A FOIL MASK SPECTROMETER

FOR

LAUE DIFFRACTION PATTERN IMAGING

by

Quentin Sean Hanley

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A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

1997
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As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Quentin Sean Hanley entitled A Foil Mask Spectrometer for Laue Diffraction Pattern Imaging and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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ABSTRACT

A foil mask spectrometer is described which allows for the simultaneous determination of position, energy, and intensity of monochromatic spots in a Laue diffraction pattern. The instrument may also be used for the quantitative determination of the intensity components corresponding to each energy contained in a spot with harmonic overlap. The spectrometer is uniquely suited to Laue diffraction applications and is demonstrated to be useful for determining unit cell dimensions and systematic absences.

This dissertation discusses the characterization of a charge injection device camera system and provides a theoretical basis for selecting a charge transfer device detector. The principles, construction, design, and limiting equations for the foil mask spectrometer are described. Equations for limiting resolution are verified and the correspondence between predicted and observed energy is shown for a variety of crystal systems. The foil mask spectrometer is then used to verify the unit cell dimensions of six compounds and to observe systematic absences due to 2\text{\textit{i}} screw axes and unit cell centering conditions. These crystals belonged to four different crystal systems including: cubic, orthorhombic, tetragonal, and monoclinic cells. The crystals had cell volumes from 179.4 Å$^3$ to 4588.3 Å$^3$. Comparison of known and re-determined cells showed good agreement (ratio of known to measured cells = 0.987±0.020). A single procedure was suitable for all unit cell determinations. Some of the crystals represent space groups containing systematic absences normally obscured by harmonic overlap when using the Laue method. These include absences due to 2\text{\textit{i}} screw axes (h, k, or l = 2n+1) and cell
centering (h+k = 2n+1). All systematic absences were identified using a combination of multiple linear regression with either stepwise elimination or stepwise inclusion and an F-test for assignment of systematic absence. The methods are discussed in detail and simulations are used to evaluate critical tolerances for future systems.
"Unfortunately, the very high degree of energy discrimination possible with semiconductor detectors is, in principle, incompatible with very high count rates; thus, they could not be used with polychromatic X-rays, e.g. in a Laue method experiment at a storage ring."

U. W. Arndt
CHAPTER 1

Introduction

In 1912, Max von Laue described the diffraction of X-ray radiation by crystals (Ewald, 1962; Amoros, Buerger and Canut de Amoros, 1975). The experiment is a simple one consisting of an X-ray source, a crystal, and a detector. Diffraction of the incident X-ray beam produced a pattern of spots on a photographic film. This experiment represents the beginning of the field of X-ray diffraction and served to establish the wave nature of X-rays, a property which was previously unverified but under much debate at the time. Motivating Laue’s experiment was the idea that if X-rays had wave properties, the wavelength could be shorter than the dimensions proposed by atomic theory. Laue’s experiment and his interpretation of it gained him the 1914 Nobel Prize in physics.

The next major development in X-ray crystallography occurred in England in the laboratories of William Henry Bragg and William Lawrence Bragg. In his paper reporting the diffraction of X-rays, Laue had argued for the existence of a few definite
wavelengths in the incident X-ray beam. The younger Bragg, after contemplating Laue's results at length, came to think that the spots in Laue's photographs were the result of a continuum of radiation being diffracted by a three dimensional lattice. Under this condition the Laue pattern appears as "reflection" off planes in the crystal. Lawrence Bragg was able to prove this using a sheet of mica. No matter what the angle of incidence, the mica behaved as a mirror reflecting the incident beam. The relationship describing this reflection condition has since become known as Bragg's law.

\[ n\lambda = 2dsin\theta \]  

1.1

The basis for this relationship is illustrated in Figure 1.1.

Bragg went on to examine other crystals, in particular the alkali halides. Upon completion of these studies, it had been demonstrated that not only do crystals diffract X-rays, but that diffraction could be used to assess the nature of crystals themselves. For this work he shared the Nobel prize with his father in 1915.

In designing the experiment that lead to the discovery of X-ray diffraction, Laue was strongly influenced by the work of Peter Paul Ewald (Laue, 1962) who was then a graduate student at the University of Munich and was in the final stages of completing his dissertation. In 1921, Ewald (Ewald, 1921) again contributed to the science of X-ray diffraction when he introduced the concept of the reciprocal lattice. In its modern form, this concept can be described as follows. The planes in a crystal giving rise to Bragg
When the difference in path length between rays scattered off planes in the crystal is an integer multiple of the wavelength, constructive interference occurs. This gives the Bragg equation $n\lambda = 2d \sin(\theta)$.
reflection can be indexed using Miller indices. Each of these Miller indices is plotted in a reciprocal space such that the distance between the origin and the reciprocal space coordinate is 1/d, where d is the interplane spacing corresponding to the given Miller indices h, k, and l. The line along which the reciprocal lattice point lies is perpendicular to the family of planes defined by h, k, and l. The resulting points in reciprocal space lie in a lattice whose axes can be defined by 1/a, 1/b, and 1/c (referred to as a*, b*, and c*) where a, b, and c are the lengths of the axes defining the unit cell of the crystal being examined.

This construction has a number of useful properties. It allows the position of diffracted beams to be computed in a straightforward manner. It allows the wavelength of X-rays which will be observed in a reflection off a particular family of planes to be predicted. It describes the extent to which a particular diffraction experiment can view reciprocal space. Finally, it allows the prediction of whether a particular family of planes is in an orientation such that it will be observed to produce a reflection.

These predictions can be made with the aid of figure 1.2. In order for a family of planes to be in a position to diffract, the reciprocal lattice point corresponding to that family must be coincident with a sphere of reflection (sometimes called an Ewald sphere). A sphere of reflection is a sphere of radius 1/λ, where λ is the wavelength of X-rays. This sphere has one point on its surface touching the origin of reciprocal space and its center along the incident beam of X-rays. The direction of the diffracted beam is given by a vector whose tail sits on the center of the sphere of reflection and passes
Figure 1.2: Ewald's Construction

Ewald's Construction illustrated in two dimensions. In order for a family of planes to be in an observable condition, the reciprocal lattice point corresponding to this family of planes must be coincident with the Ewald sphere. The direction of the diffracted beam is given by a vector whose tail sits on the center of the sphere of reflection and whose head lies on the sphere at the point where it coincides with the reciprocal lattice point.
through the reciprocal lattice point which is coincident with the sphere of reflection.

If monochromatic radiation is used, the crystal must be rotated in order to cause a particular family of planes to pass through the sphere of reflection. The region of reciprocal space which can be made to pass through the sphere of reflection is defined by what is called the limiting sphere. The limiting sphere has radius \(2/\lambda\). It should be noted that as the size of the unit cell increases, the number of reciprocal lattice points which can fit within the limiting sphere increases. As a consequence, patterns created by large unit cells tend to be more densely populated. The wavelength of X-rays needed to produce diffraction from a particular family of planes in a given orientation can be computed by solving for the radius of the required Ewald sphere. These relationships are illustrated in Figure 1.2.

The Ewald construction allows the Laue method to be compared to monochromatic methods. A given Laue experiment can be defined by a minimum wavelength, \(\lambda_{\text{min}}\), and a maximum wavelength, \(\lambda_{\text{max}}\). The monochromatic method only includes a single wavelength. The region of reciprocal space which can be observed in a particular orientation with Laue methods extends from the Ewald sphere corresponding to \(\lambda_{\text{min}}\) to that corresponding to \(\lambda_{\text{max}}\). A comparison of these two experiments is presented in Figure 1.3. What is immediately evident from the figure is that the Laue method allows much more of reciprocal space to observed in a given experiment. This has been the motivation for an enormous research effort to modernize the experiment over the last two decades. The Laue experiment experiment is potentially the fastest method for the
Figure 1.3: Comparison of Laue and Monochromatic Methods

Using Laue methods the amount of reciprocal space which is visible in a given orientation is greater than for a monochromatic experiment. In the Laue case, the region between the limiting wavelengths is potentially visible. In practice, the region available to the Laue experiment is limited relative to that shown here. The sample resolution limit, $d'_{\text{max}}$, must also be taken into consideration.
collection of data for crystal structure determination.

Historically, widespread use of the Laue method has limited due to a number of problems (Helliwell, 1992; Cassetta et al., 1993; Amoros, Beurger, and Canut de Amoros, 1975).

1. The harmonic overlap problem.
2. The wavelength normalization problem.
3. Inability to measure accurate unit cells.
4. Inability to observe some types of systematic absences.
5. Systematic under-representation of low frequency reflections.
6. Inability to perform full crystallographic analysis.
7. Until the last decade, none of these objections had been satisfactorily remedied. With the exception of 4, progress has been made toward the solution of each of these problems, but room for improvement remains in all areas. This dissertation is concerned with problems 1, 3, 4, 5, and 6. During the time in which this research was carried out, nearly complete structure analysis of a crystal has been performed. In one case, the only piece of information not obtained using Laue methods was the space group (Dodd et al., 1994). In the other case, low accuracy unit cells were obtained. The final crystal was matched to the axial ratios of a known compound (Kuriuki and Harding, 1995). The remainder of this chapter consists of a review of the literature concerning the modern Laue method and
a proposed solution to several open problems in the analysis of crystal structures using the Laue method.

1.1 Definitions

**Laue diffraction** in this work refers to any X-ray diffraction application in which a polychromatic X-ray source is used, regardless of whether the crystal is held to a fixed orientation or allowed to rotate. This is a somewhat broader definition than the traditional Laue method which consists of a stationary crystal, a polychromatic X-ray source, and a detector.

**Harmonic overlap** in this work will be used to describe the coincidence in real space position of diffracted beams from a crystal caused by X-rays of different energies from a set of Laue harmonics.

**Multiple overlap** in this work will be used to describe all types of spot overlap in a Laue diffraction pattern. This multiple overlap is divided into two categories: harmonic and spatial overlap.

**Spatial overlap** in this work will be used to describe overlapped spots created by diffraction vectors leaving a crystal at different angles but which can not be resolved under the experimental conditions used. Such overlap can, in some cases, be alleviated by using a detector having greater spatial resolution. More often it requires placing the detector at a greater distance from the crystal with a consequent loss in the acceptance
angle of the detector.

1.2 Overview of the Modern Laue Method

Laue diffraction allows more of reciprocal space to be observed simultaneously than any other X-ray diffraction technique. However, the advantages of Laue diffraction go beyond the ability to observe large regions of reciprocal space. As a polychromatic X-ray technique it is inherently an experiment providing multiple anomalous dispersion. As a crystallographic method it is potentially the fastest method for collection of data sets for structure determination (Coppens, 1992; Helliwell, 1992). Many of these capabilities are currently limited by existing instrumentation, and, as a general experiment for collection of data for structure determination, it still provides many challenges. In particular, when faced with an unknown crystal, Laue diffraction at present is unsuitable for crystallographic structure determination. Such crystals are generally pre-examined using monochromatic techniques for the determination of unit cell parameters and space groups (Helliwell et al., 1989; Gomez de Anderez et al., 1989).

When the energy bandwidth of the incident "white" beam in a Laue experiment is sufficiently wide, multiple orders of diffraction can be observed. This results in the harmonic overlap problem (Helliwell, 1992) in which reflections appear at the same position in space but with energies consisting of integral multiples of $\lambda/n$. Depending on the energy bandwidth of the incident beam, the overlapping orders may obscure the
systematic absences useful for space group determination. The reflections produced from overlapping orders represent approximately 10-20% of all reflections (Cruikshank, Helliwell, and Moffet, 1987) and are not presently used in structure refinement. It would be desirable to allow these reflections to be used for both space group determination and structure refinement. Although progress has been made toward using Laue diffraction data for unit cell determination (Carr, Dodd, and Harding, 1993), in studies where structure refinement was performed using Laue diffraction data, the space group and unit cell parameters were predetermined using monochromatic x-rays (Helliwell, Gomez de Anderez, Habash, Helliwell, and Vernon, 1989; Gomez de Anderez, et. al., 1989). Solutions to this problem involve corrections applied to images on film and require digitization of the film image for later analysis (Hao, Campbell, Harding, and Helliwell, 1993) or mathematical deconvolution of data from different crystal orientations (Campbell and Hao, 1993). A second, related problem is the spatial overlap problem (Cruikshank, Helliwell, and Moffat, 1991) in which spots from different crystal planes are sufficiently close together in space to make intensity measurement difficult. An ideal energy resolved measurement system would allow the intensities of individual components of both types of overlapping spots to be determined.

A further problem is that of wavelength normalization (Helliwell, 1992) in which it is difficult to precisely determine the response of a detector due to uncertainty about the energy of the impinging X-rays. Work has been done to solve this problem when using film; however, use of other detectors has been limited. The methods developed for film
are well advanced and probably suitable to most other detection methods. These problems could be readily solved by measurement of the wavelength dependence of the detector response and knowledge of the discrete energy or energies of the X-rays producing an individual spot. Access to energy resolved area detection would allow the Laue experiment to be routinely used for full structure and space group determinations.

1.3 Harmonic Overlap

Harmonic overlap in a Laue pattern arises from the fact that all diffracted rays produced by families of planes which are integer multiples of each other leave the crystal at the same angle. For example, if \( h, k, \) and \( l \) are the indices corresponding to a family of planes giving rise to a diffraction vector, then all the indices \( nh, nk, \) and \( nl \) will, if present, give rise to diffraction vectors having the same direction. While these vectors have the same direction, each harmonic has a distinct energy. In the energy domain, the Laue harmonics appear as integer multiples of the fundamental \( nE_o \), where \( E_o \) is the energy of the first order spot. In the wavelength domain, they appear at \( \lambda_o/n \), where \( \lambda_o \) is the wavelength of the first order diffraction. The origin of the Laue harmonics can be illustrated by considering the Ewald construction as shown in Figure 1.4.

As indicated in the Figure 1.4, an integer multiple of a particular reciprocal lattice point results in a scaling of the Ewald sphere. It does not affect the angles at which the diffraction vector leaves the crystal. In some cases, a particular harmonic may
Ewald construction shown in two dimensions, illustrating the origin of Laue harmonics. The triangles defined by the origin of reciprocal space, any set of reciprocal lattice points sharing a common positive integer multiple, and the center of the corresponding Ewald sphere are similar. Therefore the angles at which the diffracted beams leave the crystal are equivalent. The distinguishing feature of these two diffracted beams is their wavelengths.
not be in a position to diffract due to wavelength restriction on the experiment being performed.

An additional consequence of the phenomena giving rise to harmonic overlap is that for a given orientation, unit cells differing only by a scalar multiple will result in patterns that are very similar. The energy causing diffraction for a given family of planes giving rise to a particular spot in a pattern will vary, as will the density of spots. However, spots produced by planes of equivalent Miller indices will appear at the same position in space.

The problems associated with harmonic overlap were recognized early in the history of X-ray diffraction. Bragg (Bragg, 1975), in his historical treatment of X-ray diffraction, indicated that the Laue method lost favor because monochromatic methods allowed reflections of definite order to be observed. Wyckoff, who did much work in the interpretation of Laue patterns using the gnomonic projection, recommended limiting the reflections used for establishing a crystal structure to those which do not have harmonic overlap. This practice is still common in modern structure analysis using data from Laue experiments (Examples: Dodd, Hao, Harding, and Prince, 1994; Howell et al., 1992; Bartunik, Bartsch, and Qichen, 1992; Helliwell et al., 1989).

Separation of harmonically overlapped spots has been the subject of many investigations. These can be roughly classed in two groups: those involving sequential measurements of individual spots and those involving the use of area detectors.

Giessen and Gordon (1968) noted that Bragg’s law can be considered in terms of
energy. They tested the idea using a Si(Li) detector, a white X-ray source, and polycrystalline metals. Using the method they were able to separate six overlapped energies at a particular angle relative to the polycrystalline sample. This initial report led to the development of the field of energy dispersive diffractometry (c.f. Buras Niimura, and Olsen. 1978; Parrish and Hart. 1987) This approach was first applied to the Laue method by Fischer and Krane (1985) who used a Ge detector measure the effects of anomalous dispersion. Fischer and Krane argued for the feasibility of harmonic separation using the Ge energy dispersive detector.

Lange and Burzlaff (Lange and Burzlaff, 1992) described a specialized diffractometer set-up for Laue data collection. This diffractometer is used with a photomultiplier tube, scintillator, and pulse height analyzer. Using this apparatus, Lange and Burzlaff were able to show spectra from a multichannel analyzer having up to five harmonics present.

Separation of harmonically overlapped Laue diffraction spots using area detectors has been the subject of several studies. The absorption of X-rays in film packs (Helliwell et al., 1989) or calibrated absorbers (Hanley, Dunphy, and Denton, 1996), direct methods (Hao et al., 1993), mathematical deconvolution of different crystal orientations (Campbell and Hao, 1993), and a real space density modification method (Hao, Harding, and Campbell, 1995) have all been used to deconvolve the components in multiple Laue spots.

Helliwell et al (Helliwell et al., 1989) summarize experience with the collection of
Laue data using synchrotron radiation. Using data from up to six films in a film pack a procedure called UNSCRAM was used to separate doubly and triply overlapped harmonics. The method relies on the differential absorption of intensity as a function of wavelength in a set of stacked calibrated absorbers (in this case film). This method works suitably for harmonics with doubles and has been extended to treat triples; however, accumulation of errors and the limited data available from the film pack renders the method unsuitable for multiplicities greater than three.

Hao and Campbell (Hao and Campbell, 1993) developed a method applicable to detectors other than film. The technique uses multiple orientations and the wavelength normalization curve for the source and detection system. A set of harmonics observed in one orientation can appear in a separate orientation; however, the wavelengths of the harmonics will shift as will the intensities of the components in the harmonically overlapped spot. In combination with a knowledge of the wavelength normalization curve, this allows the individual intensities to be deconvolved. Using this approach, Hao and Campbell were able to separate doubles and triples. Hao et al. (Hao Campbell, Harding, and Helliwell, 1993) applied direct methods to the problem of separating Laue harmonics. Again, this allowed doubles and triples to be separated with results slightly greater than UNSCRAM. Because of experimental errors, trying to separate harmonically overlapped spots with over three components did not appear practical. Hao et al. (Hao Harding and Campbell, 1995) extended this method using an iterative procedure incorporating a modified Patterson function. This gave similar results to the
direct method procedure, but again the harmonic spots treated were restricted to doubles and triples.

Much information is hidden in the 10-20% of spots containing harmonic overlap (Cruickshank, Helliwell, and Moffat. 1987). These overlapped Laue spots contain information useful for the assignment of space groups (Amoros, Buerger, and Canut de Amoros. 1976). Further, spots containing harmonic overlap come disproportionately from low order reflections and other planes of special interest making the separation of the intensity components in these spots of particular concern. Absence of these reflections from structure refinement systematically under-represents the low frequency coefficients in the Fourier synthesis.

Sweet, et al. (Sweet, Singer and Smalas. 1993) argue for the use of a wavelength range of approximately a factor of two to eight. They base this conclusion on a desire to minimize the amount of harmonics in the resulting pattern and maximize signal to background ratios. The ability to separate harmonics in a satisfactory way would remove the wavelength range limitations arguing for the widest bandwidth achievable in the white X-ray source. The signal to background issue is incorrect as considered by these authors. The problem of measuring Laue images and getting good measurements of the intensities of weak reflections depends on the magnitude of the background noise, not the background itself.
1.4 Under-representation of Low Frequency Fourier Components

Bartunik et al. (Bartunik, Bartsch, and Qichen, 1992) assessed the accuracy of structures obtained using Laue methods and monochromatic data collection. In this comparison, it was found that structures refined from Laue data had lower accuracy than monochromatic data and the low resolution contrast in the structures was poorer. The lower accuracy was of less concern than was the poorer low resolution contrast. The lower accuracy was found to be due to imperfect correction of wavelength dependent effects. The lower contrast was the result of incomplete sampling of reciprocal space. In a single exposure of a Laue experiment, the portion of a reciprocal lattice near the origin and bounded by $\lambda_{\text{max}}$ and $\lambda_{\text{min}}$ is small. This can be thought of as a low wavelength hole in the data set. This region can be seen in Figure 1.3. The region enclosed by the $\lambda_{\text{max}}$ sphere can not be observed. Added to this problem is the conventional systematic exclusion of spots containing harmonic overlap from structure refinement. This region of reciprocal space is important for defining the low frequency components of the crystal structure.

1.5 Unit Cell Determination

Early in the history of X-ray diffraction, methods were described whereby Laue photos could be used to estimate unit cell dimensions. These methods involved
observing the low wavelength limit ($\lambda_{\text{min}}$) to the data and scaling the cell accordingly or assigning an energy to a spot and scaling the axial ratios to the energy of the spot. Bragg and Bragg (1924) described a method for single exposures. In their description, the acceleration voltage on an X-ray tube was suggested as an estimate of $\lambda_{\text{min}}$. The description contained in Bragg and Bragg is based on a treatment in a previously published paper by Aminoff which is not given a complete reference. The method is based on noting that all the observed spots must fall in a region bounded by a maximum wavelength and the minimum wavelength. Appropriate choice of axes and indices for observed spots will allow all spots to fall within the required region. Bragg and Bragg (1924) indicate that the weakness of this approach is that the exactness of the plane spacings is less than that found with monochromatic methods.

Davey (1934) described a different approach. A series of Laue pattern images are taken as the voltage on the X-ray generator is lowered step by step until a spot disappears. From this and the angle of diffraction the plane spacing can be computed using Bragg's law. Amoros, Buerger, and Canut de Amoros (1975) also indicate that the Laue method can be used to obtain approximate unit cell dimensions using a knowledge of the acceleration voltage on the X-ray source.

A modern adaptation resembling the Braggs' was described by Carr et al. (Carr, Dodd, and Harding, 1993 and Carr, Cruickshank, and Harding, 1992) who define $\lambda_{\text{min}}$ by inserting a metal foil in an incident "white" beam from a synchrotron. The foil provides a sharp cutoff in the high energy portion of the X-ray spectrum giving a $\lambda_{\text{min}}$ which is much
better defined than that provided by acceleration voltage on a source. This approach gives good results (within 0.5%) for monoclinic and orthorhombic cells having volumes in the range of \( \text{ca.} \ 5,000 \) to \( 1,000,000 \ \text{Å}^3 \). The primary limitation of this method is that it works best with large unit cells. With small cells the diffraction pattern is not well populated making application of the method difficult.

Recently, Ravelli et al. (Ravelli, Hezemans, Krabbendam, and Kroon, 1996) summarized indexing methods for use with Laue diffraction patterns. They divide the problem into four types of indexing problems:

1. When the unit cell parameters and orientation are known.
2. When the unit cell and orientation are known approximately.
3. When the cell is known but the orientation is not.
4. When the cell and orientation are unknown.

Of these only the fourth could not presently be done in automatic fashion. These authors describe a method for indexing the patterns in a semi-automatic fashion. They used a laboratory source with a Mo target. After indexing the pattern and getting an unscaled cell, they were able to scale the cell to the Mo Kβ, wavelength. The “white” spectrum of the tube has the characteristic spectrum of the Mo target superimposed. This characteristic spectrum has a signature which can be found in a plot of the corrected intensities in the Laue pattern. The reflections produced by the characteristic radiation are prominent in a plot of the Lorentz and polarization corrected intensities vs. an arbitrary wavelength (computed from the arbitrary dimensioned unscaled unit cell) scale.
Rescaling the cell gave a cell volume accuracy within 1.2%. It should be noted that this method is not generally applicable to Laue patterns in arbitrary orientations. There is no guarantee that the crystal will be in an orientation such that diffraction from characteristic radiation will be seen.

An alternative, which more closely matches that described by Davey, is to measure the energy of many spots in a Laue pattern. If such data are available, the position and energies measured can be converted directly to positions in reciprocal space. For ideal data, plotting the reciprocal space coordinates results in a recognizable lattice (See chapter 6 for details). Cell determination can proceed regardless of orientation and is suitable for small unit cells. It is this approach which will be explored in this dissertation.

1.6 Space Group Assignment

The approach of looking at X-ray diffraction as reflection of the incident beam off planes in the crystal using the Ewald construction is not a complete treatment. Sometimes a family of planes would be predicted to be present in a diffraction pattern, but is not observed. Some of these absences appear in a systematic fashion. For example, the data shown in Figure 1.5 shows a plot of the intensity observed for the h00 set of reflections. In this figure all the odd numbered reflections are missing. The origin
of systematic absences can be treated as follows. *

The intensity, I, of diffracted X-rays from a crystal is related to the periodic structure of electron density inside the crystal. For simplicity this relationship can be expressed as a proportionality.

\[ I \propto |F(hkl)|^2 \quad \text{(1.2)} \]

The quantity \( F(hkl) \) is referred to as a structure factor and is a sum over the amplitudes and phases of the scattered waves for each of the atoms in the unit cell.

\[ F(hkl) = \sum_{j=1}^{N} g_j e^{i2\pi(hx_j + ky_j + lz_j)} \quad \text{(1.3)} \]

In 1.3, \( g_j \) is the temperature corrected atomic scattering factor, \( x_j, y_j, \) and \( z_j \) are the fractional co-ordinates of the scatterer within the unit cell. A more convenient expression is to replace the complex valued exponential with the sine and cosine functions.

\[ F(hkl) = \sum_{j=1}^{N} g_j \cos(2\pi(hx_j + ky_j + lz_j)) + i \sum_{j=1}^{N} g_j \sin(2\pi(hx_j + ky_j + lz_j)) \quad \text{(1.4)} \]

If there is a 2, screw axis in the crystal parallel to the a axis, this means that for every

* The Treatment here is similar to that in Ladd and Palmer (1993) or Sands (1975).
position \((x,y,z)\) within the unit cell there is an equivalent position located at the location \((1/2+x, -y, -z)\). The combined contributions of the original object and its symmetry related “twin” will be the sum of scattering factors.

\[
F(hkl) = \sum_{j=1}^{N} g_j \left( e^{2\pi i \left( h x_j + k y_j + l z_j \right)} + e^{2\pi i \left( \frac{h}{2} + k y_j - l z_j \right)} \right)
\]

Making the substitution of 1.4 into 1.5, equation 1.6 is obtained.

\[
F(hkl) = \sum_{j=1}^{N} g_j \cos\left(2\pi i \left( h x_j + k y_j + l z_j \right)\right) + i \sum_{j=1}^{N} g_j \sin\left(2\pi i \left( h x_j + k y_j + l z_j \right)\right) + \\
\sum_{j=1}^{N} g_j \cos\left(2\pi i \left( h x_j - k y_j - l z_j + h/2 \right)\right) + \\
i \sum_{j=1}^{N} g_j \sin\left(2\pi i \left( h x_j - k y_j - l z_j + h/2 \right)\right)
\]

This equation has a special case when \(k\) and \(l\) are 0.

\[
F(hkl) = \sum_{j=1}^{N} g_j \cos\left(2\pi i \left( h x_j \right)\right) + i \sum_{j=1}^{N} g_j \sin\left(2\pi i \left( h x_j \right)\right) + \\
\sum_{j=1}^{N} g_j \cos\left(2\pi i \left( h(1/2)x_j \right)\right) + i \sum_{j=1}^{N} g_j \sin\left(2\pi i \left( h(1+1/2)x_j \right)\right)
\]

This can be further simplified using the trigonometric identities:
\[
\cos(x) + \cos(y) = 2 \cos\left(\frac{x + y}{2}\right) \cos\left(\frac{x - y}{2}\right)
\]
\[
\sin(x) + \sin(y) = 2 \sin\left(\frac{x + y}{2}\right) \cos\left(\frac{x - y}{2}\right)
\]

\[
F(hkl) = 2 \sum_{j=1}^{N} g_j \cos\left(2\pi\left(-\frac{h}{4}\right)\right) \cos\left(2\pi\left(hx_j + \frac{h}{4}\right)\right) +
\]
\[
2i \sum_{j=1}^{N} g_j \cos\left(2\pi\left(-\frac{h}{4}\right)\right) \sin\left(2\pi\left(hx_j + \frac{h}{4}\right)\right)
\]

Careful inspection of the cosine terms in 1.9 shows that if \( h \) is odd the structure factor is zero. Hence no intensity would be expected in the series of \( h00 \) reflections when \( h = 2n+1 \).

Similar treatments have been applied to all symmetry relationships possible in each of the possible space groups. Systematic absences are observed for screw axes, cell centering conditions, and glide planes. Knowledge of the systematic absences is useful for the assignment of the space group to which the crystal belongs. While it is not always necessary to know the space group in order to refine a structure from a data set it is desirable. Knowledge of the space group reduces the difficulty of phasing the data set.*

When systematic absences are considered with respect to the Laue diffraction

* Note that the observed intensity is proportional to the square of the structure factor. This results in the loss of all phase information. Recovery of the phases is necessary to obtain the structure of the crystal.
Data showing a systematic absence indicating a \(2_1\) screw axis in a crystal belonging to the \(P2_12_12_1\) space group. Data taken with monochromatic radiation. All the components with odd numbered \(h\) are missing from the diffraction pattern.
The systematic absences caused by the presence of screw axes can not be observed in a conventional Laue image. In a Laue image, all the reflections shown in Figure 1.5 will appear in the same position in space. In conventional Laue images, it can be difficult to assign absences indicative of glide planes as well.

In the case of screw axes, the number of harmonics present in a harmonically overlapped spot can be large and available methods for separating harmonics are inadequate for this purpose. Previously, it has been assumed that such absences could not be assigned using Laue methods. The author is unaware of prior speculation on methods to assign space groups using Laue images. A solution to this problem is one of the topics of chapter 6.

1.7 Full Crystallographic Structure Determination Using Laue Methods

Two papers have recently appeared in the literature which come close to the goal of complete structure analysis using Laue methods (Dodd et al. 1994 ; Kuriuki and Harding, 1995). Dodd et al. (1994) give a full refinement of a pair of crystals. However, a limited monochromatic data set was available which allowed conclusions to be checked as the structure was solved. In the Kuriuki and Harding paper (1995), a full structure was refined without knowledge of the space group for a mineral having a small unit cell. This was sufficient to match the crystal as a previously characterized substance. If these
papers do not represent full structure determination of an unknown, they are extremely close. Generally applicable methods which fully exploit the Laue experiment, however, remain to be developed.

1.8 Energy Resolved Area Detector for Laue Diffraction Pattern Imaging

This dissertation is concerned with the use of energy resolved detection of Laue patterns to solve the problems associated with unit cell determination, harmonic overlap, and space group assignment. Two approaches were proposed. the first was the possible use of charge injection devices as energy dispersive area detectors. The second was to modulate the energy distribution of the incident polychromatic X-rays using a set of metal foils. This latter technique has been termed a foil mask spectrometer. No prior work had been done on energy resolved area detection of Laue patterns and little speculation on how such a system could be made in a practicable fashion had appeared. The experimental portion of the dissertation will be presented in Chapters 2-6. Chapters 2 and 3 treat the characterization of some charge injection devices and their incorporation into systems for X-ray detection. Chapter 4 describes limiting conditions for measurements made with these devices for measurement optimization. Chapter 5 presents the development, construction, and testing of the foil mask spectrometer. Chapter 6 describes the application of the foil mask spectrometer to the determination of unit cells and systematic absences in a variety of crystals. These investigations were
made toward a longer term goal of developing a generally applicable experiment for complete structure refinement of previously unknown crystals on a laboratory scale using solely Laue methods.
Development of the foil mask spectrometer first required the construction of an X-ray area detection system. A variety of CIDs were available to form the basis of X-ray detection systems. Prior to the present work, little had been done on the use of CIDs for the detection of X-rays (Fields et al. 1992). Before characterization of their response to X-rays could be done, electro-optical characterization of the CIDs had to be performed to assess their system gain, read noise, dark current, photometric response, quantum efficiency, and fixed pattern noise. In addition, it was necessary to identify potential problems in the adaptation from the UV-Vis to the X-ray range. Four pre-amp per row CID devices were examined in some detail. The CID 17PPRA and the CID 38SG devices are commercially available devices for which prior characterizations have not been published. Although Pilon (1991) examined the CID 17PPRA for use in atomic
emission spectroscopy, this device has been re-examined in more detail here. Several of the earlier values have been amended and the characterizations performed here are considerably more comprehensive. The CID 38Q-A and CID 38Q-B are experimental devices which are not commercially available. These characterizations were performed in collaboration with True (True. 1996). The results presented here reflect only the author's work. For additional details see True (1996) and True et al. (True, Hanley, and Denton. 1996).

2.1 Description of the Devices

The CID 17PPRA is a 256x388 pixel device. Each pixel is 28x24 microns. The CID 38SG is a 512x512 device having 28x28 micron pixels. Both devices are constructed using 5Ω/cm silicon. The devices are available with several epitaxial layer thicknesses, 15, 16, 20, and 28 μm (van Gordon, 1994). The devices having 28 μm epitaxy are expected to have enhanced red sensitivity; however, no data supporting this expectation has been published. Based on the data in Hanley et al. (Hanley, Denton, Jourdain, Hochedhez, and Dhez. 1996: Appendix I. this Dissertation) increasing the epitaxy thickness without increasing the resistivity of the silicon will probably not affect the performance of the device greatly.

The CID 38Q-A and CID 38Q-B are based on the design of the CID 38SG except the Q devices are made using an all-oxide fabrication process. The structure of the
devices are proprietary at present but are similar in architecture to the CID 38SG.

Multiple motivations for the use of an all oxide process exist. The all-oxide amplifiers are thought to have lower noise than the nitride process (van Gordon, 1993). The all-oxide process requires fewer process steps and for this reason is less costly.

2.2 : System Gain

A charge injection device is read using an analog to digital converter. This conversion results in a measurement in an arbitrary scale. This scale, which is graduated in arbitrary digital units (ADUs), must be calibrated further in order to relate the value in ADU to the number of photogenerated hole pairs collected in a pixel of the device. The system gain of a device relates the number of collected electrons to the measured output in ADUs. Hence, measurement of the quantum efficiency of a charge transfer device (CTD) requires a knowledge of the system gain.

Two methods for the measurement of system gain have been described in the literature. These are: the method of mean variance (Mortara and Fowler, 1981) and the X-ray photon transfer method (Janesick, Klaasen, and Elliot, 1987). The latter method relies on exposure of the device to a low flux of X-rays, usually produced by radioactive decay. The energy of the X-ray is converted into a number of electrons. These electrons

\text{\textsuperscript{*}CIDs actually collect holes. In the characterization literature describing CIDs, collected charge is usually referred to as electrons to be consistent with the CCD literature.}
are then measured. This method requires good charge collection efficiency and low noise.

This method can not be used on the present generation of CIDs since these devices have poor collection of X-ray generated charge. For this reason, the method of mean variance must be used. This method relies on the fact that the variation of photons distributed spatially or temporally follows a Poisson distribution (Saleh and Teich, 1991).

For visible photons only one charge carrier is generated for each photon. A CTD can then be exposed to an even optical field. The Poisson, or shot, noise, \( \sigma \), of the carriers collected in the pixels is dependent on the number of carriers \( q \) as predicted by equation 2.1. The development of mean-variance presented here in equations 2.1-2.5 follows Sims (1989) and others (Bilhorn, 1987; Sweedler et al., 1987)

\[
\sigma^2 = q \quad 2.1
\]

The measured signal, \( S \), is related to the number of carriers collected by the system gain, \( G \), of the device and readout electronics.

\[
S = G^2q \quad 2.2
\]

The measured variance, \( \Delta^2 \), of the values of \( S \) is also related to the number of charge carriers.
By substituting equation 2.3 into equation 2.2 the standard mean variance expression is reached.

\[ \Delta^2 = G^2 q \]  

2.3

\[ \Delta^2 = GS \]  

2.4

The gain parameter \( G \) reflects the gain in all stages of the measurement process. It usually has components from both the on-chip amplifier and read out electronics and is not a fundamental property of the device.

Equation 2.4 implies that a plot of the set of signals measured at varying illumination levels vs. the measured variance of those signals should yield a straight line whose slope is \( G \). In real systems, there are sources of variance other than the Poisson noise from the incident photons. This variance from other processes is usually treated as an aggregate and called read noise, \( \sigma_r \). In scientific grade CTD systems, this source of noise is independent of signal strength. The combined variance from photon shot noise and read noise is given by equation 2.5.

\[ \Delta^2 = GS + \sigma_r^2 G^2 \]  

2.5

This predicts the relationship between the magnitude of a signal and its variance and
gives a way to estimate both the system gain and the read noise of a CTD system.

The read noise, $\sigma_r$, like the system gain, reflects the overall noise characteristics of the CTD system, including the device, readout electronics, and digitization noise. As measured, it does not necessarily reflect the noise from the device alone and may vary if different controller electronics are used. However, in a well designed system, the read noise will reflect the noise of the chip. This may be done by using sufficient on-chip gain such that noise added by the readout electronics is negligible.

Practical application of the mean variance equation (2.5) requires careful isolation of variance from read noise and shot noise from potential confounding factors such as fixed pattern noise and row crosstalk. The present generation of CIDs has a large fixed pattern noise (See section 2.5). This is not noise in the strictest sense. Fixed pattern noise in CIDs manifests as an offset that varies from pixel to pixel. The measured value from a pixel, $M_i$, is a sum of the pixel offset, $P_i$, and the signal due to the presence of charge carriers, $S_i$.

$$M_i = P_i + S_i$$  \hspace{1cm} 2.6

When doing the mean variance experiment based on the spatial distribution of photons the measured signals from a large number of pixels are averaged. In a CID, when the pattern noise of the device is large, it results in the mean variance plot being compromised by the pattern noise. The reason for this is that mean signal and variance
reflects the fixed pattern noise rather than the collected photons. This is shown in equations 2.7 and 2.8.

\[
\bar{M} = \frac{\sum_{i=1}^{n}(P_i + S_i)}{n} \quad 2.7
\]

\[
\Delta^2 = \frac{\sum_{i=1}^{n}((P_i + S_i) - \bar{M})^2}{n-1} \quad 2.8
\]

In 2.8, the measured variance is compromised by the values of \(P_i\). Sims (1989) described an exposure sequence that removes fixed pattern noise from a mean variance experiment by computing the variance on the difference image between a pair of matched exposures. The mean of the difference image is zero and the offsets, \(P_i\), cancel. Since variance adds when taking a difference, the resulting variance, \(\Delta_m^2\), is twice that of equation 2.5.

\[
\Delta_m^2 = 2\Delta^2 \quad 2.9
\]

A further problem with the implementation of a good mean variance experiment is assuring that the paired exposures have similar illumination levels. In all the data reported here, exposures were checked to assure that the illuminations matched. A variety of diagnostics were also checked to assure that the distributions were nearly
normal by computing the skew and curtosis of the values in the difference image. A significantly skewed distribution or one with inappropriate curtosis indicates a measurement problem and was repeated. These diagnostics were developed first for use with the CID38Q-A which had readout problems resulting in randomly appearing bad rows in images. In other devices, when a strip five pixels wide is removed from the edges of the subarrays used for measurement, the distributions were well behaved and good results were readily obtained.

A final problem in implementing the mean-variance method was encountered due to the non-linear response curve of all the CIDs examined when evenly illuminated over large areas of the device. The mean-variance method assumes a linear response to collected charge. Adaptation of the method to a non-linear system was attempted but was found to be intractable. Instead, illumination was restricted to low levels where the response closely approximates a straight line.

**CID 17PPRA Device**

A typical mean variance plot for a CID 17PPRA appears in Figure 2.1. Prior to this work no reports had been made of the variation expected to be present in a set of CID devices or in replicate measurements made on a single device. In addition, a set of well characterized devices was needed for the later X-ray studies. Since radiation damage to
Mean Variance plot for CID 17PPRA device number 16. The system gain obtained from this plot is 43.8 carriers/ADU. Data taken using a CID gain parameter of 130. This corresponds to a 16.1 kHz pixel frequency.
the devices was expected, these measurements were performed prior to exposure to X-rays.

A set of devices were studied using a standard protocol. The system gain was measured at two pixel frequencies, 16.1 and 9.43 kHz. In all cases, the exposures were kept limited such that the maximum exposure level in the mean variance experiment was less than 100,000 carriers. This level corresponds to the lower 10% of the CID's well capacity. All the mean variance experiments contained 50 exposure levels. These data are tabulated in Table 2.1. These data allow an evaluation of the reproducibility of the mean-variance measurements within a single device and between different devices. All the data shown in Table 2.1 were taken using a single board set.

Table 2.1: System Gain Data for 4 CID 17PPRA Devices

Measurements at CID Gain Parameter 130 (16.1 kHz)

<table>
<thead>
<tr>
<th>Device</th>
<th>Device mean</th>
<th>1 sd</th>
<th>2 sd</th>
<th>3 sd</th>
<th>4 sd</th>
<th>5 sd</th>
<th>mean ± 1 sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>#15</td>
<td>46.69</td>
<td>45.75</td>
<td>47.71</td>
<td>46.23</td>
<td></td>
<td></td>
<td>46.60±0.84</td>
</tr>
<tr>
<td>#16</td>
<td>43.84</td>
<td>45.58</td>
<td>45.59</td>
<td>46.40</td>
<td></td>
<td></td>
<td>45.35±1.08</td>
</tr>
<tr>
<td>#17</td>
<td>45.58</td>
<td>45.30</td>
<td>46.01</td>
<td>45.73</td>
<td></td>
<td></td>
<td>45.66±0.30</td>
</tr>
<tr>
<td>#19</td>
<td>45.78</td>
<td>44.02</td>
<td>45.25</td>
<td>45.84</td>
<td></td>
<td></td>
<td>45.2±0.8</td>
</tr>
</tbody>
</table>

Measurements at CID Gain Parameter 240 (9.43 kHz)

<table>
<thead>
<tr>
<th>Device</th>
<th>Device mean</th>
<th>1 sd</th>
<th>2 sd</th>
<th>3 sd</th>
<th>4 sd</th>
<th>5 sd</th>
<th>mean ± 1 sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>#15</td>
<td>27.61</td>
<td>27.18</td>
<td>27.71</td>
<td>29.23</td>
<td></td>
<td></td>
<td>27.93±0.90</td>
</tr>
<tr>
<td>#16</td>
<td>26.50</td>
<td>24.81</td>
<td>25.48</td>
<td>26.15</td>
<td></td>
<td></td>
<td>25.73±0.75</td>
</tr>
<tr>
<td>#17</td>
<td>25.63</td>
<td>25.87</td>
<td>24.72</td>
<td>25.77</td>
<td></td>
<td></td>
<td>25.50±0.53</td>
</tr>
<tr>
<td>#19</td>
<td>24.76</td>
<td>26.08</td>
<td>26.72</td>
<td>24.65</td>
<td></td>
<td></td>
<td>25.55±1.00</td>
</tr>
</tbody>
</table>
The data indicate that the exposure sequence used gives reasonable reproducibility. Only a few devices need to be examined and the system gain shows little variation within a single family of devices. The data taken at 9.43 kHz has a one standard deviation error of 4.9% and the corresponding error at 16.1 kHz is 2%. These tolerances are important since the measurement of the read noise and quantum efficiency relies on the system gain. Therefore, both these quantities should be assumed to have at least 2-5% error.

The CID gain parameter is an arbitrary index which controls the length of integration on a correlated double sample. As the time of integration increases, the system gain in carriers/ADU decreases. It is desirable to optimize the CID camera system by minimizing the read noise. To evaluate this, a knowledge of the system gain as a function of CID gain parameter (pixel frequency) must be known. A series of system gain measurements, taken at intervals of 10 gain parameter units, were made in a number of devices. A representative plot of such a set of measurements is shown is figure 2.2.

In the CID 17PPRA this type of plot was reasonably reproducible between devices and good measurements were typically possible from 9-80 kHz. Some instability was observed at CID gain parameters less than 20 (55 kHz).

**CID 38Q-A Device**

Two CID 38Q devices were studied. The CID 38Q-A was a first generation all
Figure 2.2: Variation in System Gain with Pixel Frequency for CID 17PPRA

Plot of the relationship between pixel frequency and measured system gain for a CID 17PPRA device. The line corresponds to the best fit straight line to the data. In an ideal system the data should match a straight line. At low frequency, the correspondence with the ideal is moderately good. At higher frequency, some curvature is apparent.
oxide prototype device which was initially expected to have lower read noise, higher radiation tolerance, and lower production cost. Only two devices were available for characterization. System Gain plots for one of these devices appear in figure 2.3.

The CID 38Q-A device performed poorly, and was generally unsuitable for scientific purposes.

CID 38Q-B Device

The CID38Q-B is a second generation all-oxide process CID. A variety of modifications were made to the original device to correct some of the problems of the CID38Q-A. system gain plot of this device appears as figure 2.4.

CID 38SG Device

The CID 38SG is a nitride process device. This device has been commercially available for several years and its design forms much of the basis for the Q device. A system plot for this device appears in figure 2.5.

2.3 Read Noise

The read noise of a device is the sum of all signal independent noise except pattern noise and dark current noise. It is commonly used as a measure of the ability of a device to detect low-level signals. In the CID, read noise is generally higher than it is in
Figure 2.3: Variation in System Gain with Pixel Frequency for CID 38Q-A

Plot of the relationship between pixel frequency and measured system gain for a CID 38Q-A device. The performance of the device was generally poor. The worst 2 outliers were removed. The remaining "poor" data points have been included and are an indication of the performance of this device.
Figure 2.4: Variation in System Gain with Pixel Frequency for CID 38Q-B

Plot of the relationship between pixel frequency and measured system gain for a CID 38Q-B device. The performance of the device was adequate.
Figure 2.5: Variation in System Gain with Pixel Frequency for CID 38SG

Plot of the relationship between pixel frequency and measured system gain for a CID 38SG device. The line corresponds to the best fit straight line to the data. The two highest pixel frequencies have been eliminated from the best fit line.
CCDs. The reason for this is that the magnitude of the output signal from a CID is limited by the total capacitance of the sense circuitry. This results in output signals of 30-50 nV/carrier before amplification. This is about two orders of magnitude lower than CCD output (Sims. 1993) and as such is more susceptible to degradation. The sensitivity decreases with device capacitance (size). Models of pre-amp per row CID performance consider row pre-amplifier noise as the greatest source of noise in the device (Carbone. 1994). In practice, other sources of noise are of concern. The ability to have output correspond to the signal from the device requires careful design of the readout electronics so that subsequent processing does not degrade the output signal. Experience has shown that interference from nearby computer monitors and electric fields seriously degraded the signal. To achieve good measurements from the CID camera systems, it is imperative to shield the readout electronics relative to other laboratory equipment.

The flexibility of the CID makes it possible to assess the read noise in several different ways. Further, the different readout sequences cannot be assumed to give the same level of measured noise. In particular, it was unclear whether readout sequences incorporating injection (charge clearing) would result in measured read noise consistent with sequences without injection.

In the CID literature, noise is an estimate of the error in a measured signal. Two statistically distinct quantities are used interchangeably and reported as read noise. Reported read noise in CIDs may be either the standard deviation of series of measurements or the estimate of the error in the mean value of a series of measurements.
Since CIDs can be read repeatedly without destroying the accumulated charge, the expected error associated with the mean signal decreases. However, it should be noted that the standard deviation of a series of measurements does not decrease with the number of measurements made. A better estimate of the standard deviation is obtained but the magnitude does not decrease. The estimate of the mean value of the distribution also improves. The error in the mean value is sometimes referred to as the error of the mean or the standard error of the mean. In this chapter, to avoid confusion, read noise will be used only to describe the standard deviation of a set of measurements made with a device and, when multiple measurements of a single packet of accumulated charge are made, the subsequent error will be referred to as read error. The CID literature does not normally make this distinction and it is sometimes difficult to ascertain the conditions of measurement responsible for reported values of read noise.

**Method A: Intercept Method**

Equation 2.5 may be used to estimate the read noise of a device. In this method, the best fit line to a mean-variance plot is computed. The slope gives the system gain, $G$, and the intercept is $G'\sigma_r^2$. Solving for $\sigma_r$ results in a value for read noise. This method is problematic since it is influenced by the photometric response of the device. Depending on the readout sequence and the quality of the device a foot is often observed in CID mean variance plots. The foot is a region of low photometric response in which charge
carriers accumulate in trap sites and other defects rather than in the potential well of the pixel. These trapped carriers are not measured which results in a decrease in the measured signal. Further, the photometric response of the CIDs examined here shows curvature at high values of mean and variance. This can result in over-estimating the device read noise. In the case of a “foot” in the plot, the read noise of the device is underestimated. In the case of curvature at the high end of the plot, the read noise is over estimated.

**Method B: Paired Subarray Reads**

A set of paired reads may be used to measure the read noise of a device. The device is cleared of all charge and a set of paired reads of a subarray on the device are measured. The difference between the two measurements is computed pixel by pixel to remove fixed pattern noise. The standard deviation of the difference is computed and divided by 2 (see equation 2.9). The standard deviation in ADU is multiplied by the system gain to obtain the read noise in carriers.

$$\sigma_r = \frac{G}{2} \sqrt{\frac{\sum_{i=1}^{n} (S_i - \bar{S})^2}{n-1}}$$  \hspace{1cm} (2.10)

In (2.10), $S_i$ is the difference signal from the $i$th pixel in the subarray and $\bar{S}$ is the mean
of the difference subarray.

Two variations of this measurement were carried out. In the first variation, the device was cleared and the same subarray is read twice to obtain the data. This type of measurement was termed read noise. In the second variation, the device is cleared of all charge, the selected subarray read, the charge was cleared from the device using the CIDs inject feature, and the subarray was then read a second time. The result of this type of measurement was termed inject noise. The purpose of the latter measurement was to determine if the process of injection introduced an additional source of noise to the measurement process.

**Method C: Standard Deviation of Rereads**

An approach unique to the CID is to use a set of rereads from a single pixel to estimate the read noise of a device. A set of reads from a pixel are made. The standard deviation is measured and then converted to charge carriers.

\[
\sigma_r = G \sqrt{\frac{\sum_{n}(S_i - \bar{S})}{n - 1}}
\]

This expression is very similar to (2.10) except that the factor of two has been eliminated and \(S_i\) represents the \(i\)th measurement of the signal in a single pixel. This expression can
be used to see if the noise is uniform over the surface of a CID.

**Method D: Moving Average in a Series of Rereads**

In most noise measurements, it is assumed that noise is white, or that the time scale of a series of measurements is such that unwanted signals appear to be "white." In practice, a system might not be well enough behaved to allow this assumption to be made. An example of a confounding noise source might be the case of a 60 Hz signal contaminating a measurement. Such noise sources are common in laboratories using 60 Hz power sources. If a series of 20 measurements are made of such a system in a burst taken at 20,000 kHz, a non-representative sample of the 60 Hz noise is obtained. The subsequent calculation of the read noise will give a spuriously low value. If the samples are made at randomly spaced time intervals over several minutes, a more representative measurement will be obtained and the read noise will be accurate.

To assess the time varying properties of the read noise, a number of experimental approaches were used. First a 20 point moving average was computed over a series of 1000 measurements. The standard deviation of the moving average was computed and converted to charge carriers and the results plotted as a function of position in the array. Plots of this type showed periodic trends and non-random behavior.

Fourier power spectra were also analyzed for this type of data. Such spectra showed expected $1/f$ (flicker noise) and constant components (white noise). They also
contained large components not attributable to either of these noise sources. The frequency of these noise sources varied depending on the pixel frequency used. It is not clear what the source of these signals was or if they were perhaps being aliased in from higher frequency signals. It is clear that the readout electronics were a major source of read noise and that it is doubtful the present generation of readout electronics allow the inherent read noise of a CID device to be assessed. The values reported here should be assumed to be high.

**CID 17PPRA**

The values for read noise of a series of CID 17PPRA devices appear in table 2.2. As can be seen, measured read noise depends on the readout electronics used for measurement.

The data in table 2.2 indicate that the intercept method is indeed inaccurate for cases where a foot is present in the photometric response curve. Where overlapping data for the other three methods are available, agreement is quite good. As seen by the first entry in the table, the position of the camera relative to computer monitors and other laboratory equipment can cause the read noise to increase. Based on these data the read noise of the CID 17PPRA device can be considered to be less than 140 e−. This level of performance, however, may not be obtainable in day to day measurements as it depends on the particular conditions and read out electronics used.
Table 2.2: Value for Read Noise Taken at 9.4 kHz

<table>
<thead>
<tr>
<th>CID 17PPRA</th>
<th>M-V* Read Noise</th>
<th>Read Noise</th>
<th>Inject Noise</th>
<th>M-A Noise†</th>
</tr>
</thead>
<tbody>
<tr>
<td># 15</td>
<td>251</td>
<td>248</td>
<td>230</td>
<td>NA</td>
</tr>
<tr>
<td>(B3FPA1)‡</td>
<td>193</td>
<td>181</td>
<td>183</td>
<td>NA</td>
</tr>
<tr>
<td>#16</td>
<td>198</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>(B3FPA1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#17</td>
<td>206</td>
<td>204</td>
<td>195</td>
<td>NA</td>
</tr>
<tr>
<td>(B3FPA1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#19</td>
<td>198</td>
<td>201</td>
<td>187</td>
<td>NA</td>
</tr>
<tr>
<td>(B3FPA1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#10</td>
<td>158</td>
<td>148</td>
<td>143</td>
<td>NA</td>
</tr>
<tr>
<td>(B1FPA2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#10</td>
<td>105§</td>
<td>141</td>
<td>141</td>
<td>140</td>
</tr>
<tr>
<td>(B1FPA2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#11</td>
<td>115§</td>
<td>139</td>
<td>140</td>
<td>139</td>
</tr>
<tr>
<td>(B3FPA2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All values in the table are in charge carriers. The characters in parentheses refer to the controller and FPA board used. A total of three controller boards and three FPA boards were examined. This table summarizes the most comparable experiments.

The read noise was measured using the intercept method over the range of pixel frequencies available to the camera system in order to determine the optimal frequency for measurement. Although many devices were examined, figure 2.6 is representative of the trends observed. Best measurements are made between 12-20 kHz.

The read noise of a CID 17PPRA was measured using the moving average method. The noise measured as a function of the position in the array of reads is plotted

* M-V Read Noise is a value of read noise obtained from the intercept of the mean variance plot.
† M-A noise is moving average noise.
‡ The first entry in the table was taken with a computer monitor close to the camera head. The second value is the same device in the same board set with the monitor at a distance.
§ This value is due to a foot in the mean variance curve. See text for discussion of the effect of a foot in the mean variance plot.
in figure 2.7. The average of a set of measurements such as those plotted in figure 2.7 agreed with those taken by other measurements. The range was over 150 carriers indicating that values of read noise should be treated with some caution and a large population is necessary to get an accurate measurement of the output of a device.

**CID 38Q-A and 38Q-B**

The read noise of the two all-oxide process devices was measured using the intercept method. These data are plotted in figure 2.8. The mean variance plots of the latter device showed a wide foot.

**CID 38SG**

Three controller board sets were tested using the same FPA board and a CID 38SG device. These data is presented in table 2.3. One of the sets of controller boards worked noticeably better than the others and was used for subsequent measurements of read noise.

A plot of the read noise of a CID 38SG obtained using the intercept method is shown in figure 2.9. The device gives a read noise of about 180 carriers over a wide range of frequencies.
All the data in the figure were taken using the same device using the intercept of a mean variance plot. The increased scatter at high frequency was common to all the devices observed. The read noise could not be reliably measured above approximately 30 kHz. Optimal measurements could be made between 12-20 kHz. It should be noted that there is no reason to use the device at pixel frequencies below 12 kHz. The full dynamic range is unavailable due to saturation of the output electronics and the noise is proportionately higher.
Figure 2.7: Moving Average Noise

The noise computed from a 20 pt moving average using a CID 17PPRA device.
Figure 2.8: Read Noise of CID 38Q-A & CID 38Q-B

Read noise of the CID 38Q-A and CID 38Q-B measured at varying pixel frequency. The filled diamonds correspond to the first generation CID 38Q-A device. The filled squares are for the CID 38Q-B.
Table 2.3: Controller Board Comparison

<table>
<thead>
<tr>
<th>Board Set</th>
<th>Read noise (carriers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>171-194</td>
</tr>
<tr>
<td>#2</td>
<td>192-220</td>
</tr>
<tr>
<td>#3</td>
<td>226-240</td>
</tr>
</tbody>
</table>

In the study of the CID 17PPRA it was noticed that there was some non-random behavior in a series of non-destructive reads. To assess this further a set of measurements were made at a variety of different pixel frequencies. The power spectra of the noise in the series of reads was measured and the data plotted as a function of frequency. These data are shown in figure 2.10. As can be seen, depending on the frequency of acquisition, strong, non-random components to the power spectra are seen. The source of this non-random noise was never found, but is thought to be an artifact from the readout electronics.

On the advice of the manufacturer, the resistance in a late stage amplifier was decreased to see if a reduction in the read noise was observed. The read out electronics are illustrated in figure 2.11. The circuit modification consisted of adding a 1.5 kΩ resistance.

The data used for this study are courtesy of Bruce True. The software as provided by the manufacturer does not allow re-reading a single pixel more than 128 times in rapid succession at a fixed pixel frequency. Dr. True made extensive modifications of the manufacturer's controller code allowing such measurements to be made and the data used here were provided by him.
Figure 2.9: Read Noise Plot for CID 38SG

Read noise plot for the CID 38SG as a function of pixel frequency.
Power spectra of a series of rereads from single CID 38SG pixels taken at varying pixel frequencies (data courtesy of Bruce True, analysis by the author). The data taken at 50 Hz shows a dominant 1/f component. The data taken at higher frequencies showed strong non-random components which do not correspond to either 1/f or "white" noise. The change in position of the peaks in the power spectra with pixel frequency suggests an aliased high frequency signal or time dependent errors in the timing circuitry.
Table 2.4: Effect of Gain Boost on System Gain and Read Noise

<table>
<thead>
<tr>
<th>Condition</th>
<th>System Gain (Carriers/ADU)</th>
<th>Read Noise (Carriers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Gain Increase</td>
<td>81.1</td>
<td>180</td>
</tr>
<tr>
<td>3X Gain Boost</td>
<td>26.9</td>
<td>200</td>
</tr>
</tbody>
</table>

resistor in parallel with the 3.01 kΩ resistor labeled R205. This modification is predicted to increase system gain by a factor of 3. The manufacturer was interested in the effect this modification would have on the read noise of the camera system. Table 2.4 shows the results of this modification.

A slight increase in readout noise was observed following the modification of the readout electronics. In other words, the system performed slightly worse than if the digital values reported by the readout electronics were multiplied by an arbitrary factor of three. It is of note that the read noise is roughly comparable to those made at 10 kHz, except that these measurements are made twice as fast. In comparison to those measurements the overall system performance has improved by a factor of 1.41. The basis for this improvement factor is given a detailed treatment in Chapter 4.

2.4 Read Error

As discussed in section 2.3, the ability to repeatedly read a single CID pixel provides a reduction in the error associated with a measured signal. This capability has been described by others (Pilon, 1991; Sims, 1989; Bilhorn, 1987). In the prior literature.
Figure 2.11: Output Amplifier Circuitry
this process has been referred to as a reduction of read noise. Using the nomenclature of section 2.3, this is a reduction in the error of a mean. It should also be noted that the ability to reduce the error in a measurement assumes that individual reads of a given pixel are dominated by white rather than flicker noise and that the reads are uncorrelated (Sims, 1989). As a result of these restrictions and the behavior demonstrated in figure 2.10, reduction of error using this technique should be treated with caution. The noise is not white when measured using the current generation of readout electronics. It should also be noted that non-white signals can be reduced provided that the time scale and sampling scheme are such that the signals appear to be white. If these conditions are not met then the expected error reduction will not be observed.

The standard deviation for a series of measurements is given by equation 2.12.

\[ \sigma = \sqrt{\frac{\sum (S_i - \bar{S})^2}{n-1}} \]  

where \( \bar{S} \) is the mean signal of the \( n \) measurements and \( S_i \) is the \( i \)th measurement. As more measurements are made, better estimates of the mean and standard deviation are obtained. The error in the mean value is related to the standard deviation by equation (2.13).

\[ s = \frac{\sigma}{\sqrt{n}} \]
This equation predicts that error in a series of measurements decreases as the number of observations increases.

In previous work (Sims, 1989; Pilon, 1991), the observed error typically exceeded values predicted by 2.13. Sims (1989) attributed this to digitization noise and to the bandwidth of the readout electronics (Sims et al., 1987a). The behavior of the new generation of devices was of interest, both to see if the theoretical noise reduction could be achieved and to optimize the readout.

**Read Error Results**

Plots of the reduction in read error as a function of the number of non-destructive reads are presented in figure 2.12. The data were taken at approximately 200 Hz. Near theoretical error reduction was observed.

**2.5 Pattern Noise**

In section 2.2 pattern noise is discussed briefly. All charge transfer devices suffer from some level of pattern noise. This may be from pixel to pixel variations in sensitivity, various types of defects, processing limitations, and other sources of random variation in pixel output. The pre-amp per row CIDs are particularly prone to this type of noise.
Figure 2.12: Read Error Plots for CID 17PPRA and CID 38SG

CID 17PPRA

CID 38SG
Figure caption for Figure 2.12. Decrease in measured signal error as a function of the number of non-destructive readouts. The connected line corresponds to the theoretically predicted reduction in error. Correspondence is particularly good for the CID 38SG device. In the other plot, a few reads of high variance at the beginning of the measurements result in an offset from the theoretical curve (solid line).
The pattern noise in CID s comes from a variety of sources: defects introduced during manufacturing, small variations in row amplifier offsets, and any other process that causes variation in row and column capacitance. Pattern noise is not "noise" in the truest sense of the word. It is fixed variation and can be removed completely by subtracting off a bias image. The total amount of variance in a series of images taken at zero exposure can be treated as a sum of individual variances. Using this approach a model can be constructed based on variance from rows, columns, pixels and reads.

\[ \sigma_{\text{total}}^2 = \sigma_{\text{col}}^2 + \sigma_{\text{row}}^2 + \sigma_{\text{pixel}}^2 + \sigma_{\text{read}}^2 \]  

2.14

The "fixed pattern" noise is due to the components from rows, columns, and pixels. To separate the components the read noise is first measured using the paired subarray technique. The total noise is measured. The column means are subtracted from each value in the corresponding column of the subarray and the remaining variance is computed.

\[ \sigma_{\text{total}}^2 - \sigma_{\text{col}}^2 = \sigma_{\text{row}}^2 + \sigma_{\text{pixel}}^2 + \sigma_{\text{read}}^2 \]  

2.15

The row means are then subtracted from each value in the corresponding row of the subarray. This leaves the pixel and read noise. The read noise is known in advance. This allows all the individual variances to be solved. Table 2.5 gives the results of these
Table 2.5: Pattern Noise

<table>
<thead>
<tr>
<th>Noise Source</th>
<th>CID38SG*</th>
<th>CID 17PPRA†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Noise (carriers)</td>
<td>4827</td>
<td>7326</td>
</tr>
<tr>
<td>Row Noise (carriers)</td>
<td>988</td>
<td>3714</td>
</tr>
<tr>
<td>Column Noise (carriers)</td>
<td>1241</td>
<td>5055</td>
</tr>
<tr>
<td>Pixel Noise (carriers)</td>
<td>4554</td>
<td>3782</td>
</tr>
<tr>
<td>Read Noise (carriers)†</td>
<td>220</td>
<td>133</td>
</tr>
</tbody>
</table>

The major source of pattern noise in each of these devices is different. In the CID 17PPRA, a first generation pre-amp per row device, far greater overall pattern noise is seen and the greatest source is column to column variation. In the second generation CID 38SG a great improvement in both row to row and column to column variation was realized. The pixel to pixel variations are somewhat larger in the CID 38SG. True (True, 1996) has suggested this modest increase is due to the larger pixels in the CID 38SG. The ratio of the pixel noise for the two devices (0.83) closely matches the ratio of pixel areas (0.85).

2.6 Conclusions for System Gain and Noise

There has been considerable speculation on the limiting source of noise in the

* CID 38SG device measurements were made at 20 kHz. Data for the CID 38SG is courtesy of Dr. Bruce True. Analysis by the author.
† CID 17PPRA measurements were made at 13.5 kHz.
‡ As noted elsewhere in the text, the measured values of read noise depend on the particular readout electronics used. The read noise reported in this table reflects the camera control unit used to make the measurements.
CID. Most reports in the literature refer to the high capacitance of the sensing circuitry as the limitation in making low noise measurements with a CID. Recently, amplifier noise on the device has been used to model CID read noise (Carbone, 1994). The present work indicates that amplifier noise is not dominant in practice. Rather, the read noise of the systems tested here seems to be limited by the readout electronics and pre-amplifier gain. The CID 17PPRA showed lower noise than did the CID 38SG. This can be explained in the following way. The ratio of read noises (1.28) is close to the ratio of row length (1.32). The row length is a rough indicator of the sense capacitance. As the capacitance increases, the output signal decreases. This makes the system gain of the larger device (CID 38SG) smaller. The smaller output signal is then degraded to a greater extent by subsequent, non-optimal readout electronics. For read noise to be equivalent to that of the CID 17PPRA, a higher gain preamplifier must be incorporated into the chip design. Future devices should strive to increase the amount of gain on the chip. This will result in larger signals leaving the device and it will take larger contaminating signals for proportional degradation. It is also apparent that the current electronics are non-optimal and need to be improved.

2.7 Photometric Response Function

The photometric response function of a device defines the signal level in terms of the incident radiation on the device. CIDs have been shown to exhibit non linear
behavior (Pilon, 1991; True et al., 1996; Sims, 1987; Bilhorn, 1987). This means that CID response is not a simple linear function of the incident light intensity. Early CIDs showed an initial “foot” or “fat zero” in the response curve (Sims, 1987). Outside of the foot region Sims observed nearly linear behavior in the CID11B. Bilhorn (1987) working with the CID17 noted that the device gave a non-linear response after the foot region was saturated. The effect could be corrected using a 2nd degree polynomial. Bilhorn attributed this behavior to diminished capacitance due to the large amount of charge transferred to the row electrode. Pilon (1991) noted in his initial work on the CID17PPRA device that the region following the “fat zero” also was non-linear. True (1996) also observed this effect while working with the CID 38SG. The effect is strongest when the device is evenly illuminated. Prior speculation (Bilhorn, 1987; Pilon, 1991) has been that the non-linearity was due to decreasing row and column capacitance as the device approached saturation. The change in voltage measured by the amplifier depends on the capacitance as shown in equation 2.16.

\[
dV = \frac{dQ}{C}
\]

Equation 2.16 suggests that as \( C \) decreases, \( dV \) will increase. This predicts a progressively increasing signal as more photogenerated charge is added to the potential well. A derivative plot should show an upward slope.
Figure 2.13 shows a photometric response plot for a CID 17PPRA and its derivative. The slope of the derivative plot is the opposite of what would be expected if the capacitance of the device is decreasing.

Previous work by Sims (1987a) showed a nearly linear response curve over much of the photometric response curve for the CID 11. Pilon (1987) found that all CID 17 generation devices showed non-linearity, both with and without row-pre-amplifiers. True (True, 1996; True et al., 1996) has shown that similar non-linear behavior is seen in the CID 38SG. In the work by True, it was shown that the output non-linearity is related to another phenomenon called row crosstalk, a relationship also suggested in Bilhorn (1987). If a CID 38SG is evenly illuminated, the extent of non-linearity increases. If only a small spot a few pixels in size is imaged, the response more closely approximates a straight line.

The existence of CIDs of a generation preceding the current pre-amp per row devices, one with good linearity another with a non-linear response, suggests that this is a problem in the readout electronics. The non-linearity in the pre-amp per row devices is more problematic. First, the row pre-amps each consist of a single FET. FETs are not inherently linear components, and, unless operated correctly, produce a non-linear response. As a result, the observed non-linearity in the CID 38SG and CID 17PPRA may be due to a combination of device architecture and readout electronics. Carbone (1996) has indicated that the problem is opposite to the prior speculation by Pilon and Bilhorn. Carbone suggests that the problem is related to row collection of charge in the present
Figure 2.13: Photometric Response Curve for CID 17PPRA

Photometric response curve for the CID 17PPRA. Heavy line is integrated intensity. Light line is a first derivative plot for the integrated intensity data. As can be seen, the device is not linear over any portion of its range.
electronics. Row collection was originally adopted by Pilon who noticed that device performance was improved when using row collection. Based on this work, row collection was adopted by CIDTEC and incorporated into the SCICAM hardware and software used in these studies. Rather than decreasing the row capacitance as the device well capacity is being reached, the capacitance increases, resulting in the behavior observed.

Sims (Sims et al., 1987b) described a method for cross-talk correction to enhance photometric response. True (True et al., 1996) has shown that injection of areas outside the region of interest improves linearity. Correcting output nonlinearity is possible provided the exposure conditions of the experiment and the calibration procedure are similar. Such a procedure was adopted by Bilhorn (1987) and also suggested by Pilon (1991) using a second order polynomial. The data in figure 2.13 may be fit to a second order polynomial up to about 80% of the maximum signal. To fit the range up to 90% of the maximum signal required a 4th order polynomial. None of these procedures are entirely satisfactory. In practice, such linearization procedures are of limited utility since the output depends on whether the entire device is illuminated or only a small portion. For practical applications, it is imperative to verify that under the conditions of the experiment suitable linearity is observed. Additional discussion of CID linearity may be found in True (1996) and True et al. (1996).

The non-linear output of the device makes calculation of the full well capacity problematic. Pilon (1991) measured the well capacity of the CID 17PPRA to be $9.6 \times 10^5$
carriers. No correction for linearity was performed. The data in Figure 2.13 indicate a well capacity of $6.9 \times 10^5$ carriers if no correction is applied. If a correction is applied, the well capacity is $1.0 \times 10^6$ carriers.

2.8 Quantum Efficiency

Quantum efficiency is a measure of a device’s ability to detect photons. There is some variation in the literature as to the definition of this term. Usually, it is the ratio of incident to detected photons expressed as a percent. Some workers have broadened the definition to be the ratio of incident photons to detected charge carriers (Barnard, 1993). This quantity is more appropriately called quantum yield. Under the usual definition, the maximum measured quantum efficiency should never exceed 100%. This definition is adopted here, since the broader definition is absurd in the X-ray region where the number of photoelectrons generated from a single photon can exceed several thousand.

In the optical range, quantum efficiency can be measured through the use of a calibrated light source. Here, a NIST traceable photodiode (EG&G UV 444BQ) was used to calibrate the output from a monochromator. The number of photons passing through the exit aperture is measured using the photodiode. The number measured using the photodiode is compared to the number of carriers generated in the CID. Quantum efficiency curves for the CID 17PPRA, the CID 38SG, and the CID 38Q-A and CID 38Q-B are shown in figure 2.14. For these measurements, some devices were coated
Quantum efficiency curves for the CID 38-A, CID 38-B, CID 38SG, and CID 17PPRA. The CID 38Q-B and the device labeled CID 38SG-2 have Metachrome II coatings to enhance UV response.
with Metachrome II to enhance UV performance. This fluorescent substance absorbs UV light and re-emits it at longer wavelengths.

The CID 17PPRA was previously examined and reported to have a QE maximum of 82% at 550 nm. This is almost double the value of 45% reported here. The value of 82% at 550 nm is also inconsistent with other measurements made on the CID17 (Sims. 1994). Given the known reflection losses off the SiO$_2$ surface layer and Al straps, the previous results are probably high.

2.9 Dark Current

Dark current can be a significant source of temporal noise in measurements made with a charge transfer device. In previous measurement with CIDs, liquid nitrogen cooling was used to reduce the magnitude of dark current. When cooled to liquid nitrogen temperatures, CIDs show negligible dark current, and (Pilon. 1991) could not be measured with any accuracy.

When cooled to liquid nitrogen temperature, dark charge generation is exceedingly slow. Even if 1000 re-reads are used, 10-20 carriers/per pixel must be generated before a measurement of reasonable accuracy can be obtained. This can take days or weeks.

There are a number of disadvantages to liquid nitrogen cooling. Liquid nitrogen is expensive, requires high vacuum, and requires frequent filling if measurements are to
be made over several days. A further problem with the use of liquid nitrogen cooling is that the rate of charge recombination is slow enough that it can be very difficult to clear accumulated charge from the device when cooled to liquid nitrogen temperatures. Great care must be exercised when using CIDs at liquid nitrogen temperatures or image ghosts may be observed in acquired images. For this reason, it is desirable to evaluate the amount of dark current generated as a function of the temperature of the device. With such data, a cooling system can be selected which is most convenient for a particular experiment.

A CID 38SG and a CID 38Q-B were supplied by Thermo-Jarrell-Ash Corporation installed in a refrigerated housing with a variable temperature refrigeration unit. Using this system the dark current was measured over the range from -100 to 0 degrees Centigrade. These data are plotted in figure 2.15. The CID 38SG device showed dark current values similar to high quality CCD devices (Strunk et al., 1993). The CID 38Q-B had a higher dark current at all temperatures of measurement and the rate of decrease with temperature was lower than seen in the CID 38SG. No CID 17PPRA devices were available for the cryogenic assembly which is used with this refrigeration system so comparable measurements could not be made.

2.10 Hysteresis Effects

Hysteresis effects in CIDs have been described by Sims (Sims, 1987). The
Figure 2.15: Dark Current of CID 38Q-B and CID 38SG

Dark current for the CID 38Q-B and the CID 38SG. The filled squares are for the CID 38SG. The solid diamonds are the CID 38Q-B. The CID 38Q-B device had between 4 and 40 times greater dark current depending on the temperature of measurement.
hysteresis reported by Sims in non-pre-amp per row CIDs is due to release of trapped charge from slow trap sites at the SiO$_2$/Si interface. A previously undescribed type of hysteresis was observed during imaging studies using the CID 38SG at liquid nitrogen temperatures. This hysteresis is observed when the device is turned on while at liquid nitrogen temperature. The first image taken with the device will appear normal. When this image is cleared a residual "ghost" image will appear. Repeated attempts to clear the charge are unsuccessful using the normal injection procedure. If the device is turned off, then turned back on the image clears completely. This type of hysteresis has since been observed by others (Joy, 1994; Jovin, 1995).

This hysteresis is due to the way in which charge is collected and stored in a CID. The charge is collected in a potential well beneath a pair of crossed electrodes. During charge collection, the electrodes are biased negatively with respect to the device epitaxy. During injection, the bias voltage is set close to the epitaxial layer. During this process the potential difference between the epitaxial layer and the inject level may vary from 0.0 V to a few tenths of a volt. Values close to zero are not recommended because a larger "fat zero or foot region is seen. This is due to de-population of trap sites. If the inject level is set slightly lower than the epitaxy, a small potential well still exists. At liquid nitrogen temperature, there is not enough thermal energy present to inject all of the stored charge. Some of it stays in the well giving rise to a "ghost" image. This type of image ghost is rarely seen in devices operated in refrigerated housing or at room temperature. Under these conditions, carrier generation in the dark fills the residual well and thermal
energy allows the trapped charge to migrate more rapidly.

Injection voltages need to be chosen carefully and for best results a bias image should be collected. A bias image must be taken after the previous image has been injected. This allows the "ghost" image to be removed. Subtraction of a bias image also raises the effective read noise in an image. Another approach to this hysteresis is to expose the entire device to a saturating light level and then inject. This leaves the potential wells filled evenly after injection.

A second type of hysteresis was observed during imaging of Laue patterns. This type of hysteresis was a ghost image which appeared even after proper collection of bias images. This type of ghost appeared intermittently during data collection. Although the exact cause is unknown, it is believed to be from partial warming of the camera system during long exposures. Under these conditions the charge trap sites de-populate based on their level of prior saturation. This type of hysteresis is probably of the type reported by Sims (Sims et al., 1987a). An image with this type of hysteresis is shown in figure 2.16.

2.11 Summary and Conclusions

The system gain of four pre-amp per row CIDs has been measured over a wide range of pixel frequencies using the method of mean variance. The exposure sequence, first proposed by Sims (1989), for removing variance due to fixed pattern noise from other sources of variance has been implemented. Further enhancements were made to
Laue image taken with a CID 38SG device using liquid nitrogen cooling. A ghost image from the previous exposure is clearly observed. Full bias subtraction was performed. The ghost image is believed to be due to release of charge from trap sites during image acquisition.
make the method more robust. A theoretical description of the method has been
developed based on the original suggestion by Sims. A series of similar devices have
been examined to evaluate the reproducibility of the method of mean variance and the
amount of device to device variation.

These studies indicate that for CIDs the method of mean variance is subject to
approximately 2-5% error depending on the pixel frequency used. Prior to this work,
similar data on the reliability of the method with CIDs had not appeared in the literature.

The read noise of the four devices was assessed using four different methods. Of
these, only one method A (the intercept method) has previously been described. Methods
similar to method B (paired subarray reads) have been described in the literature for
CCDs, but the implementation described here is based on the read sequence originally
described by Sims and has not appeared previously. Estimates of the read noise of a
device using a set of non-destructive readouts (NDROs) in either a fixed standard
deviation or based on the standard deviation of a moving average have not been
previously reported. Using these methods, good agreement was obtained when
comparable experiments were analyzed. A strong dependence on individual readout
electronics was observed. Hence, the measured values are more appropriately termed
system read noise rather than device read noise. When optimal readout electronics were
used, the measured system read noise for the CID 38SG (<180 carriers/read) and the CID
17PPRA (< 140 carriers/read) are lower than any previously measured values for CIDs.
It is worthy of note that the true device read noise of the pre amp per row generation of
CIDs remains an open question. The values reported here should be considered upper bounds.

Analysis of carefully timed rereads indicates the presence of non-random signals contaminating measurements made with a CID 38SG. This is due to non-optimal electronics and low inherent gain in the devices themselves. Adding gain at the last stage of amplification of a CID 38SG device resulted in theoretically predicted system gain increase. Contrary to the beliefs of the manufacturer, this gain boost raised rather than reduced system read noise.

Prior reports of CID read noise in the literature have used the standard deviation and the standard error of the mean value interchangeably when reporting device read noise. These are statistically distinct quantities with very different meanings and an attempt has been made to keep these quantities distinct. Using the present readout electronics, near theoretical behavior in error reduction through the use of rereads was observed. These measurements were made at low frequency which is probably responsible for their success. It is probable that prior investigations into error reduction using this method used a sampling scheme such that all noise sources did not appear white. Under these conditions the theoretically predicted improvement in the error will not be obtained.

Fixed pattern noise of the CID 38SG and the CID 17PPRA was examined. Neither device was previously characterized for pattern noise. In addition, a method has been presented for isolating the different sources of pattern noise through the construction
of a model of the overall system variance. The second generation pre-amp per row
device (38SG) showed nearly a factor of two improvement in device pattern noise over
the first generation (17PPRA) device.

The linearity of the photometric response function of the CID 17PPRA was re-
examined. The data collected for the studies presented here as well as data collected by
True (1996), Pilon (1991), Bilhorn (1987), and Sims (1989) suggest this result is not
clearly due to the presence of the on chip pre-amps, row collection, or decreasing row
capacitance as has been previously suggested (Bilhorn, 1987; Sims, 1989; Pilon, 1991;
Carbone, 1996). The effect is of considerable concern since the magnitude of the non-
linearity depends on exposure conditions of the device. While considerable attention has
been paid to this issue in this dissertation, the origin of the linearity problems of the CID
camera systems examined in these laboratories over the last 15 years should be
considered an open question. Rectification of the problem should be a high priority in the
future.

The quantum efficiency of the four devices has been measured. Data taken on the
CID 17PPRA indicate that previously reported values are high. The addition of a UV
down converter to the surface of the device results in improved UV performance while
lowering the QE in the visible slightly.

No data describing the behavior of the dark current with temperature in these
deVICES existed. Data are now available over the range from 0 to -100 degrees C for the
CID 38Q-B and the CID 38SG.
A previously undescribed form of hysteresis in CIDs has been reported and an explanation proposed. A number of other laboratories have now indicated similar problems with the devices. This type of hysteresis is correctable using appropriate bias images after image injection. Charge trap hysteresis, previously described by Sims (Sims, 1987), has been observed in the more recent generation of devices.

CIDs have previously been found to be uniquely suited to certain specialized forms of scientific imaging such as atomic emission spectroscopy. In this application, small regions of the device are exposed to light and they have excellent performance. Rigorous evaluations of the devices for other types of imaging are unavailable. The data presented here represents a first step toward evaluating CIDs for general imaging purposes.
CHAPTER 3

Evaluation of Charge Injection Devices for Use as Detectors for X-rays*

The goal of an energy resolved area detection system for Laue diffraction applications required the development and characterization of a camera system. A number of detector systems are available for detection of x-rays in crystallographic applications. These include: photographic film (Helliwell, 1992), scintillation detectors, image plates (Miyahara, Takahashi, Amemiya, Kamiya, and Satow, 1986), multiwire detectors (Xuong, Freer, Hamlin, Nielson, and Vernon, 1978), silicon intensified targets (SITs) (Arndt, 1990; Li, Phillips, Stanton, and Kalata, 1992), charge coupled devices (CCDs) (Phillips, Li, Stanton, Xie, and O'Mara, 1993; Allinson, 1989), and a variety of image intensifiers. All of these systems are in current use and they vary widely in quantum efficiency, dynamic range, and spatial resolution.

* Portions of this chapter have appeared previously in Journal of Synchrotron Radiation 2:215-228 (1995). Where required, these sections are reproduced with permission of the International Union of Crystallography.
CIDs were available for use in this project. Little prior work had been done on the application of CIDs to the detection of X-rays. CID detection offered a unique readout architecture combining many of the capabilities of other detection systems used for crystallographic applications, including direct and indirect imaging and single x-ray photon counting. At the beginning of the project, most of the properties of scientific grade CIDs in X-ray and particle detection applications were speculative. It was believed that these devices would be more radiation tolerant than equivalent grade CCDs. In addition, they had been reported as suited to detection of high energy particles due to "deep depletion" (Wentink and Carbone 1994). Based on the work included in Appendix 1, it is doubtful that this claim has any basis in fact. The first report of X-ray detection using CIDs (Fields et al. 1992) explored the use of CIDs for direct detection imaging applications. No evaluations of CIDs for crystallographic applications of any kind had appeared in the literature in either direct or indirect detection modes.

This chapter describes the construction, characterization, and evaluation of two CID camera systems for Laue Diffraction applications. The chapter will be presented in six sections. In the first section, a statement of the goals of the system will be presented as well as a brief introduction to the problems of Laue pattern detection. In the second section, the properties of CIDs will be reviewed in light of the possibilities of using them for detection of X-rays. In the third section, the systems constructed and the methods applied to their evaluation will be presented. In section four, the results generated with the prototype camera systems will be reported. These results will be discussed in section
five. The last part of the chapter presents the conclusions of this research.

3.1 Introduction and Goals

When the energy bandwidth of the incident “white” beam in a Laue experiment is sufficiently wide, multiple orders of diffraction can be observed. This results in the harmonic overlap problem (Helliwell, 1992) in which reflections appear at the same position in space but with energies consisting of integral multiples of $\lambda/n$. Depending on the energy bandwidth of the incident beam, the overlapping orders may obscure the systematic absences useful for space group determination. The reflections produced from overlapping orders represent approximately 10-20% of all reflections (Cruikshank, Helliwell, and Moffet 1987). It would be desirable to allow these reflections to be used for both space group determination and structure refinement. Although progress has been made toward using Laue diffraction data for unit cell determination (Carr, Dodd, and Harding, 1993), in studies where structure refinement was performed using Laue diffraction data, the space group and/or the unit cell parameters were pre-determined using monochromatic x-rays (Helliwell, et al., 1989; Gomez de Anderez, et al., 1989). Solutions to this problem involve corrections applied to images on film and require digitization of the film image for later analysis (Hao, Campbell, Harding, and Helliwell, 1993) or mathematical deconvolution of data from different crystal orientations (Campbell and Hao, 1993). A second, related problem, is the spectral overlap problem...
(Cruikshank, Helliwell, and Moffat, 1991) in which spots from different crystal planes are sufficiently close together in space to make intensity measurement difficult. An ideal energy resolved measurement system would allow the intensities of individual components of both types of overlapping spots to be determined.

Energy resolved measurements of X-rays can be made in a variety of ways. Traditionally, such instruments have been divided into two classes: energy dispersive and wavelength dispersive. The first class of these relies on the variation in the energies of the individual X-ray photons to create a signal which varies with energy. Examples of this include Si(Li) detectors, avalanch ed photodiodes, and CCDs. Using these devices the size of the output signal is proportional to the energy of the incident X-ray. The second class of instruments rely on the wavelength of X-ray photons to create a signal that varies with energy. These instruments use diffraction to select X-rays of a particular wavelength then many types of transduction systems may be used.

The disadvantages of the use of energy dispersive detectors for the measurement of Laue diffraction patterns are two-fold. First, the devices, even the largest CCDs, are of limited size or are unavailable in a two dimensional array format. Second, they tend to have a performance that degrades with the intensity of the incident beam. For example, the resolution of a Si(Li) detector degrades as the intensity increases. CCDs have strict limits on the number of photons per pixel per frame that can be tolerated before coincidence loss becomes problematic. Further their performance is poor at high energy and they are highly susceptible to radiation induced damage.
To properly extract the information contained in a Laue diffraction pattern, a detection system needs to be available which allows the determination of X-ray energies over a wide area of space. Such systems have precedence in the literature and include: a wide variety of scintillator based technologies (Hailey, Harrison, Lupton, and Ziock, 1989), arrays of Ge detectors, drift chambers, and CCD systems (Lumb 1990; Lumb and Nousek, 1992). None of these, however, has the combination of characteristics suitable for Laue pattern imaging.

Toward the goal of producing such a detector, the use of CIDs for indirect and direct imaging, single photon counting, and possible use as position sensitive energy dispersive analyzers was investigated.

### 3.2 Charge Injection Devices and X-ray Detection

Charge Injection Devices (CIDs) were developed by General Electric Corporation in 1973 (Michon and Burke, 1973) and have been available commercially since 1974. Currently, they are available through CID Technologies, a subsidiary of Thermo-Jarrell-Ash Corporation. Since their introduction, a variety of formats have become available ranging from single pixel devices of 1x2 mm, the CID75 (Sweedler, Denton, Sims, and Aikens, 1987), to 786x612 pixel devices, the CID22 (Zarnowski, Carbone, Carta, and Pace, 1994). CIDs have found use as detectors for atomic emission spectroscopy (Bilhorn and Denton, 1989) and commercial instruments incorporating CIDs are available.

A CID consists of a two dimensional array of pixels as illustrated in Figure 3.1. Each pixel contains a pair of crossed polysilicon electrodes over a SiO$_2$ insulating layer covering an n-doped layer of epitaxial silicon. The epitaxial layer is 15-38 microns thick with 5 ohm-cm resistivity (Van Gordan and Zarnowski. 1995) and grown on a p-doped substrate. Surrounding the crossed electrodes in each pixel is a field implant oxide which practically eliminates interpixel charge transfer, making CIDs highly resistant to the charge blooming observed in CCDs. One electrode from each pixel is connected to all other electrodes along its row with an aluminum strap. The other electrode is connected to other pixels in its column in a similar fashion. The electrodes are negatively biased such that photo generated charge is collected in the form of holes. Photo generated charge may be transferred from one electrode to the other in a procedure that is referred to as a "slosh." The ability to transfer charge within the pixel forms the basis for reading the device. Each pixel may be addressed individually in a pseudo random fashion by selecting the row and column by a set of on chip shift registers. The collected charge is not lost during the readout and a pixel may be read multiple times.

Two devices, the CID 17PPRA and the CID 38SG, were evaluated for use in X-ray detection. As described in chapter 2, both the CID 17PPRA and the CID 38SG
Figure 3.1: CID Architecture

Array architecture of a CID pre-amp per row device. Pixels of a large format array device are addressed using row and column shift registers. Electrodes consist of crossed polysilicon insulated by an oxy-nitride layer. Individual pixels are isolated by an oxide implant. All the electrodes along a row are connected with an aluminum strap, as are all the electrodes along a column. The row pre-amplifiers serve to give on chip gain which results in roughly an order of magnitude decrease in device read noise.
incorporate an on chip FET pre-amp for each row of the device and are designed for scientific imaging applications. The pre-amp per row architecture has been found to be useful for reducing device read noise by almost a factor of 10 (Michon, 1987), hence its incorporation into scientific grade devices where low read noise is desirable.

Readout of a CID depends on the change in voltage that occurs when charge is moved in or out of a capacitor. This relationship is given in equation 3.1.

\[
\frac{dQ}{dV} = \frac{1}{C}
\]

The readout process is illustrated in Figure 3.2. Several nomenclatures are in current use to designate the electrodes. CID Technologies refers to Row and Column electrodes. Other authors refer to Collect and Sense electrodes or Drive and Sense. In the pre-amp per row devices, row and sense can always be considered equivalent. Some ambiguity is introduced by the current practice of both collecting and sensing charge with the same electrode. In previous devices, either the row or the column could be used for readout or collection and collection of photo-generated charge has been done with either the row or the column electrodes. To stress the readout mechanism, drive and sense have been adopted here with the drive corresponding to whichever electrode is not used to sense charge. This usage is slightly different than is found in previous publications but best reflects the device readout used here. During charge collection (Figure 3.2 (a)) both
Schematic representation of readout in a CID. During charge accumulation and readout the drive high and sense high are held at 6.75 V. The drive low is set to -3.75 V and the sense low is held at 1.5 V. During charge recombination ("injection") both drive and sense are set to 7.70 V. Epitaxial layer is set to 8.19 V. (See text for additional details.) These voltages can be changed. For example, setting the drive low potential 0.6 V lower and sense low potential 0.3 volts lower will increase the well capacity somewhat.
drive and sense electrodes are negatively biased with respect to the epitaxial layer and the sense electrode is held more negative than the drive electrode. A pixel read is performed after disconnecting the sense electrode from its reference potential. The potential of the sense electrode is sampled before (Figure 3.2 (b)) and after (Figure 3.2 (c)) the voltage on the drive electrode is taken more negative than the sense electrode. The change in potential at the drive electrode causes the charge under the sense electrode to migrate to the drive electrode. Following read out of the pixel, the potential on the drive electrode is returned to its original value. To clear accumulated charge in the device the potential on both electrodes are collapsed (Figure 3.2(d)) and charge recombination occurs. It should be noted that readout does not affect the ability of the device to collect charge.

Readout of an individual pixel is done by selecting the row and column corresponding to the pixel with a pair of on-chip shift registers. This gives the capability of random pixel access. This is in contrast to CCDs in which each pixel must be read in a sequential fashion by first moving the collected charge to a parallel register then to an output amplifier. At present, the on-chip shift registers are unidirectional leading to the current generation of devices sometimes being described as pseudo-random access. The present generation of devices have an approximately 6-100 kHz pixel rate. This is slower than many CCDs, especially compared to CCDs with 20-30 e- of noise. CCDs of this type can operate well at pixel rates over 1 MHz. Recently, devices with pixel rates well over 1 MHz have been shown to give read noise of less than 6 e-. Many of these devices
have also been designed to allow parallel readout through multiple output nodes and amplifiers (Denton, Fields, and Hanley, 1996). In contrast to these higher speed CCDs, the advantage of CIDs is the rapid readout of individual pixels at random locations on the device, without disturbing the collected charge. A CCD must always be exposed for a specified period of time. In a CID, the option of exposing the device until a specified signal to noise ratio is reached is available.

In comparison to CCDs, CIDs typically have a slightly greater full well capacity and greater flexibility of readout. CIDs have a greater read noise (140 for a single read of a CID 17PPRA vs. 4-6 e- for typical scientific grade CCDs). Models of CID noise assume that preamplifier noise dominates all other noise sources (Van Gordon and Carbone, 1994). Such considerations place a practical limit of about 110-165 e- in the CID 17PPRA and the CID 38SG. As other sources of noise degrade the signal, a somewhat higher read noise is usually obtained.

Unlike CCDs, which are read destructively, the photo-generated charge collected in the CID imager can be read multiple times, even during image acquisition. If the charge in a pixel is read n times, the error in the measured signal, $e_m$, can be reduced by the square root of the number of reads as described in equation 3.2 (see also section 2.4 and Chapter 4). $\sigma_r$ is the noise for a single read.

$$e_m = \frac{\sigma_r}{\sqrt{n}}$$  

3.2
Use of multiple reads on each pixel lowers the full frame read rate.

The dynamic range of a CID can be extended beyond the range predicted by the full well capacity using a process referred to as random access integration (RAI). RAI involves varying the time of integration for each portion of interest in an image depending on the intensity of the region. Signal levels are monitored during exposure and signal levels recorded when a desired signal to noise ratio is reached. Using this technique dynamic ranges in excess of eight orders of magnitude have been demonstrated (Bilhorn and Denton, 1990). The dynamic range of both CIDs and CCDs can be extended through the use of co-addition of multiple pixels and frames. This topic is discussed extensively in Chapter 4.

In older CIDs, the amount of charge collected in a pixel was assessed by measuring the amount of charge “injected” into the pixel after exposure. This was a “destructive” readout method and has been almost completely replaced by the non-destructive technique. In current use, “injection” refers to the process of clearing a stored image. Three separate processes are available to perform this operation: global injection, subarray injection, and global knockdown. In a global injection, the voltages on all the row and column electrodes are set close to the voltage on the epitaxial layer. This collapses the potential well that confines the charges allowing them to recombine.

Subarray injection is similar. Instead of all the row and column voltages being set to near epitaxial voltage, only the voltages of the row and column corresponding to a particular
pixel are collapsed. This allows the charge in a single pixel to recombine. To inject a subarray, this process is repeated for each pixel in the subarray. In the case of subarray injection, the time for injection of each pixel is determined by the speed of the shift registers. In global injection, the injection voltages can be held arbitrarily long. Since the process of injection is slightly different, some hysteresis is to be expected between subarray and global injections.

Global knockdown is similar to global injection except the voltages are set to a level less than that of the epitaxial layer. This voltage may be adjusted arbitrarily within the limitations of the driver electronics. By setting the "knockdown" voltage the depth of the well under each electrode is temporarily changed. If the well depth is no longer large enough to hold all of the trapped charge the remainder recombines. The result is to clear all pixels containing more than a selected amount of charge.

Injection voltages must be selected judiciously. If the global injection voltage is set too close to that of the epitaxial layer, it can release charge confined to surface trap sites. Depletion of trap sites results in a "foot" or "fat zero" in the response function of a CID. If the voltage is set too far from that of the epitaxial layer global injection behaves like a global knockdown and ghost images will be observed after injection. This latter effect is particularly evident at liquid nitrogen temperature.

CIDs can be used for both indirect and direct detection of X-rays. In indirect detection, the X-ray photon is converted to visible light with the use of a phosphor. The phosphor can be followed by a microchannel plate, fiber optic taper, or a lens prior to
conversion of optical photons to charge in the CID. In direct detection, X-rays are allowed to directly interact with the CID. This process results in the production of multiple hole pairs being created for each X-ray photon. Replacement of CCDs in indirect X-ray imaging applications with CIDs will allow for the collection of high dynamic range images with the additional advantages of resistance to charge blooming, non-destructive readout, pseudo-random pixel access, selective pixel reset, and random access integration.

For direct detection of X-rays, CIDs offer the possibility of high speed, position sensitive, energy dispersive area detection which is currently unavailable in any detector. Although this possibility was not realized with the present generation of devices, data is presented showing the basis for such an energy dispersive detector. CCD systems have been described which perform similar functions (Janesick, Elliott, Bredthauer, Chandler, and Burke, 1988; Lumb, 1990) but the destructive readout of CCDs makes the approach described here impossible. The inability of a CCD to randomly readout individual pixels would require extremely high frame rates and 0.018 photons pixel$^{-1}$ frame$^{-1}$ has been given as a practical limit in CCDs (Lumb and Nousek, 1992). Devices with active pixels (Beker et al., 1993; Delpierre et al., 1992) could also be developed with the capability of measuring position, energy, and intensity. Such detectors are at an early stage of development at present and will remain prohibitively expensive for the immediate future.
3.3 CID X-ray Camera System and Test Methods

Characterization of the devices was performed using the method of mean variance to measure system gain and read noise (Mortara and Fowler, 1981; Sims and Denton, 1987). Fixed pattern noise is excluded from these measurements by the use of two exposures of the same subarray for each level in the mean-variance measurement (Sims, 1989). Variance is then computed on the difference between the subarray images. Knowledge of the system gain allows the quantum efficiency to be measured. A NIST traceable photodiode reference was used (UV-444-BQ EG&G) to calibrate the light source for measurements of quantum efficiency (Sims and Denton, 1987). The UV-Vis characterizations are generally applicable to any system that would use these devices for indirect detection of x-rays. Device random access was tested using 10,000 randomly positioned pixel reads at four gain settings. All characterizations were done with devices operated with liquid nitrogen cooling.

Indirect imaging of diffraction patterns used a CID 38SG device installed in a commercially available camera system (Van Gordon, Hutton, Fassett, and Carbone, 1993) (SiCAM CIDTEC Liverpool NY). This camera consists of a vacuum dewar for cooling the detector to liquid nitrogen temperatures. The indirect imaging system consisted of a 50 mm lens (Nikon) and a MIN-R (Kodak) medium x-ray phosphor. This camera was installed on the base of a modified precession camera (Enraf-Nonius) and attached to one port of an Enraf-Nonius FR571 rotating anode X-ray source with a molybdenum anode.
The unfiltered direct beam was used to generate the Laue diffraction pattern. The system operating conditions were as outlined in Table 3.1. The crystal systems used to demonstrate indirect imaging are reported in Table 3.2. A block diagram of this apparatus and a photograph of the system appear in Figure 3.3. Linearity was assessed by measuring the charge accumulated in areas corresponding to both strong and weak diffraction spots as a function of the time of illumination.

Direct imaging was performed using a CID 17PPRA device installed in a custom designed camera system. A liquid nitrogen dewar (IR Laboratories, Tucson) fitted with a 0.005 inch Mylar window allowed for passage of x-rays while providing a vacuum seal for the dewar. An additional layer of black plastic covered the Mylar window to block visible light. The camera system was mounted on the base of the precession camera previously described. X and Y position was controlled remotely using a pair of stepper motors. The Enraf-Nonius FR571 rotating anode X-ray source used for indirect imaging was used as a source for the generation of the Laue diffraction pattern. Single photon counting measurements were made on selected reflections from the Laue pattern of naturally occurring MoS₂ and using a Phillips X-ray source with a Copper target. No physical changes are required to use this direct camera for photon counting. The main difference in approach is that instead of a full frame read a single pixel is repeatedly read. The system conditions used for direct imaging and photon counting are summarized in table 3.1. The crystal systems used to demonstrate direct detection and photon counting are presented in table 3.2. Figure 3.4 gives a block diagram of this camera system and a
### Table 3.1: System Operating Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Indirect Imaging</th>
<th>Direct Imaging</th>
<th>Photon Counting</th>
</tr>
</thead>
<tbody>
<tr>
<td>CID Type</td>
<td>CID 38SG</td>
<td>CID 17PPRA</td>
<td>CID 17PPRA</td>
</tr>
<tr>
<td>CID Gain</td>
<td>100</td>
<td>100</td>
<td>240</td>
</tr>
<tr>
<td>Pixel Frequency</td>
<td>20 kHz</td>
<td>20 kHz</td>
<td>9.43 kHz</td>
</tr>
<tr>
<td>Read noise</td>
<td>178 e-</td>
<td>140 e-</td>
<td>190 e-</td>
</tr>
<tr>
<td>System gain</td>
<td>80.6 e-/ADU</td>
<td>53.2 e-/ADU</td>
<td>23.7 e-/ADU</td>
</tr>
<tr>
<td>Temperature</td>
<td>Liquid N2</td>
<td>Liquid N2</td>
<td>Liquid N2</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphor</td>
<td>Min-R</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Lens</td>
<td>Nikon 50 mm f 1.8</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Window</td>
<td>CaF2</td>
<td>Mylar</td>
<td>Mylar</td>
</tr>
<tr>
<td>Read Type</td>
<td>Full frame</td>
<td>Full frame</td>
<td>Single Pixel</td>
</tr>
<tr>
<td></td>
<td>Single read</td>
<td>Single read</td>
<td>15360 reads</td>
</tr>
<tr>
<td>X-ray Source</td>
<td>Enraf-Nonius FR571</td>
<td>Enraf-Nonius FR571</td>
<td>Enraf-Nonius FR571</td>
</tr>
<tr>
<td>Anode Material</td>
<td>Molybdenum</td>
<td>Molybdenum</td>
<td>Molybdenum</td>
</tr>
<tr>
<td>Anode Voltage</td>
<td>50 kV</td>
<td>50 kV</td>
<td>50 kV</td>
</tr>
<tr>
<td>Anode Current</td>
<td>100 mA</td>
<td>50 mA</td>
<td>50 kV</td>
</tr>
<tr>
<td>Beam Diameter</td>
<td>0.2 mm</td>
<td>0.2 mm</td>
<td>0.2 mm</td>
</tr>
<tr>
<td>Integration Time</td>
<td>0-4 minutes</td>
<td>0-30 seconds</td>
<td>0-2 seconds</td>
</tr>
</tbody>
</table>

* Gain parameter, GP, and pixel frequency in kHz, PF, are related by the equation:

\[
PF = \frac{1000}{10 + 0.4*GP}
\]

† CID read noise depends on the pixel frequency as shown in Chapter 2.

‡ A Phillips source with a Copper target was also used for single photon measurements.

§ Integration time for photon counting refers to the time of sampling. The pixel is sampled 15360 times during this integration period.
System used for indirect imaging. In this system, X-rays generate optical photons after striking a MIN-R phosphor and are imaged using a lens. The CID 38SG is installed in an evacuated dewar with liquid nitrogen cooling. The focused light passes through a CaF$_2$ window before reaching the active surface of the CID 38SG. Readout electronics are not shown. The dewar, window, and readout electronics are as supplied with the SiCAM system by CID Technologies.
Figure 3.4: Direct Camera System

System for direct imaging. In this system the window, lens and phosphor are removed and replaced with a 0.005 inch Mylar window. This allows most X-rays to pass through the window where they strike the CID 17PPRA device. The number of carriers generated per arriving X-ray photon depends on the energy of the incident x-ray. The dewar, window, and readout electronics were assembled or modified and have slightly higher system gain than is found in the standard SiCAM camera system. For most purposes direct detection can be performed with the standard instrument after replacement of the window with 0.005 inch Mylar. Shown also in the figure are readout electronics (lower left corner), Y-position motor (upper left), X-ray source (right).
Table 3.2: Crystal Test Materials

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Indirect Imaging †</th>
<th>Direct Imaging</th>
<th>Photon Counting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraphenyl-phosphonium tetrachloro-oxomolybdenum (V)</td>
<td>MoS$_2$ naturally occurring</td>
<td>MoS$_2$ naturally occurring</td>
<td></td>
</tr>
<tr>
<td>Orientation</td>
<td>Random</td>
<td>Beam parallel to c</td>
<td>Beam parallel to c</td>
</tr>
<tr>
<td>Crystal space group</td>
<td>P4/n (Carducci, 1994)</td>
<td>P63/mmc</td>
<td>P63/mmc</td>
</tr>
<tr>
<td>Unit cell parameters</td>
<td>a = 12.7306; c = 7.6845 (Carducci, 1994)</td>
<td>a$_0$ = 3.1604 Å, b$_0$ = 12.295 Å (Wyckoff, 1963)</td>
<td>a$_0$ = 3.1604 Å, b$_0$ = 12.295 Å (Wyckoff, 1963)</td>
</tr>
</tbody>
</table>

Since photon counting is done by repeatedly reading a single pixel during charge accumulation a derivative is computed to observe single photon events. Here, the derivative is computed on a 50 point moving average. As indicated by equation 3.2, this lowers the measurement noise by a factor of 7. Conversion of measurements made in (arbitrary digital units) ADU to energy values in eV were made using measured system gains in carriers per ADU and the average energy required to generate an electron hole pair in Si (3.65 eV). Single photon counting used a discriminator set to approximately 150 eV. Single events greater than this value were counted and the event height measured. This corresponds to a single event height of slightly less than 2 ADU at a CID

*All data was collected using Laue geometry and the unfiltered “white” beam from the FR571. † Linearity of the indirect camera system was assessed using MoS$_2$ under conditions identical to those used here for direct imaging.
gain parameter setting of 240.

Radiation damaged devices were annealed in a vacuum oven at 180°C for 8 hours.

Images were generated with IRAF (National Optical Astronomy Observatories, Tucson), running on a SparcStation II (Sun Microsystems).

### 3.4 CID X-ray Camera System Results

Optical characterizations of the devices can be found in Chapter 2. Figure 3.5 shows the relationship between the single pixel read rate for 10,000 randomly positioned pixels, the number of non-destructive readouts (NDROs), and the gain parameter. Figure 3.5 indicates that selected regions of the device can be read at rates much higher than would be possible for a CCD of similar size.

Indirect imaging:

Figure 3.6 shows a series of Laue diffraction patterns generated by tetraphenylphosphonium tetrachloro-oxomolybdenum (V) in a random orientation. The first image Figure 3.6a shows a typical diffraction pattern from this crystal. In the second image, Figure 3.6b, a streak extending the full width of the device appears along the row axis. This is due to row crosstalk. Crosstalk is seen in this device when some of
Figure 3.5: Read Rate for Randomly Positioned Pixels

Data showing read rates for 10,000 randomly positioned pixels on the CID 17PPRA device. The number of rereads per pixel varied from 10 to 50. The maximum read rate at a gain of 100 was 25,000 reads per second with 100 reads per randomly positioned pixel. The intercept of this plot corresponds to the time required for positioning the select registers to 10,000 randomly selected chip locations. This operation can only be done at about 380 Hz (2.6 msec/operation).
Figure 3.6: Indirectly Detected Laue Patterns

Indirect Laue pattern of tetraphenylphosphonium tetrachloro-oxo-molybdenum (V) imaged using the CID 38SG device. Figure (a) shows the image after 843 seconds of exposure. Figure (b) shows the same image after further exposure showing the development of row-crosstalk. This figure is shown using gradient filtering to allow easier visualization of the crosstalk. The crosstalk appears as a streak extending the length of the y-axis and is roughly 6 pixels high across. Saturation of the brightest reflections has occurred along these rows. Figure (c) shows the same data presented in (b) except with the application of the gradient along the row axis. This effectively removes all the observed crosstalk. In (b) the gradient was computed at a 45 degree angle to the y-axis. For more information on crosstalk see True (1996) and True et al. (1996).
Table 3.3: Linearity Results for Indirect Detection

<table>
<thead>
<tr>
<th>Reflection</th>
<th>Slope (ADU/sec)</th>
<th>Intercept (ADU)</th>
<th>$R^2$</th>
<th>Linearity (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>396.3±7.7</td>
<td>691±6320</td>
<td>0.997</td>
<td>1.9</td>
</tr>
<tr>
<td>B</td>
<td>262.0±4.4</td>
<td>804±3627</td>
<td>0.998</td>
<td>1.6</td>
</tr>
<tr>
<td>C</td>
<td>76.3±1.2</td>
<td>-773±998</td>
<td>0.998</td>
<td>1.6</td>
</tr>
<tr>
<td>D</td>
<td>5.12±0.20</td>
<td>-271±164</td>
<td>0.990</td>
<td>3.9</td>
</tr>
<tr>
<td>E</td>
<td>0.425±0.09</td>
<td>-123.2±73</td>
<td>0.790</td>
<td>21</td>
</tr>
<tr>
<td>A vs. B</td>
<td>0.6614±0.0044</td>
<td>415.5±1426</td>
<td>0.9997</td>
<td>0.6</td>
</tr>
</tbody>
</table>

* Linearity is expressed as the standard error divided by the slope.

The pixels along a row have reached saturation and has been noted previously (Sims and Denton, 1987; Bilhorn, 1987; True, 1996; True et al., 1996). Under most conditions this behavior has been eliminated, however, it may be present when pixels along a row have reached saturation. In the image shown here the effect is small representing about 20 ADU (approximately 2000 carriers). The appearance of row crosstalk can be removed from an acquired image by the application of a gradient filter. This is shown in 3.6c in which the gradient has been computed along the row axis. In Figure 3.6b, the gradient is computed at a 45 degree angle to the y axis.

Table 3.3 summarizes linearity data from a series of images of MoS$_2$ with increasing exposure time for selected spots. These data are shown in Figure 3.7. The non-destructive readout of the CID 38SG was used to record the data presented in table 3.3. Each successive image included the charge accumulated during the previous time of exposure. The large deviations from linearity in the peaks of lowest intensity are due to a "fat zero" in the response function of the CID 38SG. This is a characteristic of surface
Figure 3.7: Indirect Detection Linearity Plots

Linearity data for 5 different diffraction peaks using indirect detection with the CID 38SG device. The symbols used to represent data points correspond to the data presented in Table 3.3.
channel charge transfer devices and has been noted previously in CIDs (Sims and Denton, 1987; True, 1996; and True et al., 1996). The "fat zero" is caused by trap sites at the Si/SiO₂ interface. In the reflections with greater intensity, the majority of the deviations from linearity appears to be the result of variation in beam intensity over the time of exposure. Residuals analysis of the data for reflections A, B, and C showed that each had a similar positive deviation for time points 6 and 7 (804 and 1150 seconds respectively) suggesting instability in the incident beam. Regression of A against B, presented in table 3.3, shows clear improvement. Pre-amp per row CIDs deviate from linearity when approaching full well (Bilhorn, 1987; Pilon, 1991; True, 1996; True et al., 1996; Chapter 2, this dissertation). This deviation may be corrected by application of a second order correction to the raw data (see chapter 2 for details and limitations of this procedure). No correction was applied to the data in table 3.3. In the image with longest exposure, the ratio between spots of highest and lowest intensity is 840.

Direct detection:

Figure 3.8 shows a direct image of a portion of the diffraction pattern of MoS₂. Figure 3.9 shows linearity data for the direct detection of x-rays from MoS₂ Laue diffraction. In these exposures, no "fat zero" was seen and the linearity was slightly better than in the indirect images acquired using the CID 38SG. The better linearity is thought to be the result of the shorter exposure times employed in these experiments.
(0-30 seconds). The absence of the "fat zero" in the response function of the CID 17PPRA used here is largely due to the large number of carriers generated for each x-ray photon.

Figure 3.8 also shows a section of the device that has been damaged by exposure to x-rays. This section appears in the lower left side of the image and is unresponsive. It should be noted that this region does not affect the response of the remainder of the device. This reflects the architecture of the CID in which charge is read in place rather than moved to a register for readout. The damage to the CID 17PPRA device was the result of exposure to the direct unfiltered beam from the rotating anode generator. Best estimates of the radiation dose based on ion chamber readings of the beam indicate this region received 50,000-100,000 rads. At present these values should be considered estimates since the exact length of exposure is unknown (15-30 minutes) and the ion chamber readings from the white beam are approximate (200,000 rads/hr). Annealing in a vacuum oven at 180°C for 8 hours allowed the insensitive region indicated in Figure 3.8 to become responsive to light. Annealing of the devices resulted in a change in device fixed pattern.

Some tests were also performed in which the CIDs were flooded with UV light. Treatment of CCDs with UV light has been shown to reverse some types of radiation damage. Little improvement was observed after these treatments.*

* This work was done with the at the suggestion of Dr. Pierre Dhez.
Figure 3.8: Direct Detection Images

Direct detection of a reflection from MoS$_2$ using the CID 17PPRA device. A localized region of damage from the direct beam of the rotating anode appears in the lower left portion of the device. These images are two different representations of the same data set. The image on the left uses linear contrast. This image shows more clearly the lack of response in the damaged region. The image on the right uses gradient contrast and shows the pair of peaks due to diffraction from the MoS$_2$ more clearly.
Figure 3.9: Direct Detection Linearity

Linearity data for direct detection of diffraction from MoS₂ using the CID 17PPRA. Maximum time of exposure was 30 seconds. Overall linearity was 0.8%.
Single Photon Counting:

Figure 3.10a presents raw data showing a portion of a set of 15360 reads of a single pixel during exposure to x-rays from a reflection from naturally occurring MoS$_2$. The 15360 reads took 2 seconds to complete. Several events are clearly visible in the set of reads, appearing as steps in the amount of charge collected in the pixel. The 47 events observed in this figure correspond to approximately $5 \times 10^6$ photons/cm$^2$-sec detected by the CID. Figure 3.10b shows a similar set of reads from the same pixel with the x-ray shutter on the rotating anode closed. No events were seen in this set of reads and no general upward trend to the data was seen. Figure 3.10c and Figure 3.10d show this data plotted as a derivative to emphasize the steps corresponding to x-ray induced events. Figure 3.12 shows peak heights plotted in the form of a multi-channel analyzer while the device was being exposed to Copper K$_\alpha$ radiation. This figure indicates that roughly 25% of charge produced by a Cu K$_\alpha$ photon is collected in a single pixel.

This photon counting strategy works at both cryogenic and room temperature as shown in Figure 3.11. Under these conditions an offset is seen in the derivative plot from dark carrier generation. At the beginning of a data series higher dark carrier generation is seen. This is thought to be from release of charge from trap sites on the device which have become saturated during the previous data collection cycle.

The events observed in a similar series of reads are plotted in the form of a multichannel analyzer in Figure 3.12. Figure 3.10 and Figure 3.11 show several
Figure 3.10: Single X-ray Photon Counting - Liquid Nitrogen Cooled Camera

Each frame shows 15360 reads from the pixel at position (25,15) of the CID 17PPRA. This position contained a portion of a reflection from MoS$_2$. The lower plots show the derivative of the data in the plot above it. With the beam on a gradual increase is seen with steps from x-ray interactions. With the beam off no equivalent increase is seen: All figures incorporate 50 point smoothing. The energy axis is computed from the system gain parameter and the direct band gap energy for Si (3.65 eV). The maximum event height observed in this set of reads is 1200 eV.
Figure 3.11: Single X-ray Photon Counting - Room Temperature Camera

The data in shown here was obtained as indicated for Figure 3.10 except a room temperature camera system was used. The beam off data set shows a steady increase due to dark carrier generation. The initial rate of dark carrier generation in this plot is greater than seen later in the data series. This is thought to be due to release of charge from trap sites saturated with charge after injection of the previous data set.
Figure 3.12: Histogram of Event Energies

Histogram of events from multiple reads of the CID 17PPRA during exposure to Copper Kα radiation. Although single photon events are readily seen, energy analysis is hindered by incomplete charge collection in a single pixel. Figure indicates that roughly 25% of charge is collected in a single pixel.
limitations of the CID 17PPRA when operated as a photon counter with energy
discrimination. Much of the charge collected in the pixel is the result of interactions
below the 150 eV threshold of the discriminator. Two factors account for this behavior:
incomplete charge collection and split events in which the x-ray generated charge is
collected in several pixels. Both of these effects have been observed in CCDs used in
similar fashion (Janesick, Klaasen, and Elliott. 1987).

3.5 CID X-ray Camera System Discussion

Several features of CIDs recommend their use for area detection of indirect
diffraction pattern images. These are: the large full well capacity, the selective non-
destructive readout, real time evaluation of image quality, and selective detector reset, all
of which combine to give a wide dynamic range. With fixed exposure time and a single
read of the CID 38SG, a maximum dynamic range of 3000 is possible assuming the
minimum detectable charge accumulation in a pixel is twice the single read noise of the
device. The value of 840 measured here is roughly 1/4 of this value. This dynamic range
can be extended by using the RAI and NDRO capabilities of CIDs. An example showing
how a dynamic range of $10^8$ may be obtained is given in table 3.4. Such a wide dynamic
range is very difficult to obtain using a CCD and may be impossible if the strong and
weak peaks are present in the same row or column of the CCD. The CID gives the
capacity to accumulate continuously until a suitable signal to noise ratio has been
Table 3.4: Dynamic Range Computations

<table>
<thead>
<tr>
<th></th>
<th>Peak A</th>
<th>Peak B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge accumulation rate</td>
<td>$10^7$ e-/sec</td>
<td>0.1 e-/sec</td>
</tr>
<tr>
<td>Integration time</td>
<td>0.05 sec</td>
<td>2000 sec</td>
</tr>
<tr>
<td>Signal</td>
<td>$0.5 \times 10^6$ e-</td>
<td>200 e-</td>
</tr>
<tr>
<td>NDROs</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>Read noise</td>
<td>180</td>
<td>18.0</td>
</tr>
<tr>
<td>Dark current noise</td>
<td>$&lt; 1$ e-</td>
<td>14 e-</td>
</tr>
<tr>
<td>$S/N^\dagger$</td>
<td>1390</td>
<td>3.1</td>
</tr>
</tbody>
</table>

reached.

The CIDs used for indirect detection of X-rays have some significant limitations. While they do not have the charge blooming problems of many CCDs, care should be exercised using CIDs under saturating conditions. The devices are not linear when approaching full well capacity, and, under highly saturating conditions, eventually show a decreasing signal with increasing exposure. For better results with X-rays a polynomial correction should be applied to the raw data to obtain a more linear response. In CCDs, saturation of the device can lead to charge blooming to adjacent pixels. While CIDs rarely show charge blooming, when operated under saturating conditions they do show row crosstalk. Crosstalk is to be distinguished from the charge blooming seen in CCDs. Charge blooming in CCDs causes charge to migrate from a heavily exposed pixel to adjacent pixels in both the row and column directions. Unless the entire row or column is saturated, charge does not spread uniformly. In contrast, crosstalk in CIDs is confined to

* These values have been adjusted according to equation 3.2
† $S/N$ here is given as the measured signal divided by twice the read noise.
the row direction, never appearing in both row and column directions, and affects all pixels along the row uniformly. Crosstalk can be removed from an acquired image by the use of a gradient filter computed along the row axis. The use of gradient filtering is satisfactory in this case because the crosstalk appears exclusively along the row axis of the device and affects all pixels along the row equally. If it were charge blooming, gradient filtering would be ineffective. Gradient filtering results in some loss of information and will add to data reduction, but should prove satisfactory for most purposes as seen in Figure 3.6c. Cross-talk and device saturation occur under conditions outside the well capacities of comparable CCDs and, since CIDs can be read non-destructively during data acquisition, conditions causing these effects can be easily avoided. If cross talk is observed in an image prior to destruction of the acquired image the saturated pixels can be selectively reset and the image reread.

The “fat zero” noted here is a characteristic of surface channel charge transfer devices. At the Si/SiO₂ interface of a CID, or surface channel CCD, a large number of energy states other than the conduction and valence bands of Si are available to hold charge. These “trap” sites are located in a fixed location in the device and can exchange charge with time constants ranging from micro-seconds to hours (Sims and Denton, 1987). When charge injection is done to clear charge from a CID, these trap sites can be depleted. Subsequent exposure will generate charge which will initially fill these sites. Charge confined to trap sites is immobile and not measured during the readout process. This results in a so called “fat zero” or “foot” in the response function of the device.
Discussion of the “fat zero” here is primarily precautionary, since strategies are available to eliminate the problem. Using a procedure similar to “pre-fogging” of film, the CID can be exposed to sufficient light to fill the trap sites with charge. Subsequent use of the re-read capability allows the affects of uneven illumination during this exposure to be eliminated. Alternately, the “knockdown” feature of the CID can be employed to assure that trap sites are not depleted when the device is cleared (Van Gordon, Hutton, Fassett, and Carbone, 1993).

Direct Imaging:

Many of the advantages discussed in relation to indirect imaging apply here: the large full well capacity, the selective non-destructive readout, real time evaluation of image quality, and selective detector reset. There are a number of important drawbacks to the use of these devices in direct imaging most of which are shared with CCDs: lowered dynamic range, small device formats, and radiation induced damage. Even with a well capacity of $10^6$ electrons, assuming complete charge collection 450 Cu Kα photons in a single pixel will saturate the pixel. CCDs share this disadvantage. With a present maximum active area of 1.96 cm$^2$ for the CID 38SG, applications using a small beam diameter and a short crystal to detector distance are possible. Devices with four times the number of pixels and active area of the CID 38SG are being developed, but the utility of these devices for direct detection of x-rays from diffraction is limited.
Radiation exposure to scientific grade CCDs has been reported to cause degradation resulting in high dark current, voltage shifts, increased surface states, lowered charge transfer efficiency, and bulk damage (Roy, Watts, and Wright, 1989). Some of this damage can be reversed by annealing with heat (Herve, Lefesvre, and Dupont-Nivet), intense UV radiation (Acton, Morrison, Janesick, and Elliott, 1991), or heating in the presence of forming gas (Allinson, Allsopp, Quayle and Magorrian, 1991). CIDs show similar behavior. Although CIDs are expected to be more resilient due to the lower charge transfer efficiency requirements for readout, they are not indestructible as seen in Figure 3.8. At present the behavior of scientific grade CIDs during radiation induced degradation is not known and further work is being done at present. A specialized CID has been shown to withstand in excess of $10^6$ rads when evenly exposed (Zarnowski, Carbone, Carta, and Pace, 1994). In the study on the specialized devices, the clock voltages of the imager had to be adjusted to compensate for FET gate threshold shifts. The uneven voltage shifts produced from uneven exposure to x-rays will prove harder to compensate for than those produced during even exposure, a problem shared with CCDs. The level of radiation tolerance demonstrated in the specialized device has not yet been achieved in a scientific grade device. Both the CID 38SG and the CID 17PPRA devices were optimized for use in optical spectroscopy not X-ray detection. Even without such optimization the CID 17PPRA showed good resilience when exposed to high X-ray fluxes, performing up to approximately 50,000 rads. While some of this damage can be reversed by annealing, the long term behavior of annealed devices needs
to be investigated in more detail as does the behavior of these devices under direct X-ray exposure.

Single Photon Counting:

One of the unique uses of a CID is for single x-ray photon counting. CIDs can be used as position sensitive energy dispersive analyzers, provided the collected charge reflects the generated charge. Although CIDs will have a limited lifetime in the presence of high radiation and the active area is relatively small, they have the potential to operate at higher fluxes than do present CCDs. Figures 3.10, 3.11, and 3.12 show the strategy for using CIDs as energy dispersive detectors, and also shows the limitations of the present devices for this purpose. The shape of the curve in figure 3.12 is similar to CCDs with low charge collection efficiency (Janesick, Klaasen, and Elliott, 1987). Additionally, CIDs have a greater read noise than does a CCD. Construction of Figure 3.12 required the use of multiple NDROs of the CID 17PPRA and could not be done with single reads. The limitation of the CID for this purpose appears to be due to the shallow depletion depth of the CID 17PPRA (Appendix I). This allows charge generated in the device to spread over multiple pixels. This is shown schematically in Figure 3.13.

If a larger number of contiguous pixels are observed in order to sum the charge collected from split events, the high read noise of the CID becomes a limiting factor. For
A carrier in a charge cloud generated by an incident X-ray has several possible fates. It can recombine prior to being collected, it can be collected in the pixel in which it is generated, or it can migrate to adjacent pixels. The depletion depth in a CID 17PPRA is on the order of 5 microns. Carriers generated beneath this depletion region are not strongly attracted to the electrodes on the surface of the device.
example, using the 178 electrons of noise measured for the 38SG, a total of about 250 electrons of noise can be expected after taking the difference between the charge in a pixel before and after an x-ray event is observed. This translates into almost 1 keV uncertainty in the energy of the incident photon. While some of this uncertainty can be removed by the use of multiple rereads, as has been done here, this reduces the speed of the measurement. For example, to reduce the uncertainty in the photon energy to about 100 eV, 80 reads or more must be employed resulting in a lower effective readout rate. At these lower read rates, the only present advantage of CID s over commercially available CCDs for this purpose is a lower sensitivity to radiation induced reduction in charge transfer efficiency. In practice, as seen in Figure 3.12, it is rare that all the charge produced from an interacting x-ray photon is collected in a single pixel. This increases the difficulty of locating and measuring the x-ray generated charge. If a three by three array of pixels is sampled, the number of reads required increases accordingly. Signal to noise expressions become complicated under these conditions (full treatment is given in the following chapter). Although promising in this application, the energy dispersive resolution of the CID s investigated here is poor.

CCDs used for photon counting operation have an upper count rate limit of \( \sim 0.15 \) photons pixel\(^{-1}\) frame\(^{-1}\) for single pixel events and about 0.018 photons pixel\(^{-1}\) frame\(^{-1}\) for events spread over multiple pixels (Lumb and Nousek, 1992). Using a 7.5 kHz single pixel read rate and similar considerations, CID s have a maximum count rate of 1130 photons pixel\(^{-1}\) second\(^{-1}\) for events corresponding to greater than 5 keV. This assumes
10 times read noise for the event height and single reads. For lower energy events, this rate will be reduced by the number of rereads required to obtain a suitable signal to noise. It should be noted that CCDs and CIDs are very different in this capability. CCDs can be used as true multi-channel photon counters, a use that is limited by the high read noise of the CID. CIDs operated as described here are sequential instruments capable of higher count rates in a single pixel. A device with a pixel rate of 500 kHz, currently under development, should be able to reach rates of 15,000 photons pixel$^{-1}$ second$^{-1}$.

The devices studied here were optimized for optical spectroscopy. The CID 17PPRA device has a 14,000 Å SiO$_2$ coating over the surface of the device. This coating seriously limits the direct detection capabilities of the current device. Low energy X-rays will be heavily absorbed in the overlayer leaving only the more energetic and more penetrating, X-rays to interact with the active layer.

Several approaches can be taken to optimize the X-ray response of the devices. The first is to apply the techniques used for radiation hardening CIDs in other applications to the scientific grade of CIDs. For use in energy dispersive detectors, CIDs can be constructed of high resistivity silicon allowing for deep depletion regions to better capture charge from deep events. A second unique possibility for CIDs is the construction of a deep insulator or virtual phase between pixels. A deep implant insulator would electrically isolate pixels allowing charge generated deep in the device to be better confined to the pixel in which it was created. A virtual phase could also be used to actively repel charge carriers away from the edges of a pixel. In a CCD, these options
would be limited since the charge must be moved out of the pixel before readout.

3.6 Summary and Conclusions:

CID detectors are versatile detectors which can be placed roughly midway between image plates and CCDs. CIDs can be read more rapidly than an image plate but at present have somewhat lower spatial resolution. CIDs can compete with image plates for dynamic range using RAI, but this requires real-time analysis during data collection which can be difficult to implement. CCDs generally have faster readout and lower noise than CIDs. For this reason, CCDs are better suited to indirect low-signal imaging applications than are presently available CIDs.

CIDs may be used for direct imaging applications. There are applications where this might be of some utility such as alignment of x-ray beams, but is not generally useful for diffraction applications. Radiation damage to the CIDs investigated here was a problem and a more comprehensive study of annealing of CIDs remains for the future.

Single photon counting with CIDs is an interesting variant of methods already in use in CCDs. At present the energy resolution is poor, but the high count-rates CIDs are capable of measuring make them interesting for future work in this area.

For Laue diffraction, the primary attraction of the CID is its wide dynamic range when using RAI methods and indirect detection. Future devices may be able to measure the energy or energies of single diffraction spots at count rates suitable for Laue
diffraction applications. Such devices, however are not presently available. As presented here, the full potential of CIDs for both monochromatic and Laue diffraction applications has not been reached.

The goal of this study was to develop instrumentation which can resolve the energies of individual spots within a Laue diffraction pattern. The problems that must be solved before Laue diffraction data can be used for routine analysis of molecular structures have been reviewed by several workers (Coppens, 1992; Helliwell, 1992). The ideal detector for this type of system would be a device with the spatial resolution of a CCD or CID, the size of an image plate, and the energy dispersive resolution of a Si(Li) detector.

CIDs are limited for a variety of reasons in this application. As noted in chapter 2, their linearity is limited and, without direct evaluation of the response function under the conditions of the experiment, they can not be assumed to be suitable for a given experiment. The tests performed here showed that under the Laue diffraction detection conditions used, they have suitable linearity, provided the intensities are large enough to overcome the “fat zero” of the device.

One of the original attractions of the CID for the Laue application was the possibility of direct detection with energy resolution. The findings presented in this chapter indicate that the current generation of devices is clearly unsuited for this purpose, although it still an attractive future direction. In the course of this work it was also realized that even if CIDs had performed perfectly in this manner they would still be of
limited utility. First, their use as a device which would sequentially interrogate
individual spots in a diffraction pattern negates the primary attraction of the Laue
experiment. *Simultaneous* observation of a large area of reciprocal space. Second, the
devices are subject to a greater degree of radiation damage than anticipated. Even the
radiation hardened versions of the CIDs (the CID38Q devices presented in the previous
chapter follow an architecture believed to be of greater radiation tolerance) currently in
use would be likely to suffer under the intense radiation found in synchrotron facilities. It
is doubtful that direct detection using either CIDs or CCDs will find widespread use in
the detection of Laue patterns. Finally, the largest CIDs currently under development are
1024x1024 and do not cover a large enough area of space to be particularly useful for
direct detection of Laue patterns. For these reasons the direct detection approach was
abandoned following this evaluation.

Indirect detection was found to be of considerable utility and the indirect camera
system prototype constructed to make these evaluations was used extensively for the
detection of Laue patterns (Chapters 5 & 6). The indirect system should be treated as an
evaluation prototype and not as the best system which could be constructed using CIDs.
Specifically, the optics used are non-optimal. For this reason, no tests which were
believed to be limited by optical coupling of the CID device to the X-ray phosphor were
performed.

Three types of position sensitive detectors for X-rays were developed and tested
which use CIDs during this work. Two CID formats, the CID 17PPRA (388x256) and
the CID 38SG (512x512), were incorporated into systems performing indirect imaging, direct imaging, and single x-ray photon counting with energy discrimination. The data presented for indirect X-ray detection and photon counting represents the first work of its kind performed using these devices and the direct detection data are the most comprehensive to date.
CHAPTER 4

Detector Selection and Optimization

In chapter 2 it was found that adding additional gain to the final stage of amplification in the readout electronics used with a CID38SG device increased the system gain by a factor of 3 with a small increase in read noise. Initially, these results were treated as a negative outcome. What was not treated in chapter 2 was the possibility that higher gain might make it possible to perform a series of measurements faster. If measurements can be made with equivalent read noise, but higher frequency, an overall improvement is realized. With this result in hand, it became apparent that no prior description of the benefits obtained at a high read rate existed. In fact, no generally applicable system existed for comparing multiple charge transfer devices.

In chapter 3, it was noted that interaction of an X-ray photon with a CID resulted in a charge packet spread over several pixels. If a larger number of contiguous pixels are observed in order to sum the charge collected from split events, the high read noise of the CID becomes a limiting factor. Using the example from chapter 3, if the read noise of a CID is set to 180 carriers, a total of about 250 carriers of noise can be expected after
taking the difference between the charge in a pixel before and after an X-ray event is observed. This translates into nearly 1 keV uncertainty in the energy of the incident photon. Some of this uncertainty can be removed by the use of multiple rereads with a consequent increase in measurement time. To reduce the uncertainty in the photon energy to about 100 eV, 80 reads or more must be employed resulting in a lower effective readout rate. Knowledge of the signal to noise expressions, therefore, is imperative. The read noise in a CID is high making a determination of an incident X-ray's energy difficult. The extent to which measurement errors can be reduced by multiple reads is critical to the ability of CIDs to function as energy dispersive analyzers. These considerations led to a need for a rigorous examination of read noise limited signal to noise expressions for the CID.

Finally, considerable confusion exists in the analytical community on how to employ charge transfer devices in an optimal fashion. Charge transfer device detection in spectroscopic applications has become common in both the commercial and research laboratory. However, signal to noise expressions are not well understood and often scientific grade CTDs are used inappropriately. Compared to other detectors, CTDs offer low dark current, low read noise, and high quantum efficiency. Although CTDs have gained widespread acceptance, a theoretical treatment of the advantages of CTDs has not been presented since the early investigations of these devices. At that time, the primary comparisons made were to photomultiplier tubes (PMT) and photographic film. Since then, CTDs have become a standard detector choice and more often it is of interest to
weigh the properties of different CTDs against each other. Compared to currently available devices, CTDs of 5-10 years ago typically had higher noise, slower readout, and smaller formats. A concise general presentation of the advantages gained from the many characteristics of CTDs would allow the performance of a device to be more easily balanced against the often substantial cost.

These three factors led to the developments presented in this chapter. The goal is to allow different readout strategies and charge transfer devices to be compared. Additionally, an attempt has been made to develop read noise limited signal to noise expressions for a comprehensive set of measurement types and device characteristics. Where expressions have been developed previously, an attempt has been made to collect useful equations and present them in a common format and notation. Expressions are also developed for some devices currently under development.

The device characteristics considered here are: read noise, quantum efficiency, pixel frequency, fixed pattern noise, well capacity, dynamic range, and frame rate. Several device readout modes are considered: binning, co-addition of frames, and ability to reread the device. Practical considerations such as background subtraction and reconstruction of signals spread over several pixels are also considered.

4.1 Definitions

A measurement made with a CTD is read noise limited when the magnitude of
device read noise exceeds the combined effect of source flicker noise ($\sigma_f$), photon shot noise ($\sigma_{ps}$), and other noise sources ($\sigma_o$) by a factor of 3. This definition is chosen such that 94.9% of the final measurement noise is from read noise. (4.1)

$$\sigma_{total} = \sqrt{\sigma_{read}^2 + \sigma_f^2 + \sigma_{ps}^2 + \sigma_o^2}$$  \hspace{1cm} (4.1)

If read noise contributes 3 units of noise and all other sources combine to contribute 1, the total noise will be 3.16. 94.9% of this is from read noise. Similarly, a measurement is said to be **photon shot noise limited** when photon shot noise exceeds all other combined noise sources by a factor of 3. Consideration here will be confined solely to the portion of a measurement that depends on the transduction of an optical measurement with a CTD. Therefore, noise in an analytical measurement from source flicker, sample introduction, sample preparation, and use of standards will be neglected. It should be noted that many analytical measurements are currently limited by these factors rather than detector related issues and readers are encouraged to consult the relevant literature.

**Quantum efficiency** (QE) is the number of incident photons divided into the number of photons detected by the device. This should not be confused with *quantum yield* (QY), the product of the QE and the number of carriers generated in the device per detected photon. QE may never exceed unity. In the X-ray range, QY can be in the thousands.
**Full well capacity** is the maximum number of charge carriers which can be contained in a single pixel and accurately measured. This quantity is designated $Q_{\text{wr}}$.

A **bias image** is an image taken with no exposure. In the case of CIDs, this image represents the amplifier offsets and fixed pattern noise of the device. An **exposed image** is an image taken after exposure of the device. **Bias subtraction** is the process of generating an analytically useful image by subtracting the bias image from the exposed image.

A **type one measurement** is one in which all the optical signal is confined to a single pixel and is read out without background subtraction. A **type two measurement** is one in which the optical signal is confined to a single pixel but requires a bias subtraction. A **type three measurement** is one in which the optical signal is spread over several pixels and is read out without background subtraction. A **type four measurement** is one in which the optical signal is spread over several pixels and requires bias subtraction. A **type five measurement** is one in which an analytical signal is spread out over multiple frames and requires no background subtraction. **Type six measurement** is one where the analytical signal is spread over multiple frames and requires background subtraction.

**Binning** is reduction of a type three or four measurement into a type one or two measurement, regardless of whether the physical process used to perform this reduction is combining the carriers into a single charge packet, as is done in CCDs, or collective readout, as is being developed for CIDs.

Two systems are considered to be **equivalent** if they reach equal signal to noise in
equal time for equal numbers of incident photons. One system is said to be better if the signal to noise ratio is greater than for a second system under the conditions used to define equivalence.

4.2 Basics of the Calculation of Variance and Errors

In the following discussion all sources of noise will be assumed to be random. Four fundamental operations will be reviewed: addition, subtraction, multiplication and division. The equations presented in this section can be found in a variety of texts (Ingle and Crouch, 1988; Shoemaker et al., 1981). When two measurements, A and B, having random errors, $\sigma_A$ and $\sigma_B$, are added together or subtracted from each other their variances add.

$$\sigma_{\text{total}}^2 = \sigma_A^2 + \sigma_B^2$$  4.2

The error in the derived quantity is then given by the square root of the total variance.

$$\sigma_{\text{total}} = \sqrt{\sigma_A^2 + \sigma_B^2}$$  4.3

If the values A and B are multiplied the error in the derived quantity, A*B, is given by equation 4.4.
If the values are divided, the error in $A/B$ is given by equation 4.5.

$$\sigma_{\text{total}} = \sqrt{\frac{\sigma_A^2}{B^2} + \frac{A^2\sigma_B^2}{B^4}}$$  \hspace{1cm} 4.5

Equations 4.4 and 4.5 are often expressed as relative errors for convenience. If the relative error is computed a single expression applies in both cases (equation 4.6).

$$\frac{\sigma_{\text{total}}}{C} = \sqrt{\left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_B}{B}\right)^2}$$  \hspace{1cm} 4.6

In equation 4.6, $C$ is the derived quantity, either $A*B$ or $A/B$.

Using the definitions for the different types of measurements the expressions presented in Table 4.1 are obtained. Based on the expressions in Table 4.1 a number of conclusions can be reached.

First, the requirement to subtract a bias image imposed by some charge transfer devices results in increased noise in the difference image. Fixed pattern noise is sometimes treated as a cosmetic problem which does not affect read noise. This is literally correct, however, the error in measurements made with devices having high fixed
### Table 4.1: Read Noise Limited S/N Expressions

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Single read</th>
<th>Multiple Reads</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single pixel</td>
<td>$S = \frac{S}{N\sigma_r}$</td>
<td>$S = \frac{S}{\sqrt{N_r}\sigma_r}$</td>
</tr>
<tr>
<td>No bias</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Type 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single Pixels</td>
<td>$S = \frac{S_e - S_b}{\sqrt{2\sigma}}$</td>
<td>$S = \frac{S_e - S_b}{\sqrt{\frac{\sigma_r^2}{N_e} + \frac{\sigma_r^2}{N_b}}}$</td>
</tr>
<tr>
<td>Bias Subtraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Type 3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multiple Pixels</td>
<td>$S = \frac{\sum_{i=1}^{N_p}(S_i)}{N_p\sigma_r}$</td>
<td>$S = \frac{\sum_{i=1}^{N_R}(S_i)}{N_p\sigma_r}$</td>
</tr>
<tr>
<td>No Bias</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Type 4</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multiple Pixels</td>
<td>$S = \frac{\sum_{i=1}^{N_p}(S_{e,i} - S_{b,i})}{\sqrt{2N_p\sigma_r^2}}$</td>
<td>$S = \frac{\sum_{i=1}^{N_R}(S_{e,i} - S_{b,i})}{\sqrt{2N_p\sigma_r^2}}$</td>
</tr>
<tr>
<td>Bias Subtraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Type 5</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multiple Frames</td>
<td>$S = \frac{\sum_{i=1}^{N_f}(S_i)}{N_f\sigma_r}$</td>
<td>$S = \frac{\sum_{i=1}^{N_R}(S_i)}{N_f\sigma_r}$</td>
</tr>
<tr>
<td>No Bias</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Type 6</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multiple Frames</td>
<td>$S = \frac{\sum_{i=1}^{N_f}(S_{e,i} - S_{f,i})}{\sqrt{2N_f\sigma_r^2}}$</td>
<td>$S = \frac{\sum_{i=1}^{N_R}(S_{e,i} - S_{b,i})}{\sqrt{2N_f\sigma_r^2}}$</td>
</tr>
<tr>
<td>Bias Subtraction</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the table, $S$ is the analytical signal, $S_e$ is the signal in the exposed image, $S_b$ is the signal in the bias image, $S_i$ is the signal in the ith pixel or frame, $S_{e,i}$ is the signal in ith pixel or frame of an exposed image, $S_{b,i}$ is the signal in ith pixel or frame of a bias image, $N_p$ is the number of pixels being summed, $N_f$ if the number of frames being summed, $N_e$ is the number of reads used for the exposed image, $N_b$ is the number of reads used in the bias image.
pattern will be greater. Some of this disadvantage can be removed by taking multiple measurements of the bias image and averaging the results. This type of correction, however, is inconvenient. In the case of CID detectors, the bias image is sensitive to temperature variations and cannot be assumed to be constant. Another consequence of the fixed pattern correction is that once a threshold level of pattern noise is exceeded, greater fixed pattern noise does not degrade the measured signal further. The difference between low fixed pattern noise and high fixed pattern noise is cosmetic. The result that bias subtraction results in poorer measurement is specific to read noise limited conditions. If read noise is not the dominant source of noise these expressions become equivalent.

Second, there is no signal to noise difference between a signal which has been divided over N pixels and one which has been divided over N frames. Co-addition of the signals in multiple pixels is well accepted in the community and a treatment of the value of co-addition of pixels vs. binning has been treated extensively (Epperson 1989). What is not widely recognized is that co-addition of multiple frames is equivalent to co-addition of pixels. This conclusion is general to systems which are limited by read noise or photon shot noise. In systems limited by source flicker, this conclusion is no longer valid. In other cases they are equivalent. If multiple pixels and/or multiple frames are of interest, the sums presented in the table can be taken over all the measured pixels. The square root of $N_p$ or $N_f$ term becomes $N_{pf}$.

The expressions presented in Table 4.1 are useful for applications in which a fluorescent signal is measured. Under these conditions, analyte concentration is
Another figure of merit, in addition to the S/N ratio is the simple detection limit of a device when exposed to a photon source. In luminescence experiments the detection limit can be defined as the amount of light required to create a signal which is $k$ times the read noise of the device.

$$DL = k\sigma_r$$  \hspace{1cm} 4.7

In 4.7, $k$ is an analyst selectable quantity which defines the confidence level of the detection limit. The limitations imposed on a measurement by a background signal has not been extensively treated in the CTD literature. An example is Raman spectroscopy. In multichannel Raman spectroscopy, the growing acceptance of single grating polychromator systems has resulted in lower Rayleigh rejection in the measurement. This results in a background limited measurement. In the context of CTD detection, the limitation imposed by a background signal has not been explored. This situation also enters into limitations in the detection of spots in a Laue diffraction pattern. The Laue pattern appears as emission against a sloping background. Under these conditions, the detection limit must consider both the noise from reads and from the shot noise of the background signal. Since these are typically read together, a second read is not considered. Since the background signal noise is due to photon shot noise the variance is simply the magnitude of the background signal, $B$. 

proportional to the number of photons measured.
These expressions can be extended to include co-addition of frames, co-addition of pixels, re-reads and binning. These are tabulated in table 4.2.

Table 4.2: Luminescence Detection Limits Using CTD detection

<table>
<thead>
<tr>
<th>Detection limit</th>
<th>No Background</th>
<th>With Background Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>single pixels,</td>
<td>DL = $k\sigma_r$</td>
<td>DL = $k\sqrt{\sigma_r^2 + B}$</td>
</tr>
<tr>
<td>single frames,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>no rereads</td>
<td></td>
<td></td>
</tr>
<tr>
<td>detection</td>
<td>DL = $\frac{k\sigma_r}{\sqrt{N}}$</td>
<td>DL = $k\sqrt{\frac{\sigma_r^2}{N} + B}$</td>
</tr>
<tr>
<td>detection</td>
<td></td>
<td></td>
</tr>
<tr>
<td>multiple pixels,</td>
<td>DL = $k\sigma_r \sqrt{n_p}$</td>
<td>DL = $k\sqrt{n_p(\sigma_r^2 + B)}$</td>
</tr>
<tr>
<td>single frames,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>no rereads</td>
<td></td>
<td></td>
</tr>
<tr>
<td>detection</td>
<td>DL = $\frac{k\sigma_r \sqrt{n_p}}{\sqrt{N}}$</td>
<td>DL = $k\sqrt{n_p \left(\frac{\sigma_r^2}{N} + B\right)}$</td>
</tr>
<tr>
<td>detection</td>
<td></td>
<td></td>
</tr>
<tr>
<td>single pixels,</td>
<td>DL = $k\sigma_r \sqrt{n_f}$</td>
<td>DL = $k\sqrt{n_f(\sigma_r^2 + B)}$</td>
</tr>
<tr>
<td>multiple frames,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>no rereads</td>
<td></td>
<td></td>
</tr>
<tr>
<td>detection</td>
<td>DL = $\frac{k\sigma_r \sqrt{n_f}}{\sqrt{N}}$</td>
<td>DL = $k\sqrt{n_f \left(\frac{\sigma_r^2}{N} + B\right)}$</td>
</tr>
<tr>
<td>detection</td>
<td></td>
<td></td>
</tr>
<tr>
<td>single pixels,</td>
<td>DL = $k\sigma_r \sqrt{n_p n_f}$</td>
<td>DL = $k\sqrt{n_p n_f(\sigma_r^2 + B)}$</td>
</tr>
<tr>
<td>multiple frames,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>no rereads</td>
<td></td>
<td></td>
</tr>
<tr>
<td>detection</td>
<td>DL = $\frac{k\sigma_r \sqrt{n_p n_f}}{\sqrt{N}}$</td>
<td>DL = $k\sqrt{n_p n_f \left(\frac{\sigma_r^2}{N} + B\right)}$</td>
</tr>
</tbody>
</table>

1 These two expressions also apply to the case of binning.
The dynamic range of a measurement made with a CTD is the maximum signal divided by the minimum detectable signal (the detection limit). In the case of a single pixel and a single read and no background this is given by equation 4.9.

Table 4.3: Limiting Dynamic Range Expressions

<table>
<thead>
<tr>
<th>Dynamic range</th>
<th>No Background</th>
<th>With Background Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>single pixels, single frames, no rereads</td>
<td>$\text{DR} = \frac{Q_{\text{sat}}}{k\sigma_r}$</td>
<td>$\text{DR} = \frac{Q_{\text{sat}} - B}{k\sqrt{\sigma_r^2 + B}}$</td>
</tr>
<tr>
<td>single pixels, single frames, with rereads</td>
<td>$\text{DR} = \frac{Q_{\text{sat}} \sqrt{N}}{k\sigma_r}$</td>
<td>$\text{DR} = \frac{Q_{\text{sat}} - B}{k\sqrt{\frac{\sigma_r^2}{N} + B}}$</td>
</tr>
<tr>
<td>multiple pixels, single frames, no rereads</td>
<td>$\text{DR} = \frac{Q_{\text{sat}} \sqrt{n_p}}{k\sigma_r}$</td>
<td>$\text{DR} = \frac{(Q_{\text{sat}} - B)\sqrt{n_p}}{k\sqrt{\sigma_r^2 + B}}$</td>
</tr>
<tr>
<td>multiple pixels, single frames, with rereads</td>
<td>$\text{DR} = \frac{Q_{\text{sat}} \sqrt{Nn_p}}{k\sigma_r}$</td>
<td>$\text{DR} = \frac{(Q_{\text{sat}} - B)\sqrt{n_p}}{k\sqrt{\frac{\sigma_r^2}{N} + B}}$</td>
</tr>
<tr>
<td>single pixels, multiple frames, no rereads</td>
<td>$\text{DR} = \frac{Q_{\text{sat}} \sqrt{n_{fr}}}{k\sigma_r}$</td>
<td>$\text{DR} = \frac{(Q_{\text{sat}} - B)\sqrt{n_{fr}}}{k\sqrt{\sigma_r^2 + B}}$</td>
</tr>
<tr>
<td>single pixels, multiple frames, with rereads</td>
<td>$\text{DR} = \frac{Q_{\text{sat}} \sqrt{Nn_{fr}}}{k\sigma_r}$</td>
<td>$\text{DR} = \frac{(Q_{\text{sat}} - B)\sqrt{n_p n_{fr}}}{k\sqrt{\frac{\sigma_r^2}{N} + B}}$</td>
</tr>
<tr>
<td>multiple pixels, multiple frames, no rereads</td>
<td>$\text{DR} = \frac{Q_{\text{sat}} \sqrt{n_p n_{fr}}}{k\sigma_r}$</td>
<td>$\text{DR} = \frac{(Q_{\text{sat}} - B)\sqrt{n_p n_{fr}}}{k\sqrt{\sigma_r^2 + B}}$</td>
</tr>
<tr>
<td>multiple pixels, multiple frames, with rereads</td>
<td>$\text{DR} = \frac{Q_{\text{sat}} \sqrt{Nn_p n_{fr}}}{k\sigma_r}$</td>
<td>$\text{DR} = \frac{(Q_{\text{sat}} - B)\sqrt{n_p n_{fr}}}{k\sqrt{\frac{\sigma_r^2}{N} + B}}$</td>
</tr>
</tbody>
</table>
Extensions of equation 4.9 to include multiple pixels, frames, reads, and background appear in table 4.3.

4.3 Measurements Involving Division Operations

Two of the most common measurements made with a CTD, flat fields and absorbance, involve division operations. Field flattening is an operation used to normalize an image for uneven illumination. This is particularly useful for normalizing a field used in the detection of a fluorescent analyte. An example might be the quantitative detection of fluorescent molecules on a thin layer chromatography plate. If the illumination by the excitation source is uneven over the surface of the plate, the amount of fluorescence detected from equivalent amounts of analyte will vary over the surface of the plate. This problem is mitigated by correcting the measured intensity for variation over the surface of the plate. CTDs typically have variations in pixel sensitivity. This might be from pixel size non-uniformity, non-uniform amplification in parallel readout amplifiers, dust on the surface, or any other process which causes different pixels to behave non-uniformly. This type of variation can also be corrected by performing a flat field operation.
A simple flat field operation consists of a bias image, a flat field image, and an analytical image (Sweedler and Bilhorn, 1993; Baker and Denton, 1993). The flat field correction is performed by computing the bias subtracted images, computing the mean of the bias subtracted flat field image, then multiplying the analytical image by the ratio of the mean flat field image to the value of the flat field image pixel by pixel. These steps are presented in equation 4.10 (after Sweedler and Bilhorn, 1993; Baker and Denton, 1993).

\[
\begin{align*}
A_{b,i} & = A_{r,i} - B_i \\
F_{b,i} & = F_{r,i} - B_i \\
\bar{F} & = \frac{\sum_{i=1}^{n} F_{b,i}}{n} \\
A_{F,i} & = \frac{A_{b,i}}{F_{b,i}} \bar{F}
\end{align*}
\]  

In 4.10, \(A_{r,i}\) is the raw data value of the ith pixel in the analytical image, \(B_i\) is the bias data value for the ith pixel, \(A_{b,i}\) is the bias corrected data value for the ith pixel. The subscripts for the flat field image are identical. \(\bar{F}\) is the mean signal and \(A_{F,i}\) is the flat field corrected image. \(\bar{F}\) is only a normalizing factor and is computed to give the values in the corrected image a convenient range. Any number greater than zero can be used to re-normalize the corrected image after field flattening.

The errors introduced by this process have been partially treated by Sweedler and
Bilhorn (1993). They note that the process of performing a bias subtraction introduces a \(\sqrt{2}\) increase in measurement noise. As discussed by Sweedler and Bilhorn, the effect of bias subtraction can be minimized by making multiple measurements of the bias image and averaging. However, this is not the full treatment. If the flat field image is taken properly the effect of the bias image can be neglected. Of more concern than the bias subtraction operation is the division operation performed during the process of field flattening. Multiplication by the mean flat field image is not important since this is simply a scaling factor. The error introduced in each step is given in equation 4.11.

\[
A_{b,i} = A_{r,i} - B_i \\
F_{b,i} = F_{r,i} - B_i \\
\bar{F} = \frac{\sum_{i=1}^{n} F_{b,i}}{n} \quad \text{No error introduced here. } \bar{F} \text{ set to 1.}
\]

\[
\frac{\sigma_{A_{b,i}}}{A_{b,i}} = \sqrt{\frac{\sigma_{A_{r,i}}^2 + \sigma_i^2}{A_{b,i}}} \\
\frac{\sigma_{F_{b,i}}}{\bar{F}} = \sqrt{\frac{\sigma_{F_{r,i}}^2 + \sigma_i^2}{\bar{F}_{b,i}}} \\
\frac{\sigma_{A_{F,i}}}{A_{F,i}} = \sqrt{\left(\frac{\sqrt{\sigma_{A_{r,i}}^2 + \sigma_i^2}}{A_{b,i}}\right)^2 + \left(\frac{1}{\sqrt{\bar{F}_{b,i}}}\right)^2}
\]

The last equation in 4.11 reduces to 4.12 under shot noise limited measurement of the flat field.

\[
\frac{\sigma_{A_{F,i}}}{A_{F,i}} = \sqrt{\left(\frac{\sqrt{\sigma_{A_{r,i}}^2 + \sigma_i^2}}{A_{b,i}}\right)^2 + \left(\frac{1}{\sqrt{\bar{F}_{b,i}}}\right)^2}
\]
Under shot noise limited measurements conditions, bias subtraction does not significantly affect the outcome of a field flattening operation. It may, however, be important in the analytical image under read noise limited conditions. Equation 4.12. indicates that field flattening will not introduce more than 1% relative error provided more than 10,000 photons are collected and shot noise limited measurements are made in each pixel of the device. If greater precision is needed or a CTD with a small full well capacity is being used then good results can be obtained by co-addition of multiple frames. Under such conditions field flattening can be performed with negligible introduction of error.

Absorbance measurements involve the measurement of two images, and I_0 and I. Bilhorn (Bilhorn, 1989; Bilhorn, Epperson, Sweedler, and Denton, 1987) derived an expression for minimum detectable absorbance using a CTD system, two exposures and single pixel areas. This work was extended by Pomeroy et al. (Pomeroy, Baker, Denton, and Dickson 1995) to multiple pixels. Pomeroy et al. (1995) suggest the possibility that multiple exposures could be used for signal averaging to obtain higher precision absorbance measurements. These equations are summarized in table 4.4 and extended to include, multiple frames, background correction, and multiple rereads.

From the table a number of conclusions can be reached. As pointed out by Bilhorn, detection limits using CTD detection and absorbance are favored by shot noise limited conditions. Under these conditions there is no advantage to be gained by the
Table 4.4: Limiting Conditions on Minimum Absorbance Measured with CTDs

<table>
<thead>
<tr>
<th>Minimum absorbance</th>
<th>No Background</th>
<th>With Background Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>single pixels,</td>
<td>$A_{\min} = -\log \left( 1 - \frac{k}{Q_{sat}} \right)$</td>
<td>$A_{\min} = -\log \left( 1 - \frac{k\sqrt{2(Q_{sat} + B)}}{Q_{sat} - B} \right)$</td>
</tr>
<tr>
<td>single frames,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>no rereads</td>
<td></td>
<td></td>
</tr>
<tr>
<td>single pixels,</td>
<td>$A_{\min} = -\log \left( 1 - \frac{k}{n_pQ_{sat}} \right)$</td>
<td>$A_{\min} = -\log \left( 1 - \frac{k\sqrt{2(n_pQ_{sat} + n_pB)}}{n_pQ_{sat} - n_pB} \right)$</td>
</tr>
<tr>
<td>single frames,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>with rereads</td>
<td></td>
<td></td>
</tr>
<tr>
<td>multiple pixels,</td>
<td>$A_{\min} = -\log \left( 1 - \frac{k}{n_tQ_{sat}} \right)$</td>
<td>$A_{\min} = -\log \left( 1 - \frac{k\sqrt{2(n_tQ_{sat} + n_tB)}}{n_tQ_{sat} - n_tB} \right)$</td>
</tr>
<tr>
<td>single frames,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>no rereads</td>
<td></td>
<td></td>
</tr>
<tr>
<td>multiple pixels,</td>
<td>$A_{\min} = -\log \left( 1 - \frac{k}{n_t n_p Q_{sat}} \right)$</td>
<td>$A_{\min} = -\log \left( 1 - \frac{k\sqrt{2(n_t n_p Q_{sat} + n_t n_p B)}}{n_t n_p Q_{sat} - n_t n_p B} \right)$</td>
</tr>
<tr>
<td>multiple frames,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>with rereads</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

re-read capability of a CID. In fact, the expressions are equivalent under these conditions. The presence of a background signal, whether from dark current, source rejection, or stray light degrades CTD based detection. Furthermore, under shot noise limited conditions, there is no difference between reading from multiple pixels or frames. It has been previously recognized that co-addition of the signal (not binning) from
multiple pixels lowers the minimum detectable absorbance that can be measured with a CTD. What has not been widely realized is the enhancements obtained by co-adding multiple frames from a device. As CTD readout becomes faster, the ability to co-add signals from many frames will become more important.

It should also be noted that the expressions in table 4.4 can be used for transmission efficiency, by noting that absorbance is related to transmission efficiency (e.g.: \( A = \log(T) \)). The factor inside the logarithm is the corresponding expression for transmission efficiency.

The maximum dynamic range of a CTD based absorbance measurement presents a mix of shot noise and read noise limitation. Epperson (Epperson, 1987; Epperson et al., 1987) discussed the use of the CCDs for measurement of highly optically dense thin films. Theoretically limiting expressions were not derived for this application, although spectra with optical densities up to 5 absorbance units were presented. These expressions are presented here.

The minimum detectable photon signal is \( k\sigma \), where \( k \) is a constant selected by the analyst which defines the level of confidence desired. The maximum photon signal will be set to \( Q_{\text{sat}} \), the device full well capacity. The maximum detectable absorbance is then given by equation 4.13.

\[
A_{\text{max}} = -\log\left( \frac{k\sigma}{Q_{\text{sat}}} \right) \quad 4.13
\]
This expression can be readily extended to include multiple pixels, multiple frames, and re-reads (Table 4.5). If a background signal is present, the situation becomes more complicated. If the background is large enough such that its shot noise dominates measurement error, then the minimum detectable photon signal is given by \( k\sigma_n \). Since the background is assumed to be shot noise limited this becomes \( k\sqrt{B} \). The maximum signal is given by \( Q_{sat-B} \). Under these conditions the maximum absorbance is given by equation 4.14.

\[
A_{max} = -\log\left(\frac{k\sqrt{B}}{Q_{sat}-B}\right)
\]

4.14

As before this result may be extended to include multiple pixels, multiple frames, and re-reads (Table 4.5). Under certain special conditions, an advantage is realized by binning. These cases are included in the table.

As noted previously, the formulas in table 4.5 can be used for transmission efficiency by simply noting the logarithmic relationship between transmission efficiency and absorbance.

The relationships in Table 4.5 indicate that under some conditions binning the signal gives an advantage when making high absorbance measurements. As is the case for minimum absorbance, maximum absorbance measurements are best made under conditions where negligible background signal exists. In the case of minimum
detectable absorbance. the improvement obtained through the use of co-addition from multiple frames of data is identical to that obtained by co-addition of multiple pixels. In the case of the read noise limited measurements of minimum photon signals required for maximum absorbance measurements a slight difference is obtained. Since it is impossible to bin across multiple frames of data, only a $\sqrt{n_f}$ improvement in absorbance is realized. Use of these equations indicates that the maximum dynamic range of a device is not limited by the full well capacity. The full well capacity only defines a simple dynamic range which is readily extended by co-addition of multiple pixels and frames of data.

4.4 Consideration of Device Speed

The system gain in a CID can be changed by adjusting the length of integration in a correlated double sample. Plots of this type of behavior are found in chapter 2 for 4 different CID devices. The read noise of the CID also varies with the pixel frequency. In prior work with CIDs, similar plots of read noise and system gain vs. pixel frequency, such as are found in Chapter 2, were not presented. Faced with such data, an analyst may wish to know how to determine the best range in which to work. Further, is it better to optimize for read noise or speed? An analytical solution to this problem exists. Although it was developed with the CID in mind it also applies to the case of skipper amplifier CCDs which repeatedly sample a single charge packet.
<table>
<thead>
<tr>
<th>No Background</th>
<th>With Background Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maximum absorbance</strong></td>
<td></td>
</tr>
<tr>
<td>single pixels, single frames, no rereads</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{max}} = -\log \left( \frac{k \sigma}{Q_{\text{sat}}} \right)$</td>
<td>$A_{\text{max}} = -\log \left( \frac{k \sqrt{B}}{Q_{\text{sat}} - B} \right)$</td>
</tr>
<tr>
<td>single pixels, single frames, with rereads</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{max}} = -\log \left( \frac{k \sigma}{Q_{\text{sat}} \sqrt{N}} \right)$</td>
<td>$A_{\text{max}} = -\log \left( \frac{k \sqrt{B}}{\sqrt{n_p} (Q_{\text{sat}} - B)} \right)$</td>
</tr>
<tr>
<td>multiple pixels, single frames, no rereads, no binning</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{max}} = -\log \left( \frac{k \sigma}{\sqrt{n_p Q_{\text{sat}}}} \right)$</td>
<td></td>
</tr>
<tr>
<td>multiple pixels, single frames, with rereads</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{max}} = -\log \left( \frac{k \sigma}{Q_{\text{sat}} \sqrt{n_p N}} \right)$</td>
<td>$A_{\text{max}} = -\log \left( \frac{k \sqrt{B}}{\sqrt{n_f} (Q_{\text{sat}} - B)} \right)$</td>
</tr>
<tr>
<td>single pixels, multiple frames, no rereads</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{max}} = -\log \left( \frac{k \sigma}{\sqrt{n_f Q_{\text{sat}}} \sqrt{N}} \right)$</td>
<td></td>
</tr>
<tr>
<td>single pixels, multiple frames, with rereads</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{max}} = -\log \left( \frac{k \sigma}{Q_{\text{sat}} \sqrt{n_f N}} \right)$</td>
<td>$A_{\text{max}} = -\log \left( \frac{k \sqrt{B}}{\sqrt{n_f n_p} (Q_{\text{sat}} - B)} \right)$</td>
</tr>
<tr>
<td>multiple pixels, multiple frames, no rereads</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{max}} = -\log \left( \frac{k \sigma}{n_p Q_{\text{sat}} \sqrt{n_f N}} \right)$</td>
<td></td>
</tr>
<tr>
<td>multiple pixels, multiple frames, with rereads, with binning*</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{max}} = -\log \left( \frac{k \sigma}{n_p Q_{\text{sat}} \sqrt{n_f N}} \right)$</td>
<td>Binning not advisable with shot noise limited background signal</td>
</tr>
</tbody>
</table>

* Binning in this table only refers to binning of the I image. Binning of the Io image is detrimental and should be avoided. It may cause register blooming and is never advisable under shot noise limitation.
Two parameters must be considered, the length of time of sampling and the rate of sampling. To determine an optimal range, the time, \( T \), is held fixed and several pixel frequencies are considered. The first point to note is that the error in the measurement of an analytical signal may be reduced as indicated in chapter 2.

\[
s = \frac{\sigma_r}{\sqrt{N}} \tag{4.15}
\]

In 4.15, \( s \) is the error in a measurement. The number of samples, \( N \), which can be taken in a period of time depends on the pixel frequency, \( f \).

\[
N = fT \tag{4.16}
\]

Making the substitution of 4.16 into 4.15 an expression for \( s \) as a function of the time of measurement and the pixel frequency is obtained. It should be noted that \( N \) only takes integer values.

\[
s = \frac{\sigma_r}{\sqrt{fT}} \tag{4.17}
\]
Using 4.17, the optimal region of measurement can be selected unambiguously. It may also be used to determine relationships defining equivalent systems. For example, consider two devices, one having a read noise of 100 carriers, the other 200 carriers. Equation 4.17 indicates that an equivalent system exists if the device with greater read noise can be read 4 times faster than the one with less noise.

\[ s_1 = \frac{100}{\sqrt{f_1}} = s_2 = \frac{200}{\sqrt{4f_1}} \]  

4.18

These considerations indicate that read noise can double for every 4 fold increase in pixel frequency without loss of performance. If the noise levels of the two systems are set equal then the system with the higher read rate is better.

### 4.5 Consideration of Quantum Efficiency

Quantum efficiency is a measure of the ability of a device to detect light of a particular wavelength. If all other factors are equal, devices of higher quantum efficiency will give superior performance. Under such conditions, they will reach shot noise limitation sooner and in a read noise limited regime will always have higher signal to noise ratios. The signal generated in a CTD is a product of the quantum efficiency, Q, the photon flux, \( \Phi \), and the time of exposure, \( t \).
In 4.19, \( t \), the time of exposure, should not be confused with \( T \), the time of readout. The error in this measurement is the sum of the read noise of the device and the photon shot noise (an ideal photon source is assumed).

\[
\sigma_t = \sqrt{\sigma_t^2 + S} \quad 4.20
\]

In a system where re-reads are possible, expression 4.17 can be used for computing the total error.

\[
\sigma_t = \sqrt{\frac{\sigma_t^2}{fT} + S} \quad 4.21
\]

A signal to noise expression (4.22) can be derived by combining 4.21 and 4.19. Note that in this expression the \( N \) in the denominator is the noise.

\[
\frac{S}{N} = \frac{Q\Phi t}{\sqrt{\frac{\sigma_t^2}{fT} + Q\Phi t}} \quad 4.22
\]
This expression allows a combination of quantum efficiency, pixel frequency, time of readout, photon flux, and exposure time to be evaluated. In photon shot noise limited measurements, it reduces to the standard square root S/N dependence. In the read noise limited case, it gives an ability to predict a better system. In the case of the best scientific grade CCDs (those having noise of 2 e- per read), it is mostly an academic exercise since shot noise limited measurements begin after 36 photoelectrons have been collected. It is very rare that useful chemical measurements are made based on 36 photoelectrons. Background would be likely to limit such measurements. Equation 4.22 can be readily adapted for use with a background photon signal.

While CIDs have more substantial read noise, equation 4.22 can be used to predict the behavior of CIDs of various characteristics. For example, consider two systems. System 1 has a QE of 30%, a read noise of 100 electrons, and a read rate of 40 kHz. System 2 has a QE of 90%, a read noise of 150 electrons, and a read rate of 10 kHz. Based on equation 4.22, these systems are equivalent under read noise limited conditions, despite the substantially higher QE of system 2.

It should be noted that these considerations are for read noise limited measurements. If the signal becomes shot noise limited then System 2 will be better.
4.6 Binning Schemes

Binning (Epperson and Denton, 1989; Epperson, 1987; Carbone, 1995) is a readout technique which allows the charge collected in a number of pixels to be readout using a single read. In a CCD this is done by combining the charge from many pixels into a single pixel for readout. Binning gives the advantage of adding signals from multiple pixels, while only performing a single read. This can improve the quality of measurements, lower data storage and handling requirements, and decrease the time required to obtain a data set. Users of CCDs employ this technique extensively. The possibility of binning CIDs has not been widely discussed. This has been due to device architecture in the past. Recently, CIDs have been under development which allow binning to be performed. A binnable CID allows the possibility of re-reads to be performed on the collected charge in pixels randomly combined along a row of the device. The signal from multiple rows can also be combined, however this occurs after the signal has passed through the row amplifier. As such, it is not clear whether this will give the full advantage predicted by standard binning expressions. These devices are still under development and it is unclear whether binning the pixels at two vertices on a diagonal of a rectangular region can be read in isolation from the remaining vertices. The ability to perform re-reads on a binned signal and to bin randomly along a row of the device allows for capabilities not previously discussed.

A signal to noise advantage is accrued through the use of binning under read noise.
limited conditions. Under these conditions the total charge in the set of pixels is combined into a single packet. The total signal measured is the sum of individual signals.

\[ S_i = \sum_{i=1}^{N_p} S_i \]  \hspace{1cm} 4.23

Since only a single read is made, read noise is still \( \sigma_r \). In comparison, if each pixel were read individually and the resulting values co-added after readout, the combined error in the measurement is \( \sigma_r \sqrt{N_p} \). When a bias subtraction must be performed an additional square root of two increase is predicted. Under read noise limited measurement conditions the advantage to be realized by binning is then the square root of the number of binned pixels.

\[ \frac{\text{SNR}_{\text{binned}}}{\text{SNR}_{\text{co-add}}} = \frac{\sigma_r}{\sqrt{N_p} \sigma_r} = \frac{1}{\sqrt{N_p}} \]  \hspace{1cm} 4.24

As noted previously, there is no advantage to binning under shot noise limited measurement. For more discussion of this issue see Hanley et al. (Hanley, Earle, Pennebaker, Madden, and Denton, 1996).

The error associated with binned measurements made with reread capability can be treated similarly to the simple binning case. By using equation 4.15.
The use of the reread capacity gives an additional square root of $N$, improvement in the measurement error.

4.7 Hadamard Binning

One of the unique possibilities of the ability to randomly select a pixel while maintaining reread capability is the possibility of applying Hadamard encoding to the selected pixels. The resulting measurements can be decoded using a Hadamard transform. Hadamard encoding can be thought of as a weighing scheme (Harwit and Sloane, 1979). As a simple example, consider the determination of the masses of three objects using a laboratory balance. The usual approach is to weigh the objects one by one and then report the results. An alternative is to weigh the objects in pairs. In the first measurement the first and second objects are weighed. The second measurement involves weighing the second and third objects. Finally the first and third objects are measured. The resulting measurements give a set of linear equations which can be solved for the mass of each object. In this example, if the measurements were 11, 13, and 12 grams respectively the results can be expressed in matrix form (4.26).
This equation can be solved by multiplying both sides by the inverse of the 3x3 matrix.

\[
M^{-1}Y = (M^{-1}M)X \Rightarrow X = M^{-1}Y
\]

For the equation given the solution is \( x=5 \), \( y=6 \), and \( z=7 \).

The three by three matrix in 4.26 is an example of a Hadamard matrix. There are two types, true Hadamard matrices which are made up of ones and negative ones and S-matrices which, like the one in 4.26, contain only zeroes and ones. The matrices can be used to specify an experimental weighing scheme in a wide range of applications. The matrix coefficients are sometimes referred to as an encoding scheme. In optical spectroscopy and imaging, Hadamard matrices have been widely used (Treado and Morris, 1990). CID devices have been previously designed specifically to incorporate Hadamard encoded readout (Michon, Burke, Vogelsong, and Merola, 1977; Michon and Burke, 1984). These devices employed an off-chip driver to produce a Hadamard transformed output. These devices were designed for guided missile applications. The Hadamard transform lowers the communication bandwidth of remotely controlled weapons, making them less susceptible to jamming.
The possibility of noise reduction through the use of Hadamard encoding has not been previously described in the context of CID detection. In other optical spectroscopic applications, the use of Hadamard transform methods are often limited by a multiplex disadvantage due to shot noise from large signals contaminating weaker signals. In most conventional uses of the Hadamard transform in optical spectroscopy, a series of images are taken and the encoding applied to the multiple images. The use of multiple exposures results in shot noise and flicker being present in the images which must be taken over a period of time. Application of Hadamard encoding to CID pixels during binned readout has no such disadvantage. Once the charge in a set of pixels is generated the amount present in the device is fixed. Therefore, full signal to noise reduction occurs even when both strong and weak signals are present along a row of a device.

If a series of $N_p$ pixels is read using an S-matrix masking scheme such that one S-masked read is made per pixel a total of $N_p$ reads is made. A signal to noise advantage is realized through the use of this scheme. The error in the signal for the $i$th pixel, $\sigma_h$, after S-matrix decoding, may be computed using equation 4.28 (This equation is the square root of equation 3-42 in Harwit and Sloane (1979).†

$$\sigma_h = \frac{2\sqrt{n_h \sigma_r}}{(n_h + 1)}$$

† The author would like to acknowledge the assistance of Michael Schappert in the derivation of the Hadamard signal to noise expressions.
If the number of pixels read using the S-matrix encoding, \( n_h \), is large equation 4.28 reduces to 4.29.

\[
\sigma_h = \frac{2\sigma_r}{\sqrt{n_h}} 
\]

Equation 4.29 indicates that if the 1024 pixels along a row of a CID are read using S-matrix encoding the error in measurement of the charge in a pixel is decreased by a factor of 16. A total of 1028 reads are made. If a bias image is subtracted then 4.30 is obtained.

\[
\sigma = \sqrt{\left(\frac{2\sigma_r}{\sqrt{n_h}}\right)^2} + \left(\frac{2\sigma_r}{\sqrt{n_h}}\right)^2 = 2\sqrt{\frac{2}{nh}}\sigma_r 
\]

Using the same example as given above the advantage is a factor of 11, slightly lower than what is obtained if no bias image is needed.

Substitution of equation 4.15 into 4.29 gives an expression for Hadamard binned readout where each segment is read N times. This result is presented in equation 4.31

\[
\sigma_{h, \text{reread}} = \frac{2\sigma_r}{\sqrt{Nn_h}} 
\]
The corresponding equation to 4.30 for rereads is 4.32.

\[
\sigma = \sqrt{\left(\frac{2\sigma_r}{\sqrt{Nn}}\right)^2 + \left(\frac{2\sigma_r}{\sqrt{Nn}}\right)^2} = 2\sqrt{\frac{2}{Nn}}\sigma_r
\] 4.32

The consequence of these equations is that as the size of the imager increases the S/N advantage increases for the Hadamard binnable imager. For example, a device with 4096 pixels along a Hadamard binnable row will have an advantage of 32. A CID device might have a read noise of 180 electrons. Reduction of this by 32 results in roughly 6 electrons of read noise. There is no increase in the total number of reads required to obtain this S/N reduction. If the device is binnable along both rows and columns then the advantage increases rapidly. This level of read noise is directly comparable to scientific grade CCDs. CCDs, however, do not have the same flexibility of readout.

### 4.8 Event Reconstruction

In the present generation of CIDs, binning is not possible. When making observations of X-rays, a method for reconstructing events spread over multiple pixels was desired. CIDs offer the possibility of locating an event, then choosing a readout strategy based on the type of event and its location.

If an event is spread over multiple pixels the expressions presented in table 4.1 for
type 1-4 events may be applied. Using these equations the following rules can be found for read noise limited conditions

1) If an event is spread over multiple pixels, it can be treated as a single pixel if the number of rereads per pixels is equal to the number of pixels.

2) When designing an analytical strategy, a measurement of lowest type class should always be used where possible.

3) Where possible, rereads should be performed.

In the case of photon shot noise limited measurement none of these rules apply. Under shot noise limited conditions, there is no advantage to rereading the device or binning and there is no disadvantage to spreading signals over multiple frames or pixels.

4.9 Read Noise and Co-addition

In the context of CID s, it is sometimes argued that the higher full well capacity justifies the somewhat higher read noise of the devices. This argument depends generally on the rate at which the lower noise device can be read. For low-light level measurements, however, the importance of low read noise can not be stressed too strongly. It is instructive to compare the number of co-adds that can be performed before the combined read noise equals the noise of a single read of another device. If some
number, $N_e$, of frames are co-added the resulting combined read noise is given by equation 4.33.

$$\sigma_{\text{co-add}} = \sigma_r \sqrt{N_e}$$  \hspace{1cm} 4.33

Using this expression, the number of co-adds that can be performed under the read noise floor of a device having greater noise can be solved. For example, if the level of noise desired after co-additions is 180 e- and the read noise of the device under consideration is 5 e-, $N_e$ becomes 1296. This means that 1296 frames of the device with 5 e- of read noise can be co-added before the combined noise is equivalent to the noise of a single 180e- read.

### 4.10 Summary and Conclusion

The basis for a systematic comparison of CTDs has been defined. Using the definitions a set of rules has been proposed for the collection and reconstruction of signals spread over multiple pixels. In the case of CID, the impact of quantum efficiency, read noise, time of readout, and pixel frequency have been combined into a single expression allowing the trade off of these different factors to be evaluated. The use of these expressions is most important under read noise limited conditions.

Little prior work has been done on the influence of background photon signals in
the context of charge transfer device detection. An extensive set of equations for signal to noise ratios, detection limits, minimum detectable absorbance, and maximum detectable absorbance, given signals spread over multiple pixels or frames, read out with and without rereads, and in the presence and absence of background signals have been presented. These equations begin to define the optimal way to use CTDs for the detection of many analytical signals.

Finally, a theoretical study of the possibilities available for the readout of a binnable CID device has been presented. While such devices are currently under development and not available for use at this time, they have properties which allow even a noisy device to compete more directly with CCDs for detection of low light level images. With the use of a Hadamard encoded binning scheme, a device having reread capability can equal or exceed the performance of the best scientific grade CCDs. When such devices become available, they may be the best scientific imaging devices for low level signals yet produced.
"The ultimate in rapid diffraction could be achieved with simultaneous energy and position analysis using an area detector with energy resolution. Further technical developments are required for implementation of such comprehensive analysis techniques."

Philip Coppens

*Synchrotron Radiation Crystallography* (1992)

"These objections [the multiplicity problem] are fundamental in the sense that an energy-sensitive detector with the additional properties of high spatial resolution, high count rate and high absorption efficiency is not available."

John R. Helliwell

*Macromolecular Crystallography with Synchrotron Radiation* (1992)
CHAPTER 5

A Foil Mask Spectrometer for Laue Diffraction Pattern Imaging

Following the investigations presented in Chapter 3, it was concluded that the CID would not, by itself, be capable of energy dispersive detection. The only suitable mode of operation was indirect detection using a phosphor to convert X-rays to visible light. This process removes all energy information when detected with an integrating detector like the CID. Presented with the limitations of the device, a new approach had to be adopted to make use of the energy insensitivity of the systems available for detection.

In optical spectroscopy, there are two well-documented ways to turn an energy insensitive detector into an energy sensitive one. Both of these methods involve encoding schemes in which an incident beam is somehow modulated in an energy dependent manner resulting in intensity domain encoding of spectroscopic information.

* Portions of this chapter have appeared previously in Journal of Synchrotron Radiation 3:101-111 (1996). Where required, these sections are reproduced with permission of the International Union of Crystallography.
One popular example of these techniques, the Fourier transform infrared spectrometer, encodes wavelength information in the intensity domain through the use of a Michelson interferometer. The interferogram is sampled at regular intervals and the wavelength domain reconstructed using Fourier transform methods. A less common technique involves the use of a Hadamard transform (see chapter 4 for a brief introduction to Hadamard encoding).

In one type of Hadamard transform spectrometer, spectral segments are added or removed from an incident beam using a mask placed at the focal plane of a spectrometer (Harwit and Sloane, 1979). The key to this method is wavelength domain encoding by either completely turning on or off the signal from a particular spectral segment.

The idea of energy domain encoding incorporated into the Foil mask spectrometer borrows heavily from Hadamard techniques. The main difference is that the masks in this case do not completely mask a particular spectral segment completely and the type of masking possible is limited by the availability of absorbing materials. The idea of "masking" which is borrowed from the Hadamard transform remains in the name of the spectrometer.

This chapter is concerned with the design, construction and testing of a foil mask spectrometer for energy resolved detection of Laue diffraction patterns. A description of the spectrometer in terms of design and principle of operation begins the chapter. This section is followed by a set of simulations investigating the properties of such a spectrometer. This is followed by experimental tests of the system. The chapter will end
with a summary of the system's capabilities and conclusions based on the tests of the devices.

5.1 Considerations for an Energy Resolved Area Detector

The Laue experiment has a variety of features that need to be considered when creating an energy resolved detection system. The spots observed typically appear at high spatial frequency requiring the detector to have a large number of elements, ideally over a large area. Each detected reflection contains energy information characteristic of the crystallographic plane that produced it. Some points in space contain multiple energies corresponding to overlapping orders of diffraction (Helliwell, 1992). The most demanding environment for the detection of energy resolved Laue diffraction patterns is that found in synchrotron facilities where incident beam intensities are very high. The detector for this application needs to be able to cover a large area, have fast response at the energy of the spots and be able to handle a large number of X-ray photons simultaneously. Prior to the beginning of this project there was no high resolution energy resolved measurement system suitable for use with Laue diffraction at synchrotron facilities and little or no speculation had been made about how to produce such a system. If an area detection system were available that allowed the determination of position, intensity, and energy simultaneously, additional features of the Laue experiment could be unlocked. This chapter describes the design and properties of a foil mask spectrometer
uniquely suited to Laue diffraction.

The foil mask spectrometer for X-rays relies on wavelength modulation of the incident beam using a series of metal foils of varying composition and thickness. Modulation of the intensity of the resultant Laue diffraction image is encoded in a series of images taken through the foils measured in the intensity domain. These intensity domain images are then used to compute an energy image which could be used for determination of unit cell parameters. The foil mask spectrometer is capable of producing high resolution energy measurements on the monochromatic reflections which make up the majority of reflections from the Laue diffraction pattern (Cruikshank, Helliwell, and Moffet, 1987). These monochromatic reflections may be used to determine the unit cell parameters (see chapter 6). Knowing these parameters, the energies corresponding to reflections containing overlapping orders of diffraction can be predicted and the intensity of the overlapped orders can be determined for space group assignment.

This chapter describes the design, properties, and limitations of such a spectrometer and discusses its application to Laue diffraction. Three primary modes of operation are available. It can be used as a low resolution system for broadband radiation. It may be used as a high resolution system for monochromatic X-rays. Finally it can be used to separate intensity components of Laue harmonics of known energy. This last case also applies to X-ray beams which can be represented as a sum of monochromatic components and not specific to the case of Laue harmonics.
5.2 High Resolution Energy Determination of Monochromatic X-rays.

A block diagram of a simplified foil mask spectrometer is illustrated in Figure 5.1. The spectrometer works on the principle that materials absorb X-rays based on their elemental composition. Pure metal foils have an X-ray absorption spectrum characteristic of the thickness and electronic properties of the element composing the foil. Foils composed of alloys could also be used, but the presence of multiple K edges in the material would make subsequent analysis more complicated. The spectrometer consists of a series of foils arranged in a "color wheel", an X-ray source, and a detector. The foils are used to partially or completely "mask" spectral regions in a predictable way. By modulating the incident beam in the energy domain, the energy information can be encoded in a series of measurements made with an energy insensitive detector.

Let \( T(\lambda) \) be the mathematical relationship between the transmission efficiency of a foil and the energy of the incident beam. In practice, this relationship is measured at particular wavelengths or may be computed from tabulated data. When applied to Laue diffraction the incident polychromatic beam passes through a given foil and is attenuated in an energy dependent manner described by \( T(\lambda) \) of the particular foil. The attenuated beam subsequently hits the crystal and is diffracted. The diffracted beams form a pattern of spots on an area detector. In a Laue diffraction pattern, the majority of these spots are

* All symbols used in this chapter are given in Table 5. 1.
† All the tabulated data used in computations of \( T \) values are from the CRC Handbook of Spectroscopy Volume 1. J.W. Robinson (ed.) CRC Press, Cleveland Ohio, 1974.
Figure 5.1: Block Diagram of a Foil Mask Spectrometer

Schematic representation of a ten element foil mask spectrometer. Although not shown here post-foil collimation must be applied. In this figure the elemental foils are introduced before the beam reaches the sample. While this arrangement is not required, it is advantageous. If the foil is placed after the crystal a parallax correction must be applied to correct for the angle $\theta$ between the incident beam and the foil. Under such conditions the transmission efficiency for a given energy will be: $T = e^{-\mu(\frac{x}{\cos\theta})}$. Where $x$ is the thickness of the foil, $\theta$ the angle of incidence, and $\mu$ the linear absorption coefficient. This reduces the intensity rapidly at high angle and aggravates the $\sin(\theta)/\lambda$ fall off in intensity in diffraction applications. For this reason the geometry illustrated here has been adopted. (Artwork Courtesy of Sean Madden)
created by monochromatic X-rays (Cruikshank, Helliwell, and Moffet, 1991). A series of measurements of the intensity of the beam before and after each metal foil is placed in the beam are made. The transmission efficiency corresponding to each foil is evaluated and the energy of the X-rays is estimated by comparing the measured transmission efficiency with a set of tabulated transmission efficiencies in a look-up table containing transmission and energy. The energy, or energies corresponding to this transmission efficiency are then reported. This process is illustrated in Figure 5.2 for the case of a 50 μm aluminum foil.

A foil mask spectrometer can be used in two ways. These include a high resolution spectrometer for measuring the energy of a monochromatic source or a low resolution spectrometer for measuring the energy distribution of a polychromatic source. The theory describing the properties of the low resolution spectrometer will be presented. The first is applicable to determining the energy of x-rays in monochromatic reflections in a Laue diffraction pattern.

5.3 Propagation of Noise from the Intensity Domain into the Energy Domain

The energy resolution of a foil mask spectrometer is limited by the error in the determination of transmission efficiency and the derivative of the equation relating energy to transmission efficiency. Transmission efficiency is defined in equation 5.1.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T(\lambda)$</td>
<td>Function relating the transmission of x-rays through a foil to the energy of the incident x-ray.</td>
</tr>
<tr>
<td>$\vec{T}$</td>
<td>Row vector containing values of $F(\lambda)$ at particular energies.</td>
</tr>
<tr>
<td>$\vec{T}_{el}$</td>
<td>$\vec{T}$ for a particular element. Example: $\vec{T}_{Cu}$ contains values of $\vec{T}$ for the element copper.</td>
</tr>
<tr>
<td>$T$</td>
<td>Matrix consisting of $n$ rows with each row corresponding to a different set of $\vec{T}$ values.</td>
</tr>
<tr>
<td>$S(\lambda)$</td>
<td>Function relating the energy of an X-ray photon to the Intensity of the X-ray source at that wavelength.</td>
</tr>
<tr>
<td>$\vec{S}$</td>
<td>Column vector containing values of $S(\lambda)$ at particular energies.</td>
</tr>
<tr>
<td>$I$</td>
<td>An intensity measurement made with an energy insensitive detector on an X-ray beam after passing through an foil.</td>
</tr>
<tr>
<td>$\vec{I}$</td>
<td>A column vector of intensity measurements passing through a set of foils as defined in an $T$ matrix.</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle of incidence between the foil mask and the X-ray beam.</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Linear absorption coefficient.</td>
</tr>
<tr>
<td>$x$</td>
<td>Foil thickness.</td>
</tr>
<tr>
<td>$T$</td>
<td>Transmission efficiency of a foil mask at a particular energy, defined as the intensity after absorption divided by the incident intensity.</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density.</td>
</tr>
</tbody>
</table>
Figure 5.2: Conversion of Transmission Efficiency to Energy

Illustration of the principle behind a foil mask spectrometer. A measured transmission efficiency of 0.78 results in an energy of 12 keV. Data is for a 50 micron Al foil.
\[ T = \frac{I_{\text{mask}}}{I_0} \]  

The theoretical best case for the error in measurements of \( I_{\text{mask}} \) and \( I_0 \) are determined by Poisson statistics.

\[ \sigma_{I_{\text{mask}}} = \sqrt{I_{\text{mask}}}; \sigma_{I_0} = \sqrt{I_0} \]  

Propagating these errors into the determination of \( T \) results in equation 5.3.

\[ \sigma_T = \sqrt{(1 + T) \frac{T}{I_0}} \]  

In this analysis it is assumed that the published tables of transmission efficiency and energy are well measured and do not represent a large source of error. The error defined by equation 5.3 then propagates by a factor of the derivative of the relationship between transmission efficiency and energy, \( |dE/dT| \).

\[ \sigma_E = \left| \frac{dE}{dT} \right| \sqrt{(1 + T) \frac{T}{I_0}} \]
This equation represents a theoretical best case for a system limited by Poisson noise. Other sources of error, such as source flicker or detector read noise, will degrade this performance.

Equation 5.4 has several consequences that allow the resolution of a foil mask spectrometer to be optimized. First, $|\frac{dE}{dT}|$ can be minimized by selection of foil thickness and composition. Second, the incident beam intensity, $I_0$, should be as large as possible. Selection of foils represents a compromise allowing a wide energy range to be measured. Figure 5.3 shows the error function defined by equation 5.4 plotted for increasing values of $I_0$ for a 25 micron Nb foil. Figure 5.4 shows a plot of $|\frac{dE}{dT}|$ as a function of energy for Nb foils of varying thickness.

Equation 5.4 also assumes that the full width at half maximum (FWHM) of the energy distribution of the incident X-ray beam is much smaller than $\sigma_E$. The energy measured by the spectrometer shows a dependence on the FWHM (see section 5.9). This dependence is complex and depends on the foil and the energy of the incident beam.

5.4 Low Resolution Determination of Broad Band X-ray Sources Having Broad Spectral Features

Using the definition of $T(\lambda)$ developed in section 5.2, assume that $T(\lambda)$ is measured at $n$ different values of $\lambda$. These values of $T$ are stored in a row vector, $\bar{T}$. If
Figure 5.3: Modeled Energy Resolution for Varying X-ray Photon Levels

Plot of equation 5.4 for increasing values of $I_0$. Solid squares - $I_0 = 10$ photons, solid diamonds $I_0 = 100$ photons, solid triangles - $I_0 = 1000$ photons, solid circles - $I_0 = 10000$ photons, and open squares - $I_0 = 100000$ photons. Plot uses a 25 μm Nb foil. Discontinuity is due to the K edge of Nb.
Figure 5.4: Derivative of Energy with Respect to Transmission Efficiency

Derivative of the energy with respect to transmission efficiency for Nb foils of varying thickness. Open squares -5 μm, open diamonds - 15 μm, open triangles - 25 μm, open circles - 50 μm, filled squares - 100 μm. Discontinuity is due to the Nb K edge. The thinnest foil allows for optimum resolution at low energies but the 5 μm foil has a limited range. 25 μm represents a compromise giving a wide range of utility.
the incident intensity of an X-ray source as a function of \( \lambda \) is given by the function \( S(\lambda) \). this can be represented as a column vector, \( \mathbf{S} \), when evaluated at known intervals. As is the case with \( T(\lambda) \), in practice \( \mathbf{S} \) is measured at particular wavelengths. The product of \( \mathbf{T} \) and \( \mathbf{S} \) gives the total intensity, \( I \), of an X-ray beam after passing through a foil mask.

\[
I = \mathbf{T} \cdot \mathbf{S} \tag{5.5}
\]

If many such masks are available then \( T_{\text{el}}(\lambda) \), the transmission spectrum for each elemental mask, can be defined and the intensity of an x-ray beam passing through each mask can be computed. \( T \) is defined as a matrix, each row of which corresponds to a different mask and to the transmission efficiency at a particular wavelength interval. Equation 5.6.

\[
\mathbf{I} = \mathbf{T} \cdot \mathbf{S} \tag{5.6}
\]

The quantity of experimental interest is \( \mathbf{S} \), the energy spectrum of the incident beam. \( \mathbf{I} \) and \( \mathbf{T} \) are the known quantities, while \( \mathbf{S} \) is unknown. \( \mathbf{S} \) can be determined by computing the inverse matrix \( \mathbf{T}^{-1} \) and applying it to \( \mathbf{I} \). equation 5.7.
Equation 5.7, which assumes that the inverse matrix $\mathbf{T}^{-1}$ can be computed, is a simplified expression defining a low resolution X-ray spectrometer for polychromatic radiation. There are a number of limitations. First, as many masks must be employed as there are desired energy resolution elements. Second, the spectral features must be broad relative to the width of each resolution element (see section 5.9). Additionally, propagation of uncertainty is far more complex in this system than in the spectrometer for high resolution measurements of monochromatic X-rays. In practice, use of a spectrometer of this type would probably require an over determined multiple linear regression approach to the data analysis since some foils will have near zero transmission efficiency. While intriguing, such a spectrometer is of limited utility and will not be developed further here.

5.5 Application to Laue Diffraction

The Laue experiment consists of an incident polychromatic beam of radiation. This polychromatic beam may come from either a laboratory scale source or a synchrotron. While the incident beam is polychromatic, two features of the diffracted beams from the Laue experiment allow the application of the foil mask spectrometer to the problem. First, the majority of reflections from the crystal produce monochromatic

\[ \mathbf{\tilde{S}} = \mathbf{T}^{-\mathbf{f}} \]
X-rays (Helliwell, 1992; Cruickshank et al., 1987). Second, the remaining reflections either contain harmonic overlaps or spatial overlaps. The considerations in Part 5.2 are sufficient for measuring the position, energy, and intensity of monochromatic reflections. The intensity of each component in a position containing harmonic or spatial overlap may also be treated using the foil mask spectrometer provided the energies are previously known. In Laue diffraction, if the unit cell parameters and the orientation matrix of a crystal are known then the energies present in all spots may be computed. Knowing the energies present, the intensity of the spot may be partitioned among the energies present by setting up a system of linear equations. For example, let a set of Laue harmonics produce diffracted X-rays with energies $\lambda_1, \lambda_2, \lambda_3, \ldots, \lambda_n$. Let each harmonic component of the incident beam have intensity $H_{\lambda_1}, H_{\lambda_2}, H_{\lambda_3}, \ldots, H_{\lambda_n}$. Let $T_1(\lambda), T_2(\lambda), T_3(\lambda), \ldots, T_n(\lambda)$ be the functions relating energy to transmission efficiency for masks 1, 2, 3, \ldots, n, and let $I_1, I_2, I_3, \ldots, I_n$ be the measured intensities through each mask in the spectrometer. If the energies are known, this reduces to the system of the linear equations 5.8.

$$
\begin{bmatrix}
I_1 \\
\vdots \\
I_n
\end{bmatrix}
= 
\begin{bmatrix}
T_{1,1} & \ldots & T_{1,n} \\
\vdots & \ddots & \vdots \\
T_{n,1} & \ldots & T_{n,n}
\end{bmatrix}
\begin{bmatrix}
H_1 \\
\vdots \\
H_n
\end{bmatrix}
$$

5.8

It should be noted that these equations may also include the trivial case of no mask at all.

A consequence of this set of equations is that the maximum number of harmonics which
may be resolved into individual intensity components depends on the number of masks in
the spectrometer. In practice, equation 5.8 will usually represent an over determined
system of equations and should be evaluated using standard statistical procedures (See
chapter 6 for details). Additionally, these equations could presumably be used to resolve
spatially overlapped reflections, those which are not sufficiently separated in space to be
distinguished. Such conditions are common in proteins when the crystal to detector
distance is small. Again this requires a knowledge of the spatial resolution of the detector
system and computation of energy and position for the multiply overlapped reflections.

5.6 Instrumental Considerations - Detectors

The ideal detector for use with a foil mask spectrometer would have unity gain
at all energies and 100% quantum efficiency. While such a detector would be desirable,
it is not a requirement. Detectors that might be used for this purpose are silicon
intensified targets (SITs) (Arndt, 1990; Li, Phillips, Stanton, and Kalata, 1992), charge
coupled devices (CCDs) (Phillips, Li, Stanton, Xie, and O'Mara, 1993; Allinson, 1989),
charge injection devices (CIDs) (Hanley, True, and Denton, 1995), image plates
(Miyahara, Takahashi, Amemiya, Kamiya, and Satow, 1986), multiwire detectors, and
even photographic film. It should also be noted that single channel detectors such as
avalanched photodiodes, GM counters, scintillation counters, and ion chambers could
also be used. Single channel detectors incorporating a foil mask spectrometer could be
used as low cost alternatives to Si(Li) detectors for assessing the amount of overlap in beams using multilayers for monochromation, particularly in very high flux environments.

5.7 Eliminating K edge ambiguities in Energy determinations

Inclusion of elements having K edges in the range from 4-40 keV results in ambiguity in the determination of the energy of the incident X-ray beam. A given transmission efficiency can result in three separate values for energy. This behavior is illustrated in Figure 5.5. It is important to determine ways to eliminate K edge ambiguities so as to obtain an unambiguous measurement of the energy of an incident beam of monochromatic x-rays. This may be done by selecting regions over which the transmission efficiency curve for a particular foil is single valued. Such regions are tabulated for the foils used here in Table 5.2.

A further problem is that reliable estimates of energy depend on good measurements of T. Foils for which the estimated error is large as predicted by equation 5.4 need to be excluded from the determination of energy. If a scintillation counter or multiwire detector is used, evaluation of the estimated error associated with a measurement may be done through the use of equation 5.4. In other cases a rough rule is
The region between a transmission efficiency of approximately 0.15 to 0.75 results in ambiguous values of energy due to the K edge of Nb. From data processing the matches can be restricted to regions where |dE/dT| is positive. This avoids the K edge. Selection of the remaining from among the remaining two values is done by applying the criteria in part 6. Data presented is for a 25 micron Nb foil.
to limit the use of foils where the transmission efficiency is less than 0.10 or greater than 0.80.

For a particular position in a measured Laue pattern, the transmission efficiency is first evaluated for each foil. The energy or energies corresponding to the measured transmission efficiency are computed, including ambiguous values. Energy values from each foil are evaluated in order of appearance in Table 5.2 to eliminate those outside the transmission efficiency criteria (0.1 < T < 0.8). The first foil meeting the criteria is used to set a target energy for eliminating K edge ambiguities. If a K edge for a particular foil is within 0.8 keV of the target energy, then data from that foil are excluded. In the case of ambiguity, the value closest to the target energy is selected. Selected values meeting all of these conditions are averaged to obtain an initial estimate of the energy.

The initial estimate of the energy is refined using least squares minimization of the difference between the measured and predicted transmissions efficiencies. When a minimum is reached the energy value is reported. Quality of the measurement of the energy is assessed using the final sum of squares.

5.8 Design

The design of the Foil Mask Spectrometer was selected based on three primary factors. An energy resolved detection capability from 4-40 keV was desired. These limits were approximately matched to the available wavelengths from a Rotating anode source operating in atmosphere with an acceleration voltage of 40 kV. The ambiguity
introduced into the measurements of energy by K edge effects must be resolvable in a simple fashion. Finally, the spectrometer needed to be constructed at low cost with readily obtainable materials.

The energy range criteria required that foils of several materials be used to allow energy dependent attenuation of the incident beam over the full range. The following materials were considered when designing the spectrometer system: Al, Au, Fe, In, Mo, Ni, Pd, Rh, Ta, Ti, Y, Co, Nb, Zr, Sn, Cu, Ag, and bronze alloy. Rare earth metals were also considered but were rejected due to sensitivity to oxidation by air. There is no reason such elements cannot be used if given a thin polymer coating, but given project constraints these were rejected. After simulations of the Au foil, the behavior of elements having high atomic charge were eliminated for use with this target energy range due to prominent L edges. The L edges of these elements introduce additional ambiguities into the assignment of energy from a foil. Elements of the final transition should be considered if the energy range of the spectrometer is extended. Here, however, the high cost of appropriate thickness foils could not be justified.

Foil thickness was chosen in a compromise between wide energy range and spectrometer resolution. As illustrated in Figure 5.4 resolution is enhanced by increasing the magnitude of the derivative of Energy with transmission efficiency (dE/dT). For best results a set of foils should seek to have several different foils having transmission efficiencies in the range from 0.1<x<0.9 for any value of energy.

Based on these design criteria a 12 foil spectrometer was designed. The foils and
suppliers are found in Table 5.2. The indium foil was not used in the final spectrometer system due to difficulty calibrating its thickness.

The foils were mounted in a brass wheel which served two purposes: mechanical support of the foils and post-foil re-collimation of the X-ray beam. The crystallites in the metal foil behave similarly to a powder resulting in scatter of the incident beam in addition to absorption. A drawing of the wheel may be found in Figure 5.6.

5.9 Simulations

The initial idea for the foil mask spectrometer was similar to the low resolution spectrometer discussed in section 5.4. It was thought that the matrix approach could be applied using a series of increasingly more accurate T matrices. For example the T matrix might initially include 11 spectral elements each of which would represent the average value over an energy range of 4 keV (for a 0 to 40 keV). The energy would be computed in crude fashion and a new T matrix more finely tuned to the data would be constructed. Suppose the true energy was 11 keV. In this situation it was supposed that the third energy resolution element (8-12 keV) would show the majority of the signal. The new T matrix would be constructed to only cover the 8-12 keV range. The process would be repeated until the energy was found. This approach was simulated using 1000 element T vectors applied to the energy distributions represented by 1000 data points. Each energy distribution was assigned a σ of 0.25 keV. Source models of this type or presented in Figure 5.7. The full 1000 points were multiplied by the 1000x11 T matrix.
Color wheel is constructed of 0.5 inch brass. Holes are 1/16\(^{th}\) inch diameter drilled on 18 degree centers 2.5 inches from the center. A photo of the device appears on the left. The foils set on the photo matches that reported later in the chapter.
Source models for simulated X-ray sources having 0.25 keV $\sigma$. These sources, when multiplied by an appropriate $T$ matrix give an Intensity matrix. The values in the intensity matrix correspond to the measured intensity through a particular foil.
Figure 5.8: Reconstruction of a 22 keV Source Using an 11x11 Inverse Matrix

A reconstructed energy distribution of a source having a 0.25 \( \sigma \) distribution. As can be seen with this simulation the reconstruction using this method of a narrow band source is extremely poor. Negative intensities are computed and ringing outside the range of the true source is seen. In this case, the strongest intensity components are found roughly in the same location as the centroid of the incident source. The ringing outside the range of interest is due to the average value of the transmission efficiency being a poor representation of the transmission efficiency at the energy of the “monochromatic” source. This behavior is particularly bad in the vicinity of a K edge in a foil.
Figure 5.9: Reconstruction of a 26 keV Source Using an 11x11 Inverse Matrix

A reconstructed energy distribution of a source having a 0.25 \( \sigma \) distribution. As seen in the previous figure, the reconstruction using this method of a narrow band source is extremely poor. Negative intensities are computed and ringing outside the range of the true source is seen. Unlike the previous example, the strongest intensity components are not found clearly in the vicinity of the centroid of the incident source. The ringing outside the range of interest is due to the average value of the transmission efficiency being a poor representation of the transmission efficiency at the energy of the “monochromatic” source. This behavior is particularly bad in the vicinity of a K edge in a foil.
This results in a simulated intensity vector corresponding to what would be measured by a detector on the other side of each foil. An inverse T matrix (11x11) was used to recover the energy distribution.

The simulation showed that the initial idea would not work readily. In the best cases the low resolution computations involving the 11x11 matrix resulted in "ringing" behavior in the vicinity of the true energy Figure 5.8 and Figure 5.9. The observed behavior is the result of the average value of the transmission efficiency over the width of the energy bin is a poor representation of the transmission efficiency of a "monochromatic" source of X-rays. In the case of a K edge being present for a foil in the range of an energy bin this behavior is particularly pronounced. The result is ill-behaved reconstructions that are not suitable for further analysis. For these reasons, the matrix approach for monochromatic X-ray sources was discarded in favor of the approach described in section 5.7.

It is possible that selecting energy bin boundaries to match with the K edges of a particular foil set might reduce this effect. This approach was not tried. Additionally, it might be possible to store a look up table of intensity vectors for monochromatic sources and, using least squares matches to these vectors, to obtain the incident source distribution. Again this approach was not tried.

An additional concern in the case of "monochromatic" radiation in the incident beam was the effect of the peak width in the energy domain of the "monochromatic" incident beam. This is of concern in cases where mosaic spread in a crystal is high and
the resulting energy distribution broader. To assess this an incident source with a mean energy of 8.0 keV was simulated. The full width at half maximum (FWHM) was allowed to vary from 0.05 to 6.4 keV. The simulated source was assumed to interact with a Cu foil and the energy computed using a single foil. The results of these simulations are found in Figure 5.10. The method is robust up to an FWHM of about 0.4 keV. This simulation indicated that for most purposes the FWHM can be assumed to be much smaller than the resolution of the spectrometer. Further investigation of this relationship could be of use. The full relationship between peak bandwidth and the measured energy is presumably very complex as it will depend on the position of K edges and the thickness of foils. The relationship was not investigated beyond this one simulation.

Table 5.2: Foil Compositions and Thickness

<table>
<thead>
<tr>
<th>Element</th>
<th>Purity (%)</th>
<th>Nominal Thickness ((\mu m))</th>
<th>Measured Thickness ((\mu m))</th>
<th>Supplier</th>
<th>Single valued areas 4-40 keV&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>99.0</td>
<td>12.5</td>
<td>11.2</td>
<td>Goodfellow</td>
<td>Entire Range</td>
</tr>
<tr>
<td>Al</td>
<td>99.5</td>
<td>25.4</td>
<td>25.4</td>
<td>Alfa</td>
<td>Entire Range</td>
</tr>
<tr>
<td>Al</td>
<td>99.0</td>
<td>50</td>
<td>50.2</td>
<td>Goodfellow</td>
<td>Entire range</td>
</tr>
<tr>
<td>Ti</td>
<td>99.6+</td>
<td>15</td>
<td>16.2</td>
<td>Goodfellow</td>
<td>&gt; 12.5 keV</td>
</tr>
<tr>
<td>Ni</td>
<td>99.5</td>
<td>25</td>
<td>25.0</td>
<td>Alfa</td>
<td>&gt; 20 keV</td>
</tr>
<tr>
<td>Cu</td>
<td>99.9</td>
<td>12.5</td>
<td>13.2</td>
<td>Alfa</td>
<td>&gt; 20 keV</td>
</tr>
<tr>
<td>Zr</td>
<td>99.99+</td>
<td>25</td>
<td>20.0</td>
<td>Alfa</td>
<td>&lt; 8 keV</td>
</tr>
<tr>
<td>Nb</td>
<td>99.8</td>
<td>25</td>
<td>25.0</td>
<td>Alfa</td>
<td>&lt; 8 keV</td>
</tr>
<tr>
<td>Mo</td>
<td>99.95</td>
<td>12.7</td>
<td>13.5</td>
<td>Alfa</td>
<td>&lt; 9 keV</td>
</tr>
<tr>
<td>Ag</td>
<td>99.9</td>
<td>25</td>
<td>24.7</td>
<td>Alfa</td>
<td>&lt; 12 keV</td>
</tr>
<tr>
<td>In</td>
<td></td>
<td>127</td>
<td></td>
<td></td>
<td>20 &lt; E &lt; 25.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> - a 1 keV margin of error has been included when selecting these regions and the energy range has been restricted to 4-40 keV.
Simulated relationship between the FWHM of the energy distribution of an incident X-ray source and the Energy determined using a single foil. Simulation used an 8.0 keV source and a single Cu foil. Although exhaustive modeling of the relationship was not performed, the behavior indicates that if the source energy distribution is narrower than the resolution of the spectrometer little impact on the measurements is expected.
5.10 Experimental

Foils of Cu, Ag, Al, Nb, Mo, Zr, and Ni were obtained from Alfa Aesar (Ward Hill MA). All remaining foils were obtained from Goodfellow (England). Specifications and purity of these foils are presented in Table 5.2. The thicknesses were measured by determining the transmission efficiency of the foil using Mo and Cu Kα radiation.

Verification of equation 2.4 was done by making a series of measurements of $I_0$ and $I$ for a monochromatic X-ray beam of known energy. A total of twenty five values of transmission efficiency were obtained for each foil. The energy was computed for each of the foils at each individual measurement of transmission efficiency. The reported measured random error is the standard deviation of the series of measurements through each foil. The predicted error was computed based on $I_0$, $I$, and equation 5.4. The X-ray source in these experiments was a sealed tube Mo source followed by a graphite monochromator. The 0, -1, 0 reflection from 2-dimethylsulfurylidene-1,3-indandione (Christensen and Thom, 1971) was used to produce an X-ray source of appropriate intensity. The difference between the literature value for the Mo Kα radiation and the mean value of energy measured with each foil is reported as systematic error.

A series of Laue diffraction images of tetraphenyl-phosphonium tetrachloro-oxomolybdenum (V) were taken using an indirect charge injection device camera system previously described (Hanley, True, and Denton, 1995: Chapter 3, this dissertation). Exposures were taken with and without the foils attenuating the incident beam. X-rays
were generated using an Enraf-Nonius FR571 rotating anode X-ray source with a Mo anode. A photograph of the assembled system appears as Figure 5.11. The unfiltered direct beam was used to generate the Laue diffraction pattern. The system operating conditions and the crystal system parameters are outlined in Table 5.3. The orientation of the crystal was found and refined using the program LAUEGEN. Prediction of the energies present at locations of known index were made using the simulation option of LAUEGEN. Additional image processing was done using the Image Reduction and Analysis Facility (IRAF) written by the National Optical Astronomical Observatories (NOAO) running on a Sparc Station II (Sun Microsystems). Peak search and integration was done using the IRAF PHOT subprogram. Separation of harmonic overlaps into component intensities was done using multiple linear regression with stepwise inclusion of components having P values less than 0.05. Since each integrated value was

<table>
<thead>
<tr>
<th>Table 5.3: System Characteristics and Cell Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
</tr>
<tr>
<td>Crystal space group</td>
</tr>
<tr>
<td>(Carducci, 1994)</td>
</tr>
<tr>
<td>Unit cell parameters</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>(Carducci, 1994)</td>
</tr>
<tr>
<td>X-ray Source</td>
</tr>
<tr>
<td>Source Voltage</td>
</tr>
<tr>
<td>Source Current</td>
</tr>
<tr>
<td>Detector</td>
</tr>
<tr>
<td>“Raster Size”</td>
</tr>
<tr>
<td>Image Size</td>
</tr>
</tbody>
</table>
Figure 5.11: Foil Mask Spectrometer System

Photograph of the assembled foil mask spectrometer. The system consists of an area detector, a white X-ray source, and a "color wheel" for modulating the incident X-ray beam. Also shown is an Enraf-Nonius CAD-4.
background corrected the regressions were forced to include the origin. This initial analysis was done using the SPSS computer program.

5.11 Results

Calibration:

The measured X-ray thickness of each foil is given in Table 5.2. The results of a comparison of expected random error and measured random error in determinations of the energy of Mo Kα radiation are plotted in Figure 5.12. The 12.5 micron Al foil and the 25 micron Zr foil do not appear in this figure. The 12.5 micron Al foil does not attenuate the beam sufficiently. The 25 micron Zr foil, while significantly attenuating the beam, has a K edge very close to the Mo Kα emission energy. This results in poor estimates of energy. Systematic errors for these same foils are charted in Figure 5.13. The data for expected random error, measured random error, and systematic error are tabulated in Table 5.4. The average energy using all foils meeting the criteria outlined in section 3.7 is $17.5 \pm 0.1$ (s.e) keV. remarkably close to the literature value of 17.48 keV. Similar measurements made using Cu Kα gave a value of $8.08 \pm 0.05$ (s.e) keV. again close to the literature value of 8.05 keV.
Figure 5.12: Comparison of Predicted and Measured Random Errors

Plot of expected random error Vs measured random error for 8 foils measuring Mo Kα X-rays. The thinnest Al foil and the Zr foil are excluded from this plot, see text for details. Slope of the line is $0.73 \pm 0.06$. True error is slightly degraded from the theoretical best case. In all cases the value of $I_O$ was approximately 45500 counts.
Figure 5.13: Systematic Errors for Each Foil

Systematic errors for each of the foils in preceding figure. Under conditions of measurement the aluminum foils would be excluded due to the large expected error based on the shot noise model. Under conditions where the number of counts is unknown $T$ should be constrained between 0.10 and 0.8.
Table 5.4: Comparison of Predicted and Measured Errors

<table>
<thead>
<tr>
<th>Foil</th>
<th>Estimate Random Error(^a)</th>
<th>Measured Random Error(^b)</th>
<th>Systematic Error(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 25.4</td>
<td>1.7</td>
<td>2.3</td>
<td>1.38</td>
</tr>
<tr>
<td>Al 50</td>
<td>0.76</td>
<td>1.2</td>
<td>0.91</td>
</tr>
<tr>
<td>Ti 15</td>
<td>0.30</td>
<td>0.46</td>
<td>-0.03</td>
</tr>
<tr>
<td>Ni 25</td>
<td>0.058</td>
<td>0.11</td>
<td>-0.36</td>
</tr>
<tr>
<td>Cu 12.5</td>
<td>0.095</td>
<td>0.14</td>
<td>-0.19</td>
</tr>
<tr>
<td>Nb 25</td>
<td>0.14</td>
<td>0.25</td>
<td>0.39</td>
</tr>
<tr>
<td>Mo 12.7</td>
<td>0.21</td>
<td>0.30</td>
<td>0.17</td>
</tr>
<tr>
<td>Ag 25</td>
<td>0.087</td>
<td>0.11</td>
<td>0.12</td>
</tr>
</tbody>
</table>

\(^a\) Random error estimates were computed using equation 5.4 and the measured I and I\(_o\).
\(^b\) The standard deviation of a series of energy measurements is reported as measured random error.
\(^c\) The difference between the literature value of Mo K\(_\alpha\) radiation and the mean value of a series of measured energies is reported as systematic error.

Crystal Orientation and Pattern Indexing:

Figure 5.14 is the I\(_o\) Laue diffraction pattern image taken of tetraphenylphosphonium tetrachloro-oxomolybdenum (V). The center of the pattern was found using conic centering. Twenty reflections were selected interactively using LAUEGEN and the orientation of the diffraction pattern was found based on the known unit cell parameters and crystal class. The orientation angles, crystal to detector distance, and detector parameters (bulge, tilt, and twist) were further refined after entry of 156 reflections matching the simulated pattern. Refined parameters are summarized in Table 5.5. Figure 5.14 also shows the predicted pattern superimposed on the observed image.
Energies for observed reflections consisting of monochromatic or harmonic overlaps were simulated using LAUEGEN based on the refined orientation.

Eleven images of the Laue pattern were measured. Each corresponded to one of the foil masks or the $I_n$ image. The ten mask images are shown in Figure 5.15. The spots in the image were selected interactively using IRAF and the intensities integrated. Energy analysis was attempted on a total of 118 positions, regardless of the existence of multiple harmonic overlaps. Of these 118 positions 92 were predicted to be monochromatic, 14 were doubles, 4 were triples, 6 were quadruples, and 2 were sextuples.

Table 5.5: Detector Characteristics and Crystal Orientation

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phix</td>
<td>91.80°</td>
</tr>
<tr>
<td>Phiy</td>
<td>3.51°</td>
</tr>
<tr>
<td>Phiz</td>
<td>107.89°</td>
</tr>
</tbody>
</table>

Refined Detector Characteristics

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal to Detector Distance</td>
<td>68.99 mm</td>
</tr>
<tr>
<td>X Center</td>
<td>237.4</td>
</tr>
<tr>
<td>Y Center</td>
<td>243.1</td>
</tr>
<tr>
<td>&quot;Twist&quot;</td>
<td>44.589 (0.01°)</td>
</tr>
<tr>
<td>&quot;Tilt&quot;</td>
<td>75.578 (0.01°)</td>
</tr>
<tr>
<td>&quot;Bulge&quot;</td>
<td>17.516 (0.01°)</td>
</tr>
</tbody>
</table>
Figure 5.14: Observed and Predicted Laue Pattern

Image on the left is the Laue diffraction pattern of tetraphenylphosphonium tetrachlorooxomolybdenum(V). The Image on the Right is the same pattern with the predicted pattern superimposed. The predicted pattern was simulated based on known unit cell parameters and LAUGEN.
Figure 5.15: Intensity Images Taken Using Each of the Foils

Example data set taken using the foil mask spectrometer. Each image is the result of diffraction from a beam which has been modulated in an energy dependent fashion. The difference is difficult to detect with the eye. The best way to tell that the incident beam has been altered is by noticing the appearance and disappearance of horizontal streaks due to row crosstalk from the CID detector.
Monochromatic Energy Comparison:

Using the simulated pattern the reflections containing monochromatic components were selected. The 92 reflections were sorted in order of increasing sum of squares as defined in part 6. These were divided in half with the best 46 and the worst 46 in separate groups. The two groups are plotted against the predicted energy in Figure 5.16. The ratio of predicted to measured energy is $0.993 \pm 0.034$ for the best group and $0.767 \pm 0.298$ for the worst group.

Harmonic Overlaps:

Harmonic overlaps were present in 26 of the observed spots. The estimated number of harmonics present in these spots ranged from 2-6. Of the 31 positions predicted to contain harmonic overlap, 14 were doubles, 4 were triples, 6 were quadruples, and 2 were sextuples. Regression analysis for each type of overlap are summarized in Table 5.6. Further analysis was not done since the wavelength normalization curve for the detector system is unknown.

5.12 Discussion

Calibration

Figure 5.12 and Figure 5.13 demonstrate the potential of the foil mask
### Table 5.6: Regression Analysis of Harmonics Using SPSS

<table>
<thead>
<tr>
<th>Harmonic Type</th>
<th>(h. k. l)</th>
<th>Energy</th>
<th>Intensity</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Double</strong></td>
<td>(-1, 1, 3)</td>
<td>10.8</td>
<td>1694 ± 304</td>
<td>0.0003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.6</td>
<td>643 ± 237</td>
<td>0.0237</td>
</tr>
<tr>
<td>Regression Statistics:</td>
<td>R² = 0.977</td>
<td>F = 196</td>
<td>Significance &lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>Regression = 2</td>
<td>Residual = 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Triple</strong></td>
<td>(-1, -1, -2)</td>
<td>9.27</td>
<td>431 ± 94</td>
<td>0.0018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.54</td>
<td>451 ± 134</td>
<td>0.0099</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.80</td>
<td>428 ± 121</td>
<td>0.0080</td>
</tr>
<tr>
<td>Regression Statistics:</td>
<td>R² = 0.994</td>
<td>F = 452</td>
<td>Significance &lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>Regression = 3</td>
<td>Residual = 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Quadruple</strong></td>
<td>(-1, -2, -1)</td>
<td>10.57</td>
<td>3159 ± 145</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.14</td>
<td>5295 ± 217</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.71</td>
<td>1224 ± 170</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>42.28</td>
<td></td>
<td>N. S.</td>
</tr>
<tr>
<td>Regression Statistics:</td>
<td>R² = 0.999</td>
<td>F = 12.203</td>
<td>Significance &lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>Regression = 3</td>
<td>Residual = 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sextuple</strong></td>
<td>(1, 1, -1)</td>
<td>5.61</td>
<td></td>
<td>N. S.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.23</td>
<td></td>
<td>N. S.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.84</td>
<td>4046 ± 172</td>
<td>0.0000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.45</td>
<td>4263 ± 173</td>
<td>0.0000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.07</td>
<td></td>
<td>N. S.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33.68</td>
<td></td>
<td>N. S.</td>
</tr>
<tr>
<td>Regression Statistics:</td>
<td>R² = 0.999</td>
<td>F = 15.126</td>
<td>Significance &lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>Regression = 2</td>
<td>Residual = 9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Correspondence between predicted and measured energy for best (top) and worst (bottom) measurements of monochromatic reflections. Measurement quality is assessed using the squared difference between the predicted transmission efficiency and measured transmission efficiency. Correspondence degrades rapidly as the sum of squares exceeds 0.2. The line in each figure is for ideal 1:1 correspondence.
spectrometer system. Random errors show a clear correlation with equation 5.4. This shows the resolution of the spectrometer is predictable and can be optimized by increasing the incident X-ray flux and decreasing the value of $|dE/dT|$. With a high incident flux, the random error of the energy measured with a foil mask spectrometer decreases by the square root of the intensity. The value of the slope of measured error versus expected error is 0.73. It is unclear why the slope differs from unity.

At present, systematic errors vary depending on the foil. Several factors may account for these errors in the present spectrometer system. First, a linear interpolation algorithm was used between points giving some inherent error to the computed values of energy. Second, impurities in the foils will result in systematic errors in computed energies. Finally, the measured X-ray thicknesses represent the average of the values obtained using Mo and Cu K$_\alpha$ radiation. As such they represent a compromise. Future systems should seek to calibrate the transmission efficiency of the foils at a variety of energies rather than relying on published values of $\mu/\rho$ as was done here. For example, the transmission efficiency could be measured every 50 eV, resulting in improved energy estimates. Despite these limitations, the average value of energy using these foils is remarkably close to the literature values reported for both Mo and Cu K$_\alpha$ radiation.

Monochromatic Energy Comparison

The data presented in Figure 5.16 shows that the performance of the spectrometer
on images is degraded somewhat from the results obtained for monochromatic Cu and Mo Kα sources. The first fifty percent of the data shows excellent agreement with the predicted values. The sum of squares used to refine the energy values appears to be a good a priori index of data quality. For the system described here, the energy values can be considered reliable provided the sum of squares is kept under 0.2. After this point is reached, the quality of the data degrades rapidly. While it is justifiable to exclude values when the sum of squares gets large, it is more desirable to improve the measurements of transmission efficiency. A sum of squares value of 0.2 obtained from 10 separate masks represents an average disagreement of 0.045 transmission efficiency units. Further development of the technique should be able to improve these measurements considerably. A reasonable target for future systems is to measure all the transmission efficiencies to better than 0.02 transmission efficiency units. This criteria is currently being met by only 4 of the monochromatic spots. If this criteria were to be met the final sum of squares would be less than 0.05. Reaching this level of precision might bring an added benefit by being able to separate spots containing harmonic overlap from monochromatic spots based on a priori considerations.

Harmonic Overlaps

The data in Table 5.6 shows the capability of separating multiple components of a spot containing harmonic overlap using the system of foil masks. The major components
of the overlapped positions can be separated and an error assigned. The data presented here is primarily for demonstration purposes since the wavelength normalization curve of the detector is not known. Without further characterization of the detector the "true" relative intensities can not be verified. Future work in this area should allow this to be tested in more detail.

The method for separation of intensity components containing harmonic overlap described here is similar to the UNSCRAM procedure previously described by Helliwell et al. (Helliwell et al. 1989). UNSCRAM applies to the use of stacked absorbers for unscrambling the intensity components in overlapped spots. The UNSCRAM procedure is general to any system of stacked calibrated absorbers between detecting elements.

While UNSCRAM is most applicable to the use of film as a detector, the analysis described here is general to all systems of absorbers. The instrumental adaptation described has a number of advantages. It is computationally simplified since no parallax correction is needed, a condition which is unavoidable in film systems. It avoids the problems involved in the use and digitization of film images. The use of a solid state detector allows for the possibility of real time assessment of image quality. The system of foils only needs to be calibrated once. In the case of film each lot must be calibrated separately. Finally, since the method is not dependent on a particular detector, the "color wheel" may be physically removed and installed with another detection system without loss of calibration.
5.13 Summary and Conclusions

There are several features of the foil mask spectrometer described here that are attractive for Laue diffraction, particularly at synchrotron facilities. The spectrometer is robust with respect to radiation damage, components are inexpensive to replace, and the method is general to any area detector currently in use. It is well suited to modern solid state camera systems. Unlike energy dispersive detectors, the energy resolution of a foil mask spectrometer improves with the square root of the incident beam intensity. Si(Li) detectors and CCDs used as direct X-ray detectors have degraded performance at high incident beam intensities. The foil mask spectrometer is adaptable to detection systems ranging from single channel scintillation counters to large format CCDs. The primary fundamental limitation of the foil mask spectrometer system is that it requires multiple exposures.

For Laue diffraction, combining crystallographic refinements and position and energy measurements from a foil mask spectrometer should allow complete determination of the space group and unit cell parameters of an unknown crystal. The procedure consists of first determining the energy of each of the monochromatic reflections in the Laue diffraction pattern. These measurements of position and energy can be used to deduce the unit cell of the unknown crystal. Once these are known, the energies that should be present in reflections containing overlapping orders of diffraction can be computed. Knowing the energies that must be present, a set of linear equations
can be set up to measure the intensities of overlapping reflections. In conventional Laue
diffraction, such information is not available and prior monochromatic examination of
crystals is necessary.

Considerable development of the foil mask spectrometer system is still needed. There are three main areas needing improvement. First, improving the precision of
measurements of transmission efficiency will allow a greater portion of observed spots to
be used for later unit cell determination. Second, a detection system needs to be
characterized sufficiently to allow wavelength normalization to be applied to the
collected data. Finally, automated image processing needs to be applied to allow
convenient extraction of peaks from an image. When these problems are solved the
spectrometer system may be useful for full crystallographic structure determination using
Laue diffraction.

The long term goal of this research is to develop instrumentation allowing
complete structure and space group determination using a single instrument and Laue
diffraction. Such instrumentation requires the development of area detectors with high
energy resolution. The foil mask spectrometer meets many of the required properties of
such an instrument. Further development should allow more widespread use of the Laue
diffraction method.
"Even if additional [Laue] photographs are taken with other directions of the X-ray beam, the presence of screw axes can never be fixed, for the absences characteristic of them occur in rows \([h00]^*\), \([0k0]^*\), and \([00l]^*\), which are densely packed with reciprocal-lattice points and which are therefore never available in first order reflections only."

Amoros, Buerger, and Canut de Amoros

*The Laue Method* (1975)
CHAPTER 6

Application of Energy Resolved Measurements to Laue Diffraction

In the previous chapter, the foil mask spectrometer was described. Briefly, this instrument allows the measurement of the energy of a monochromatic, or nearly monochromatic X-ray source to be determined with high resolution. In addition, the intensity components of Laue harmonics may be separated, provided the energies of the harmonically overlapped spots are known. Using the data shown in Figure 5.16 the unit cell for the crystal of tetraphenylphosphosphonium tetrachlorooxomolybdenum(V) could be re-determined within 2% absolute error (Campbell, 1996). The full application of energy resolved measurements needed to be investigated. Specifically, it was unknown how generally applicable the energy resolved Laue auto-indexing (ERLAI) program

* Portions of this chapter are based on a paper which has been submitted to the Journal of Synchrotron Radiation under the title Application of Energy Resolved Measurements to Laue Diffraction: Determination of Unit Cell Parameters, Deconvolution of Harmonics and Assignment of Systematic Absences with co-authors JW Campbell and MB Denton. Where required, these sections are reproduced with permission of the International Union of Crystallography.

† The author is grateful to Dr. John Campbell for the interest he took in this project. See acknowledgments.
(Campbell. 1996) was whether space group assignments could be made based on foil mask spectrometer data, and the extent to which the system could be used to separate harmonics.

This chapter describes the processing and use of energy resolved Laue data for the determination of unit cell dimensions, separation of harmonically overlapped Laue spots, and assignment of systematic absences. It consists of two approaches: 1) simulations are used to explore different limitations of the method and to define critical parameters for data acquisition and 2) data obtained from a foil mask spectrometer system are used to measure unit cells and separation of harmonics. Further verification of the foil mask spectrometer is included using the known cells. The analyses presented were done with the foil mask spectrometer in mind, however, the results are thought to be general to any system capable of making similar measurements using a system of calibrated absorbers.

6.1 Theory - Unit Cell Determination

Energy resolved Laue diffraction data give a direct view of the reciprocal lattice from which they came. The data can be converted directly to reciprocal space coordinates. The direction of any observed diffraction vector measured at a distance $z$ from a crystal corresponds to the direction of a vector from the center of an Ewald sphere of radius $1/\lambda_{\text{meas}}$. If $\lambda_{\text{meas}}$ is known, the position of the point in the reciprocal lattice responsible for producing the diffraction may be calculated using 6.1.
\[
x' = \frac{x}{\lambda \sqrt{x^2 + y^2 + z^2}} \\
y' = \frac{y}{\lambda \sqrt{x^2 + y^2 + z^2}} \\
z' = \frac{z}{\lambda \sqrt{x^2 + y^2 + z^2}} - \frac{1}{\lambda} \tag{6.1}
\]

These relationships are illustrated in Figure 6.1.

With ideal data the observed spots form a readily indexable reciprocal lattice. In practice, the foil mask spectrometer system produces imperfect energy data. Data sets may include reflections containing harmonic overlap, or spots for which the energy measurements are poor. The effect of such points may be minimized by selecting the best portions of the data set, but they cannot be completely eliminated \textit{a priori}. For this reason the indexing method of Duiisenberg (1992) was adopted and coded into the program ERLAI by Campbell (1996) (see Appendix II for details). Briefly, the method consists of generating triplets created by the end points of three reciprocal space vectors corresponding to three reflections. If the reflections belong to a single reciprocal lattice, the normal to the triplet is a direct lattice vector. Reflection vectors are projected onto the triplet normal and the line projection searched for the one dimensional lattice with the shortest period giving a ‘t’ vector. The three ‘t’ vectors best fitting the data are used to determine a unit cell. This Campbell-Duiisenberg process is summarized in Figure 6.2 and Figure 6.3.
Illustration of the relationship between real and reciprocal space co-ordinates in a Laue diffraction pattern. Knowledge of the energy of the X-rays creating a spot in real space coordinates (X, Y, Z) allows the reciprocal lattice co-ordinates (x', y', z') to be computed directly. The relationships are slightly different than the convention used by the program ERLAI.

* In the Laue case, the distinction between the direction vector in the Ewald construction and the diffracted beam should be maintained. The origin of real space and reciprocal space coincide. The diffracted beam originates at (0,0,0) in real space. In the monochromatic case, this distinction can be ignored. Although some texts indicate the reason for this is that the experiment views the diffracted beam at infinite distance (cf: Stout and Jensen, 1989), it is the use of monochromatic radiation which allows this approximation to be made. Some authors use a convention in which the crystal is placed at the center of the sphere of reflection, others also use a normalized sphere of reflection having radius d/λ (Ladd and Palmer, 1993; Helliwell, 1992). While such conventions can be used in the Laue case, they are somewhat inconvenient, difficult to visualize, and should be used with caution. The conventions used here are similar to Bragg (1975, p 111).
Figure 6.2: Computation of Triplet Normal in ERLAI

- Compute triplets
- Compute unit normals
  \[ N = \frac{\mathbf{v}_i \times \mathbf{v}_j + \mathbf{v}_j \times \mathbf{v}_k + \mathbf{v}_k \times \mathbf{v}_l}{|\mathbf{v}_i \times \mathbf{v}_j + \mathbf{v}_j \times \mathbf{v}_k + \mathbf{v}_k \times \mathbf{v}_l|} \]
- Project each reflection vector on the unit normal
- Result is a one-dimensional lattice

A triplet consists of the end points of three reflection vectors in reciprocal space. The first step is to generate all possible triplets in a the subset of a data set meeting the criteria of equation 6.14. The normal to each triplet is then computed as indicated and each reflection vector projected onto the normal.
The second step in the indexing procedure is to look for periodicity in the one-dimensional lattice formed by projecting the reflection vectors onto the triplet normals. The parameter MAX DISTANCE is the greatest distance between two projections in the one-dimensional lattice. CELL MAX is set by the user and represents the shortest distance allowed in the search for periodicity. The period fitting the most projections is stored. After all the one-dimensional lattices are searched the three best ‘t’ vectors are used to compute the unit cell parameters.
6.2 Theory - Separation of Harmonics

Assignment of intensities to the components of multiply overlapped spots using a system of calibrated absorbers can be described by a multiple linear regression model of the form:

\[ Y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \ldots + \beta_n x_n + \varepsilon \]  

where \( Y \) is the measured intensity, \( x_i \) is the known value of the transmission efficiency, \( \beta_i \) is the \( i \)th component of the multiply overlapped Laue spot, and \( \varepsilon \) is the error. This is a standard multiple linear regression model except that the model is assumed to have zero intercept. This is due to the physical system in which no intensity is expected when all values of \( x_i \) are zero. A least squares solution exists for this over-determined system of equations. Using the matrix notation (Hanley, Dunphy, and Denton, 1996; Chapter 5) developed for the foil mask spectrometer the intensity components are given by 6.3.*

\[ \bar{H}_h = (T^t T)^{-1} T^t \bar{I}_m \]  

The variance explained by the multiple linear regression model is given by equation 6.4.

* In this equation the superscript 't' refers to the matrix transpose and the superscript '-1' refers to the matrix inverse. \( H \) is the column vector containing each of the intensity components in the harmonic, \( T \) is the transmission efficiency matrix, and \( I_m \) is the measured intensity through each of the foil masks.
The total variance is given by equation 6.5.

\[ SS_{\text{tot}} = \sum (I_i)^2 \]  

6.5

The residual variance is given by equation 6.6.

\[ SS_{\text{resid}} = SS_{\text{tot}} - SS_{\text{reg}} \]  

6.6

R² is the ratio of the variance explained by the multiple linear regression model divided by the total variance. An adjusted R² value which takes into account the number of degrees of freedom in the model and the number of measurements made is given by equation 6.7.

\[ \text{Adj } R^2 = 1 - \left(1 - R^2\right) \frac{n}{n - k} \]  

6.7

Where n is the number of measurements (masks) and k is the number of intensity components in the harmonically overlapped spot. Statistically rigorous errors can be
assigned to each intensity component in the model by first computing the mean squared residual 6.8.

\[
\text{MS}_{\text{res}} = \frac{\text{SS}_{\text{res}}}{n-k} \quad \text{6.8}
\]

The standard error of the \(i\)th intensity component in an overlapped spot can be computed from the mean squared residual 6.9.

\[
\text{se}_i = \sqrt{\text{MS}_{\text{res}} (\mathbf{T}^\mathbf{t} \mathbf{T})^{-1}_{ii}} \quad \text{6.9}
\]

In equation 6.9, the quantity \((\mathbf{T}^\mathbf{t} \mathbf{T})^{-1}_{ii}\) corresponds to the diagonal elements in the inverse matrix computed in 6.3. The significance of each intensity component is then tested using Student's t.

\[
t_i = \frac{I_i}{\text{se}_i} \quad \text{6.10}
\]

If the value corresponds to a probability less than 0.025 the component is included, otherwise it is eliminated.

The value of \(\varepsilon\) in 6.2 is limited by three types of noise: detector noise, source flicker, and Poisson noise. The Poisson, or shot, noise may be divided into components
from the background and signal of interest (see Chapter 4 for more details). An ideal system, one with no detector noise, a perfectly stable X-ray source, and negligible background, will be limited by the Poisson, or shot, noise of the detected X-rays. The critical property of Poisson noise is that the magnitude depends on the strength of the incident signal.

\[ \sigma_I = \frac{I}{\sqrt{2}} \]

6.11

For this reason, a component of a multiply overlapped spot having an intensity less than twice the standard deviation of the largest component should be assigned a value of zero.

6.3 Theory - Assignment of Systematic Absences

Assigning systematic absences based on measurements of reflections in a monochromatic experiment is usually done using relationships between signal level and noise. A common procedure is to mark a reflection as absent if the intensity of the reflection is less than \( k \) times the noise level.\(^1\) This is a statistically “interesting” approach in that reflections might be marked as “systematically absent” which might be “statistically present” with 95% confidence. Although initial mis-assignments of space

\(^1\) k here is a constant defining the desired significance level. Values of \( k \) vary somewhat depending on the researcher and the data set being confronted, but values of 1, 2, and 3 are common.
groups are encountered when using this approach, experience has shown such procedures
to be useful.

Assigning an absence to a reflection in a multiply overlapped spot in a Laue
pattern may proceed in a similar fashion. Considering reflections on an individual basis,
the following criteria are proposed for assigning an absence when using a system of
calibrated absorbers. A reflection is present if:

a) it has a regression coefficient with a significance level of 97.5% or greater
when using equation 6.2.
b) it has positive magnitude.
c) it has a magnitude greater than twice the square root of the intensity of the
largest overlapped reflection.

If the reflection does not meet these three criteria it is designated as absent. It should be
noted that using these criteria may result in exclusion of some reflections that might be
present and that all reflections present in a multiply overlapped spot are not equally
weighted in the measurements of spot intensity. The wavelength normalization curve of
the detection system inherently under-represents the reflections at some wavelengths.
There is no way to correct for this prior to deconvolution of the harmonics using a system
of calibrated absorbers.

Assigning a "systematic absence" to a set of reflections in a multiply overlapped
spot or spots is slightly more complicated. Here the example of a 2₁ screw axis is treated. This may be done by considering two models, one is designated a complete model, the other a reduced model. The complete model is given by equation 6.2. The reduced model 6.12 consists of 6.2 except that all the coefficients having odd numbered coefficients have been removed (see Chapter 1 for the reasons the odd components are absent).

\[ Y = \beta_2 x_2 + \beta_4 x_4 + \ldots + \beta_{2n} x_{2n} + \epsilon \]  
\[ \text{(6.12)} \]

The hypothesis being tested is that of systematic absence (e.g.: \( \beta_1 = \beta_3 = \beta_5 = \ldots = \beta_{2n+1} = 0 \)). The \( F \) statistic corresponding to this hypothesis, 6.13, may then be used to confirm a systematic absence when \( F > F_{n,k}^{(\alpha)} \).

\[
F = \frac{\left( SS_1 - SS_2 \right)}{k - g} \frac{k - g}{SS_2} \left( \frac{n - k}{n - k} \right)
\]
\[ \text{(6.13)} \]

where: \( SS_1 \) is the sum of squared errors for the reduced model computed using 6.6.

\( SS_2 \) is the sum of squared errors for the complete model computed using 6.6.

\( k-g \) is the number of absent intensity components.

\( k \) is the number of intensity components in the complete model.

* This treatment is based on one given in Scheaffer and McClave (1982).
n is the total sample size.

\( v_1 \) is \( k-g \), the number of degrees of freedom in the numerator of 6.13.

\( v_2 \) is \( n-k \), the number of degrees of freedom in the denominator of 6.13.

\( \alpha \) is the desired significance level.

This \( F \) statistic tests whether the null hypothesis, that a systematic absence is present, may be rejected.

### 6.4 Data Collection

The foil mask spectrometer system has been previously described (Hanley, Dunphy, and Denton, 1996). Data were collected using an indirect CID camera system (Hanley, True, and Denton, 1995) an Enraf-Nonius FR571 X-ray source equipped with a Cu rotating anode, and a CAD4 goniometer. Images were processed using the Image Reduction and Analysis Facility (IRAF). Within IRAF, spot positions were entered manually, centered, and intensities integrated. Energies were computed as previously described and sorted using 6.14 as a figure of merit.

\[
FOM = \sqrt{\frac{\sum (T_e - T_m)^2}{n}}
\]
where FOM is the figure of merit, $T_e$ is the calculated transmission efficiency at the energy measured, $T_m$ is the measured transmission efficiency, and $n$ is the number of masks used in the computation of energy. Only spots having measured energies with FOMs < 0.05 were included in unit cell parameter computations. The CID camera system crystal to detector distance and spatial distortions were calibrated using a sample of MoOCl$_4$PC$_{24}$H$_{20}$.

Six crystals were selected for study: NaCl, KCl, C$_{19}$H$_{28}$O$_2$, MoOS$_4$N$_4$C$_{28}$H$_{40}$, C$_{19}$H$_{31}$MoBN$_6$O$_3$, and MoOCl$_4$PC$_{24}$H$_{20}$. Crystals were mounted in a random orientation.

### 6.5 Computations

Several programs were used to evaluate the system and perform computations on the collected data. These programs are ERLAI (Campbell, 1996), EMATCH (Campbell, 1996), EINDEX, ESIMUL, ESEP, and EAN.* ERLAI is used for the determination of unit cell parameters and orientation using a set of energy resolved measurements. EMATCH rescales unit cells determined by ERLAI following refinement using LAUEGEN and reduction by TRACER. EINDEX assigns indices, multiplicity, and harmonic increments to spots in a Laue diffraction pattern. ESIMUL generates a simulated energy resolved data set given an LDM file. ESEP separates harmonics and tests for 2$_1$ (and related systematic absences) and 4$_1$ screw axes. EAN adds Gaussian

* Although minor modifications were made to ERLAI and EMATCH by the author, these programs were written by Dr. John Campbell. The programs EINDEX and ESIMUL, were based substantially on the program EMATCH. The programs ESEP and EAN were written solely by the author.
noise to a set of energy resolved Laue data.

For additional details on the programs ERLAI and EMATCH see Appendix II.

The program EMATCH, EINDEX, and ESIMUL make use of the Laue Data Module (LDM) routines (Campbell, Clifton, Harding, and Hao, 1995) from the Daresbury Laboratory Laue Software Suite. EINDEX works in a similar fashion to EMATCH, except all the data in the list, rather than only those with low FOMs, are processed. In assigning a match, only the distance between the predicted and observed position is used. ESIMUL generates the position and energy of spots in a Laue pattern based on an LDM file. The first 249 of these are written to a file in ERLAI input format.

The program ESEP is an adaptation of the constrained multiple linear regression procedures outlined in sections 6.2 and 6.3. The matrix manipulation was performed using published algorithms (Embree and Kimble, 1991). F and t tests performed by the program are based on published algorithms (Vetterling et al., 1988). The program constructs the T matrix using the data produced by EINDEX for the number, type, and increment of the harmonics. The regression performed by ESEP is forced to include the origin and negative coefficients are rejected. When the predicted number of harmonics is $\leq 4$ a backward elimination procedure is used to eliminate components with P values $> 0.025$. When the predicted number of components exceeds 4, a forward inclusion procedure is used to iteratively select components whose coefficients have P values $< 0.025$. The program was verified against the SPSS program using data from selected spots.
The program EAN was used to validate ERLAI. EAN operates on files in ERLAI input format and adds user specified amounts of Gaussian noise to the xy positions or energies contained in the file. EAN is based on a published random number generator (Vetterling et al., 1988).

6.6 Data Analysis

The procedure for obtaining unit cells from the measured energies and positions consisted of five steps. First, the positions and energies are measured as described in Chapter 5. Second, the measured positions and energies were submitted to the program ERLAI to obtain cell dimensions and orientation matrices. During processing with ERLAI, an estimated maximum cell length was obtained by an iterative procedure. Typically a large increase in the number of spots fitting the computed cell was observed when the cell maximum was 1/2 of the longest unit cell dimension. The value of 1/2 reflects the computation algorithm used by ERLAI. In the region of rapid increase, a series of estimated values were entered in 0.5 Å increments until the lowest maximum cell length with the largest number of fitting spots was selected for cell determination. An example of this behavior is found in Table 6.1.

Third, the cell dimensions and orientation matrices were entered into LAUEGEN and both sets of parameters were refined. Fourth, the refined unit cell was submitted to
Table 6.1: Number of Fitting Vectors with Choice of CELL MAX

<table>
<thead>
<tr>
<th>Cell Max (Å)</th>
<th>Number of Fitting Spots</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>7.5</td>
<td>14</td>
</tr>
<tr>
<td>8.0</td>
<td>14</td>
</tr>
<tr>
<td>8.5</td>
<td>14</td>
</tr>
<tr>
<td>9.0</td>
<td>26</td>
</tr>
<tr>
<td>10.0</td>
<td>26</td>
</tr>
<tr>
<td>15</td>
<td>24</td>
</tr>
</tbody>
</table>

TRACER to obtain a reduced cell. If necessary, the third and fourth steps were repeated until a good correspondence between the Laue pattern and the predicted pattern was obtained. Finally, predicted and observed energies were compared using the program EMATCH to ascertain whether the final cell needed rescaling. This last step is necessary because the position of spots is unaffected by rescaling a unit cell by a constant factor. If successive refinements and cell reduction are performed, the cell axis lengths begin to lose fidelity to the original data. Rescaling the cell following refinements and cell reduction guards against this and against the possibility of spurious cell axis doubling during data reduction. Once a rescaled unit cell is found the energy resolved data list is indexed using EINDEX and separation of harmonics proceeds using ESEP.

Simulated data was treated using a slightly different procedure. Since image data was not always available, the LAUEGEN refinement step was excluded in these cases. The output from ERLAI was submitted directly to TRACER.
6.7 Calibrations

A sample of the MoOCl$_4$PC$_{24}$H$_{39}$ crystal was placed in the beam of the instrument and a standard Laue photo taken. The crystal orientation was found using LAUEGEN and the known cell parameters. A total of 227 spots were used, refining to a final rms of 0.093. The resulting parameters for the CID camera system are found in Table 6.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal to detector distance</td>
<td>77.57 (mm)</td>
</tr>
<tr>
<td>X center position</td>
<td>234 (rasters)</td>
</tr>
<tr>
<td>Y center position</td>
<td>264 (rasters)</td>
</tr>
<tr>
<td>X center offset</td>
<td>0.052 (mm)</td>
</tr>
<tr>
<td>Y center offset</td>
<td>0.051 (mm)</td>
</tr>
<tr>
<td>Detector Twist</td>
<td>4.761 (x0.01 degrees)</td>
</tr>
<tr>
<td>Detector Tilt</td>
<td>22.748 (x0.01 degrees)</td>
</tr>
<tr>
<td>Detector Bulge</td>
<td>-106.195 (x0.01 degrees)</td>
</tr>
</tbody>
</table>

All energy data meeting the criteria for inclusion in unit cell computations are plotted in Figure 6.4. Figure 6.4 includes data in which multiples were predicted to be present. From this data, it appears that applying the inclusion criteria selects for spots containing either spots that are singles or multiples in which only one harmonic dominates.

6.8 Unit Cell Determination - Simulated Data

Table 6.3 presents three simulations. Simulation one consisted of a cubic system
Correspondence between predicted and observed energies for the spots used for the determination of unit cells. The line in the figure is for ideal 1:1 correspondence.
Table 6.3: Simulation Results - Unit Cell Parameters

<table>
<thead>
<tr>
<th>Simulation #</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial Parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a=6.0</td>
<td>a=10</td>
<td>a=30.365</td>
<td></td>
</tr>
<tr>
<td>b=6.0</td>
<td>b=27.1096</td>
<td>b=8.373</td>
<td></td>
</tr>
<tr>
<td>c=6.0</td>
<td>c=9.0</td>
<td>c=19.649</td>
<td></td>
</tr>
<tr>
<td>α=90</td>
<td>α=98.265</td>
<td>α=90</td>
<td></td>
</tr>
<tr>
<td>β=90</td>
<td>β=92</td>
<td>β=113.28</td>
<td></td>
</tr>
<tr>
<td>γ=90</td>
<td>γ=85.7056</td>
<td>γ=90</td>
<td></td>
</tr>
<tr>
<td><strong>Parameters obtained with 0% added noise</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a=6.0</td>
<td>a=10</td>
<td>a=30.366</td>
<td></td>
</tr>
<tr>
<td>b=6.0</td>
<td>b=27.11</td>
<td>b=8.370</td>
<td></td>
</tr>
<tr>
<td>c=6.0</td>
<td>c=9.0</td>
<td>c=19.65</td>
<td></td>
</tr>
<tr>
<td>α=90</td>
<td>α=98.26</td>
<td>α=90</td>
<td></td>
</tr>
<tr>
<td>β=90</td>
<td>β=92</td>
<td>β=113.27</td>
<td></td>
</tr>
<tr>
<td>γ=90</td>
<td>γ=85.7</td>
<td>γ=90</td>
<td></td>
</tr>
<tr>
<td><strong>Parameters obtained with 1% added noise</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a=5.99</td>
<td>a=10.07</td>
<td>a=29.195*</td>
<td></td>
</tr>
<tr>
<td>b=5.99</td>
<td>b=26.2964</td>
<td>b=8.45</td>
<td></td>
</tr>
<tr>
<td>c=5.99</td>
<td>c=9.1188</td>
<td>c=19.53</td>
<td></td>
</tr>
<tr>
<td>α=90</td>
<td>α=98.79</td>
<td>α=90</td>
<td></td>
</tr>
<tr>
<td>β=90</td>
<td>β=90.1285</td>
<td>β=108.77</td>
<td></td>
</tr>
<tr>
<td>γ=90</td>
<td>γ=87.1923</td>
<td>γ=90</td>
<td></td>
</tr>
<tr>
<td><strong>Parameters obtained with 2% added noise</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a=6.02</td>
<td>a=30.662</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b=6.02</td>
<td>b=8.417</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c=6.02</td>
<td>c=19.796</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α=90</td>
<td>α=90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β=90</td>
<td>β=113.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ=90</td>
<td>γ=90</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Parameters obtained with 2% added noise</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a=5.95</td>
<td>a=30.568</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b=5.95</td>
<td>b=8.426</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c=5.95</td>
<td>c=19.795</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α=90</td>
<td>α=90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β=90</td>
<td>β=113.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ=90</td>
<td>γ=90</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* No refinement was used for this determination
with a 6 Å unit cell with all missetting angles set to zero. Simulation 2 consisted of a triclinic system viewed in a random orientation. Simulation 3 was an idealized case corresponding to \( \text{C}_19\text{H}_3\text{MoBN}_6\text{O}_3 \). The simulation was run using the orientation of the known cell and orientation, allowing refinement in LAUEGEN.

In all cases, a combination of ERLAI and TRACER found the cell parameters of the simulated pattern without subsequent refinement in LAUEGEN. When 1% random noise was added to the idealized data, a cell resembling the original cell was obtained. To obtain the cells reported after addition of 1% noise in Table 6.3 sometimes required increasing the fit level parameters and the value of DEL used in TRACER. The agreement between the parameters used in the simulations and those recovered was degraded somewhat with the lower symmetry cells relative to the cubic cells.

Without refinement in LAUEGEN it was difficult to recover the original cells when the noise level reached 2%. With refinement, agreement within 1% of the original parameters was readily obtained, even after addition of 3% noise.

### 6.9 Separation of Harmonics - Simulated Data

Table 6.4 shows the results of three simulations of a harmonic consisting of 4 Poisson intensity components. Initially the intensity components are 100, 1000, 10000, and 100000 having standard deviations of 10, 31.6, 100, and 316 respectively. The intensity of the spots is then modeled as each intensity component grows by an order of
magnitude. This would correspond to the case of increasing the length of exposure by factors of ten. In each simulation, the intensity components are summed after attenuation by a T matrix to obtain an I. As the intensity of the I vector increases the ability to separate the intensity components in the spots also increases. When insufficient signal is present the weaker components become lost in the noise from those of high intensity.

Table 6.4: Harmonic Overlap Simulations

<table>
<thead>
<tr>
<th>Simulated Intensity</th>
<th>Simulated Standard deviation</th>
<th>Recovered Intensity</th>
<th>Recovered error</th>
<th>t-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>10</td>
<td>NS</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>31.6</td>
<td>NS</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>100</td>
<td>10,801</td>
<td>690</td>
<td>15.6</td>
</tr>
<tr>
<td>100,000</td>
<td>316</td>
<td>100027</td>
<td>690</td>
<td>145</td>
</tr>
<tr>
<td>R^2&gt;0.9999</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>31.6</td>
<td>NS</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>100</td>
<td>8893</td>
<td>2661</td>
<td>3.34</td>
</tr>
<tr>
<td>100,000</td>
<td>316</td>
<td>102852</td>
<td>2859</td>
<td>35.97</td>
</tr>
<tr>
<td>1,000,000</td>
<td>1,000</td>
<td>998,733</td>
<td>2164</td>
<td>461.36</td>
</tr>
<tr>
<td>R^2&gt;0.9999</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>100</td>
<td>NS</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>100,000</td>
<td>316</td>
<td>93571</td>
<td>16381</td>
<td>5.71</td>
</tr>
<tr>
<td>1,000,000</td>
<td>1,000</td>
<td>1025503</td>
<td>17600</td>
<td>58.27</td>
</tr>
<tr>
<td>10,000,000</td>
<td>3160</td>
<td>9984703</td>
<td>13300</td>
<td>749.25</td>
</tr>
<tr>
<td>R^2&gt;0.9999</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NS - Not significant

6.10 Unit Cell Determinations - Real Data

A total of 6 crystals were examined. Each of these crystals have been previously
characterized using monochromatic methods. A summary of each crystal is presented in Table 6.5.

The Laue pattern from NaCl had 29 spots. Of these, 10 spots had \( \text{FOMs} \leq 0.05 \) and were submitted to the program ERLAI. The pattern from KCl had 21 spots. Twelve of these had \( \text{FOMs} < 0.05 \). Three orientations of the crystal of \( \text{C}_{19}\text{H}_{28}\text{O}_2 \) were viewed. Each orientation was submitted to energy analysis. Orientation 1 ("0k0") had 102 spots. Of these, 34 had \( \text{FOMs} < 0.05 \), and 50 of which were harmonics. Orientation 2 ("h00") had 109 spots with 20 having \( \text{FOMs} < 0.05 \), and 50 of which were harmonics. Orientation 3 ("00l") had 91 spots of which 10 had \( \text{FOMs} \leq 0.05 \), and 48 of which were harmonics. A cell could not be refined for orientation 3. Examination of the 10 spots meeting inclusion criteria showed that only one was a true monochromatic reflection, the remainder contained harmonic overlap. The values in Table 6.5 are for orientations 1 and 2. The pattern from \( \text{MoO}_4\text{N}_4\text{C}_{28}\text{H}_{40} \) had 121 spots of which 26 had \( \text{FOMs} < 0.05 \), and 39 were harmonics. The pattern for \( \text{C}_{19}\text{H}_{31}\text{MoBN}_6\text{O}_5 \) had 122 spots with 51 having \( \text{FOMs} < 0.05 \), and 39 were harmonics. The pattern from \( \text{MoCl}_4\text{PC}_{24}\text{H}_{20} \) had 188 spots of which 44 had \( \text{FOMs} < 0.05 \), and 38 were harmonics.

### 6.11 Separation of Harmonics

The NaCl and KCl data sets contained no spots with harmonic overlap and were
Table 6.5: Unit Cell Information Summary

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal System</th>
<th>Space group</th>
<th>Known Cell Parameters</th>
<th>Measured Cell Parameters</th>
<th>Rescale of Known Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl*</td>
<td>Cubic</td>
<td>Fm3m</td>
<td>(a = 5.6402 \text{ Å})</td>
<td>(5.60\pm0.09 \text{ Å})</td>
<td>(5.60 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\alpha = 90^\circ)</td>
<td>(\alpha = 90^\circ)</td>
<td>(\alpha = 90^\circ)</td>
</tr>
<tr>
<td>KCl(^1)</td>
<td>Cubic</td>
<td>Fm3m</td>
<td>(a = 6.2929 (1) \text{ Å})</td>
<td>(3.08\pm0.05 \text{ Å})</td>
<td>(6.155 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\alpha = 90^\circ)</td>
<td>(\alpha = 90^\circ)</td>
<td>(\alpha = 90^\circ)</td>
</tr>
<tr>
<td>C(<em>{19})H(</em>{22})O(_2)(^2)</td>
<td>Orthorhombic</td>
<td>P(_{2_1}2_1_2_1)</td>
<td>(a=11.333 (3) \text{ Å})</td>
<td>(11.30\pm0.23 \text{ Å})</td>
<td>(11.139 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(b=12.813 (4) \text{ Å})</td>
<td>(12.72\pm0.25 \text{ Å})</td>
<td>(12.593 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(c=11.2904 (2) \text{ Å})</td>
<td>(11.22\pm0.22 \text{ Å})</td>
<td>(11.096 \text{ Å})</td>
</tr>
<tr>
<td>MoOS(<em>2)N(<em>2)C(</em>{20})H(</em>{40})(^8)</td>
<td>Monoclinic</td>
<td>P(_2_1/n)</td>
<td>(a=8.911 (3) \text{ Å})</td>
<td>(8.87\pm0.15 \text{ Å})</td>
<td>(8.858 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(b=10.211 (6) \text{ Å})</td>
<td>(10.16\pm0.17 \text{ Å})</td>
<td>(10.151 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(c=15.414 (1) \text{ Å})</td>
<td>(15.38\pm0.26 \text{ Å})</td>
<td>(15.323 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\alpha=\gamma=90^\circ)</td>
<td>(\alpha=\gamma=90^\circ)</td>
<td>(\alpha=\gamma=90^\circ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\beta=103.42 (3)^\circ)</td>
<td>(\beta=103.58^\circ)</td>
<td>(\beta=103.42^\circ)</td>
</tr>
<tr>
<td>MoOCl(_4)PC(_2)H(_3)</td>
<td>Tetragonal</td>
<td>P(_4/n)</td>
<td>(a=12.7379 (4) \text{ Å})</td>
<td>(12.11\pm0.43 \text{ Å})</td>
<td>(12.119 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(b=12.7379 (7) \text{ Å})</td>
<td>(12.11\pm0.43 \text{ Å})</td>
<td>(12.119 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(c=7.6871 (3) \text{ Å})</td>
<td>(7.31\pm0.26 \text{ Å})</td>
<td>(7.313 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\alpha=\beta=\gamma=90^\circ)</td>
<td>(\alpha=\beta=\gamma=90^\circ)</td>
<td>(\alpha=\beta=\gamma=90^\circ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(c=7.313 \text{ Å})</td>
<td>(c=7.313 \text{ Å})</td>
<td>(c=7.313 \text{ Å})</td>
</tr>
<tr>
<td>C(_{19})H(_3)MoBN(_6)O(_3)(^{**})</td>
<td>Monoclinic</td>
<td>C(_2/c)</td>
<td>(a=30.365(4) \text{ Å})</td>
<td>(30.1\pm1.0 \text{ Å})</td>
<td>(29.847 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(b=8.373(1) \text{ Å})</td>
<td>(8.29\pm0.30 \text{ Å})</td>
<td>(8.230 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(c=19.646(2) \text{ Å})</td>
<td>(19.50\pm0.70 \text{ Å})</td>
<td>(19.311 \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\alpha=\gamma=90^\circ)</td>
<td>(\alpha=\gamma=90^\circ)</td>
<td>(\alpha=\gamma=90^\circ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\beta=113.28(1)^\circ)</td>
<td>(\beta=113.25^\circ)</td>
<td>(\beta=113.28^\circ)</td>
</tr>
</tbody>
</table>

* Data from Donney & Ondik 1972, error assumed to be ±1 in final decimal place.
† Data from Donney & Ondik 1972.
‡ Data from Kasal et al. 1996.
§ Data from M. Bruck 1996.
** Data from Xiao Z., et al. 1995.
not analyzed further. Of the remaining data sets, 260 spots contained harmonic overlap. The number of predicted spots contained in these harmonics ranged from 2-12. The maximum number of frequency components into which any given spot was separated was

6.12 Assignment of Systematic Absences

Although the harmonics containing information for assigning screw axes were of most interest, only a very small number of spots of this type were observed. As a result, spots predicted to have systematic absences due to unit cell centering were also examined. These summary of these results are presented in Table 6.6.

6.13 Discussion - Simulations

The simulations indicate that the determination of unit cell parameters using energy resolved data is applicable to a wide range of cell sizes and types. It allows all three axes to be determined in any orientation. The previously described methods (Carr, Dodd, and Harding, 1993; Carr, Cruickshank, and Harding, 1992) fail under some rare conditions. With the exception that the energy measurements must be of sufficient quality, the unit cell determination methods described here appear to be general. The
Table 6.6: Assignment of Systematic Absences

<table>
<thead>
<tr>
<th>Compound</th>
<th>type of symmetry</th>
<th>reflection condition</th>
<th>range of harmonics</th>
<th>harmonics found</th>
<th>harmonic type</th>
<th>systematic absence found</th>
<th>correct?</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{19}H_{31}MoBN_{6}O_{3}</td>
<td>Centering</td>
<td>h+k=2n</td>
<td>2-4</td>
<td>2 &amp; 4</td>
<td>(0,-1,3)</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>C_{19}H_{31}MoBN_{6}O_{3}</td>
<td>Screw</td>
<td>l=2n</td>
<td>3-14</td>
<td>4, 8, &amp; 10</td>
<td>(0,0,1)</td>
<td>yes†</td>
<td>no†</td>
</tr>
<tr>
<td>C_{19}H_{31}MoBN_{6}O_{3}</td>
<td>Centering</td>
<td>h+k=2n</td>
<td>2-8</td>
<td>2, 6, &amp; 8</td>
<td>(1,0,-2)</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>C_{19}H_{31}MoBN_{6}O_{3}</td>
<td>Centering</td>
<td>h+k=2n</td>
<td>2-4</td>
<td>2</td>
<td>(0,-1,0)</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>C_{19}H_{25}O_{2}</td>
<td>Screw</td>
<td>k=2n</td>
<td>1-6</td>
<td>2 &amp; 4</td>
<td>(0,-1,0)</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>C_{19}H_{25}O_{2}</td>
<td>Screw</td>
<td>l=2n</td>
<td>2-10</td>
<td>4 &amp; 6</td>
<td>(0,0,-1)</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>C_{19}H_{25}O_{2}</td>
<td>Screw</td>
<td>l=2n</td>
<td>1-6</td>
<td>2 &amp; 4</td>
<td>(0,0,1)</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>C_{19}H_{25}O_{2}</td>
<td>Screw</td>
<td>k=2n</td>
<td>1-7</td>
<td>2 &amp; 4</td>
<td>(0,1,0)</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>MoOCl_{2}PC_{2}H_{20}</td>
<td>none</td>
<td>none</td>
<td>2-7</td>
<td>3 &amp; 4</td>
<td>(0,0,1)</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

* Systematic absence was assigned if either the F-test or the stepwise regression method revealed an absence of the type indicated.
† F-test could not be performed, the number of coefficients exceeds the available data.
simulations indicate that the tolerances required for the energy resolved method are relatively loose. One percent random error in energy measurements is easily tolerated and does not require refinement. If a refinement step is introduced, higher noise in the data may be present. These simulations indicate that a system capable of making energy resolved measurements with less than 1% error should be suitable for most applications. More can be tolerated, but this represents a good design goal, regardless of the method by which the measurements are made.

The results of the simulation of non-random errors such as inaccurate determination of the crystal to detector distance, or the xy position of spots indicate that these sorts of errors propagate nearly linearly into inaccuracies in cell parameters. Consideration of equation 1 suggests why this occurs. If there is an inaccuracy in the determination of the square root term in the denominator, it will result in an error in the reciprocal space position of the spot position. The exact magnitude of the inaccuracy depends on the relative magnitudes in the errors of the measurements of the X, Y, and Z co-ordinates. Under special conditions, such as the case where X, Y, and Z are each off by a factor of 2, the inaccuracies will cancel.

The separation of the intensity components in a harmonically overlapped spot is limited by Poisson noise in the collected X-ray photons. The simulated harmonic separation illustrates that while a limitation exists, separation of harmonics is favored by high beam intensity. Like the energy measurements from a foil mask spectrometer system (Hanley, Dunphy, and Denton, 1996), the ability to separate harmonics improves
with the total number of X-ray photons measured. The theoretical limitation is imposed once the intensity level is set. This limitation can be thought of as being similar to the multiplex disadvantage encountered in optical spectroscopy (Ingle and Crouch, 1988; Harwit and Sloane, 1979). The multiplex disadvantage occurs in encoded systems when shot noise from a large feature contaminates weak features.

As noted in section 2.2, the error, $\varepsilon$, in the multiple linear regression model also may contain contributions from detector dark current noise, read noise and source $1/f$ (flicker) noise. Read noise in the measurement of X-rays varies depending on the system of measurement used. Use of photographic film can result in a large amount of read noise during digitization of the image. In this context, it is interesting to compare the use of stacked film (UNSCRAM) to the foil mask spectrometer system. Film will have greater uncertainty associated with the digitization of the image, however, a unique feature of the UNSCRAM approach is that the images are coincident in time, effectively eliminating source flicker noise. In contrast, the foil mask spectrometer collects a series of images which are separated in time, making it sensitive to source instability during data collection. In environments where the X-ray source is not stable, corrections may be necessary. If it were possible to construct an image plate which, like film, was semi-transparent to X-rays, and could be stacked, the UNSCRAM approach could become a method of choice for both energy determination and harmonic separation. It would also have the advantage of simultaneous acquisition of the multiple required images and, unlike film, could be calibrated once and reused repeatedly.
6.14 Discussion - Real Data Sets

Analysis of the real data sets indicates that the foil mask spectrometer gives energies that are suitable for unit cell determination. In all cases, moderate agreement with the known cells was obtained while requiring a minimum of operator intervention. A single procedure was suitable for all data sets suggesting that many steps could be automated. The combination of the programs ERLAI, LAUEGEN, and EMATCH do a good job of analyzing the data from energy resolved measurements of Laue patterns. The cells obtained using these programs fit the data nearly as well or better than did the known cells. This indicates that the measurements of cell parameters using this method is presently limited by the quality of the energy measurements. This conclusion is corroborated by the facility with which ERLAI was able to obtain cells using simulated data with low noise.

In comparison to previous work with Laue methods, the energy resolved measurements result in unit cell dimensions of similar quality. The demonstration on small unit cells, provides a complement to previously described methods (Carr, Dodd, and Harding, 1993; Carr, Cruickshank, and Harding, 1992). Using either method, it is clear that measurements obtained using Laue methods are of lower quality than those made with monochromatic methods. However, another order of magnitude increase in the precision of energy measurements may be possible in the future and the present level
of accuracy is within the range of utility. Further, the level of accuracy which is typically reported in the small molecule literature from monochromatic experiments is unnecessary for many purposes. For standard structure refinement, cell parameters only need to be of sufficient accuracy to allow the position of reflections to be found for the purpose of making intensity measurements and to assign appropriate indices to the data. Beyond this, 1% errors are not of great concern.

Additionally, this method may be a useful complement to previously described studies of very small crystals (Kariuki and Harding, 1995). The dimensions of the alkali halide crystals used here are in the range of many crystalline minerals. A single orientation was sufficient for the determination of the cell dimensions. Moreover, laboratory scale instrumentation was sufficient for the present work.

The use of the foil mask spectrometer allows for identification of the most important intensity components in a harmonically overlapped spot. Careful attention to the residual variance after extracting the most significant components allows an upper bound to be placed on the magnitude of the harmonics which are not significantly present. For example, if the significant components explain 99.9% of the variance, all remaining components combined can account for no more that 0.1%. This is of particular importance in light of the systematic loss of low frequency components in refinements which do not use data from harmonically overlapped spots. Using the foil mask spectrometer data, at least the most important of these will be identified.

It is also of interest that in the data sets collected and analyzed here, it was usually
found that the number of predicted harmonics exceeded the number observed. Usually, one or two intensity components dominate. Some of this is due to the theoretical limitation discussed previously. It will never be possible to reliably separate harmonics in which the intensity of a weak harmonic is much less than the Poisson noise of a dominant component using a system of absorbers.

The data in Table 6.6 demonstrates that Laue data can be used for assignment of systematic absences corresponding to screw axes. There has been little speculation in the prior literature about how this type of analysis could be done. In the data sets examined here, the combination of the F-test and stepwise regression correctly identified the known systematic absences in all cases. In one case, the number of harmonics predicted to be present, 12, exceeded the number of masks, 11. Under these conditions, the F-test can not be performed and successful assignment of systematic absences appears to be quite sensitive to the scaling of the unit cell dimensions. Two approaches can be used to minimize the possibility of misassignment of systematic absences in future systems. First, as with the energy measurements and the separation of harmonics, assignment of systematic absences will also be favored by an increase in the number of X-ray photons measured. Second, the foil mask spectrometer system used here is still a first generation instrument. Improvement of both the foil sets used and the detection system should be able to substantially improve its performance. Finally, in cases where a large number of harmonics may be present there is a statistical multiple comparisons problem which may influence the outcome of the separation procedure. In cases which are statistically
marginal. Initial refinements using a space group of lower symmetry may be advisable to provide additional support for the procedures described here.

6.15 Summary and Conclusion

The use of energy resolved measurement for the determination of unit cells, separation of harmonics, and assignment of systematic absences has been demonstrated. The tolerances required for the measurement of energy are relatively loose, in simulations as much as 3% random error in energy still resulted in satisfactory measurements of the unit cell. When used with a foil mask spectrometer, all aspects of the method improve with the intensity of the measured X-rays. The method complements methods previously described in the literature and are of similar quality.
CHAPTER 7

Conclusion and Future Directions

The goals for this research were two-fold. The first goal was the development of experiments allowing the full use of the information available in a Laue diffraction pattern. The second goal was to create laboratory scale instrumentation implementing Laue methods which would allow full structure refinement without recourse to monochromatic methods. Pursuit of these goals resulted in the results reported in chapters 2-6. Chapters 2 and 3 were concerned with the characterization and use of charge injection devices for detection of both optical photons and X-rays. The experience working with these devices and applying them to particular types of problems led to the considerations presented in chapter 4. This material as much as possible was intended to be general to a wide range of charge transfer devices. Chapters 5 and 6 describe the development and use of a spectrometer system based on calibrated absorbers which meets the goal of an energy resolved detection system for Laue diffraction applications.
This final chapter gives a summary of the accomplishments of the research. Since each chapter represents a definable segment of the research the organization of this final chapter will be divided accordingly. At the end of this chapter is a discussion of the limitations of the current system and suggestions for future research.

7.1 Electro-optical Characterization of Pre-amp per Row CIDs

Four pre-amp per row CIDs were examined in the course of these studies. These CIDs were tested in a variety of hardware systems, some of which are available from the manufacturer, the remainder were assembled, constructed, and/or modified in the Denton group laboratories. Data are now available for a wide range of device characteristics for the CID 17PPRA, CID 38SG, CID 38Q-A and CID 38Q-B. It has been shown that current measures of device noise are limited by the electronic readout of the camera systems used. This result was supported by four separate approaches to the measurement of read noise. In addition, the read noise levels reported here are the lowest values ever measured for single reads of any CID previously reported. Prior to the current work, no investigations of the temperature dependence of dark current in pre-amp per row CIDs with temperature had been made. Considerable effort was made to assess the reliability of electro-optical characterizations of CIDs. Toward this end a set of CID 17PPRA devices and controller boards were evaluated. The data presented in this dissertation suggests that measurements made using a particular set of readout electronics do not
necessarily apply to other board sets obtained from the manufacturer, particularly in the case of read noise. On the other hand, in the case of the CID 17PPRA devices, device to device variability does not appear to be very great. Experience with the devices indicates that in cases where linearity or read noise are critical to the performance of an analytical system, these characteristics need to be assessed under the conditions of measurement. The devices, while extensively characterized for the purposes of atomic emission spectroscopy, have not been extensively investigated for general scientific imaging purposes. This work and the work of True (True et al., 1996; True, 1996) suggest that they have some serious limitations for this purpose.

7.2 Evaluation of Charge Injection Devices for X-ray Detection

Two prototype camera systems were constructed in the course of this research. One of these was designed for direct detection and incorporated a plastic vacuum seal allowing X-rays to directly interact with the sensing region of the device. The other X-ray camera system was designed for indirect detection applications. This camera used an X-ray phosphor which converted the incident X-rays to visible photons which were imaged with a lens. Software for driving these camera systems was written which allowed for calibration, rapid single pixel address, and general imaging.

Prior to the work undertaken for this dissertation the capabilities of CIDs for detection of X-rays was mostly speculative. The only prior work was on direct detection
in imaging applications. The use of CIDs for indirect X-ray detection and for X-ray photon counting was first reported in the course of the work done for this dissertation (Hanley, True, and Denton, 1995). This work was done with Laue diffraction in mind. In indirect imaging applications, under the conditions of the tests with Laue patterns, linearity of the CID camera system was adequate, but can not be assumed to be so generally. The extent of linearity problems was not understood at the time of the initial report on this device (Hanley et al., 1995). Outside of this limitation, which should be corrected in later device revisions, the CID can be considered to hold a place midway between the image plates and the CCD in terms of read out speed. The formats are smaller than competing technologies. They have wider dynamic range than typical CCDs when using the random access integration capability of the CID. This situation is complicated if multiple CCD frames are co-added, a situation which is treated at length in Chapter 4.

The use of rapid interrogation of single pixels for single X-ray photon counting represents an intriguing possibility for the future. The CID could become a room temperature energy dispersive analyzer for X-rays. At present this possibility is limited due to the shallow depletion depth of the current CID structures. Similar methods employing intensification optics could be used to do optical photon counting with CIDs. Other direct detection imaging applications could use the devices, however, in the context of Laue diffraction it is doubtful that direct detection using CIDs or CCDs will be a viable technology in the foreseeable future. The CIDs studied here were damaged by the
X-ray beam. Solving this problem in a satisfactory fashion will be difficult. Under the uneven exposures likely to occur doing diffraction studies, suitable performance will be difficult to achieve. The Laue experiment, like many diffraction experiments, is best served by a detector system which can cover a large region of space. All the current CIDs and those presently under development are relatively small when compared to image plates or indirect imaging systems. Finally, the attraction of the CID initially for these studies was the possibility of performing energy dispersive analysis on a pixel by pixel basis. Even if such a scheme were to work perfectly, it represents a sequential approach to the detection of a Laue pattern. The primary advantage of the Laue experiment is its ability to simultaneously observe large regions of reciprocal space. Reducing this to a sequential experiment removes its primary advantage.

7.3 Charge Transfer Device Selection and Optimization

An extensive theoretical treatment of charge transfer device signal to noise expressions has been assembled and developed. The purpose of this treatment was to collect existing noise expressions for measurements made with charge transfer devices and to extend them to include the ability to add, subtract, multiply, divide, bin, and reread pixels in a CTD. This treatment allows the optimization of measurements commonly made with CTDs. In the context of the present work this treatment was initiated to find rules for reconstructing X-ray events which might be spread over multiple pixels and to
be able to compare multiple generations of CIDs. The expressions developed can also be used to find the best conditions of measurement for transmission efficiency, absorbance, and flat fields.

This treatment anticipates the capabilities of a family of CIDs currently under development. The RACID (random access CID) family of devices is being designed to have both true random access readout and binning capability. A theoretical treatment of this device suggests that the application of a Hadamard mask to the readout gives considerable advantage for very low light level applications. On an effective per read basis, such a device should be able to equal or exceed the performance of the best CCDs. In addition, the advantage obtained increases with the number of pixel included in the Hadamard binning procedure making it particularly applicable to very large scale devices.

7.4 Foil Mask Spectrometer for Laue Diffraction Pattern Imaging

An X-ray spectrometer for simultaneous position, intensity, and energy determinations suitable for Laue diffraction applications has been developed. The foil mask spectrometer consists of a series of metal foils of varying composition and thickness which are used to modulate the energy distribution of an incident X-ray source. Three modes of operation have been described: a high resolution spectrometer for measurement of nearly monochromatic X-rays, an intensity discriminator for partitioning the intensity from a small number of spatially overlapped monochromatic X-ray sources.
and a low resolution spectrometer for polychromatic X-rays with broad spectral features. The first mode of operation was designed to allow the energy of monochromatic or nearly monochromatic Laue reflections to be measured with a resolution suitable for determination of unit cell parameters. The second mode of operation was designed to allow the intensity of each component in a spatial region containing overlapping orders or spatially overlapped reflections to be discriminated for use in refinements or space group assignment. The third mode of operation was presented for completeness.

The theory behind each mode of operation has been described. The energy resolution of the spectrometer improves with the square root of the intensity of the incident beam. It also increases linearly with the change in energy with respect to transmission efficiency of a particular foil. In theory, the resolution of the spectrometer can exceed 50 eV over a wide range of energies depending on the foils used and the incident X-ray photon flux. Determinations of the energies of Mo Kα and Cu Kα radiation using a ten foil spectrometer gave values of 17.5 ± 0.1 keV and 8.08 ± 0.05 keV respectively. Treatment of random error shows good correspondence with a Poisson model. The spectrometer was demonstrated using a sample of tetraphenyl-phosphonium tetrachloro-oxomolybdenum (V). Comparison of predicted and observed energies shows good agreement over a wide range of energies. The ratio of predicted to measured energy for the first 50 measurements was 0.9918 ± 0.0344. The system was found to be capable of separating Laue harmonics. The capabilities of the foil mask spectrometer system
demonstrated the feasibility of using Laue diffraction to completely determine the crystal structure of a molecule without recourse to monochromatic methods.

7.5 Application of Energy Resolved Measurements to Laue Diffraction

Data from the foil mask spectrometer was first shown to be suitable for unit cell determinations by Campbell (Campbell, 1996). Based on this first result, a set of crystals were studied to see if the method was general to a wide range of sizes and crystal systems. The ability to measure unit cells was then extended to the ability to assign systematic absences from the Laue pattern. Seven different crystals having previously known unit cells were re-examined using Laue diffraction methods. These crystals included four different crystal systems including: cubic, orthorhombic, tetragonal, and monoclinic cells. The crystals had cell sizes from 179.4 Å$^3$ to 4588.3 Å$^3$. Comparison of known and re-determined cells showed good agreement (ratio of known to measured cells = 0.987±0.020). A single procedure was suitable for all unit cell determinations. The accuracy of the method is presently limited by the quality of the available energy measurements. The set of crystals examined using the energy resolved detection system contained some examples with space groups having systematic absences normally obscured by harmonic overlap when using the Laue method. In particular, included in this set of crystals were examples of absences due to 2, screw axes (h, k, or l = 2n+1) and cell centering (h+k = 2n+1). A multiple linear regression model was developed for the
separation of harmonics and an F-test was applied to the assignment of systematic absences. All systematic absences were identified using a combination of the multiple linear regression model with either stepwise elimination or stepwise inclusion and the F-test for assignment of systematic absence.

An extensive set of simulations were performed to evaluate the tolerances required and to evaluate the theoretical limitations of harmonic separation. Based on this set of simulations it appears that the separation of harmonics is limited by the Poisson noise of the different intensity components of the harmonics. This limitation is probably general to all presently available methods for separating Laue harmonics. If the magnitude of a particular component is less than the noise associated with the other components of greater intensity, separation of its intensity will be impossible in any system of calibrated absorbers. In cases in which exposures are taken of multiple orientations, separation will also be limited by the Poisson noise of the measured X-rays. This limitation can be considered analogous to the "multiplex disadvantage" often encountered in optical spectroscopic methods which use encoding schemes. The multiplex disadvantage occurs when the photon shot noise of a strong feature contaminates or obscures weak features in a spectrum. In the case of harmonic separation, the ability to separate a set of harmonics improves as the number of X-rays sampled increases. This condition improves nearly all measurements made with a foil mask spectrometer.
7.6 Future Directions

The research presented in this dissertation suggests that all the tools needed for full implementation of the Laue experiment for complete structure determination are available. Implementation of such experiments on either a laboratory scale or synchrotron facility scale to the extent where they become competitive with monochromatic methods for most purposes will need considerable experiment and development. The directions in which this future work can proceed can be divided into five areas: X-ray sources, detectors, data collection, calibration methods and analysis. Possible future directions for each of these areas are discussed in detail in the following sections.

7.7 X-ray Sources

The power available in laboratory scale "white" X-ray sources is limited at present. The commonly used sources are sealed X-ray tubes and rotating anode X-ray sources. These devices have been primarily engineered for monochromatic X-ray use. They are stable over long periods of time. The power output of these devices, however, is limited by the ability to remove the large amount of heat generated as a byproduct of the X-ray generation process. If the rated power is exceeded the target can be damaged.
The Laue experiment has several features which can be considered when designing a source. For Laue applications, the stability required of a source under some conditions is less critical than in monochromatic data collection. Since multiple spots can be observed at once they can be normalized to each other, hence removing the effects of source instability, and since redundant data is easily collected when multiple orientations are observed, multiple orientations can also be normalized to each other without difficulty. This allows a source to be engineered for high power with less of a need for high stability.

The limitation of the power output from a rotating anode is the ability to remove heat. The target anode material can be damaged due to melting of the anode or destruction of the target material by vaporization. One possible way to avoid the problems of melting and anode damage is to construct the anode of a material which can reform if melted or vaporized from local heating effects. An approach to such a source is to construct the anode of a molten metal target material. Three elements that are appropriate for this type of approach are Hg, Pb, and Bi. These substances have low melting points which could be maintained under soft vacuum without difficulty. Since the rate of thermal transfer is proportional to the temperature difference between a material and its surroundings, maintaining a molten metal target at elevated temperatures would improve the rate of thermal cooling. Refluxing mercury is the basis for mercury diffusion pumps suggesting that a mercury target might be suitable for both target
material and for maintaining vacuum. Some of the properties of these elements are presented in Table 7.1.

Table 7.1: Properties of Mercury, Lead and Bismuth Targets

<table>
<thead>
<tr>
<th>Property</th>
<th>Mercury</th>
<th>Lead</th>
<th>Bismuth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>80</td>
<td>82</td>
<td>83</td>
</tr>
<tr>
<td>Atomic Weight</td>
<td>200.59</td>
<td>207.2</td>
<td>208.94</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>-38.9</td>
<td>328</td>
<td>271</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>356.58</td>
<td>1740</td>
<td>1560</td>
</tr>
<tr>
<td>Temp where vapor Pressure =1x10⁻³ (mm Hg) °C</td>
<td>-23.9</td>
<td>1156</td>
<td>474</td>
</tr>
<tr>
<td>Thermal Conductivity @ 100 °C (W cm⁻¹K⁻¹)</td>
<td>0.0947</td>
<td>0.344</td>
<td>0.0722</td>
</tr>
</tbody>
</table>

There are a variety of advantages to the use of these elements for target material. They can easily exist in vacuum in the molten state. They are of high atomic number, representing 3 of the 4 highest stable elements in the periodic table. The yield of continuum X-rays from a target is approximately linear with the atomic charge.

The molten metal could be pumped in direct contact with a coolant to maintain constant temperature. The metal target could be subjected to current pulses or used in a continuous mode of operation. If the power level gets too high in such a system no ill effects are anticipated as it will only disrupt the target surface until the current level is reduced and the target surface can recover. Two target configurations could be used. The first would be to simply allow the molten metal to form a pool. The second is to pump
the molten metal through a nozzle to form a jet.*

The advantage of a jet is that it allows more configurations to be attained. The use of a gravity formed pool requires that the resulting X-ray beam be directed upward from the target. A jet could be directed in a convenient orientation. The resulting X-ray beams could even be directed downward. The other advantage of the molten metal jet is that the jet velocity could be adjusted to keep the target region from being locally over heated.

The primary concern with the use of such a source would be fouling of the window with high atomic mass metals. If vaporization of small amounts of the metal occur from the pool or jet it is possible that some of this material could condense on the window material. To avoid this, a small counter flow of He gas from the direction of the window toward the source could be used to deflect the vaporized metal.

Schematic representations of two molten metal sources appears in Figure 7.1 and Figure 7.2. It should be noted that these are intended to be conceptual drawings and will probably require modification before a useable source can be constructed.

7.8 Detectors

As discussed in chapters 2 and 3, the CIDs used in this study have a variety of

* The author would like to acknowledge Dr. Michael Bruck who suggested the use of a jet during the course of a conversation with the author.
Figure 7.1: Molten Metal Anode X-ray Source - Gravity Pooled Target

Outline for a gravity pooled molten metal anode X-ray source. The anode material is pumped to control temperature. See text for details.
Figure 7.2: Molten Metal Anode X-ray Source - Liquid Jet Target

Outline for a molten metal jet anode X-ray source. See text for details.
limitations. Of particular concern is the non-linear behavior of the photometric response function of the CID. In the context of atomic emission spectroscopy, this behavior is of less concern since it can be corrected by the use of a standardization curve. In X-ray crystallography, standardization of the response of an unknown crystal in an unknown orientation is unrealistic. Further, the camera system used had low light collecting abilities. Exposure times were long using this system. The combination of slow optical response and poor photometric accuracy of the CID system were cause for concern throughout this work. While the detection system was sufficient for the studies performed here, the entire detection system could be redesigned and several orders of magnitude improvement in performance could probably be realized.

The exposure times used in chapters 5 and 6 were typically 40-60 minutes per exposure. Some preliminary work with a CCD system employing a fiber optic taper was done toward the end of this project. Two images from this system appear as Figure 7.3 and Figure 7.4. The figure showing the Laue diffraction pattern of lysozyme was taken in 2 minutes per exposure. The figure showing the Laue pattern of tetraphenylphosphonium tetrachlorooxomolybdenum (V) was taken using a 25 second exposure. This camera system is over an order of magnitude better than the CID camera system described in Chapter 3 and used throughout this work. Both patterns were obtained using a Cu rotating anode generator. With the use of a W or Au anode roughly a factor of 2-3 increase in continuum X-rays could be achieved. Combining the faster optical system

* This CCD camera system was constructed for MAR research by Gary Sims of Spectral Instruments.
and the higher intensity source should allow nearly 2 orders of magnitude improvement over the current system.

An added advantage of going to the CCD system is that improved linearity would be expected. It should also be noted that there are a variety of other X-ray area detectors which have good linearity. These include: image plates, multi-wire detectors, and SITs. Retrofitting the foil mask spectrometer to one of these existing detectors should give equal or better performance than the camera system used in these studies.

In chapter 6, the possibility of using a redesigned image plate system as an alternative to the foil mask spectrometer idea was briefly discussed. One of the fundamental limitations of the foil mask spectrometer is that it requires multiple exposures which are separated in time. A system which allows the information obtained from a foil mask spectrometer to be obtained in a single exposure would be desirable. As discussed in Chapter 1, the UNSCRAM approach used the attenuation of X-rays in stacked photographic film for the purpose of separating harmonically overlapped spots in Laue patterns. There are many problems with the use of film in this application.

The general idea of stacked absorbers is a good one which has considerable promise. If a system based on image plate technology could mimic the role of film in this experiment, it would solve the problem of the multiple exposures required by the foil mask spectrometer. Currently available image plate technology has been engineered for maximal detective quantum efficiency. If an image plate were instead engineered to be.
Figure 7.3: Laue Pattern of tetraphenylphosphonium tetrachlorooxomolybdenum (V) Taken with CCD System

Laue pattern from tetraphenylphosphonium tetrachlorooxomolybdenum (V) crystal in a random orientation. Exposure time was 25 seconds.
Laue pattern from Lysozyme crystal in a random orientation. Exposure time was 2 minutes.
semi-transparent to X-rays, they could be used to collect data similar to that presented in chapters 5 and 6

Implementing such a system may be complicated to eliminate K-edge ambiguities, however, it should be possible to selectively dope individual plates or to carefully place foils between plates to eliminate energy ambiguities. Implementation of this system, if possible, would allow the full potential of the high speed Laue experiment to be realized even under synchrotron source conditions. Unit cell determination, harmonic separation, and systematic absence conditions could be determined using data obtained from a single exposure.

7.9 Data Collection

It is anticipated that the use of the Laue method on a laboratory scale will require automated data collection. The data collection problems associated with the Laue method are somewhat different than those of the monochromatic techniques. In monochromatic methods the crystal is rotated in such a way that the desired reflection or reflections become coincident with the Ewald sphere characteristic of the wavelength of the X-rays used. Using Laue methods a large portion of reciprocal space is simultaneously visible. In this latter case, one would like to survey as much of reciprocal space as possible using the minimum number of exposures and the minimum amount of redundant data.

Amoros et al. (Amoros, Buerger, and Canut de Amoros, 1975) present a
description of the systematic Laue method. The systematic Laue method is an approach
to the collection of a full record of the reciprocal space available to the diffraction
experiment. In the treatment of Amoros et al., it is shown that there is considerable
advantage to be obtained using a cylindrical film for recording such photographs. Of the
modern detection systems, the image plate is probable the only one that lends itself to a
curved format. Regardless of the detection system, developing an automated data
collection system based on the systematic Laue method would be advantageous.

7.10 Calibration Methods

The foil mask spectrometer system described here had limited calibration. To
obtain the results presented, it was sufficient to use a two point measurement of the X-ray
thickness of the foils used. The remainder of the expected transmission efficiency curves
were obtained from tabulated data and linear interpolation. Further, no wavelength
normalization was applied to the data. While it would be possible to obtain a calibration
of the transmission efficiency of the foils using a point by point approach a more elegant
and useful way is to use a crystal of known unit cell and structure. The crystal can be
introduced into the diffractometer and the Laue pattern recorded through each of the foils.
Since the crystal is known the energies or energy of each recorded spot is known. Using
this data a multi-point calibration of the transmission efficiency can be obtained for each
foil. Alternately, this data can be entered into a model and a least squares fit to the
thickness can be performed. The ideal crystal for this approach would be with a large unit cell to give a large number of spots in the Laue pattern. It is also possible to predict the relative intensities of the observed spots using a crystal of known structure. Using a plot of the relative intensity observed vs. the relative intensity predicted as a function of energy it would be possible to generate a wavelength normalization curve for the source and detector. Using a crystal with a large unit cell and well known structure the characteristics of the spectrometer, detector, and source could be readily determined in a straightforward manner.

7.11 Analysis

At present the analysis of data generated by the foil mask spectrometer system is done by a number of separate programs. Consolidation of the programs into a single program allowing start to finish analysis of Laue patterns would be a desirable convenience. In addition, the software described here and other programs currently available do not allow for certain types of analysis. First, the method described for separating harmonics, in theory is equally applicable to spatially overlapped spots. This type of overlap is caused by multiple non-harmonic spots which are not sufficiently spaced to allow them to be resolved with the detector system used. If the number and energies of the spatially overlapped spots are known a multiple linear regression model of the region can be generated in a fashion analogous to that described for harmonics. A
program for generating such models is somewhat complicated and remains to be implemented.

The program ERLAI, in its present form is designed to analyze single Laue patterns. The use of a systematic Laue method data collection method would result in Laue data from multiple orientations. It would be advantageous to be able to use the multiple orientations simultaneously to obtain a single self-consistent unit cell. As seen in Table 6.4, two orientations of the same crystal resulted in slightly different unit cell dimensions. It is probable that if simultaneous refinement of the data from all three of the orientations of this crystal for which data was collected were possible, a more accurate unit cell measurement would have been obtained. At present no software exists to perform such refinements.

7.12 Motivation for Future Research

Assume that the following are available: an X-ray source with 10 times the output of the one used for the data collection reported in Chapter 6, a detector with the capabilities of the CCD system used for the preliminary measurements presented earlier in this chapter, a combination of detector and foil set calibration giving \(1/10^{th}\) the error of the current systems, and an optimized data collection procedure. Such a system would have the following capabilities for a strongly diffracting crystal such as the molybdenum compound used in chapters 3, 5, and 6:
1) Unit cell accuracy of 0.2% or less.

2) Exposure times of 2.5 seconds per image.

3) Data collection for unit cell determination in 27.5 seconds.

4) Standard Laue photos or 100 orientations in 4.5 minutes.

5) Foil mask analysis of 10 orientations in 5 minutes.

6) Combined data collection for full structure analysis in 11 minutes.

For samples like the lysozyme crystal, equivalent data collection could be performed in 45 minutes. The author believes the assumptions are realistic and expects that such a system will be implemented in the near future. This would make the Laue method very attractive as a method of analysis on both the laboratory and the synchrotron facility scale.

The Laue method has long held the promise of very high speed structure determination. It is hoped that the research presented in this dissertation will allow that promise to be finally realized.
Appendix I

Appendix I: Depletion Depth Evaluation for CID 17PPRA
(Hanley, Denton, Jourdain, Hochedez, and Dhez 1996)

I INTRODUCTION

Charge Injection Devices (CIDs) are, like the more widely known Charge Coupled Devices (CCDs), members of the Charge Transfer Device's (CTD) family of optical imaging detectors. CIDs have the capability of performing high speed single pixel address, random access integration, real time evaluation of image quality, and non-destructive readout during image acquisition. Due to its unique combination of readout modes and signal integration possibilities, CIDs open a new area in spectroscopy and imaging. While the characteristics of CIDs in the optical photon range have been

* The material in this appendix has been published previously in Recent Developments in Scientific Optical Imaging by the Royal Society of Chemistry, 1996. Under the terms of its publication, the authors retain the rights to reproduce it.
published, little work has been done to date on the efficiency of CIDs in the far UV and soft X-ray range. The purpose of this paper is to present X-UV Quantum Efficiency (QE) measurements achieved on a CID (CID 17PPRA made by CIDTEC) initially designed for sensing visible light.

This study will be presented in four parts. First, the interaction of photons with Si internal photo effect devices will be summarized. This section will focus on the physical properties of Si that allow CIDs to be used as detectors for the X-UV. In a second part, measurements obtained at the SACO synchrotron facility of LURE are presented. Third, a simple model is compared to the measured results in order to explain the main features of the QE curve and to evaluate depletion depth and oxide layer thickness. Finally, conclusions will be reached with regard to the utility of the devices as detectors in the X-UV range and suggestions made for future optimization of CIDs for this purpose.

These measurements represent the first evaluation of depletion layer thickness in CIDs and also the first reported measurements of the variation in response of a CID with the energy of incident photons.

2 SILICON IMAGING DEVICE IN THE VISIBLE AND X-UV RANGES

The two most important parameters controlling the X-UV detection efficiency in CTDs
are the oxide over layer thickness and the depletion depth. Figure 1 is a plot of the penetration lengths of photons having energies from 1-10000 eV in Si and SiO₂. The penetration length corresponds to the depth at which 1/e of the incident photons are absorbed (according to the Beer-Lambert law). From such curves it is easily seen that CTDs, despite being designed for visible light, might be useful over a limited region of...
the X-UV range. The main drawback to the use of devices without specialized engineering for the X-UV is that the SiO$_2$ layer is very absorbing outside the visible range. In the devices used here, this SiO$_2$ layer formed a "dead" layer on the order of one micron.

3 EXPERIMENTAL QE MEASUREMENTS FROM 1.7 TO 6 KEV.

A CID 17PPRA device was mounted in a dewer providing liquid nitrogen cooling. Radiation was generated by the LURE Synchrotron Radiation source and photons of appropriate energy were selected using a double crystal monochromator. The photon flux was measured using a calibrated proportional counter as a reference photon detector.

The CID 17PPRA device is a pre-amp per row architecture device fabricated on 5Ω-cm$^{-1}$ silicon. The epitaxial layer of the devices varies from 15-38 microns, depending on the particular device. The CID 17PPRA is a 256 X 388 pixel device in which each pixel is 28 X 24 microns.

The QE of the CID 17PPRA was calculated from the integrated signal in the device using Equation 3.1

$$QE = \frac{S \times 3.65 \times G}{nbph \times E}$$

3.1
In equation 3.1:

- $S$ is the signal in the CID summed over all irradiated pixels (after a dark image subtraction has removed the dark current and the pixel non-uniformity) expressed in ADU (Arbitrary Digit Unit)

- $n_{p\text{h}}$ is the number of photons reaching the CID based on calibration of the beam with the proportional counter.

- $E$ is the photon energy.

- $3.65$ is the energy in eV of an electron-hole pair creation.$^5$

- $G$ is the system gain$^6$ of the camera at which the images have been generated expressed in carriers/ADU.

### 3.1 Experimental results

Figure 2 shows the absolute QE of the CID 17PPRA over the range from 1.7-6.0 keV. The CID QE curve exhibits two regions of interest. First, the QE varies rapidly in the range near the Silicon K edge (1750 eV). Second, the QE decreases smoothly with
energy in the higher energy region. This latter case is due to the penetration length being comparable to, or larger than, the expected depletion depth.

For contrast, Figure 3 shows a Si transmission curve obtained with the same monochromator plotted over the same range as the QE measurements made with the CID. This transmission curve is consistent with that expected for a given energy and the silicon edge features of the CID.

The QE variation around the silicon K edge and the decrease in QE with energy was then selected for more detailed study. Analysis of the latter region indicates the energy at which the depletion depth of the CID becomes smaller than the X-ray penetration depth in silicon. Analysis of these regions gives access to the CID depletion depth.

4 DATA INTERPRETATION.

It is possible to model the two segments of the data presented in the preceding section using a "crude" model. Application of the model to the data allows the depletion depth of the device and the thickness of the SiO₂ to be estimated. The simplest model explaining
Figure 2 Absolute QE measurement from 1.7 keV to 6.0 keV

Figure 3 Absolute QE measurement over the Si_k edge
the main observed features rests on two assumptions. First, a single absorbing SiO₂ over layer is assumed to account for all the photons absorbed before they reach the active silicon region where photoelectrons are efficiently collected. Second, a fully efficient silicon layer having a thickness equal to the depletion depth is assumed to account for all the signal generated in the device.

Figure 4 shows computed QE curves generated using this model. For these curves the SiO₂ dead layer was set to 2 μm, and the thickness of the active silicon layer was

**Figure 4** Energy vs quantum efficiency for various depletion depths using the “crude” model and an assumed SiO₂ upper layer of 2 μm thickness
allowed to vary from 5-1000 microns. It should be noted that 1000 microns is much
greater than X-UV penetration length. Therefore, no decrease of QE versus energy is
seen.

Two points may be noted from this curve. First, the energy at which a given QE
curve departs from the 1 mm curve depends heavily on the depletion depth of the device.
Second, the QE amplitude variation and the shape of the curve in the region of the Si\text{\textk}
edge also depends on the depletion depth.

Figure 5 shows the results of different fits of our "crude" model to the data. Data at
high energy, above the Si\text{\textk} edge, allow both the thickness of the SiO\text{\textg} dead layer and the
CID depletion depth to be estimated. To check the robustness of the model, a series of
fits were made selecting data over different energy ranges, enabling evaluation of the
perturbation introduced by the rapidly changing QE in the vicinity of the Si\text{\textk} edge.

All fits indicated a CID 17PPRA depletion depth of about 5\textmu m. It should be noted
that the "crude" model neglects phenomena at the Si-SiO\text{\textg} interface and does not account
for collection of charges generated outside the depletion region.

5 CONCLUSION

QE measurements in the X-UV have allowed an estimate of the depletion depth of the
CID 17PPRA to be estimated. The value of 5 microns measured here is consistent with values expected for a device fabricated on relatively low resistivity silicon. These measurements can bring important information on the CID structures (such as depletion depth and upper layer). As indicated above and clearly shown in Figure 1, the SiO₂ layer should be made as thin as possible. The thickness of the SiO₂ is the primary determinant of quantum efficiency below the Si₅ edge. Therefore, as has been done with CCDs, construction of a CID with a thin SiO₂ layer is of interest. For the energy range above 3 keV, the best way to enhance quantum efficiency is to increase the depletion depth. This

*Figure 5  Fits of the data with the “crude” model*
enhancement may be obtained by fabrication of CIDs on high resistivity silicon. It is also of interest to perform the same measurements at lower energies to explore the aluminum electrode structures and possibly to more precisely account for the different layers in our model. The "crude" model described here does not take into account the aluminum strap connecting the row electrodes or the nitride passivating layer.

References


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Appendix II

Description of the Programs ERLAI and EMATCH

(Excerpt from Hanley, Campbell, and Denton 1996)

The method of Duisenberg (1992) was adopted and coded in the program ERLAI. The program first converts the spot positions and energies into reciprocal lattice coordinates. The auto-indexing procedure is then carried out. All triplets (the end points of three reflection vectors) are generated for the selected input reflections and the origin reflection. The normals to such triplets define direct-lattice vector directions if the three reflections belong to the same reciprocal lattice. Taking each triplet in turn, all the selected reflections are projected onto it and the line projection is searched for the one dimensional lattice with the shortest period (above a given minimum) that fits the maximum number of the reflections within a requested tolerance (FIT LEVEL and FIT INDEX) giving a 't' vector which is stored. In ERLAI all triplets are examined from the start rather than taking a random selection initially as done by Duisenberg. The 't' vectors
list is sorted in descending order of NFIT (the number of fitting reflections) and the determined reciprocal distance vector 'd*'. The first vector in the sorted list is chosen to be the first direct lattice vector. The list is then searched to find the next vector which is at least a user defined minimum angle (default 30 degrees) from the first selected vector. This defines the second direct lattice vector. The search continues to find a third vector which is at least a user defined minimum angle (default 30 degrees) from the first two vectors. The three selected 't' vectors are then refined as described by Clegg (1984). The reflections which index well using the three vectors are found and if there are a sufficient number of these (e.g. at least half of the starting set of reflections) then the three selected 't' vectors are re-refined using only the fitting reflections. If the vectors form a left handed set then they are converted to a right handed set. The cell and crystal orientation are then determined and output to a file in a suitable format for input to the LAUEGEN program.

EMATCH predicts the reflection positions on an image and their energies given the current crystal and orientation parameters. For each observed reflection, the program finds the predicted reflection which is closest to the observed position. It is treated as a match if the distance between the observed and predicted position is less than a user defined number of rasters (default = 2) and the fractional wavelength difference is less than another user defined value (default 20%). The user may choose to include spots believed to be multiples if desired. Using the matching spots, a least squares calculation determines the scaling factor to apply to the cell to give the best match between the
predicted and experimentally determined energies. Details of the spots found and matched are listed and the rescaled cell values are output.
REFERENCES


in a Heavy-Ion Experiment. Nuclear Instruments and Methods in Physics Research A332:188-201


Bragg, W. L. 1975. The Development of X-ray Analysis G. Bell and Sons Ltd London.


Jovin, T. 1995. Personal Communication


Sons, Inc.

