the situation is very different. Integrating devices, such as CCD detectors, can have a significant read noise. The read noise is introduced by the detector and associated electronics in reading out a single charge packet.

The read noise in scientific CCD detectors is usually very low, however. This is because they use a sequential transfer of charge from the photosensitive area to a low-noise amplifier. This eliminates the multiplexing circuitry necessary in other types of multichannel detectors, which greatly reduces the capacitance on the amplifier input (a primary source of noise in other multichannel detectors).

The presence of dark current is an additional concern in low-light-level applications. It is important to ensure that photon shot noise from dark current does not exceed preamplifier noise or photon shot noise from the signal even when long integration times are used. This is usually accomplished by cooling the CCD detector chip. CCD detectors can be chilled to approximately -60° C by use of
thermoelectric cooling. At this temperature, dark current is typically reduced to 1 electron/pixel/second. For extremely long exposures, liquid nitrogen is used to cool the detector to \(-120^\circ\text{C}\). This can reduce the dark current to <5 electrons/pixel/hour.

**Signal-to-Noise Ratio**

The figure of merit that describes the performance of a system is the signal-to-noise ratio (SNR).\textsuperscript{67} A strong signal and low system noise level will give a large SNR which will often reduce the time required to acquire data. A weak signal, on the other hand, will necessitate a low system noise level and will usually require long data acquisition times. The minimum acceptable SNR ratio is typically set at two.

If it is assumed that photons from a steady Poisson source are incident on a CCD or PMT detector, the signal (after subtraction of any dark current) is given in counts by\textsuperscript{68}

\[ S = \eta \Phi t \]  

(9)

where \( \eta \) is the detector quantum efficiency or the probability that a photon will interact to produce a detectable event, \( \Phi \) is the mean photon flux rate, and \( t \) is the total flux observation time.
For a PMT, the principle noise sources are shot noise in the incident photon stream and the shot noise in the dark current. This gives a noise level for the PMT of

\[ N_{\text{PMT}} = \sqrt{t(\eta \Phi + \Phi_d)} \]  

where \( \Phi_d \) is the mean dark current count rate. The overall SNR for a PMT is then

\[ \text{SNR}_{\text{PMT}} = \frac{\eta \Phi t}{\sqrt{t(\eta \Phi + \Phi_d)}} \]  

CCD detectors have a finite read noise which contributes to the noise expression in addition to the two shot noise terms present in the PMT case. This gives an overall SNR expression for the CCD detector of

\[ \text{SNR}_{\text{CCD}} = \frac{\eta \Phi t}{\sqrt{[N_r^2 + t(\eta \Phi + \Phi_d)]}} \]  

where \( N_r \) is the rms read noise.

**CCD Charge Summation**

The quality of Raman spectra acquired with a CCD detector can be improved by summing together charge from multiple pixels. As previously discussed, the two methods of summing the charges are summing the analog signal on the chip and digital summing in computer memory. The manner of
summing the photogenerated charge directly affects the signal-to-noise ratio (SNR) and dynamic range of the measurement of spectral line intensities.

The SNR advantage of summing the analog signal on chip, as opposed to digital summing in memory, is that the summed charge is subject to only one read operation and thus has only the noise associated with one read. Digitally summing, on the other hand, adds the read noises from each element. In extreme low-light-level situations where the dominant source of noise is detector read noise, the summing in computer memory gives a higher noise level by a factor equal to the square root of the number of summed elements. This is because when N pixels containing a finite readout are digitally summed, the SNR improvement will be $N^{1/2}$. If the charge from N pixels are binned and read out, the readout noise is the noise for only one pixel, and this means that the SNR improvement is directly proportional to N. Binning, however, yields this SNR advantage over digital summation only when readout noise is a significant noise component.

In Raman spectroscopy, the ability of the CCD detector to bin charge from multiple detector elements can increase the sensitivity of a measurement. Some resolution loss is incurred, however, because the large number and small size of the original resolution elements is not being fully utilized. In many spectroscopic applications, this resolution loss may not be significant.
CHAPTER IV
MICROPROBE DESIGN AND MODIFICATIONS

Introduction

The Raman microprobe used in this thesis was originally designed and constructed by Yaney, Schneider, and Wager in 1984. It is uniquely configured to study advanced ceramic materials and has been used for this purpose since that time. The system has gone through a series of modifications over the years, with each new graduate student adding some new component or capability to the system to better study and understand these very complicated materials. A comprehensive description of the time evolution of the microprobe is given by Jennings in Reference 75 for the interested reader.

The purpose of this chapter is to highlight the components of the microprobe that are related to this thesis. Special emphasis will be placed on how each component helps enhance the microprobe’s unique capability for the study of advanced ceramics. Modifications and upgrades performed for this thesis will also be explained as they pertain to the measurements that were carried out.

Microprobe Design

A schematic of the microprobe used in this work is shown in Figure 9. It is typical of a modern Raman microprobe, and
consist of four basic parts: 1) a laser excitation system, 2) a sample holder or sampling cell, 3) a light dispersing system, and 4) a light detection system.

Figure 9. Schematic of Raman microprobe optical system. (Key to diagram: M-mirror, I-iris, NDF-neutral density filter, CL-cylindrical lens, L-lens, PMT-photomultiplier tube.)

The heart of the microprobe is a pulsed Chromatix model 1000E Nd:YAG laser. This "baby YAG" has a maximum power output of \( \approx 100 \text{ mW} \), and a spectral linewidth of \( 1 \text{ cm}^{-1} \). It is run in a Q-switched, frequency doubled mode that provides a 532 nm, \( \text{TEM}_{00} \) output. The Q-switch is normally set to provide a burst of 8 to 12, 150 ns pulses, for each flash lamp pulse operated typically at a repetition rate of 59 Hz. Synchronous gating of the signal collection electronics
around these 150 ns pulses provides an effective means of suppressing fluorescence background that can often be a problem from impurities in the ceramic.\textsuperscript{76}

The output from the laser is highly polarized along the horizontal axis, and a $\lambda/2$ waveplate positioned just after the laser provides orientation control of the polarization axis. This waveplate, in combination with a Glan-Thompson polarization analyzer placed in the signal collection path, allows complete control over the selection of different modes of vibration in the ceramic.

A unique cylindrical lens spatial filter system produces a fine line of laser light on the specimen surface. This allows high spatial resolution across the line, while averaging over a sizeable length along the line. As pointed out by Lander,\textsuperscript{77} this dramatically reduces local specimen heating problems and reduces bleaching delays due to fluorescence. In addition, the short focal length cylindrical lens, which determines the length of the line of light, can be defocused to control the length of the line and further reduce specimen heating.

The microprobe is configured in a backscatter geometry and uses a 70/30 beamsplitter that transmits 30\% of the incident laser energy to the specimen, and 70\% of the scattered Raman light to the collection optics. This 70/30 combination was chosen based on an analysis done by Jennings\textsuperscript{78}
which predicted a maximum Raman signal for minimum specimen heating with this transmission-to-reflection beamsplitter ratio.

The "micro" part of the Raman microprobe is supplied by an assortment of interchangeable microscope objectives (5x to 100x magnification powers), which focus the incident laser beam (≈6 mm long by 1 mm wide) down to a size comparable to the dimensions of the ceramic grains (20 μm to 0.1 μm). Sizes of the line of light on the specimen surface range from approximately 25 μm x 10 μm for the 5x objective to 1.4 μm x 0.72 μm for the 100x objective. These values are based on calculations using Gaussian beam propagation and a focused image at the specimen. This allows microsampling of individual grains on the order of one micron, which is desirable for characterization of polycrystalline ceramics.

Visual observation of the ceramic surface/topography is provided by an auxiliary white light source and pair of viewing binoculars. This system is used to adjust the focus of the laser light on the specimen surface, and to accurately place the line of light on a particular grain or region of the ceramic. A sharp cut red filter (Corning C.S. No. 3-66) provides safe viewing of the scattered laser light through the viewing binoculars by filtering out close to 100% of the light at and above the laser excitation frequency.

The scattered light is collected by the same microscope objective used in illumination. It then proceeds to a 200 mm
focal length achromatic lens that focuses the light down to a scanning slit designed and built by Fettig. The line of light is oriented perpendicular to the scanning slit, and for the 40x objective used in this research, it has been magnified by 48.2 times. The slit can be adjusted in width to transmit any fraction of the line image, and is mounted on a motor-actuated stage capable of 0.1 μm resolution. This allows the probed area to be scanned as a function of position with any desired resolution down to the diffraction limit of the optics involved as permitted by the intensity of the scattered light.

The scanning slit is imaged onto the entrance slit of the "triple" spectrometer using a second 200 mm achromatic lens. The spectrometer is a Spex model 1401 double spectrometer coupled to a Spex 1442 monochromator. The double spectrometer is a 0.85-meter focal length Czerny-Turner type and is equipped with a pair of 1200 grooves/mm gratings that provide a theoretical limit of resolution of 0.154 cm$^{-1}$ at 532 nm. This provides adequate spectral resolution of the ceramic phonon bands (typically 4-12 cm$^{-1}$ FWHM) and good laser light and stray light rejection, both of which are essential for quality spectra to be taken from the weakly scattering ceramic materials.

A thermoelectrically cooled (-20°C) RCA C31034A photomultiplier tube is used to detect the spectral light output from the triple spectrometer. Photon counting
electronics along with the synchronous gating mentioned earlier provided a dark count rate of effectively zero. This provides a system that is signal-noise limited, which gives the microprobe the ability to detect very weak Raman signals.

An IBM PC/AT provides data acquisition control. The data reduction and analysis process uses Asyst software written by Pruchnic. This includes background subtraction, data smoothing, and Raman peak comparison algorithms that can provide quantitative information about the ceramic microstructure.

**System Upgrades**

One of the primary objectives of the thesis was to obtain quantitative microstructural information from mechanically stressed Si$_3$N$_4$. The addition of two major components to the existing microprobe have made it possible to conduct these types of studies. These include a four-point bend fixture placed at the microprobe's specimen stage assembly, and a charge-coupled device (CCD) detector placed at the exit plane of the double spectrometer.

**Four-Point Bend Fixture**

The four-point bend fixture was designed by Mr. Leon Chuck of the UDRI Metals and Ceramics Division. It was constructed and assembled by the UDRI machine shop and Mr. Steve Goodrich. The fixture was designed to be used with a 3 mm x 4 mm x 50 mm Norton/TRW NT-154 Si$_3$N$_4$ flexural test
specimen. The overall dimensions of the fixture are 25 mm wide by 88 mm long by 47.5 mm high. A schematic diagram of the four-point bend fixture is shown in Figure 10.

Figure 10. Schematic diagram of four-point bend fixture used in mechanical load studies.

Four steel rods (1 inch long by 1/8 inch diameter) provide the load points to the Si₃N₄ specimen. Two are located above the specimen spaced 40 mm apart, and two are located below the specimen spaced 10 mm apart. The bars are positioned by v-notches cut in the support structure.

Load to the bar is provided by a screw/nut loading actuator at the bottom center of the fixture. The nut can be tightened or loosened with a standard 7/8 inch wrench. When tightened, the screw rises and produces a flexural moment on the Si₃N₄ test specimen. A load cell made from an aluminum cylinder is located between the specimen and the loading actuator. The cylinder is thin walled and has steel caps on either end to ensure even load distribution through the thickness of the cylinder. It was designed to provide
stability for the center support of the fixture and efficient transfer of load to the test specimen. The load cell has a pair of strain gages attached to opposite sides of the aluminum cylinder which provide a relative measure of the amount of load on the bar. The strain gages are a standard 120 $\Omega$ resistance design, and they change their length (resulting in a small change in resistance) when a compressive or tensile load is applied. This very small change in resistance is measured with a Wheatstone bridge configuration and a picoammeter which provides a current readout proportional to the amount of microstrain present in the strain gages. This configuration is typical of a standard strain indicator. A schematic diagram of the circuit used is shown in Figure 11.

![Figure 11. Schematic diagram of Wheatstone bridge/picoammeter circuit used to measure strain.](image-url)
The two strain gages were originally calibrated by Mr. Steve Goodrich of the UDRI Metals and Ceramics Division using a Vishay Instruments Model P-350A strain indicator and known loads. This same strain indicator was then used to calibrate the strain gages with our Wheatstone bridge/picoammeter configuration. A plot of the calibration curves for each strain gage using our configuration is shown in Figure 12. The two curves differ because of small differences in the resistance characteristics of each strain gage. As shown in the plots, they both have the same general response.

Figure 12. Calibration curves for the two strain gages.
CCD Array Detector Characteristics

The CCD detector used in this thesis was a Princeton Instruments model LN/CCD-576 detector. This model is liquid nitrogen cooled and has a pixel format of 576 columns x 384 rows. The detector has excellent quantum efficiency (~30% @ 532 nm), exceptionally low noise and high dynamic range. These characteristics make it ideal for Raman spectroscopy work where extremely low light level signals require long signal integration times.

The detector is controlled by Princeton Instrument's ST-130 Detector Controller. The controller provides the necessary power, thermostating, and timing signals to the detector head; coordinates data gathering with the experiment; sets exposure times; digitizes and averages data; and transmits it to the computer. Two 50-conductor shielded cables connect a Direct Memory Access (DMA) board in the ST-130 to an IBM/AT adapter board. The IBM/AT adapter board provided by Princeton Instruments is plugged into one of the eight slots available in the IBM/AT computer.

This arrangement gives the ST-130 free access to the computer's 16-bit data bus, the DMA channels and the I/O channel signals, all of which are essential for rapid DMA data transfer. The data bus is used bidirectionally by the computer to send control information to the controller and to receive raw data. The controller is able to digitize and transmit acquired data in real-time to be manipulated and/or
stored by the computer via the DMA. The specification and performance characteristics important to this thesis that are specified by Princeton Instruments are summarized in Table 1.

Table 1. Princeton Instruments LN/CCD-576 specifications and performance characteristics.

<table>
<thead>
<tr>
<th>LN/CCD-576 Performance Characteristics</th>
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</thead>
<tbody>
<tr>
<td>Array Type/Format: Thompson-CSF model TH7883CDA array/ 576 (row) x 384 (column) pixel format</td>
</tr>
<tr>
<td>Pixel Dimensions: 23 x 23 μm²</td>
</tr>
<tr>
<td>Spatial Resolution: # of pixels @ FWHM of spectral line &lt;1.5 pixels</td>
</tr>
<tr>
<td>Geometrical Distortion: Less than 1 pixel</td>
</tr>
<tr>
<td>Readout Noise: 1 - 1.2 counts rms</td>
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<tr>
<td>Spectral Response: Typically 400 - 1060 nm</td>
</tr>
<tr>
<td>Dynamic Range: 14 bits ADC (16,384:1)</td>
</tr>
<tr>
<td>Response Linearity: Better than 1% over the entire range</td>
</tr>
<tr>
<td>Response Nonuniformity: 5-10% typically, depending on the dimension of the super-pixels (binning of pixels)</td>
</tr>
<tr>
<td>Operating Temperature Range: Variable from -80°C to -100°C</td>
</tr>
<tr>
<td>Dark Charge: @ -110°C : 6-8 electrons/pixel/hour</td>
</tr>
<tr>
<td>Exposure (Integration Time): Up to 23 hours in increments of 5 milliseconds</td>
</tr>
<tr>
<td>Frame Readout Rates: 0.0684 to 2.278 msec @ 100kHz depending on number of bins</td>
</tr>
<tr>
<td>Shutter Open/Close time: 5ms/6ms (energized to full open/close)</td>
</tr>
</tbody>
</table>
The entire CCD system is controllable through software provided by Princeton Instruments. This software takes full advantage of the high scan rate of the controller, and utilizes the capabilities of the computer to achieve real-time data storage and near-real time graphics display and manipulation. It uses window-based graphics, and features pull down menus, and mouse selected options. This allows the data to be easily and rapidly viewed, analyzed and compared.

Integration of the CCD Detector into the Microprobe

The integration of the CCD detector head into the Raman microprobe included several steps. The first step involved the actual physical placement of the detector in the system. It was decided to place a ‘swing’ mirror in the double spectrometer 6 1/2 inches before the exit slit, in order to intercept and redirect the light out of the side of the spectrometer. This would allow operation of the microprobe with either the PMT or the CCD detector by just swinging the mirror in or out of position. A 1 3/4 inch hole was cut in the spectrometer side to accommodate the exiting light. This situation is shown schematically in Figure 13. A ray trace analysis was initially performed to help with placement of the hole and the swing mirror and to determine the feasibility of this approach.
The next step was to design and build a suitable mount for the detector. The mount needed a high degree of stability and adjustability in order for the CCD detector to function properly. The mount that was designed and eventually built has six degrees of freedom including two tilt adjustments, two translation adjustments (lateral and transverse), a height adjustment, and a rotation adjustment. A picture of the CCD detector and mount is shown in Figure 14. The various components were bolted together using 1/4 - 20 socket cap screws, and the whole assembly was securely bolted to the optics table.
The next step in integrating the CCD detector into the microprobe involved correcting for astigmatism present in the output image plane of the spectrometer. The astigmatism was due to the off-axis nature of the Czerny-Turner design based on spherical mirrors. This design produces two distinct image planes, one located at the tangential focus and the other located at the sagittal focus (this problem and our solution are covered in more detail in the Appendix).

The astigmatism was reduced by inserting a 150-mm-focal-length cylindrical lens between the exit hole of the spectrometer and the detector image plane. The cylindrical lens in effect brought the two focal planes into coincidence. A custom mount was designed and built for the cylindrical
lens, and like the detector mount, it was provided with the six necessary degrees of freedom for adjustability.

With the cylindrical lens in position, the system produces an adequately focused spectral image at the output focal plane of the spectrometer. An example of this is shown in Figure 15, where the 16462.8 cm\(^{-1}\) (6074.3 Å) and 16403.7 cm\(^{-1}\) (6096.2 Å) neon emission lines are each shown illuminating approximately one pixel (a 10 μm wide by ≈25 μm high image was used at the entrance slit of the spectrometer).

![Figure 15. Spatial and spectral focus using cylindrical lens.](https://example.com/fig15.png)

The intensities of both spectral lines in Figure 15 drop off sharply as you move up or down one pixel, and go to zero
as you move up or down two pixels, which is an indication of a sharp focus in the vertical (spatial) direction. In the spectral direction, each emission line has a linewidth (FWHM) of approximately 2 pixels, which corresponds to \( \approx 0.67 \text{ cm}^{-1} \) (\( \approx 0.24 \text{ Å} \)). This indicates that there is a sharp focus in the spectral direction.

For alignment purposes the 17087.5 \text{ cm}^{-1} (5852.5 \text{ Å}) emission line of a medium pressure neon lamp was used. The lamp was oriented vertically at the scanning slit position so that it was imaged onto the entrance slit of the spectrometer. Rough adjustments were then made to the various translation adjustments of the CCD mount, so that a sharp, well-resolved line was imaged vertically on the center pixels of the array. Fine adjustments were then made to the tilt and rotation adjustments so that the image was uniform and not tilted in any way in the vertical direction.

It was determined early in the CCD detector characterization that the light emanating from the spectrometer was not filling the entire CCD detector array area. With the center slit of the spectrometer opened to its maximum extent (width) of 3 mm, and the entrance slit closed down to 10 \( \mu \text{m} \) wide, we found that we were limited to a working pixel area of about 250 pixels in the horizontal (spectral) direction. It was later found that as the center slit of the spectrometer was narrowed, the working pixel area narrowed by a proportional amount, indicating that the center
slit was acting as the limiting aperture in the spectral direction.

The vertical (spatial) direction of the CCD detector was similarly limited to a working pixel area of about ~210 pixels, in this case being limited by an iris in the 50 mm focal length lens used to focus the light onto the entrance slit of the double spectrometer. The effective working pixel area (window) of the CCD detector array taking these two limitations into account is depicted in Figure 16. This effective area is only 24% of the total CCD detector area available for imaging. These limitations will have to be removed in the future in order to optimize the use of the CCD detector.

![Figure 16. Effective pixel work area (window) on CCD imaging surface due to limiting apertures of microprobe.](image-url)
It was found that the 1200 groove/mm gratings in the double spectrometer dispersed light across the CCD detector at 0.487 nm/mm (0.0112 nm/detector element). In wavenumbers (cm⁻¹) this works out to be 14.56 cm⁻¹/mm (0.335 cm⁻¹/detector element). This is in reasonable agreement with the reciprocal linear dispersion specification given for the double spectrometer of 0.48 nm/mm or 17 cm⁻¹/mm. The difference between these specified and measured values may be attributed (in part) to the cylindrical lens used to correct for astigmatism, which changed the effective focal length (0.85 meter) of the second half of the spectrometer.

The resolution of the CCD detector in the spatial (vertical) direction was checked using the scanning slit and the 17087.5 cm⁻¹ emission line from the neon lamp. The neon lamp was positioned just before the scanning slit, and the scanning slit was used to limit the spatial extent of the neon line in the vertical direction. With the slit narrowed to 100 μm, only one pixel stripe (23 μm) in the vertical (spatial) dimension of the CCD was illuminated. This gave an approximate demagnification in the vertical (spatial) direction of ≈5x from the scanning slit position to the CCD detector.

A more accurate measure of this demagnification factor was obtained using the actuator encoder-based positioning capability to position the slit. By moving the actuator a known and precise amount, and noting the movement of the
image on the CCD detector, an overall demagnification factor of 4.85 was determined. This can be used to calculate the size of one pixel element (23 μm) at the specimen surface for the different magnification objectives available for use in the microprobe, thereby giving a measure of the spatial resolution available at the specimen surface with the CCD detector. These results are tabulated in Table 2.

Table 2. Resolution of CCD pixel elements on specimen surface for different microscope objectives.

<table>
<thead>
<tr>
<th>Objective Magnification</th>
<th>Effective Focal length</th>
<th>Magnification at Scanning Slit</th>
<th>23 μm Pixel Size at Specimen Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>5x</td>
<td>50.2 mm</td>
<td>x3.98</td>
<td>28.0 μm</td>
</tr>
<tr>
<td>10x</td>
<td>16.3 mm</td>
<td>x12.27</td>
<td>9.09 μm</td>
</tr>
<tr>
<td>20x</td>
<td>8.3 mm</td>
<td>x24.10</td>
<td>4.63 μm</td>
</tr>
<tr>
<td>40x</td>
<td>4.3 mm</td>
<td>x46.51</td>
<td>2.40 μm</td>
</tr>
<tr>
<td>LWD 40x</td>
<td>5.19 mm</td>
<td>x38.54</td>
<td>2.89 μm</td>
</tr>
<tr>
<td>ELWD 60x</td>
<td>3.49 mm</td>
<td>x57.31</td>
<td>1.95 μm</td>
</tr>
<tr>
<td>100x</td>
<td>2.52 mm</td>
<td>x79.37</td>
<td>1.41 μm</td>
</tr>
</tbody>
</table>

The long working distance (LWD) 40x microscope objective (Nikon CF M-plan achromat #78730) shown in Table 2 was used in all of the characterization studies described in Chapter V. The long working distance was primarily needed to keep the objective a safe distance from the specimen during the
mechanical loading experiments. The objective has a working distance of 3 mm and an effective focal length of 5.19 mm, which produced a laser line image on the specimen of \( \approx 2 \) \( \mu \)m wide \( \times \) 60 \( \mu \)m long. The 60 \( \mu \)m dimension was imaged onto the CCD detector in the spatial direction (vertical), and covered \( \approx 20 \) pixels as illustrated in Figure 17. This gave a spatial resolution on the specimen surface of \( \approx 2.89 \) \( \mu \)m per pixel along the laser line image.

![Schematic diagram showing the size of the long dimension of laser line on the specimen, and corresponding image size on CCD array.](image)

The detector was calibrated using the five neon emission lines listed in Table 3. Each spectral line could be positioned on the center pixel (No.290) with an accuracy of \( <0.5 \) Å. The spectral lines are representative of the range scanned in the Raman experiments presented in this thesis.
Table 3. Calibration data for CCD using neon emission lines.

<table>
<thead>
<tr>
<th>CCD Channel #</th>
<th>Wavenumber Reading (cm⁻¹)</th>
<th>λ Observed (Å)</th>
<th>λ True (Å)</th>
<th>λ Deviation From True (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>17087.5</td>
<td>5852.23</td>
<td>5852.488</td>
<td>0.258</td>
</tr>
<tr>
<td>290</td>
<td>15666.8</td>
<td>6382.92</td>
<td>6382.991</td>
<td>0.071</td>
</tr>
<tr>
<td>290</td>
<td>15619.5</td>
<td>6402.25</td>
<td>6402.246</td>
<td>0.004</td>
</tr>
<tr>
<td>290</td>
<td>14236.0</td>
<td>7024.45</td>
<td>7024.050</td>
<td>0.400</td>
</tr>
<tr>
<td>290</td>
<td>14219.4</td>
<td>7032.85</td>
<td>7032.410</td>
<td>0.240</td>
</tr>
</tbody>
</table>

**CCD Detector Cooling and Evacuation**

The CCD detector is normally cooled cryogenically to -100°C with liquid nitrogen. This decreases the CCD dark charge leakage due to thermally-generated electrons by approximately a factor of 2 for each reduction of array temperature by approximately 4-7°C. This permits longer signal integration times and, consequently, better SNR performance.

Before liquid nitrogen can be added to the detector, the detector head (dewar jacket/front enclosure) requires evacuation. This is primarily needed to prevent internal condensation which, if contacted the CCD chip, could damage it permanently. The system is therefore evacuated by a fore pump/diffusion pump system to approximately 5 x 10⁻⁶ Torr before liquid nitrogen is added. The evacuation normally lasts one week before a re-evacuation is required, which
takes approximately one hour to perform.

The effect of cooling the detector is shown in Figure 18, where the 576.9 nm, 578.9 nm, and 579.0 nm emission lines of a low pressure mercury lamp are recorded for the detector at room temperature (top spectrum) and at -100°C (bottom spectrum). Both spectra were obtained with a five second integration time and a single row of pixels readout of the detector (the center row of pixels of the detector- #192). The light from the Hg lamp was focused onto the entrance slit of the spectrometer, which was set to 10 μm wide by 0.2 cm high. The effect of cooling the detector to -100°C effectively reduced the noise level from 96 counts to 0.93 counts and the background level from 2463 counts to 66 counts for this 5 second integration example.

Figure 18. Mercury emission spectra showing the effect of cooling the CCD detector to -100°C.
The liquid nitrogen dewar requires approximately 1 1/2 liters of liquid nitrogen to fill it. Filling and cooling takes about one hour to reach -100°C. Once filled, the liquid nitrogen keeps the detector cooled to this temperature for 12-15 hours.

One final addition was needed to the microprobe system to make the CCD operational. The CCD requires the center slit of the double spectrometer be opened to its maximum extent for proper and optimum operation. This is not how the double spectrometer is meant to be used. As a result, the spectrometer does not reject stray light as effectively as it was originally designed. This produces spurious lines in the spectrometer, that show up as an increase in noise, background, and even spurious lines in the Raman spectrum. It was determined that the spurious reflections were mainly due to the very intense reflected laser light from the specimen which scatters off of the imperfections of the mirrors and gratings in the spectrometer.

It was decided to place one of two sharp cutoff high-wavelength-pass filter (Corning C.S. No.3-67 or No.3-68) in the microprobe system just before the entrance slit of the spectrometer. These filters allow less than 0.5 % transmittance of light at all wavelengths shorter than 524 nm for No.3-67 and 507 nm for No.3-68, and attenuate the intense laser light at 532 nm without dramatically altering the intensity of Raman lines away from this wavelength. A
comparison of the unfiltered light, and the transmitted Raman light for the C.S. No.3-67 (designated orange due to its orange coloring), and C.S. No. 3-68 (designated yellow) is shown in Figure 19. The plots should show a single 864 cm\(^{-1}\) Si\(_3\)N\(_4\) Raman peak at the left of the plot sitting on an elevated plateau. The orange filter permits measurements down to \(\approx 700\) cm\(^{-1}\) Raman shift before it attenuates the signal to an unacceptable level while the yellow filter allows measurements down to \(\approx 190\) cm\(^{-1}\) Raman shift.

Figure 19. Spectra of Si\(_3\)N\(_4\) 864 cm\(^{-1}\) Raman line showing the effect of adding yellow and orange sharp cutoff filters before the spectrometer slit to minimize spurious spectral signals due to internal scattering of the laser light.
CHAPTER V
EXPERIMENTAL STUDIES

The Raman lines for Norton/TRW NT-154 Si$_3$N$_4$ were studied in the experimental work presented in this chapter. A PMT survey spectrum of Norton/TRW NT-154 Si$_3$N$_4$ is presented in Figure 20. The spectrum agrees with that expected for crystalline $\beta$-Si$_3$N$_4$, where 10 of the 11 known Raman lines were observed in our spectrum. It includes three relatively intense Raman lines at 183, 206, and 224 cm$^{-1}$, and seven weaker lines at 449, 619, 729, 864, 928, 938, and 1047 cm$^{-1}$. The lines were measured with an accuracy of ± 1 cm$^{-1}$ and are in agreement to within ± 2 cm$^{-1}$ with published reports.

Figure 20. PMT survey spectrum of Norton/TRW NT-154 Si$_3$N$_4$ (bar #54).
**CCD Characterization**

Four studies were done to characterize the performance of the CCD array detector. They included 1) a comparison of the SNR performance of the CCD detector with the microprobe’s PMT detector, 2) an investigation of the CCD detector’s binning properties, 3) the effect of fluorescence signals on the CCD Raman spectrum, and 4) an example of the CCD detector’s line-imaging capability.

**PMT/CCD Detector SNR Comparison Study**

The 206, 224 cm^{-1} and 864 cm^{-1} Raman lines of Norton/TRW NT-154 Si$_3$N$_4$ were used to compare the SNR performance characteristics of the PMT and CCD detectors. The entrance slit width of the double spectrometer was set to 100 μm for all of the PMT and CCD runs presented in this section. For the PMT runs, the center and exit slits were both set to 100 μm, while for the CCD runs, the center slit was set to either 1.5 mm or 3.0 mm, and the exit slit was not used. These slit width values provided a spectral bandpass of ≈1.67 cm^{-1} for the PMT and allowed all of the available Raman light to pass through the spectrometer. The 100 μm entrance slit width and 23 μm CCD pixel dimension provided a spectral resolution using the CCD detector of ≈1.46 cm^{-1}. The spectrometer was stepped at 0.333 cm^{-1} per data point for the PMT runs which is comparable with the 0.335 cm^{-1} per pixel spectral dispersion value for the CCD detector scheme. The
input laser power was set to 40 mW, which produced an incident power level at the specimen of ≈1.5 mW. Forty CCD pixels (#172 - #211) in the vertical direction were binned together on the CCD chip before they were read out (these were the pixels illuminated by our image in the vertical direction).

Figure 21a. shows the 206 cm\(^{-1}\) and 224 cm\(^{-1}\) Raman lines of Norton/TRW NT-154 Si\(_3\)N\(_4\) produced by the PMT and CCD detectors for the same total integration time of 75 minutes. For the PMT run, this corresponded to 20,000 Q-switch laser pulses (≈50 seconds) per data point. For the CCD run, all available pixels were illuminated for the entire 75 minutes.

![Figure 21. Si\(_3\)N\(_4\) Raman spectra for CCD and PMT detectors for equal total integration times and equal single element integration times. The spectra are normalized and have been arbitrarily offset.](image-url)
The noise level of each plot was measured using the standard deviation of the intensity (in counts) between 210 and 220 cm\(^{-1}\). This along with the peak intensity value (in counts) of the 206 cm\(^{-1}\) line (after background subtraction) was used to calculate the SNR of each line. A conversion factor of 20 electrons per count was also used in the SNR calculation for the CCD detector. The calculated value of SNR for the 206 cm\(^{-1}\) line in the CCD spectrum was \#178 and in the spectrum acquired with the PMT was \#22. It is clear that the added integration time occurring across the entire CCD spectrum produces greatly improved signal-to-noise ratios.

Figure 21b. shows the same Si\(_3\)N\(_4\) Raman lines as Figure 21a., but with the PMT and CCD spectra in this case being compared on a detector-element-by-detector-element basis. The PMT spectrum was again scanned with 20,000 laser pulses (\#50 seconds) per data point for a total of 90 points. The CCD spectrum in this instance was acquired with a 50 second integration time, which corresponds to the single-point PMT time. The SNR of the two spectra are comparable, with the CCD having a SNR \#37, and the PMT having a SNR \#22. The CCD spectrum was acquired 90 times faster, however. The higher SNR for the CCD detector is due in part to a higher quantum efficiency of \#30% compared to \#20% for the PMT detector.

A test of the improvement in sensitivity using the CCD detector is given in Figure 22, which shows an acceptable record of very weak Raman signals with as little as 50 \(\mu\)W of
incident power at the specimen surface. The figure depicts the 864 cm\(^{-1}\) Raman line of Si\(_3\)N\(_4\) obtained using the CCD and PMT detectors for power levels at the specimen surface between 0.05 and 3.0 mW. Low power levels are important when studying Si\(_3\)N\(_4\) because they are normally required to minimize specimen heating effects in these materials. The CCD spectra exhibit excellent SNR for moderate power levels between 1.5 and 3.0 mW and only 10 minute integration time, and adequate SNR for very low power levels below 1.5 mW and integration times on the order of one hour. The PMT spectra were acquired with a four hour total integration time (40,000 Q-switch pulses per point, or about 2 min, for 160 total points), and show adequate SNR for moderate power levels between 3.0 and 1.5 mW. The SNR for low power levels below 1.5 mW are below the minimum acceptable SNR of 2, however.

Figure 22. Comparison of CCD and PMT sensitivity of weak 864 cm\(^{-1}\) Si\(_3\)N\(_4\) Raman line for low incident power levels. The spectra have been arbitrarily scaled and offset.
**CCD Charge Binning**

The effect of binning in the spatial and spectral directions of the CCD detector array were studied using the 864 cm\(^{-1}\) Raman line of Si\(_3\)N\(_4\). The spectrum for each study was dispersed across the CCD for a 10 minute integration time. The entrance and center slit widths of the double spectrometer were set to 100 μm and 3 mm, respectively. This produced a spectral image covering approximately 250 of the 576 columns of the CCD detector, and provided a wavelength coverage of approximately 70 cm\(^{-1}\), and 0.335 cm\(^{-1}\) per detector element, for a spectral resolution of \(\approx 1.46\) cm\(^{-1}\).

The result of parallel binning along the slit height to increase the SNR is shown in Figure 23. The four spectra were for equal integration times (10 minutes) and incident laser power levels (40 mW and ND=0.5), and are the result of different combinations of binning and digitally summing the charge intensities from the 40 illuminated rows using parallel binning factors of 1x, 4x, 10x, and 40x (a binning factor of 1x is a normal readout). For example, in the case of 4x binning, the 40 rows of charge were binned 4-fold into 10 rows and read out, followed by the summation of the 10 digitized rows in computer memory. Each spectrum represents the detection of the same amount of photogenerated charge. The SNR for the 1x, 4x, 10x, and 40x bins are 14, 23, 28 and 29, respectively. The increased SNR achieved by charge
binning is realized at the expense of spatial resolution along the slit height.

Figure 23. The effect of charge binning in the spatial direction (slit height) of the CCD array. The spectra are arbitrarily offset.

The result of binning in the direction of wavelength dispersion on the Si₃N₄ Raman spectrum under the same conditions as above is shown in Figure 24. A binning factor of 40x was used in the spatial direction for all spectra, while bins of 1x, 4x, 8x, and 16x were used in the spectral direction. The SNR for the 1x, 4x, 8x and 16x bins depicted in Figure 26 are 37, 53, 82 and 112, respectively. In this case, binning increases the SNR, but at the expense of spectral resolution. However, due to the relatively broad spectral features, a certain amount of binning is tolerated without loss of spectral information. The ability to bin in
both directions allows the effective detector element size to
be conveniently adjusted to match the requirements of
wavelength resolution and sensitivity.

Figure 24. The effect of charge binning in the spectral direction
(wavelength dispersion direction) of the CCD array. The
spectra are arbitrarily offset.

**Fluorescence**

In many solid specimens, the existence of fluorescence
can pose a problem when recording a weak Raman spectrum.
Even traces of fluorescing impurities in a material can
completely mask a Raman spectrum. This is primarily due to
the fact that the quantum yield in fluorescence processes is
typically more than a million times that in Raman
spectroscopy.

When fluorescence is a problem, various methods can be
employed to lessen, and in some instances completely eliminate, its effects on weak Raman signals. The gated photon counting detection scheme described in Chapter IV, for example, uses synchronous gates of the PMT's signal and the laser's Q-switched pulses to discriminate against fluorescence. This gated detection scheme could not, however, be employed with the new CCD detector. This set of experiments was done in an attempt to determine the effect of fluorescence signals on the CCD Raman spectrum.

Because fluorescence is often specimen dependent, two different types of Si$_3$N$_4$ were examined in this study. They included a GTE/PY6 Si$_3$N$_4$ specimen and Norton/TRW NT-154 Si$_3$N$_4$ specimen. GTE/PY6 is an injection molded and hipped $\beta$-Si$_3$N$_4$ with 6% Y$_2$O$_3$ (an oxide sintering aid), while Norton/TRW NT-154 is a sintered and hipped $\beta$-Si$_3$N$_4$ with 4% Y$_2$O$_3$. Their compositions and fabrication are typical of Si$_3$N$_4$ ceramics currently being used in high-temperature engineering applications.

The effect of a fluorescence background on a weak Raman spectrum is shown in Figure 25, where the time evolution of the 206 and 224 cm$^{-1}$ Raman lines for a GTE/PY6 and Norton/TRW NT-154 Si$_3$N$_4$ are compared. The Raman spectra for each specimen were taken sequentially in time with each spectrum having an integration time of 30 seconds. The input power level at the specimen was ~1.5 mW for both sets of spectra.
The spectra in Figure 25 show the existence of a fluorescence background signal that decays over time. This decaying fluorescence signal over time is commonly referred to as specimen bleaching. A detailed description of the bleaching process is provided by Fettig.\(^7\) As shown in the spectra in Figure 25, the fluorescence background decays to a negligible level within \(\approx 15\) minutes for the GTE/PY6 specimen, and is almost non-existent for the Norton/TRW specimen. The difference in the fluorescence levels present in the two sets of spectra is most likely due to differences in the impurity levels present in the specimens.

**CCD Line Imaging Capability**

An example of the line imaging capability of the CCD detector is shown in Figure 26. The figure shows a line
image of the 864 cm\(^{-1}\) Si\(_3\)N\(_4\) Raman line with spectral information in one direction, spatial information in another, and intensity in the vertical direction. Because binning was not used when the image was taken, a ten-hour exposure was needed to get the SNR shown in the figure. This long exposure time produced many cosmic ray spikes that were removed with software provided by Princeton Instruments. The image covers \(\sim 70\) cm\(^{-1}\) wavenumbers in the spectral direction and \(\sim 50\) \(\mu\)m in the spatial direction. The vertical scale is the recorded counts less the background signal count. The overall profile in the spatial direction is due to the Gaussian profile of the laser beam along the length. Small variations of amplitude around 23 \(\mu\)m can be attributed to the granular character of the specimen. No discernable change in peak position was observed from spectrum to spectrum.

Figure 26. Example of line imaging capability of CCD detector.
Si₃N₄ Mechanical Load Studies

All pertinent parameters such as input power levels, spectrometer drive position and slit widths, optical setup, etc. were kept constant for all of the mechanical load studies. This helped insure reproducibility of data, and consistency between different loading conditions. In effect, the only thing that was changed between different mechanical load studies and runs was the amount of load applied to the Si₃N₄ specimens. The pertinent parameters held constant for all of the mechanical load studies are listed in Table 4.

Table 4  Experiment parameters used for all mechanical load studies.

<table>
<thead>
<tr>
<th>Mechanical Load Experiment Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Flashlamp Voltage</td>
<td>340 volts</td>
</tr>
<tr>
<td>Flashlamp Repetition Rate</td>
<td>59 Hz</td>
</tr>
<tr>
<td>Q-Switch Pulses/Lamp pulse</td>
<td>6-8</td>
</tr>
<tr>
<td>Average Power on Specimen</td>
<td>1.05 mW</td>
</tr>
<tr>
<td>Microscope Objective</td>
<td>LWD 40x</td>
</tr>
<tr>
<td>Sharp Cut Filter</td>
<td>Corning CS #3-68</td>
</tr>
<tr>
<td>Spectrometer Entrance Slit</td>
<td>60 μm x 0.2 cm</td>
</tr>
<tr>
<td>Spectrometer Center Slit</td>
<td>3 mm wide</td>
</tr>
<tr>
<td>CCD Binning (vertical)</td>
<td>Stripes 172-212</td>
</tr>
<tr>
<td>CCD Integration Time</td>
<td>90 minutes</td>
</tr>
</tbody>
</table>

A preliminary mechanical loading study of one of the Norton/TRW NT-154 test specimens showed noticeable shifts in the Raman frequencies for 7 of the 10 observed Raman lines. The 864 cm⁻¹ Raman line showed the largest change in
character, so it was decided to use this spectral line for future loading studies. All of the work presented in this thesis, shows changes in the character of the $\text{Si}_3\text{N}_4$ 864 cm$^{-1}$ Raman line exclusively.

A Lorentzian line fit was performed on each of the Raman spectral lines used in the mechanical load studies to get a better measure of their shifted positions with applied load. The fitting code was provided in the Igor plotting program (version 1.2) available on a Macintosh IIIsi computer. An example of a fitted $\text{Si}_3\text{N}_4$ 864 cm$^{-1}$ Raman line is shown in Figure 27. The exceptionally good fit to the raw data indicates that we were close to the theoretical resolution for this particular Raman line. The fitting program also provided error analysis information related to the fit that helped determine the precision of our measurements.

![Figure 27. Example of Lorentzian-line fit to the 864 cm$^{-1}$ Raman line of $\text{Si}_3\text{N}_4$. The center frequency uncertainty is $\pm 0.019$ cm$^{-1}$.](image-url)
**Comparison of Stressed & Unstressed Flexural Test Specimen**

The first mechanical load study involved comparing the Raman spectrum of an unstressed \( \text{Si}_3\text{N}_4 \) test specimen with the Raman spectrum of a specimen under a moderate load. The specimen was placed in the four-point bend fixture in a stable, centered, and unloaded state. The strain indicator was zeroed and checked for calibration, and a Raman spectrum of the 864 cm\(^{-1}\) line was taken using the CCD detection system. Because of the very weak Raman signal levels from \( \text{Si}_3\text{N}_4 \), a 90 minute integration time was required to obtain an adequate SNR. After the unstressed 864 cm\(^{-1}\) spectrum was taken, the test specimen was loaded to 70-lbs using the strain indicator illustrated in Figure 11. For these specimens, this load corresponds to a stress of 261 MPa. A 90 minute Raman spectrum was then taken of the 864 cm\(^{-1}\) line for this 70-lb load case. The two normalized spectra are plotted for comparison in Figure 28. A downward shift in the peak position of 1.95 cm\(^{-1}\) was observed for the stressed -vs- unstressed case as shown in the figure. The absolute values of the frequencies of the Raman bands could be measured with a precision of \( \pm 0.75 \) cm\(^{-1}\), while the changes in the frequencies could be measured with a precision of \( \pm 0.018 \) cm\(^{-1}\). The applied load was maintained (no relaxation of the \( \text{Si}_3\text{N}_4 \) specimen in the bend fixture) throughout the 90 minute run time.
It was decided to incorporate an 'internal standard' into the Raman microprobe as a reference to the observed Si₃N₄ line shifts. This internal standard was a clear liquid that was placed at the scanning slit position in the microprobe so that the laser light reflected from the Si₃N₄ specimen would traverse the liquid and generate the Raman spectrum of the liquid. The reference line of the internal standard would remain unchanged when the Si₃N₄ line was shifting due to applied load, and could, therefore, be used to very accurately reference the amount of shift due to external stress on the specimen.

**Internal Standard**

Figure 28. Shifting of Si₃N₄ 864 cm⁻¹ Raman line with applied mechanical stress.

![Graph showing Raman shift with and without load](image-url)
Several candidate liquids were examined with the final choice being nitromethane (CH$_3$NO$_2$) because of its strong vibrational Raman mode at 915 cm$^{-1}$. Since this spectral line was in close spectral proximity to the 864 cm$^{-1}$ Si$_3$N$_4$ Raman line, it could be observed at the same time while being sufficiently removed from the 864 cm$^{-1}$ line so as not to interfere with it.

The 70-lb load study was repeated using 80-lbs of load and the internal standard. The addition of the internal standard into the system required very precise alignment so that the Raman light was properly focused onto the entrance slit of the spectrometer. In addition, the internal standard reduced the amount of Raman light from the specimen entering the spectrometer by ≈50%.

The results of the 80-lb load study with the internal reference in place are presented in Figure 29. A noticeable shift in the 864 cm$^{-1}$ line of 1.74 cm$^{-1}$ was observed, and as expected, no shift was observed in the nitromethane reference line at 915 cm$^{-1}$. The shift of 1.74 cm$^{-1}$ for this 80-lb load study was 0.21 cm$^{-1}$ less than the 1.95 cm$^{-1}$ shift observed in the initial 70-lb load study. There are several possible explanations for this smaller shift. First, the 0.21 cm$^{-1}$ difference is actually within the overall uncertainty of 0.315 cm$^{-1}$ of the measurement. This will be discussed in the next section. It is also possible that the Si$_3$N$_4$ specimen may have changed its character slightly with repeated loading and
unloading (the specimen had been loaded and unloaded several times before this experiment). If the material had fatigued at all with repeated loading, this would have shown up as a reduced shift. One additional possibility is that the probe position on the specimen may have been displaced slightly between the two experiments. Minor variations in the amount of shift could result from different probe positions on the specimen (this will be discussed in the final experiment of this chapter).

Figure 29. Shift of Si$_3$N$_4$ 864 cm$^{-1}$ Raman line with applied stress and with nitromethane internal reference line in place.

Reproducibility Study

The reproducibility of the experiment was checked by taking four consecutive unloaded spectra in sequence. The
resulting spectra are given in Figure 30. Each of the four spectra shown were taken under identical conditions, with each spectrum taking 90 minutes to record. The Raman shift of the Si$_3$N$_4$ line was reproducible to within 0.414 cm$^{-1}$ while the internal reference line was reproducible to within 0.106 cm$^{-1}$. By aligning all of the reference lines the Raman shift of the Si$_3$N$_4$ line was reproducible to within 0.315 cm$^{-1}$. Minor differences in lineshape and relative intensities were observed. It should be noted that the shift results of the initial 70-lb load experiment and the subsequent internal standard 80-lb experiment presented above agree within this uncertainty.

Figure 30. Spectra showing reproducibility of data.

**Incremental Loading Study**

The second mechanical load study involved an incremental
rather than "full" loading of the Si₃N₄ test specimen. The same general procedure was followed for set up and loading, but the load was applied in increments of 20-lbs starting with 0-lbs and finishing with 80-lbs. As in the initial 70-lb load study, the integration time for each spectrum was 90 minutes and there were no variations in the applied load (as given by the strain indicator) during each load phase.

The fitted peak positions for each load level, along with the relative shift away from the 0-lb load case, are tabulated in Table 5 and the resulting incremental-load spectra are shown in Figure 31. The peak positions, which have been fit to Lorentzian curves, are also shown in the figure. It is interesting to note that the 80-lb load resulted in a relative shift of only 1.03 cm⁻¹ for this incremental loading study. This is only about two-thirds the value obtained in the 80-lb full loading study described earlier (1.74 cm⁻¹).

Table 5. Incremental load data.

<table>
<thead>
<tr>
<th>Amount of Load (lbs)</th>
<th>Fitted Peak Position (cm⁻¹)</th>
<th>Fit Quality (cm⁻¹)</th>
<th>Relative Shift from 0-lb Load Value (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>864.40</td>
<td>±0.018</td>
<td>0.00</td>
</tr>
<tr>
<td>20</td>
<td>863.86</td>
<td>±0.017</td>
<td>0.54</td>
</tr>
<tr>
<td>40</td>
<td>863.62</td>
<td>±0.013</td>
<td>0.78</td>
</tr>
<tr>
<td>60</td>
<td>863.45</td>
<td>±0.014</td>
<td>0.95</td>
</tr>
<tr>
<td>80</td>
<td>863.37</td>
<td>±0.017</td>
<td>1.03</td>
</tr>
</tbody>
</table>
Cyclic Loading Study

The third mechanical load study involved cyclic loading of the test specimen from 0 lbs to 80 lbs, twice in succession. The same general procedures were again followed for set up and loading the specimen. The fitted peak positions, along with the relative shift away from the 1st 0-lb load case, are tabulated in Table 6 and the resulting cyclic-load spectra are shown in Figure 32. The peak positions, which have been fit to Lorentzian curves, are also shown in the figure. As shown in Figure 32 and Table 6, the initial 80-lb loading produced a substantial shift of 1.56 cm\(^{-1}\). When the load was removed, the 864 cm\(^{-1}\) line did not return to the initial unstressed position, but showed a shift
relative to the initial wavenumber position of 0.74 cm\(^{-1}\). The second 80-lb loading shifted the line approximately 1.44 cm\(^{-1}\) referenced to the original unstressed position.

Table 6. Cyclic loading data.

<table>
<thead>
<tr>
<th>Load Applied</th>
<th>Fitted Peak Position (cm(^{-1}))</th>
<th>Fit Quality (cm(^{-1}))</th>
<th>Peak Position Relative to 1st 0-lb Load (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st 0 lbs</td>
<td>864.03 ±0.022</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>1st 80 lbs</td>
<td>862.47 ±0.018</td>
<td>1.56</td>
<td></td>
</tr>
<tr>
<td>2nd 0 lbs</td>
<td>863.29 ±0.018</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>2nd 80 lbs</td>
<td>862.59 ±0.018</td>
<td>1.44</td>
<td></td>
</tr>
</tbody>
</table>

Figure 32. Shifting of Si\(_3\)N\(_4\) 864 cm\(^{-1}\) Raman line with cyclic loading.
**Spatial/Temporal Variation Study**

A final mechanical loading study recorded the spatial and temporal variations of strain in the specimen for a constant load of 80-lbs. Seven spectra were initially taken (90 minutes per spectra) at different locations on the specimen for the unstressed case. The relative position on the specimen of each data run is shown in Figure 33. They were symmetrically placed about the center of the specimen, five along the axis of the specimen, and two perpendicular to the axis. The specimen was then loaded to 80-lbs, and an additional seven spectra were taken for comparison, one at each location. Temporal changes were checked by leaving the specimen under 80 lbs of load for 36 hours, and taking a spectrum at the same location on the specimen at 0, 4, 18, and 36 hours after initial loading.

![Figure 33. Relative positions of measurement points used for the study of spatial variations of the load-induced Raman shifts.](image_url)
The results of the spatial variation study are tabulated in Table 7 and plotted in Figure 34. Each of the shifting Si₃N₄ Raman peaks were fit to a Lorentzian lineshape and were referenced to the internal standard line. As shown in Figure 34, spatial variations in the load-induced shift of the 864 cm⁻¹ Raman line were recorded ranging from a 0.459 cm⁻¹ shift to a 1.282 cm⁻¹ shift. These two extreme values were observed at the two positions located perpendicular to the specimen axis. The remaining five shift values along the axis showed variations ranging from 1.212 to 0.648 cm⁻¹.

Table 7. Spatial variations of stress on the test specimen.

<table>
<thead>
<tr>
<th>Position Relative to Center of Bar (µm)</th>
<th>Fitted Peak Positions (cm⁻¹)</th>
<th>Fit Quality (±cm⁻¹)</th>
<th>Shift From 0 lb Position (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center</td>
<td>0 lb - 864.27</td>
<td>0.045</td>
<td>1.008</td>
</tr>
<tr>
<td></td>
<td>80 lb - 863.26</td>
<td>0.071</td>
<td></td>
</tr>
<tr>
<td>178.5 left of ctr</td>
<td>0 lb - 864.26</td>
<td>0.048</td>
<td>1.282</td>
</tr>
<tr>
<td></td>
<td>80 lb - 862.98</td>
<td>0.067</td>
<td></td>
</tr>
<tr>
<td>178.5 right of ctr</td>
<td>0 lb - 864.22</td>
<td>0.061</td>
<td>0.459</td>
</tr>
<tr>
<td></td>
<td>80 lb - 863.76</td>
<td>0.079</td>
<td></td>
</tr>
<tr>
<td>102.5 above ctr</td>
<td>0 lb - 864.14</td>
<td>0.057</td>
<td>0.794</td>
</tr>
<tr>
<td></td>
<td>80 lb - 863.35</td>
<td>0.128</td>
<td></td>
</tr>
<tr>
<td>102.5 below ctr</td>
<td>0 lb - 864.36</td>
<td>0.046</td>
<td>1.212</td>
</tr>
<tr>
<td></td>
<td>80 lb - 863.15</td>
<td>0.068</td>
<td></td>
</tr>
<tr>
<td>203.5 above ctr</td>
<td>0 lb - 863.93</td>
<td>0.062</td>
<td>0.648</td>
</tr>
<tr>
<td></td>
<td>80 lb - 863.28</td>
<td>0.078</td>
<td></td>
</tr>
<tr>
<td>203.5 below ctr</td>
<td>0 lb - 864.25</td>
<td>0.080</td>
<td>1.134</td>
</tr>
<tr>
<td></td>
<td>80 lb - 863.12</td>
<td>0.060</td>
<td></td>
</tr>
</tbody>
</table>
The results of the temporal variation study are presented in Table 8. All of the measurements for this study were arbitrarily taken at the top center position on the test specimen (102.5 μm above the center position). As with the spatial variation study, each Si₃N₄ Raman peak was fit to a Lorentzian lineshape and referenced to the internal standard line. A mean value of 863.45 cm⁻¹ was attained with an rms spread of ±0.079 cm⁻¹. This corresponds, from Table 7, to a load-induced shift of 0.69 cm⁻¹ which is in agreement with the overall uncertainty, with 0.794 cm⁻¹ for this position given
in Table 7. Thus, there was no statistically significant change in the shift over the 36 hour period.

Table 8. Temporal variation of 864 cm\(^{-1}\) Raman peak under 80-lb load.

<table>
<thead>
<tr>
<th>Time of Measurement</th>
<th>Fitted Peak Position (cm(^{-1}))</th>
<th>Fit Quality (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 hr</td>
<td>863.40</td>
<td>0.075</td>
</tr>
<tr>
<td>4 hr</td>
<td>863.35</td>
<td>0.128</td>
</tr>
<tr>
<td>18 hr</td>
<td>863.56</td>
<td>0.074</td>
</tr>
<tr>
<td>36 hr</td>
<td>863.47</td>
<td>0.075</td>
</tr>
</tbody>
</table>
CHAPTER VI
DISCUSSION OF RESULTS

CCD Detector Characterization

The CCD detector proved to be a valuable addition to the Raman microprobe. The very weak Raman signals produced by Si₃N₄ require that a detector have a high sensitivity, low read noise, large dynamic range, low dark count rate, and a linear, well-behaved response. The Princeton Instruments LN/CCD-576 detector provided these and other features that helped make the Raman studies of these complicated advanced ceramics possible.

The addition of a 150 mm-focal-length cylindrical lens between the double spectrometer and the CCD detector provided a means of correcting the astigmatism aberration created by the off-axis spherical optics of the spectrometer, and produced an adequately focused, two-dimensional image on the CCD array. Resolution measurements of the system gave a spectral resolution of 1-2 pixels FWHM of a sharp spectral line (neon 640.2 nm line), which is in good agreement with the specification of <1.5 pixels FWHM given by Princeton Instruments. In the spatial direction (slit direction) of the CCD array the resolution was measured to be ~2 pixels or 30-40 μm. This is slightly larger than the optimum value of
1 pixel (23 μm), but is in relatively good agreement with values obtained in the analysis presented in Appendix A, which gave an rms blur value between 10 and 40 μm for the normal operating conditions used in the experiments in this thesis.

The current system is limited to a working area on the CCD array of about 250 pixels wide and 210 pixels high, or about 24% of the 384 x 576 array dimensions available. This corresponds to \( \approx 70 \text{ cm}^{-1} \) in the spectral direction with the light being dispersed across the CCD array at \( .335 \text{ cm}^{-1} \) per pixel. The multichannel advantage of the CCD detector in the spectral direction allows a spectrum to be acquired 250 times faster than is possible with the monochannel PMT detector under similar operating conditions. If the current system were optimized to use the entire 576 pixels available in the spectral dispersion direction, the acquisition time could be increased an additional 2.3 times to a maximum of 576 times faster compared to PMT detection. The spectral coverage would also increase to a range of \( \approx 193 \text{ cm}^{-1} \).

The vertical direction (slit height) of the CCD array is currently limited by the maximum vertical extent of the line of laser light imaged onto the entrance slit of the double spectrometer. The current length of the image with the LWD 40x objective is \( \approx 595 \mu\text{m} \), which corresponds to only 25 pixels being used in the vertical direction. To fully utilize the available 384 pixels in the vertical direction,
the image on the entrance slit would need to be magnified or
lengthened an additional 15 times, to a length of 8832 μm or
8.832 mm. This could further enhance SNR performance through
spatial binning, and could increase the current spatial
resolution from 2.89 μm (with the LWD 40x objective) down to
the diffraction limit of the system (~0.7 μm) with a redesign
of the current optical system.

The CCD/PMT SNR comparison study showed the performance
levels of the two detectors to be similar when compared on a
detector-element-by-detector-element basis. For equal single-
point integration times of 50 seconds, the CCD detector gave
a SNR of ~37 for the 206 cm⁻¹ Raman line of Si₃N₄, while a SNR
of ~22 was obtained with the PMT detector. The difference is
due, at least in part, to a higher quantum efficiency for the
CCD detector since all sources of noise, except photon shot
noise, were minimized. For moderate signal levels, photon
shot noise is the dominant noise source and Equations 11 and
12 given in Chapter III then take the familiar form

\[ \text{SNR} \approx \sqrt{\eta \Phi t} \quad (13) \]

where \( \eta \) is the detector quantum efficiency, \( \Phi \) is the incident
flux, and \( t \) is the integration time. The slightly higher
quantum efficiency of the CCD detector (30% for the CCD -vs-
20% for the PMT) gives rise to a slightly higher SNR
performance level. Using Equation 13, a rough estimate of the
SNR advantage of a CCD detector element over the PMT detector
would be \((0.3/0.2)^{1/2} = 1.22\) times better. This is in
reasonable agreement with the measured SNR values just
presented which showed the CCD to be \(\approx 1.68\) times better.

The real advantage of the CCD array detector comes from
its ability to detect hundreds of spectrally resolved
features simultaneously. This is often referred to as the
multichannel advantage of the CCD array detector. This
multichannel advantage was demonstrated experimentally by
comparing the SNR performance of the PMT and CCD detectors
for equal total integration time, spectral resolution, and
spectral coverage. For the same total integration time of 75
minutes, the CCD detector provided a SNR of \(\approx 177\) for the 206
cm\(^{-1}\) Raman line of Si\(_3\)N\(_4\), while the PMT provided a SNR of \(\approx 22\).
This corresponded to an increase in SNR of \(\approx 8.0\) times for the
CCD array detector compared to the single-channel PMT. In
each case, the same information was obtained in the same
amount of time, but the CCD detector provided a much cleaner
representation of the data.

The multichannel advantage of the CCD array detector,
coupled with its slightly higher quantum efficiency, also
provided more sensitivity than the PMT. Sensitivity
measurements of the 864 cm\(^{-1}\) Raman line of Si\(_3\)N\(_4\) indicated that
the CCD detector adequately detected this line with less than
50 \(\mu\)W of incident power and 1 hour integration. The PMT,
however, was incapable of detecting the presence of this line with incident power levels lower than 100 μW for 4 hours total integration time. It can be estimated that the limit of detection with the CCD detector for this very weak Raman line is ~10 μW with integration times on the order of 1 hour. This limit of detection represents an improvement of more than an order of magnitude relative to PMT detection.

The effect of binning charge on the CCD chip was studied using the 864 cm⁻¹ Raman line of Si₃N₄. The spatial binning study was limited to binning ~40 pixel rows in the vertical direction (slit height) of the CCD array due to the limited extent of the line of laser light imaged onto the entrance slit of the double spectrometer. Even with this limited binning capability we were, however, able to show a factor of two increase in SNR. This factor of two increase in SNR was actually realized in the lowest 4-fold binning case in the study, where the SNR increased from ~14 for 1x binning (i.e. no binning) to ~23 for 4x binning. This follows (approximately) the N¹/² increase in SNR mentioned in Chapter III. Very little increase in SNR was observed at higher binning levels. In all cases spatial resolution was lost in the slit dimension.

The effect of charge binning in the direction of wavelength dispersion showed a factor of three increase in SNR for the 16-fold binning. This also follows (approximately) the N¹/² increase rule. Spectral resolution
was quickly lost, however, and, for the 16x binning case, it increased to an unacceptable level of 5.36 cm\(^{-1}\) resolution.

The CCD detector was able to detect the existence of a fluorescence background in two different types of Si\(_3\)N\(_4\) ceramic. The amount and level of interference with the weak Raman signals was found to be spatially and specimen dependent, and can most likely be attributed to the different levels and locations of impurities in the specimens. The effect of bleaching the specimen was observed and indicated that the fluorescence background decays to a reasonable level within 15 to 30 minutes and, in most cases, to a virtually undetectable level within \(\approx\)1 hour. If fluorescence does become a problem with CCD detection of weak Si\(_3\)N\(_4\) Raman signals, the laser should be moved to a different position on the specimen that doesn’t fluoresce, the specimen should be allowed to bleach out, or a different excitation wavelength should be used.

An example of the line imaging capability of the CCD detector was used to examine the spatial character of the 864 cm\(^{-1}\) Si\(_3\)N\(_4\) Raman line on the specimen surface. The image showed an expected Gaussian intensity distribution in the spatial direction, with minor variations that can most likely be explained by the inhomogeneous regions of Si\(_3\)N\(_4\) grains in the specimen. The LWD 40x objective used in this study produced an image \(\approx\)60 \(\mu\)m long by 2 \(\mu\)m wide on the specimen surface. This line was imaged onto \(\approx\)20 CCD pixels giving a
spatial resolution in the vertical direction of ≈2.89 µm. This is comparable with the dimensions of the Si₃N₄ grains so that it is possible to resolve individual Si₃N₄ grains in the polycrystalline ceramic. The line image could be extended to a maximum of 384 pixels on the CCD array in the vertical direction to cover a greater distance on the specimen surface or to increase the spatial resolution down to the diffraction limit of the system (≈0.7 µm). Groups of pixels in the spatial direction could also be binned together to increase the SNR of the line image at the expense of spatial resolution. This would greatly reduce the long integration time needed to detect weak Raman signals, which for the image presented in Chapter IV took 10 hrs of exposure to produce.

**Si₃N₄ Mechanical Load Studies**

One of the primary objectives of this thesis was to obtain quantitative measurements of Si₃N₄ material parameters using the Raman technique. The mechanical load studies focussed on obtaining strain information from the shifting Raman lines due to applied stress on a Si₃N₄ test specimen. A starting point for this analysis involves the evaluation of the proportionality constant, K, in Equation 8 (p. 30) of Chapter III.

Equation 8 deals with the application of stress/strain to a pure crystalline solid. NT-154 is not a pure
crystalline solid, but a complicated polycrystalline ceramic. It is composed primarily of Si₃N₄ grains (crystallites) of different shapes, sizes and orientations. In addition, there is a glassy interface material that exists between the grains. When an external stress is applied to NT-154, both the Si₃N₄ grains and the glassy interface material react to the applied stress and show strain effects.

The Raman spectra obtained with the microprobe are due to the normal vibrational modes of the Si₃N₄ grains alone, and not in general, to the bulk material. The measurements only indirectly reflect changes in the character of the bulk material, which includes both the Si₃N₄ grains and the glassy interface material. Equation 8 provides a means for understanding how the Si₃N₄ grains react to an applied stress to the NT-154 specimen.

In order to estimate the amount of strain present in the Si₃N₄ grains using Equation 8, two assumptions will need to be made. The first assumption is that the Si₃N₄ grains are not being stressed to inelastic deformation in any of the mechanical load studies. This implies that Young’s modulus is constant and the strain being measured in the grains is proportional to the amount stress being applied to the grains. For the low stress levels used in these experiments, it is unlikely that the Si₃N₄ grains have been pushed beyond the elastic limit.
The second assumption is that the Young's modulus for pure crystalline Si₃N₄ can be approximated as the Young's modulus for NT-154 Si₃N₄. This assumption is needed to obtain a value for K in Equation 8, and was unavoidable because single crystal Si₃N₄ information was not available.

The Raman mode frequency shift of the initial 70-lb load study presented in Chapter V will be used as a calibration tool to obtain a value for the proportionality constant K. In that study an untouched NT-154 specimen was loaded to 70-lbs for the first time. This initial 70-lb case was chosen for the reference because it was not known whether the material's character had changed after the repeated loadings that followed.

Independent flexural strength measurements by the UDRI Metals and Ceramics Division on Norton/TRW NT-154 Si₃N₄ indicated that an applied load of 70 lbs represented a stress on the 3 x 4 x 50 mm test specimen of 260.8 MPa (37.82 ksi). NT-154 Si₃N₄ has a Young's modulus @ 20°C of 310 GPa (44.6 million psi). A strain of 8.5 x 10⁻⁴ is calculated using Equation 7 in Chapter III and the values obtained for Young's modulus and stress. The 1.95 cm⁻¹ shift in the 864.27 cm⁻¹ Si₃N₄ Raman line for the 70-lb mechanical load (Chapter V) can be used to determine the constant K.
Recalling Equation 8 from Chapter III

\[ \frac{\Delta \omega}{\omega_0} = K \frac{\Delta V}{V} \approx K \varepsilon \]

we obtain a value for K of:

\[ K \approx \frac{\Delta \omega}{\varepsilon \omega_0} = \frac{1.95 \text{ cm}^{-1}}{(8.5 \times 10^{-4}) (864.27 \text{ cm}^{-1})} = 1.9827 \]

This result can now be used to obtain additional strain information from stressed Si₃N₄ test specimens using the shift of the 864 cm⁻¹ Raman line for different applied mechanical loads. Using the shift values presented in Tables 5 and 6 in Chapter V for the full, incremental and cyclic load studies, along with Equation 8 and \( K = 1.9827 \), it is possible to obtain effective strain values for each of these load studies. The resulting effective strain values are tabulated in Table 9.
Table 9. Effective strain for mechanical loading studies.

<table>
<thead>
<tr>
<th>Amount of Load (lbs)</th>
<th>Relative Shift From 0 lb Load Value</th>
<th>Effective Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>1.95 cm(^{-1})</td>
<td>8.5 \times 10^{-4}</td>
</tr>
</tbody>
</table>

### Full Load Study

<table>
<thead>
<tr>
<th>Amount of Load (lbs)</th>
<th>Relative Shift From 0 lb Load Value</th>
<th>Effective Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.54 cm(^{-1})</td>
<td>3.15 \times 10^{-4}</td>
</tr>
<tr>
<td>40</td>
<td>0.78 cm(^{-1})</td>
<td>4.55 \times 10^{-4}</td>
</tr>
<tr>
<td>60</td>
<td>0.95 cm(^{-1})</td>
<td>5.54 \times 10^{-4}</td>
</tr>
<tr>
<td>80</td>
<td>1.03 cm(^{-1})</td>
<td>6.01 \times 10^{-4}</td>
</tr>
</tbody>
</table>

### Incremental Load Study

<table>
<thead>
<tr>
<th>Amount of Load (lbs)</th>
<th>Relative Shift From 0 lb Load Value</th>
<th>Effective Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st 80 lbs</td>
<td>1.56 cm(^{-1})</td>
<td>9.11 \times 10^{-4}</td>
</tr>
<tr>
<td>2nd 0 lbs</td>
<td>0.74 cm(^{-1})</td>
<td>4.32 \times 10^{-4}</td>
</tr>
<tr>
<td>2nd 80 lbs</td>
<td>1.44 cm(^{-1})</td>
<td>8.41 \times 10^{-4}</td>
</tr>
</tbody>
</table>

A comparison plot of effective strain -vs- applied load for the full loading and incremental loading studies is presented in Figure 35. As shown in the plot, the two different loading situations show fairly good agreement below 30-lbs load, but above 30-lbs load, a nonlinear behavior occurs. One possible explanation for this phenomenon is a relaxation or material fatiguing process initiated above 30
lbs load. This results in an increase in compliance in the specimen, reducing the amount of observed strain in the Si$_3$N$_4$ grains, producing a smaller shift in frequency.

![Graph](image.png)

*Figure 35. Plots showing material fatiguing in Si$_3$N$_4$ test specimen for applied incremental loading.*

The results of the cyclic loading study are presented in Figure 36. The first 80-lb loading on the test specimen resulted in an effective strain comparable to that measured for the initial 70-lb load study presented above. When the load was removed the strain did not shift back to its original unstressed value. As shown in Figure 36, the strain remained at an intermediate value approximately half-way between the 0-lbs and 80-lbs load effective strain positions. The second 80-lbs load showed an effective strain
similar to the first 80-lbs load position. This may be explained by the presence of residual strain present in the Si₃N₄ grains after the first mechanical loading sequence that affects the second loading sequence. This behavior is typical of a hysteresis type phenomenon.

![Graph showing effective strain vs. applied load](image_url)

**Figure 36.** The effect of cyclic loading of the Si₃N₄ specimen showing residual strain in the ceramic.

The final mechanical load study carried out involved looking for spatial and temporal variations in strain on the stressed Si₃N₄ test specimen. As described in Chapter V, spatial and temporal variations in the shift of the 864 cm⁻¹ Raman line were noticed at different positions on the specimen and for different times. These variations in terms of the effective strain are tabulated in Table 10.
Table 10. Effective strain for spatial and temporal variation studies.

<table>
<thead>
<tr>
<th>Position Relative to Center of Bar (µm)</th>
<th>Shift from 0 lb Position (cm⁻¹)</th>
<th>Effective Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center</td>
<td>1.008</td>
<td>5.88 x 10⁻⁴</td>
</tr>
<tr>
<td>178.5 left of center</td>
<td>1.282</td>
<td>7.48 x 10⁻⁴</td>
</tr>
<tr>
<td>178.5 right of center</td>
<td>0.459</td>
<td>2.68 x 10⁻⁴</td>
</tr>
<tr>
<td>102.5 above center</td>
<td>0.794</td>
<td>4.63 x 10⁻⁴</td>
</tr>
<tr>
<td>102.5 below center</td>
<td>1.212</td>
<td>7.07 x 10⁻⁴</td>
</tr>
<tr>
<td>203.5 above center</td>
<td>0.648</td>
<td>3.78 x 10⁻⁴</td>
</tr>
<tr>
<td>203.5 below center</td>
<td>1.134</td>
<td>6.62 x 10⁻⁴</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time of Measurement</th>
<th>Relative Shift From 0 lb Load Value (cm⁻¹)</th>
<th>Effective Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 hrs</td>
<td>0.794</td>
<td>4.63 x 10⁻⁴</td>
</tr>
<tr>
<td>4 hrs</td>
<td>0.745</td>
<td>4.35 x 10⁻⁴</td>
</tr>
<tr>
<td>18 hrs</td>
<td>0.585</td>
<td>3.41 x 10⁻⁴</td>
</tr>
<tr>
<td>36 hrs</td>
<td>0.675</td>
<td>3.94 x 10⁻⁴</td>
</tr>
</tbody>
</table>

The theoretical stress distribution for four-point bending predicts a uniform stress distribution between the
two inner load points where the spatial measurements were taken. This is shown in Figure 37, where the shaded area represents the tensile stress, ranging from zero at the upper supports of the bend specimen to a maximum at the midspan, and being uniformly maximum along the entire midspan gage section of the flexural specimen.

The spatial distribution of effective strain measured in this study is illustrated in Figure 38. It shows a nonuniform distribution of effective strain with some trends that may be an indication that the specimen was slightly out of alignment when the measurements were taken. Another possible explanation for this nonuniformity could be a sensitivity of the measurement to the relative orientations of the individual Si$_3$N$_4$ grains being probed. The small number of data points prevents a substantiated conclusion. Further measurements of this type need to be taken to fully determine
how sensitive the observed strain is to misalignment of the specimen in the bend fixture.

Figure 38. Spatial variation of effective strain on bar for 80 lbs of load.

Temporal variations were also noticed for measurements taken at the same location on the specimen (102.5 μm above center position on specimen) for 0, 4, 18, and 36 hours after loading to 80-lbs. As mentioned in Chapter V, these variations were within the measurements uncertainty. Minor variations were also noticed on the strain gage readings during this time period.
CHAPTER VII
CONCLUSIONS AND RECOMMENDATIONS

An upgraded Raman microprobe has been used to characterize the microstructure of mechanically stressed Norton/TRW NT-154 Si₃N₄. The addition of a 4-point bend fixture and a liquid-nitrogen-cooled CCD array detector made this possible. Both qualitative and quantitative information were obtained from the stressed Si₃N₄ specimens that provides a better understanding of the mechanical behavior.

CCD Detector Characterization

The performance characteristics of the CCD array detector were investigated, and these studies showed that this detector offers significant advantages over conventional PMT scanning, both for time-resolved studies and for spatial resolution. These advantages include improvements in signal-to-noise ratio (SNR), increased sensitivity and shortening of the recording time, all leading to easier access to the very weak Raman lines from the Si₃N₄.

The CCD and PMT detectors proved to have similar SNR performance characteristics when compared on a detector-element-by-detector-element basis. The CCD detector did, however, show a slight SNR performance edge (~1.68 times better) that can most likely be attributed to a
slightly higher quantum efficiency.

When the CCD detector’s multichannel advantage was taken into consideration, the CCD detector dramatically outperformed the PMT. The current optical system of the microprobe permits the CCD detector to detect 250 spectrally-resolved elements simultaneously, which means that it can reduce the data acquisition time of a Raman experiment by as much as 250 times compared to the PMT. This can translate into an increase in SNR and sensitivity when the two detectors are compared on the basis of equal total data acquisition time.

The CCD array detector also has a line imaging capability that provides Raman spectral information in one dimension and spatially-resolved information in the other dimension. This replaces the time-consuming scheme of the slit scanning along the image previously used to obtain spatial data.

A line image of the 864 cm⁻¹ Raman line of an NT-154 Si₃N₄ specimen showed minor variations in the intensity of the Raman line in the spatial direction that could prove interesting in future studies. These minor variations in intensity can be attributed to the inhomogeneous character of the ceramic and its polycrystalline nature.

The CCD detector’s ability to bin the charge collected on the CCD chip in both the spectral and spatial dimensions of the array provides an added flexibility to the detector.
Charge binning has two positive effects on spectral quality. First, it allows dynamic configuration of the size and shape of the effective resolution elements of the array. Second, it provides a SNR improvement by combining signal charge noiselessly. A SNR improvement factor of four times was observed for 16-fold binning, but this was realized at a substantial loss in resolution.

The CCD characterization studies done for this thesis showed the CCD detector to be a very capable addition to the Raman microprobe. To fully benefit from the advantages of this technique, however, it is not sufficient to simply replace the photomultiplier at the output of the spectrometer with the CCD detector. The whole optical system needs to be carefully redesigned to meet appropriate requirements. Stray light rejection, high throughput and optimized optical matching are three areas of further study that could dramatically effect the quality and quantity of the Raman spectra taken with the microprobe.

**Si₃N₄ Mechanical Load Studies**

The Si₃N₄ mechanical load studies presented in Chapters V and VI demonstrated that the Raman technique is a sensitive tool for studying microscopic stress-strain behavior in advanced ceramic materials. The first set of studies included a comparison of full, rapid loading versus incremental loading of the NT-154 Si₃N₄ flexure specimen. The
results obtained in these studies showed possible fatiguing effects in the specimen for loading levels above 30 lbs for incremental loading. The cyclic-loading study showed a similar nonlinear behavior in the test specimen that can be explained by the presence of a residual strain in the material after the first loading sequence. The cyclic-loading study also showed a hysteresis type behavior.

Spatial and temporal variations of strain were observed on the stressed Si$_3$N$_4$ test specimens. It is possible that the spatial variations were due to the specimen being slightly out of alignment in the 4-point bend fixture. However, the design of the bend fixture and the wide spacing of the load points relative to the width of the test specimen makes it unlikely that this alone can explain the large range of strain values given in Figure 39. More studies are needed before any firm conclusions can be drawn. The temporal variations of strain were small, and were accompanied by minor variations in the strain gage readings over the 36 hour duration of the experiment. No consistent trends were observed and further studies are needed to reveal the cause of these apparent temporal variations.

Quantitative measures of the microscopic strain present on the mechanically stressed Si$_3$N$_4$ specimens were obtained in all of the loading experiments. The strain was on the order of 800 $\mu$in/in for a moderate stress of 37.82 ksi (70 lbs load) on the flexural test specimens. This applied stress
level is well below the expected failure level for NT-154 Si₃N₄ (132 ksi). Future studies should work towards approaching this failure level in order to characterize the ceramic under more extreme conditions.

Future studies should be conducted to reproduce the results obtained in the incremental-load and cyclic-load studies. Time restrictions limited the number of experiments that could be performed, and in most cases the loading experiments conducted were only repeated one or two times. A greater number of repetitions are required to more fully characterize the strain behavior obtained.

The results of the spatial variation study indicate a possible sensitivity to the alignment of the specimen in the 4-point fixture which should be further studied. A more substantial alignment procedure needs to be developed to ensure reproducibility of load on the specimens.

As previously mentioned, one of the primary objectives of this thesis was to obtain quantitative strain information using the Raman technique. The results presented in Chapters V and VI accomplished this objective. The analysis used to obtain these results, however, was on the most basic level possible. Si₃N₄ is actually a very complicated polycrystalline material that deserves a much more rigorous mathematical treatment than was done in this work. The results obtained are still valid, but computer simulation programs and other more detailed analysis schemes should be
examined in an effort to better understand the results.

In any program of materials characterization, the use of Raman microprobe techniques can be expected to yield new answers to problems only incompletely solved by conventional techniques. With the steadily expanding range of successful applications and advancements in instrumentation for optical spectroscopy, the future of Raman microprobe analysis looks promising indeed.
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APPENDIX A

Cylindrical Lens for Astigmatic Correction to CCD Detector

When an object point lies some distance from the axis of a concave or convex mirror, the incident rays, whether parallel or not, will make an appreciable angle $\phi$ with the mirror axis. When this is the case, instead of a point image, two mutually perpendicular images are formed. This effect is known as astigmatism, and is illustrated in Figure 39, which depicts an off-axis object point at infinity, as formed by a concave spherical mirror.\(^9\)

![Figure 39](image)

*Figure 39.* Astigmatic image of an off-axis object point at infinity, as formed by a concave spherical mirror. The lines T and S are perpendicular to each other.\(^9\)
As shown in Figure 39, the cross-section of the beam as it leaves the mirror is initially circular, but it gradually becomes elliptical with the major axis in the sagittal (vertical) plane, until at the tangential (or meridional) focus, T, the ellipse degenerates into a line (using third order theory).⁹⁰ All object point rays traverse this line, which is known as the primary image. Beyond this point the beam's cross section opens out until it is again circular at L. The image at this point is a circular blur known as the circle of least confusion. Moving further from the mirror, the beam's cross-section again takes the form of a line, called the secondary image. This time the line is in the meridional (horizontal) plane and is at the sagittal focus, S.

Conventional wide-aperture off-axis Czerny-Turner spectrometers employ spherical collimating/focussing mirrors which produce severely astigmatic images at the output plane.⁹¹ The main consequence of the astigmatism is that, if good spectral resolution is to be obtained, the dispersed spectral features are imaged as vertical lines instead of point images at the output. A consequence of this is that multiple discrete spectral sources input at the entrance slit of the spectrometer will be combined into a single confused spectrum at the spectrometer output. This limits conventional spectrometers to processing spectra from only one source at a time, and usually excludes them from being
used in imaging applications with multiple sources.

A simple conventional off-axis spectrograph using two spherical mirrors is depicted graphically in Figure 40. Astigmatism takes a point light source and images it as a vertical line at the tangential focus, T, and a horizontal line at the sagittal focus, S. Since the diffraction grating disperses the spectra along the horizontal plane, to obtain maximum spectral resolution, conventional spectrographs operate at the tangential focus.

![Figure 40. Image of a point source as produced by a conventional off-axis spectrograph.](image-url)
The SPEX model 1401 double spectrometer used in this thesis is a conventional wide-aperture off-axis Czerny-Turner spectrometer that employs spherical collimating/focussing mirrors. It suffers from the astigmatism mentioned above and produces two distinct image planes. The tangential image plane was measured to be 210 mm ± 5 mm from the center of the flip mirror located in the spectrometer, while the sagittal image plane was measured to be 215 mm ± 5 mm from the center of the mirror. This is depicted schematically in Figure 41.

2nd Half of Double Spectrometer

Figure 41. Schematic diagram showing measured positions of tangential and sagittal foci of double spectrometer due to astigmatism.
The integration of the Princeton Instruments CCD detector into the microprobe required the tangential and sagittal image planes be brought together. It was decided to correct this astigmatism problem with the insertion of a cylindrical lens between the CCD detector and the output of the double spectrometer. This situation was modeled by Steve Ernst and Dr. Yaney using Beam 4 Optical Ray Tracer software on the IBM/AT computer. Beam 4 has an auto adjust feature that optimizes any optical component’s position or angle based on an RMS approximation of a specified ray goal. The ray tracer was also able to plot out rays at any surface as a two dimensional spot pattern or a one dimensional histogram. Plots could also be enhanced with a random ray generator which shows the concentration of rays at a surface. All of these features allowed the system to be modeled using the cylindrical lens, and helped with the selection of an appropriate focal length lens, and the positioning of the swing mirror, the cylindrical lens, and the CCD detector.

A 150 mm focal length plano-convex cylindrical lens of 1 inch diameter was eventually chosen, and was positioned ±160 mm ±5 mm from the center of the swing mirror. This position brought the sagittal and tangential foci together, and produced an adequately focused spot at ±215 mm ±5 mm from the swing mirror. This is depicted schematically in Figure 42.
An example of the focussing ability of this system was shown in Figure 15 in Chapter IV, where the 16462.8 cm\(^{-1}\) (6074.3 Å) and 16403.7 cm\(^{-1}\) (6096.2 Å) neon emission lines were each shown illuminating approximately one pixel (a 10 µm wide by ~25 µm high image was used at the entrance slit of the spectrometer). The intensities of both spectral lines dropped off sharply as you moved up or down one pixel, and went to zero as you moved up or down two pixels. This indicated that there was a sharp focus in the vertical (spatial) direction. In the spectral direction, each
emission line had a linewidth (FWHM) of approximately 2 pixels, which corresponded to \( \approx 0.67 \text{ cm}^{-1} (\approx 0.24 \text{ Å}) \). This indicated that there was a sharp focus in the spectral direction.

The focusing ability of the system in the vertical direction was further demonstrated using the 15766.8 cm\(^{-1}\) (6402.2 Å) emission line of neon. The neon lamp was oriented and positioned so that a vertical image was focused onto the entrance slit of the double spectrometer. This produced a vertical image on the CCD array detector covering approximately 200 vertical pixels on the detector as shown in Figure 43.

![Figure 43. Line Image of neon 15766.8 cm\(^{-1}\) emission line showing vertical focus of CCD array.](image-url)
As shown in Figure 43, the focus in the vertical direction of the CCD array is maintained for the entire extent of the line. The lineshape and linewidth (FWHM) of the neon line was consistently within 1-2 pixels. This indicates that there is a good focus in the vertical direction of the detector array.

One final check of the focus involved looking for variations in lineshape and linewidth of the same 15766.8 cm\(^{-1}\) neon emission line for the nine positions shown in Figure 44. Each of the three columns in the figure was from a different run, where the spectrometer had been scanned to move the emission line to a different position laterally on the detector.

![Figure 44. Variation of Neon 15766.8 cm\(^{-1}\) lineshape and intensity for different positions on CCD array.](image-url)
Minor variations in lineshape can be seen in the spectral lines in Figure 44, but linewidths (FWHM) are within 1-2 pixels at all locations. The lineshape variations can be attributed to the emission line striking the pixels slightly offset from one column to another. These observations are consistent with the previous two examples, and again point to a good focus across the entire surface of the array.

The addition of the 150 mm cylindrical lens effectively brought the tangential and sagittal foci into coincidence and, thus, eliminated the optical distortion caused by astigmatism. The resolution measurements of the system gave a spectral resolution of 1-2 pixels FWHM of a sharp spectral line (neon 640.2 nm line), which is in good agreement with the results of the Beam 4 ray trace analysis done by Steve Ernst and Dr. Yaney, the results of which are shown in Figures 45, 46, and 47. A representative spot diagram is shown in Figure 47, where an rms blur value is shown that was typical of the 10 to 40 μm range obtained for rays originating off axis and hitting the detector array at various positions. The measured focussing ability of the cylindrical lens correction scheme of 1-2 pixels corresponds to 20-40 μm, which is in good agreement with the ray trace analysis. True stigmatic imaging was then achieved - a point source at the input is imaged to a point at the output.
Figure 45. Spectrometer layout.

Figure 46. Ray trace at focus.

Figure 47. f=150mm, λ₀, Y=0.