SINGLE-PHOTON-COUNTING TECHNIQUE
FOR LUMINESCEENCE SPECTRA AND DECAY MEASUREMENTS

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TO MY PARENTS
&
BROTHER
ABSTRACT

A time-correlated single photon counting (TCSPC) method, which has very high sensitivity and a linear dynamic range, has been increasingly used to determine short luminescence lifetimes. Unlike virtually all other techniques that utilize relatively high emission intensities, single photon counting (SPC) depends on the intensity being low.

The time-correlated single-photon counting (TCSPC) technique has as its basis the timing of individual emission photons relative to a zero-time determined by the onset of the excitation pulse. By using a repetitive laser beam operating at a high frequency it is possible to rapidly record a histogram representing the probability of photon emission as a function of time after excitation.

The key instruments in an SPC system, are an excitation source, a start photomultiplier, a stop photomultiplier, a time-to-amplitude converter (TAC), and a multichannel analyzer (MCA) used in the pulse height analysis mode. The TAC generates an output pulse whose amplitude is directly proportional to the time between the start and the stop pulses. The MCA digitizes the height of the input pulse and increases by one the contents of the memory channel corresponding to this digital value.

The objective of this research is to design, build and characterize a single-photon counting apparatus based on the latest state-of-the-art time
resolving technique, and to develop the necessary software for computer control.

The effort is to use this apparatus to measure the luminescence emission and kinetic properties of rare-earth-doped ZnS crystals. The characteristic properties of rare earths in a ZnS lattice will then be related to the experimental conditions of temperature and concentration of rare earth doping in the ZnS.

A single photon counting system has been developed for making spectral and lifetime measurements in luminescent phosphors. The system's most novel feature is its ability to switch rapidly between spectral and kinetic measurement modes.

The time-correlated single-photon counting technique has several advantages over alternative techniques for lifetime measurements, all of which use analog detection. This is because it offers a combination of single-photon sensitivity, the precision of a mainly digital technique, a wide dynamic range, and a time resolution that still surpasses the capabilities of the fastest photomultipliers.

The construction details and performance characteristics for a SPC apparatus are described. The system utilizes a photomultiplier tube for signal detection, a monochromator for scanning, and a multichannel analyzer and computer for data acquisition and analysis.
Monochromator scanning is interfaced to an IBM-PC and Modulynx stepping motor controller. Detailed circuit diagrams and supporting software are presented. Suggestions for adoption to meet different experimental conditions are given.

To have some general agreement on the method of publishing experimental results, so that it will be of maximum value to others, the recorded spectra are corrected and a reference made to a 'correction curve' for our particular TCSPC system and experimental condition employed. The calibration of the monochromator and detector is accomplished with a tungsten lamp operated at a standard color temperature (2860 K). The monochromator wavelengths were calibrated by means of standard reference lines of mercury lamp.

Data acquisition is done in a ratiometric mode to compensate the excitation source intensity variations when measuring luminescence emission spectra and to keep the statistical noise of the reference signal constant. The Delayed coincidence method is used for kinetic measurements. This system uses laser excitation that is chopped by an acousto-optic modulator for decay measurements.

Electron transit time is minimized by the application of a high voltage between photocathode and the first dynode of the photomultiplier tube (PMT), as well as some modification of the electronic system. Several operating configurations of the TAC were examined to evaluate its performance in the TCSPC experiment. The inverted configuration has been proved to be optimum.
The resulting data are analyzed to obtain pertinent parameters such as luminescence emission peaks and excited state lifetimes. Tests of the apparatus have demonstrated that luminescence decay times as short as a few picoseconds can be analyzed by the system.

The photoluminescence emission (in MCS mode) and kinetic (in PHA mode) properties of rare-earth doped ZnS crystals (ZnS:Pr$^{3+}$ and ZnS:Nd$^{3+}$) were investigated using the apparatus, and experimental results and analysis are summarized in this thesis.
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INTRODUCTION

a) CONCEPTS

Experimental spectroscopy encompasses methods of observing the flux density or intensity of radiation as a function of wavelength, time and state of polarization. The most frequently investigated relationship is that of intensity as a function of wavelength, which is called the 'spectrum'.

Ever since the discovery of spectral concept and analysis, no one could doubt that the language of the atom could be understood if one learned how to interpret atomic spectra [1]. What we hear today, the language of spectra is a true 'music of the spheres' of the atom, chords of integral proportions, an increasing order and harmony. For all times, the theory of spectral lines will bear the name of Bohr. All integral laws of spectral lines originate from the quantum theory.

The spectroscopist is interested in the whole wavelength region in which spectra of atoms and molecules can be observed. The experimental information on the energy levels of atoms, with the predictions of quantum mechanics, through the observation of the spectrum of light emitted by atomic vapours, transitions of electrons is more precise. Survey of different spectral regions requires a special experimental technique of investigation.
It is assumed that the reader is familiar with the elementary principles of atomic structure and with the spectroscopic notations and units. The information about band structure and energy levels is available in varying depths of treatment in a number of literature sources.

When an atom makes a transition from one energy level to another, with the emission of light, one can learn more than the mere fact that there are two levels in the atom separated by the energy of the transition. This is because certain selection rules exist which place restrictions on the type of level to which a given level may decay.

The analysis of a spectrum involves an interesting experience: given a set of spectrum lines, to construct the array of atomic energy levels, transitions between which produce the observed spectrum. Evaluation of a spectrum consists of determining the wavelengths of the lines as well as their relative intensities. The characteristic feature of a continuous spectrum is that its intensity is a function of the wavelength (intensity distribution).

Spectral line intensities are mostly determined by comparison according to an arbitrary scale, in which the brightest is the strongest line and the weakest is barely recognizable. With a recording instrument, the distance between lines, the line intensities, and the
The positions of the energy levels in an atom are measured in wave numbers,

\[
\sigma = \frac{1}{\nu} = \frac{\lambda}{c}
\]

where

- \( \lambda = \) wavelength in vacuum (meters)
- \( c = \) velocity of light \((3 \times 10^8 \text{ m/s})\)

and \( \nu = \) the frequency (Hz)

One can distinguish between emission and absorption spectra according to whether the atom under consideration emits the wavelength in question, or absorbs it out of the continuous wavelength range of the incident radiation. The width of a spectral line depends on the perturbation/disturbance of its emitting or absorbing atoms by its environment.

To observe an emission spectrum, the atoms or ions under investigation must be 'excited', the physical meaning of which has been explained in the later chapters.
b ) PHOTON COUNTING

Discussing the basic understanding of spectral lines and spectrum, it is essential to know how the spectrum is recorded and what are the instruments needed for recording a spectrum.

Photon counting is a technique for measuring low light levels. Any system used to measure the intensity of light at a specified area in a beam or as a spot on a sample must have a detector, a signal processing unit (e.g., counter) and an output indicator (digital display or analog meter). Light can be described in terms of photons or discrete bundles of energy propagating in the light beam direction.

In an ideal light measuring system, the detector should have the property of giving out a perfectly defined pulse every time a photon strikes the detector's sensitive area, the photocathode. Furthermore, it should not give out a pulse in the absence of light. The signal processing would then simply consist of a counter that stored these output pulses, which would be a number that represents the number of pulses accumulated in a specified measurement interval.

The general counting system shown in fig. 1 provides for counting all detector events that produce an output with an amplitude greater than the threshold set on the discriminator.
The usual choice of discriminator setting is just high enough to reject the background noise present at low amplitudes.

Flash lamps, high pressure mercury or xenon lamps, and more recently lasers have been used as excitation sources and photomultiplier tubes as the detectors. Convenience and precision of measurement is the choice of the individual experimenter.
c ) OBJECTIVE of this research:

The objective of this research is to design, build and characterize a single-photon counting apparatus based on the latest state-of-the-art time resolving technique, and to develop the necessary software for computer control.

The effort is to use this apparatus to measure the luminescence emission and kinetic properties of rare-earth-doped Zinc sulphide (ZnS) crystals. The characteristic properties of rare earths in a ZnS lattice will then be related to the experimental conditions of temperature and concentration of rare earth doping in the ZnS.

The analysis of experimental data with the energy level scheme/transition assignments to be accomplished relating to the free ion spectra of trivalent rare earth ions.
II. EXPERIMENTAL TECHNIQUES:

Introduction

Many factors are considered in the design of a photon counting experiment: an adequate excitation source, a detection system and procedures for data collection and analysis.

This thesis focuses on a single-photon-counting (SPC) technique for spectral measurements and a time-correlated single-photon-counting technique (TCSPC) for decay kinetics (time response) measurements on luminescent materials. This very sensitive technique allows the determination of the time of emission of a single photon from a sample. Since single photons can be detected, this technique provides useful information at extremely low light levels.

The overall system has been described because it is a versatile apparatus for studying luminescent phenomena (electroluminescence and photoluminescence).
Single-Photon Counting (SPC)

As the incident light intensity drops, the output of the PMT is no longer a pulse, but a sequence of single photon pulses, the mean number of which in a given time interval is proportional to the photon intensity in that interval.

Single-photon counting is a technique by which the occurrence of single photoelectrons produced by photons incident on the photocathode are counted. The mean transit time in a multistage (12 or 14 stages) photoelectron multiplication is reduced by timing when the leading edge of the PMT output pulse reaches a certain threshold. This can be performed by a leading-edge type discriminator, which produces a timing output whenever an incoming pulse crosses the input threshold. The pulse amplification of the photomultiplier depends on the energy of the incident photon and differs for photons incident on different parts of the photocathode. There is also a spread in the secondary-electron amplification factors. This resulting variation in pulse amplitude will lead to a timing 'jitter' (fig.2a) which can be reduced if only a small part of the photocathode is used. However, it is preferable to use 'constant-fraction timing', since maximum aperture can then be retained.

In the constant-fraction timing method, one uses a discriminator whose threshold for timing occurs when the pulse has reached a fixed fraction of its maximum. By assuming that the ratio of the heights of the pulses is the same at any point on the pulse, all the variation is removed [18,19] (fig.2b).
Time-correlated single-photon counting (TCSPC)

In an ideal time-correlation experiment, a pulse of light excites a luminescent sample and the time at which each photon is emitted by the sample is detected by the photomultiplier and recorded [2]. This experiment is repeated to build up the time correlation or the decay spectrum. In practice, one cannot measure the time of arrival of all the photons emitted by the luminescence sample as a result of one single excitation pulse. The time of arrival of the first photon is recorded only if it arrives in a given time interval after the pulse (excitation). Each time there is a pulse, a synchronized pulse (START) initiates the time sweep of a time-to-amplitude converter (TAC), and if a pulse is received from the photomultiplier during the sweep it acts as a STOP. The TAC then generates an output signal whose voltage is proportional to the time difference between START and STOP.
Block diagram of a conventional single-photon counting apparatus
The luminescence-detection photomultiplier output could also be used as a START [18], while the excitation pulse, through a suitable delay can activate the STOP. This sequence reduces the number of unconsummated STARTs [20].

There is an inherent delay between the excitation and the earliest possible photon detection due to photomultiplier transit time, light-path length, cable delay and discriminator delay. On a short TAC range, only the latter half of the range is used unless the START pulse is delayed to bring it closer to STOP. On longer ranges the finite time for the TAC to STOP after STARTing is taken into account. In this manner, the initial non-linear region of the TAC is avoided by delaying the STOP. Thus both the START and STOP pulses are suitably delayed by a length of coaxial cable or by the delay generator to ensure that the linear section of the full range of the TAC is utilized.

The pulse output of the TAC is fed to a biased amplifier whose gain is used to sample a section of the TAC range and expand it to cover the full range of the MCA. In the analyzer, the counts in each channel are proportional to the probability of luminescence emission in the time interval $\Delta t$ at time $n\Delta t$, where $n$ is the channel number and $\Delta t$ the channel width. The analyzer thus stores the distribution of time intervals, up to a given maximum, for the arrival of the first photon from successive pulses. The maximum is set by the TAC-BA combination with an ultimate resolution of less than 10 psec.
a) Excitation Source

A Laser Ionics model 553A argon ion laser has been used as the photoluminescent excitation source. During our measurements we set the excitation intensities in the range of 18 mW to 100 mW during spectral recording. The laser beam was filtered through a laser filter monochromator (Photo Physics) to suppress all the plasma lines and make it monochromatic. All of the argon laser lines 457.9 - 514.5 nm (2.7076 eV - 2.4097 eV) were used.

The continuous-wave (CW) laser beam was pulsed by an acousto-optic modulator (AOM) for decay-time measurements. The AOM was used to intensity modulate the laser-light optical frequency by the applied acoustic frequency. To obtain maximum modulation depth and minimum rise time, the laser beam diameter in the modulator sound field was reduced to 0.104 mm, using a lens of focal length, f=50 mm. The acoustic frequency was derived from a pulse generator (HP 8013 B).

Rotation of the AOM in a plane defined by the light beam and sound field (optimum at Bragg angle) gave maximum intensity in the first-order diffracted light. The undiffracted or zero-order beam was blocked by a diaphragm and only the diffracted beam was passed through an aperture and recollimated on the sample by a lens of f=75 mm.

Whenever and wherever possible, for a series of experiments, the excitation spot was maintained at the same location on the sample.
to avoid variation of sample parameters with position on the sample (since the sample might be non-homogeneous).

b) Detection

The detection system is organized primarily for photon counting. Using a Hamamatsu R928 high gain, side-on type photomultiplier tube (PMT), a spectral range of 400 - 930nm (3.1 eV - 1.33 eV) is obtained.

The PMT is cooled with a thermoelectric cooler to -20°C to keep the dark-count rates to within 40 - 45 counts per second. The PMT was operated at 1250 Volts and 1350 Volts, with the modified dynode chain, by a regulated high-voltage power supply (Pacific Instruments).

When it is desirable to minimize the dark count, the standard procedure of cooling should be adopted [38,39]. There is a voltage-dependent component of the dark count which can be minimized empirically by monitoring the signal-to-noise plus noise-to-signal ratio as interdynode voltages [37].

In applications where the incident light is in the form of pulses, the anode output signal should reproduce a waveform faithful to the incident pulse waveform. This reproducibility is related to the anode pulse rise time and the electron transit time as illustrated in fig.3. The anode pulse rise time is defined as the time to rise from 10% to 90% of the peak amplitude when the whole photocathode is illuminated by a delta function light pulse. The
electron transit-time is the time interval between the arrival of a delta function light pulse at the photocathode and the instant when the anode output pulse reaches its peak amplitude. Both parameters are affected by the dynode structure and the applied voltage.

![Figure 3: Anode pulse rise time and electron transit time](image)

As explained before, the time width of the response curve mainly comes from the pulse duration of the exciting light, electron-transit time variation of the photomultiplier, and "jitters" in the electronic system. Using mode-locked lasers, stable pulses with very short duration and precision electronic instruments, minimum jitter can be accomplished. Therefore, the most important contribution to broadening of the response curve is the electron transit time variation of the PMT.

Shuichi Kinoshita [21] observed that, both the peak position of the response curve, which corresponds to the electron transit time variation, and the pulse width, which corresponds to the transit time variation, varied appreciably with the photocathode position along the shorter side.
Narrower response curves can be obtained by applying a higher voltage between the photocathode and the first dynode of the photomultiplier. This is because the velocity distribution of the emitted electrons from the photocathode affects the transit time variation more significantly than the distribution from the dynodes \([34,35]\). Therefore, the application of a high voltage between the photocathode and the first dynode makes the electron transit time dispersion considerably smaller. Though the width of the response curve decreases with increasing applied voltage, a value between 200 and 400 Volts between photocathode and the first dynode, proves to be the best, when breakdown of insulation is taken into account.

Silvio et al \([36]\) report that the wavelength dependence of the single-photon-counting instrument response curve is due to the distribution of the velocity of photoelectrons that are generated by photons of different wavelength. Increasing the voltage reduces the transit-time jitter and also the wavelength dependence of the response curve.

Photomultiplier tube (Hamamatsu R928) specifications indicate a transit time of 20 psec when operated at 1250 Volts. No attempt was made to investigate the actual transit time in the response curve. However, the features of shorter transit time are accomplished by modifying the voltage-divider network and operating the PMT at 1350 Volts (fig.4).

The typical current gain of Hamamatsu R928 PMT is around \(1.0 \times 10^7\) at 1000 Volts, but when operated at 1350 Volts the gain is of the order of \(4.0 \times 10^7\).
Output current pulses corresponding to single photons were amplified ten times by a fast preamplifier (Ortec 9301S) and connected to a timing filter amplifier (Ortec 474) through a 50 ohm coaxial cable, which is used to minimize stray noise and degradation in the detected signal during passage from the PMT housing to the signal counting electronics.

c ) Data acquisition

The sample emission spectra are taken by a Jarrel Ash 1M grating monochromator. A computer-controlled stepper motor scanned the monochromator synchronously with the memory channel sweep of the multi-channel pulse height analyser (MCA) which recorded the spectrum.

A modular photon-counting system has been chosen because of the variety of timing functions desired and control pulses may be interconnected with simplicity and ease.

During spectral recording, the MCA is operated in multichannel scaling (MCS) mode. In this mode, the analyzer accumulates all the incident photon counts (constant amplitude pulses) until the preset time for each channel, and then advances to the next channel and again records the constant amplitude pulses until it switches to the next channel
Fig. 4. Circuit diagram of the modified voltage divider network.
Direct method of spectrum recording.
and so on. The MCA thus records in 1024 channels during each sweep [22]. As the wavelength is scanned synchronously with MCA sweep, the profile of counts displays the emission spectra of the sample.

In many experiments, data recording over a longer period of time will be distorted by the intensity fluctuations of the excitation source during measurements. A ratiometric data acquisition mode [23] is used to compensate for excitation intensity variations and to keep the statistical noise of the excitation signal constant.

In a ratiometric mode, the emission and reference PMT signals are sent to their respective signal counters (as shown in fig.5). The reference counter is preset (say to 1000 counts) and initialized to count down from that preset value. Signal accumulates in the multichannel analyzer (MCA) until the preset reference count has been acquired. Although the MCA indicates one number in each channel, the measurement is effectively the ratio of emission to reference counts, with the count value of the reference set to a constant [23].
Fig. 5. Schematic representation of the ratiometric method.

**Ratiometric measurement circuit**

Data acquisition and wavelength control were accomplished by interconnecting between the COM1 and COM2 ports of an IBM PC, the ENABLE function feature of the Canberra 2071A dual counter/timer and the programmable MODULYNX motion controls SLO-SYN stepping motor indexer card. The MCA is run in EXT.CLK mode for its MCS setting (channel advance).
Ratiometric method of spectrum recording
The Dual counter-timer CANBERRA 2071 A has an ENABLE function feature which provides a logic "low" output when the unit is enabled for counting. When the counter is started this way, it is the master unit in the system. The enable line will be held low by this unit until its preset is reached, thus enabling all other units in the system.

The Multichannel analyzer (ORTEC 7100) accepts TTL inputs for EXT.CLK operation. EXT.CLK is used to start an MCS sweep. If EXT.CLK is held low, MCS will not begin until EXT.CLK goes high. If EXT.CLK is brought back low within 1 ms after the sweep starts, then MCS will stop at the end of one sweep. If EXT.CLK is not brought back to the low state within 1 ms, the sweep will be continuous. If no input is presented to EXT.CLK, it will be held positive and MCS will not be affected.

EXT.ADVANCE needs TTL input. When in MCS collect ext., this input is used to advance the MCA to the next channel. MCA channel advance occurs on the negative-going edge of EXT.ADVANCE, which should be high for a minimum of 2 μsec before going low.

The SCA feature delivers a TTL output. In MCS, SCA goes high for 1 μsec (minimum) each time an input pulse to the ADC satisfies the LLD and ULD limits of the analyzer.

In the programmable commands for stepping motor,
- KYLn load IOD009 Output Y, command controls the programmable outputs of the IOD009 indexer card.
KYWn Wait for input Y, command are wait commands that are associated with input Y of IOD009 card. This command tells the indexer card to hold further program execution until the specified input is in specified state.

A 74121 pulse stretcher is used to meet the EXT ADVANCE conditions for the MCA. 74LS00 SR flip-flop is used to advance the stepping motor to the next wavelength and to reset the counter.

The setting sequence of these instruments are shown below and the interconnections are shown in fig. 6.
Interface board

For interfacing the MCS and the stepper motor computer and the dual counter/timer. To be used for external control of the channel advance in MCS mode on the basis of photon counts.

Fig. 6. Circuit diagram and interface for ratiometric method.
We have used a delayed-coincidence method for measuring time decay. In the delayed-coincidence technique, an ensemble of events consisting of the time difference between a trigger signal and the arrival of the first photon after trigger are measured \[24\] (fig.7).

The delayed-coincidence technique depends upon a regime in which only one photon is detected per interval, $T$, and the fact that there is an equal probability of detecting a photon in any interval. In this limit, the number of counts in any channel is proportional to the intensity at the time corresponding to that channel.

The time of photon arrival had to be referred to the time of arrival of the laser excitation at the sample. A pulse output from the pulse generator (HP 8013B) which modulates the acousto-optic modulator represents the switching of the laser beam and thus the excitation pulse. This signal is constant in amplitude from pulse to pulse, hence a leading-edge discriminator (100 MHz Ortec 453) is adequate. Before entering the discriminator, the signal is delayed (through Ortec gate & delay generator). This delay is to compensate for the delay in the optical path, PMT, and current amplifiers, and an additional delay is added so that the reference timing pulse will arrive after the pulse from the photomultiplier tube. The PMT and reference timing pulses are used as the 'start' and 'stop' pulses for a time-to-amplitude converter (TAC) respectively.
The TAC can be thought of as a capacitor charging up in a linear scale. Charging starts when the start pulse triggers the TAC and capacitor charging stops when the stop pulse arrives. The voltage on the capacitor is a function of the elapsed time between start and stop. The output of the TAC is accumulated in a multichannel pulse height analyzer (MCA).

The TAC will recognize only one start pulse for each excitation period of the source. Therefore, the data would be biased if more than one photon was detected for a given excitation pulse. To avoid multiple photons in one period, the count rate is usually limited to <10% of the excitation repetition rate. Samples luminescing with low efficiencies at low excitations will automatically satisfy this requirement, but strongly luminescing samples require attenuation of the photoluminescence (attenuator inserted in front of the monochromator entrance slit, and slit widths reduced) to lower the count rate.

The TAC accepts a stop signal only if it has received a start signal; if a cycle occurs with no stop signal after a start, no output occurs. Only valid events are presented to the time-to-pulse height analyzer [26].

The reason for using the photon timing pulse as a start pulse rather than as the stop pulse can be better understood at this point [25]. Since a photon will be produced only once out of every 100 cycles or even less often, if the laser reference pulse had been the
Fig. 7 Schematic diagram of our computer-controlled TCSPC apparatus.
start pulse, the TAC would have started each period and stopped no more than 1% of the time. It is better to start the TAC only when it is needed, since the TAC ignores stop pulses which are not preceded by a start pulse. The instrument will perform better and more efficiently under such conditions, having less dead time. The only drawback of this configuration is that the resulting multichannel analyzer decay curves run backwards in time, so the data must be reversed when it is analyzed.

The voltage pulses from the time-to-pulse-height analyzer are accumulated according to the amplitude. Over time, the analyzer collects voltage pulses corresponding to decays from many different photons and makes histograms which represent the luminescence decay of the sample. Collection over a longer period of time reduces the signal-to-noise ratio in the data.

In all the time-correlation experiments, if the count rate for luminescence photons exceeds a few percent ( < 10 - 15% ) of the excitation repetition rate, 'pulse pileup' error will result [19].

Methods, both electronic and numerical, exist for correcting this error, which can enable counting at higher repetition rates [18].

Multiple photons or pulse-pileup elimination can be accomplished electronically by utilizing a digital inhibit circuit. If the output of the TAC is delayed by a suitable length of cable, then a pulse counter can be used to
gate the input of the analog-to-digital converter (ADC). The pulse counter will inhibit storage of the luminescence event if more than one photon of luminescence is detected following a single excitation pulse. With this technique, data collection rates (time-to-amplitude converter rate/excitation pulse rate) of up to 20% can be utilized. Since the probability of photon emission peaks sharply and then falls off either exponentially or as a sum of exponentials, if multiple photon events occur they will most likely occur with a small time separation. This method will be blind to precisely those multiple photon events which are most likely to occur, especially when short photoluminescence lifetimes are being measured [39].

Correction of emission spectra

It is desirable to have some general agreement on the method of publishing experimental results, so that they will be of maximum value to other researchers.

All spectrometers record 'apparent luminescence emission or excitation spectra' which, in some regions of the spectrum, are grossly distorted versions of the true spectra. Nevertheless, for one instrumental set-up the results can be reproducible and therefore may be used directly for analytical work without any correction. However, they are likely to differ considerably from the results obtained in another laboratory with an instrument of a different type. It is clearly desirable that the published spectra be corrected and a reference made to a 'correction curve' for the particular instrument and the experimental conditions employed [27].
The calibration of a monochromator and detector for the measurement of spectral distribution of luminescence is accomplished with a tungsten lamp operated at a known color temperature [28,29].

The principle of calibrating a monochromator is to determine the exact relationship between the wavelength of the emergent beam of monochromatic radiation and the scale divisions on the counter used to rotate the diffraction grating.

For this purpose gas discharge lamps are commonly used to provide a source of radiation with a line spectrum, i.e., individual lines of precisely determined wavelengths.

In calibration, the spectra of a number of standard reference lamps are examined by means of the monochromator and the position of the individual spectral line is determined with respect to the divisions on the monochromator scale. The results of measurements of several spectra serve as a basis for finding the relation between the monochromator scale divisions and wavelength by interpolation [30].
The standard reference lines are listed below:

**Wavelength of lines in radiation from discharge lamps**

<table>
<thead>
<tr>
<th>Monochromatic wavelength (nm)</th>
<th>Type of discharge</th>
<th>Monochromatic wavelength (nm)</th>
<th>Type of discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>253.7</td>
<td>Mercury</td>
<td>307.6</td>
<td>Zinc</td>
</tr>
<tr>
<td>313.0</td>
<td>Mercury</td>
<td>636.2</td>
<td>Zinc</td>
</tr>
<tr>
<td>365.0</td>
<td>Mercury</td>
<td>326.1</td>
<td>Cadmium</td>
</tr>
<tr>
<td>404.7</td>
<td>Mercury</td>
<td>506.8</td>
<td>Cadmium</td>
</tr>
<tr>
<td>435.8</td>
<td>Mercury</td>
<td>589.3</td>
<td>Sodium</td>
</tr>
<tr>
<td>546.1</td>
<td>Mercury</td>
<td>377.6</td>
<td>Thallium</td>
</tr>
<tr>
<td>578.0</td>
<td>Mercury</td>
<td>535.0</td>
<td>Thallium</td>
</tr>
</tbody>
</table>

An ORIEL Mercury spectral lamp was used for calibration of Jarrel-Ash monochromator. The monochromator counter divisions were specifically tested for the 435.8 nm and 546.1 nm lines.

To determine the calibration factor and the correction curve, a halogen tungsten lamp was used as the source of radiant energy whose color temperature was set to 2860 K (standard color temperature) as measured using an Optical Pyrometer (Leeds & Northup Co.). It was introduced in
front of the inlet slit of the monochromator and the energy emerging from the exit slit measured as a function of wavelength. Direct visual indication of the emerging energy as a number of photons was accomplished by a Quantum Photometer (PRA 1140) and recorded by the multichannel analyzer in the scaling mode.

The overall calibration of the monochromator has a quantitative relation with

- the spectral sensitivity \( R(\lambda) \) of the photomultiplier tube (PMT)
- the monochromator dispersion \( I(\lambda) \)
- the relative transmission \( \tau(\lambda) \) of the monochromator, owing to non-uniformities of the reflection and transmission characteristics of the optical elements in the system.

The product of these three functions constitutes a spectral relation characteristic for a given arrangement of monochromator and photomultiplier. Knowledge of the individual factors is not necessary for measuring the spectral response characteristics of a phosphor, since in this case the method employed is that of calibrating the instrument by means of a reference source of light. Such a source is a tungsten lamp whose spectral distribution is determined by measuring the color temperature.

On the basis of measurement on the tungsten lamp over a range of wavelengths, the number of photons (intensity counts) is recorded as a function of wavelength \( \lambda \).
This relation can be expressed as:

\[ N(\lambda)_{\text{BBD}} = \phi(\lambda)_{\text{STD}} [ I(\lambda) T(\lambda) R(\lambda) ] \]

where: \( \phi(\lambda)_{\text{STD}} = \) spectral distribution of tungsten lamp

\( N(\lambda)_{\text{BBD}} = \) number of photons for the color temperature 2860 K

\( [I(\lambda) T(\lambda) R(\lambda)] = \) the product of the dispersion, the monochromator transmission, and the sensitivity of the detector.

Similarly, for an unknown emission one can write

\[ N(\lambda)_{x} = \phi(\lambda)_{x} [ I(\lambda) T(\lambda) R(\lambda) ] \]

the ratio of the number of photons from the unknown to the number of photons from the black body will give

\[ N(\lambda)_{x}/ N(\lambda)_{\text{BBD}} = \phi(\lambda)_{x}/ \phi(\lambda)_{\text{STD}} \]

Thus we have,

\[ \phi(\lambda)_{x} = (N(\lambda)_{x}) x (S(\lambda)) \]

The calibration factor \( S \) was thus calculated from

\[ S(\lambda) = \phi(\lambda)_{\text{STD}} / N(\lambda)_{\text{BBD}} \]

\( S(\lambda) \) is the factor by which the photomultiplier readings must be multiplied to give the true counts/sec.
Monochromator wavelength calibration spectra using standard lines of mercury spectral lamp

(Wavelength (nm))

(Intensity, arbitrary units)

435.8
404.7
365.0
546.08
579.1

(Hundreds)
Emission spectra for a Tungsten lamp at a color temperature of 2860 K.
Black-Body radiation as number of photons

Intensity, arbitrary units

Wavelength (nm)
III. LITERATURE REVIEW

In this portion of the thesis, a comprehensive survey of the known electron-hole radiative recombination mechanisms will be explained.

Luminescence emission involves radiative transitions between electronic energy levels of the material, and the emission is the characteristic of the material. The transition originates on some excited electronic level, and after the emission of a photon, occupies a lower electronic level.

Photoluminescence is the optical radiation by a physical system resulting from excitation to a non-equilibrium state by irradiation of light.

In photoluminescence, three processes can be distinguished:

- creation of electron-hole pairs by absorption of exciting light
- radiative recombination of electron-hole pairs
- escape of the recombination radiation from the sample.

The process of excitation and luminescence in a hypothetical material having an electronic energy scheme is shown in fig.9. A line with an arrow upwards indicates excitation and the line with an arrow downwards indicating radiative recombinations, the dotted line showing the non-radiative decay process.
Fig. 9. The process of excitation and luminescence in a hypothetical material having an electronic energy level scheme is shown above.

At low-temperature and in the absence of any exciting mechanism level 0 alone is occupied; after excitation level 5 is occupied. Because levels 2 to 5 are close, the excitation drops to level 2 by a non-radiative cascade process. If the gap between level 2 and the next lower level is large enough, the excitation in level 2 cannot be dissipated non-radiatively. With such a large gap the transition from level 2 to level 1 or 0 may occur radiatively by emission of a photon, that is by the emission of luminescence [74].

Luminescence is efficiently excited in semiconductors through processes which produce large excess concentrations of free electrons and holes in the energy bands of the crystal. Transitions induced by lattice defects or impurities usually predominate in the recombination process.
An electron excited to a high energy state in the conduction band will eventually recombine with a hole in the valence band. Some of the possible electronic transitions which may take place with the emission of radiation are shown schematically in fig.10, and are described in detail below.

Electron-hole recombinations usually occur predominantly at impurities or lattice defects, either introduced intentionally or otherwise, but radiative intrinsic interband electron-hole recombinations, which occur in perfect crystals, have been observed. Recombination processes which involve the participation of impurities or lattice defects ('extrinsic recombinations) include transitions in which:

1. free carriers recombine with carriers trapped at impurities, (free-to-bound transitions)
2. electrons bound at donor impurities recombine with holes trapped at acceptor impurities (donor-acceptor pair recombinations).
3. excitons bound to charged or neutral donor or acceptor impurities recombine radiatively(both resonance' and 'two-electron', 'bound exciton' transitions)

Excitons are bound electron-hole pairs which can be described in terms of 'hydrogenic' levels close to the conduction band.
4. excitons bound to neutral donor or acceptor impurities recombine non-radiatively ('Auger' recombination)
5. excitons bound to impurities with the same number of valence electrons as the host atom which they replace (isoelectronic traps) recombine radiatively.
In thermal equilibrium, the several processes of carrier generation and recombination exactly balance.

Fig. 10. Representation of recombination processes (Lumb [74]).

C \rightarrow V \text{ is band-to-band transition}
E \rightarrow V \text{ is the decay of excitons (free-to-bound)}
D \rightarrow V \text{ is the loosely bound electron on the neutral donor-free hole transition}
C \rightarrow A \text{ is the free electron-neutral acceptor transition}
DD \rightarrow V \text{ and } C \rightarrow DA : \text{ the deep donors (DD) and deep acceptors (DA) give rise to transitions whose photon energies are well below the band gap.}
a) Energy band description of electron states in crystals

The energy band description of the energy states available to an electron in a crystal forms the basis of the empirical classification of crystalline solids into metals, semiconductors, and insulators in accordance with their electrical and optical properties [74]. Nonmetallic crystals have a finite energy gap between the highest energy level which is completely filled with electrons for the perfect crystal and the next band of allowed energy states. The magnitude of this energy gap, $E_g$, relative to the thermal energy, $kT$, at room temperature ($\approx 25$ meV) determines whether the crystal is an intrinsic semiconductor or an insulator.

b) Excitation processes

If the crystal is in an excited state, there are electrons near the bottom of the conduction band and charge-compensating 'holes' at the top of the valence band.

The crystal can be excited by illumination with light, with frequency $\nu$, greater than $E_g/h$, where $h$ = Planck's constant, by the impact of ionizing radiation. The equilibrium or ground energy state of the crystal is reached through the recombination of these electrons and holes. The general advantages of optical excitation are that luminescence can be observed both from uniformly doped and from highly purified crystals.
c) Direct and Indirect gap semiconductors

i) Perfect crystals: The momentum of the electron is given by $\hbar k_e$, where $k_e$ is a wave vector of the electron. The Figure 11. shown below, details the band structure of a crystal.

![Band structure of a crystal](image)

Fig.11. Band structure of a crystal

Semiconductors are classified as direct gap or indirect gap according to whether or not the absolute minimum of the conduction band occurs at the same wave vector as the absolute maximum of the valence band. The importance of this distinction is based upon excitation of an electron between these extrema through the absorption of a photon. The wave vector $k_{\text{phot}}$ of the photon is negligible on the scale of $k_e$. Since energy and momentum must both be conserved in this elementary excitation:

$$\hbar \nu = E_c - E_v \quad \text{and} \quad k_{\text{phot}} = (k_e)_c - (k_e)_v \approx 0$$

where $c$ and $v$ refer to the conduction and valence bands.
Absorption at an indirect energy gap in a perfect crystal involves a direct transition to a virtual energy state and interaction with a quantum of lattice vibration (phonon), having energy $\hbar \omega$ and wave vector $k_{\text{phon}}$, to scatter the electron between this virtual energy state and the real states at the band extremum [52]. At the absorption threshold, considering low temperatures when only one phonon-emission process occurs:

$$\hbar \nu = E_c - E_v + \hbar \omega \quad \text{and} \quad k_{\text{phon}} = (k_e)^c - (k_e)^v$$

Absorption and emission processes between a pair of electronic states are related by a detailed balance. The recombination rate constant is proportional to the absorption coefficient. The magnitude and form of the absorption coefficient depends on the nature of the transition [53].

ii ) Heavily doped crystals: In a direct gap crystal the initial and final states are no longer subject to the momentum selection rule, since momentum can be conserved through ionized impurity scattering.

d ) Intrinsic luminescence:

I ) Indirect gap compounds: intrinsic transitions have not been identified in the low-temperature luminescence of the indirect gap III-V compounds. They may make a small contribution to the room temperature luminescence recorded from some GaP diodes with exceptionally high efficiency for near band-gap transitions [53]. This is evidence of the imperfect state of these materials compared with specially purified crystals.
of the group IV elements. Intrinsic luminescence has been detected from all of the indirect gap semiconductors formed from group IV elements [53].

II ) **Direct gap compounds**: the evidence for intrinsic luminescence comes from the spectra of purified single-crystal material. The intrinsic components are weak compared with residual impurity induced bands at low temperatures. The intrinsic transitions become prominent at higher temperatures because of thermal dissociation of carriers from the impurity centers responsible for the lower-energy bands (donor-acceptor pair bands).

e ) **Extrinsic luminescence in indirect gap compounds**:

I ) **Bound Exciton transitions at neutral donors and acceptors**

   i) **Radiative recombinations**: as discovered in silicon, no-phonon indirect recombinations of excitons bound to impurity centers are possible since momentum can be conserved through coupling to the impurity. The no-phonon transition strong line observed in absorption spectra shows the Zeeman pattern for recombinations of an exciton at a neutral donor center [54]. The position of low energy lines below the no-phonon line varies according to the differences in the donor ionization energies. This low energy spectrum is the two-electron transition in which the donor center is either left in the excited bound state or the donor electron is ejected into the conduction band by the decay of the bound excitation. The energy of the emitted radiation is therefore less than the energy of the bound...
exciton (given by the position of no-phonon resonance line) by the excitation energy of the donor electron.

ii) **Non-radiative (Auger) recombinations**: the lifetimes observed for the bound exciton transition are about 500 times shorter than the value calculated from the absorption cross section using a detailed balance. It is believed that the decay rate is dominated by Auger recombinations in which all of the exciton transition energy appears as kinetic energy of the electron which is ejected deep into the conduction band.

III) **Bound Exciton recombinations at isoelectronic impurities**:

Zeeman analysis shows that the transition has the character of an exciton bound to an uncharged point defect in an absorption-emission line close to the energy gap of the compound.

It has been shown in the low-temperature photoluminescence spectra of GaP that the emission spectra arise from excitons bound at nitrogen impurities, which are isoelectronic substituents for phosphors [54]. Nitrogen has a relatively exposed nuclear charge compared with phosphorus, and the nitrogen impurity is believed to introduce a narrow potential well to which an electron can be bound by a short-range non-coulomb potential. The resulting negatively-charged center can then bind a hole to form the localized exciton; i.e., the center acts as an isoelectronic acceptor [55].
III) Donor - Acceptor pair recombination

The ionized donors and acceptors in a compensated crystal have large capture cross sections for excess electrons and holes [56]. At low temperatures, equilibrium can be restored only by an inter-impurity recombination resulting from a wavefunction overlap between the electron or hole on each center and the holes or electrons on the surrounding centers of opposite type. The resulting transition energy is very large compared with the phonon energy for typical shallow donor and acceptor centers in a wide band gap semiconductor, and the radiative transition probability is therefore dominant [53].

f) Extrinsic luminescence in direct gap compounds:

1) Free-to-Bound vs Donor-Acceptor pair recombinations:

Impurity-induced bands close to the energy gap of direct III-V compound semiconductors, prominent at low temperatures, are often attributed to the recombination of free carriers at neutral impurity centers. The observed line shape for these transitions is similar to that for intrinsic direct recombinations.

It is difficult to decide solely from the spectral position of the prominent luminescence band, whether the transitions are free-to-bound or whether the electrons are trapped on shallow donors before luminescence occurs. Gross et.al. have observed a deeper luminescence band which shifts with
increasing excitation intensity. This band is attributed to pair recombinations involving a deep donor. The magnitude of the observed shift rate with excitation intensity suggests a possibility that the effect is due to band-filling involving the recombination of free electrons in a donor impurity band at neutral acceptor centers.

II ) Recombinations at multivalent centers: A number of substitutional impurities in the III - V compounds form multivalent carrier traps, similar to the well-known behavior of the transition and noble metals in silicon and germanium. In the photoluminescence spectrum, the position of the emission band agrees roughly with the ionization energy, provided that the line width is mainly attributed to phonon interactions.

g ) Exciton emission

i ) Free excitons: The free exciton is an excited state in a crystalline solid, where an electron and a hole orbit each other at distances large compared with atomic dimensions. The observation of free exciton edge emission is observable at temperatures well above liquid helium temperatures, where the exciton is usually part of a bound complex. The ionization energy of the bound complex which is needed to give a free exciton is generally much smaller than the ionization of the free exciton, hence the observation of free exciton emission at intermediate temperatures.

ii ) Bound excitons: Excitons have a tendency to form bound exciton
complexes with natural defects which are a common feature in crystals of the II - VI compounds. The bound exciton complexes are created by the optical excitation of the crystals. The emission spectra which result from the disintegration of these bound exciton complexes occur on the long wavelength side of the free exciton emission spectra.

The different types of bound exciton complexes have been analysed from the magneto-optical behaviour of the emission spectra (Zeeman effect). The characterization of the three observed bound exciton conditions associated with the top-most valence band is:

i) an exciton bound to a neutral acceptor exhibits emission that splits into a doublet when the magnetic field $H$ is perpendicular to the c-axis of the crystal. The line splitting depends linearly on the magnetic field which suggests a single unpaired electronic charge. The intensity ratio of the doublets is unaffected by temperature variation for the ground state.

ii) an exciton bound to a neutral donor shows a linear dependence of the emission peak energy in the magnetic field. Temperature dependence of the emission intensities of the doublet confirms that an exciton is bound to a neutral donor.

iii) an exciton bound to an ionized donor has been observed in the absorption spectrum. The zero field splitting arises from an exchange interaction of an unpaired electron and an unpaired hole in the upper state and characterizes an exciton bound to an ionized defect. Emission
intensities of the doublet are independent of temperature and indicate a single ground state (ionized donor or acceptor). The small binding energy of the exciton to the ionized defect distinguishes the ionized donor from the ionized acceptor defect.

**h) Shaffer and Williams theory**

In semiconductors the movement of charge is possible, whereby the energy of recombination of an excited donor-acceptor pair is transferred to the luminescing atom. One situation is where the excited donor-acceptor pair transfers its energy to a distant point luminescing atom and the other situation occurs when the luminescing atom is intimately involved as either the donor or acceptor of the donor-acceptor pair so that the energy of the electron-hole recombination is transferred to the core states of one of the centers.

---

Fig. 12. Shaffer Williams recombination model
Luminescence in II - VI compounds

The rare earth ions in II - VI semiconductor lattices form an interesting system to study because of the energy transport and transfer mechanisms which come into play. The host lattice plays an important role in the excitation of the rare earth luminescence. Since we are dealing with semiconductors, energy transport can take place via hole and electron motion. The lattice can give up large quanta of energy in electron-hole recombination, and these phenomena determine the emission properties of the system.

Phosphors consisting of II - VI compounds containing rare earth activators have a discrete ion as the principal source of luminescence emission, with the $f - f$ transitions yielding narrow emission bands or lines. Interest in the optical spectroscopy of rare earth doped II-VI compounds centers in physical discussions of such impurity systems (radiative and non-radiative transitions) because the dopant is incorporated on several different sites [2,3]. This leads to optical spectra generally consisting of an enormous number of lines, whose assignment to the various types of sites is rather difficult [4].

The coexistence of many types of sites can be related:

i ) to the fact that triply-positive rare earth ions are involved, which tend to associate with negatively-charged defects.
ii) to the occurrence of both substitutional and interstitial incorporation.

The existing literature on f - f transitions and narrow emission lines is very confusing, since the results obtained are often contradictory and appear to involve the synthesis procedures utilized by the individual investigators.

The energy levels of trivalent rare earths can generally be obtained in considerable detail from the absorption and emission spectra of the ions embedded in host lattice [14].

Because the spectrum of praseodymium, Pr$^{3+}$, is relatively simple compared to other rare earth spectra, it is one of the most often studied rare earth ion spectra in different host lattices and one of the best understood [15-17]. The luminescence emission of Pr$^{3+}$ doping is bright and there is no difficulty in observing appreciable luminescence.

**Luminescence in Rare-earth-doped Zinc sulphide crystals**

The luminescence emission spectra of II- VI compounds containing rare earth ions, particularly of the zinc sulfide family, show three main characteristics:

1. broad band emission
2. sharp line f-f rare earth emission and
3. various mixture of broad band and sharp lines.
In Zinc sulphide (ZnS) -type crystals, the incorporation of activator of group I elements (Cu, Ag, Au) with the nature of acceptor and/or coactivator of group VII elements (Cl, Br, fluorides) or group III elements (Al, Ga, In) with the nature of donor, creates various kinds of luminescence centers. In some cases, native lattice defects also participate in the formation of the centers. The atomic structure of these centers as well as the nature of the electronic transitions responsible for these luminescences have been studied for many years by several investigators.

With regard to the luminescence transition in ZnS-type crystals, there are three well-known models:

1. Schon - Klasens model which states that, luminescence is caused by an electron transition from the conduction band to a localized level located above the top of the filled band.

2. Lambe - Klick model attributes the luminescence to a hole transition from the filled band to a localized level located below the bottom of the conduction band.
3. Prener - Williams model assumes that an electron transition from the excited or ground state of donor to the ground state of acceptor gives rise to the luminescence.

There have been a number of discussions and disputes about the model of the luminescence transition in ZnS. So far as the luminescence caused by the incorporation of Ib activator and/or VIIb or IIIb coactivator are concerned, it is considered that the types of luminescence transition suggested in the mentioned three models include all of the types which one can assume to be responsible for the luminescence observed. Then the problem to be solved is reduced to deciding which type of transition gives rise to the luminescence in question.

It is well known that trivalent rare earth ions in ZnS phosphors show emission spectra with a narrow line structure, characteristic of the transitions in the $4f^n$ electron configurations \[3,5\].

The subject of photoluminescence (PL) in solids has been widely studied for the purpose of understanding impurity levels, energy transfer mechanisms, the effect of crystal field on transitions, as well as electroluminescence (EL) device mechanisms. Rare earth ions have been introduced into a number of host lattices, since it is possible to obtain emission lines corresponding to the orbital transitions of these ions. Y.S.Chen et.al [6] have reported the room-temperature PL results of a new material system in which the rare earth fluoride molecules are incorporated within a host lattice, especially thin films of ZnS:TbF$_3$. Their
main purpose was to study the energy transfer mechanisms together with the efficiencies of such processes; they also studied the emission and excitation spectra as a function of the fluoride concentration. The molecular center, TbF$_3$ in ZnS can be pumped directly and efficiently at levels below the energy gap of ZnS. This is true presumably for any host lattice and any rare earth fluoride dopant. The conversion efficiency, which is enhanced greatly in a dilute system, can be close to 100%. The same centers can be excited via energy transfer from electron-hole recombination if pumped at energies above the forbidden gap of the host lattice, although the efficiency for this process is very poor.

Anderson [7] has investigated the emission properties of the terbium-doped ZnS phosphors. From the infrared-stimulation spectrum of ZnS:Tb at 77 K, he interprets the sharp peak at 1.02 eV to be a deep-hole trap (possibly copper) and trivalent Tb$^{3+}$ ion as a donor in ZnS substitutionally replacing Zn. He has proposed a model of the recombination process. Based on Piper-Williams model, he shows that the inner shell levels of the rare earth be somewhere below the valence band. The donor level associated with Tb$^{3+}$ is due to the valence electrons, 6s$^2$5d$^1$, not the inner shell 4f$^8$ electrons which are shielded from the lattice. He explains the recombination kinetics as, after intense UV excitation, the hole traps will be saturated and electrons will be loosely attached to the donors. At 77 K the donors are not ionized thermally, and the process of recombination is possible between the donor Tb$^{3+}$ level and the trap, modelled as shown (fig.13). Based on the model, the observed effectiveness of Tb$^{3+}$ as a recombination center, and some of the known
properties of ZnS, he estimated the relative probability of a direct radiative recombination compared to a resonant energy transfer process at the recombination center. Using a hydrogenic model of the rare earth donor, he found the electron Bohr orbit about the Tb$^{3+}$ ion to be around 0.25 nm, i.e., the electron moving over to the four nearest-neighbor S$^{2-}$ ions. In an ionic model of the bonding in ZnS, the donor electron can recombine when a hole moves onto to one of these four nearest-neighbor sulfurs.

Fig. 13. Model of recombination process by Anderson
A necessary condition for resonance energy transfer is an overlap between the emission spectrum of hole-electron recombination and the absorption spectrum of the rare-earth ion. The mechanism being, when one $4f^8$ energy level is nearly resonant with the recombination transition, energy transfer takes place between the rare-earth ion and the transition by the resonance due to the electric dipole-quadrupole interaction. The excited $4f^8$ can relax to a lower energy rapidly by cascading through a number of closely spaced levels to the metastable level from which it will then radiate giving the characteristic rare-earth emissions.

Nakazawa and Shionoya [47] conclude from their investigation on Tb$^{3+}$ that the energy transfer taking place in the optical region between trivalent rare earth ions in inorganic solids is caused by the resonance due to the electric dipole-quadrupole interaction.

Langer and Weichert [67] report that the relative location of electronic levels of some deep luminescence centers, e.g., transition or rare earth centers, with respect to the host lattice were accessible to experimental investigations in the past only in those cases where charge transfer was observable. They measured the kinetic energy distribution of electrons emitted from samples due to X-ray excitation; and thus determined the energy location of a number of atomic levels of Zn, S and Mn in the samples of ZnS, MnS and ZnS:Mn (3%). Experimental evidence indicated that the Mn 3d level lies approximately 3 eV below the top of the ZnS valence band.
Kingsley et al. [2] found that the luminescence of rare earth ions in ZnS is sensitized by addition of Cu or Ag ions and the sensitization is due to the addition to the non-radiative energy transfer from Cu or Ag luminescence centers to rare earth centers.

Shionoya [8,9] experimentally found that the excitation of rare earth ions is caused by energy transfer from self-activated centers.

Shosaku [10] explains the mechanism of the sensitization effect based on the transient behavior of emission of rare earth in ZnS added with Cu, Er, Na and experimentally observed that:

i) rare earth emission in ZnS is caused by the non-radiative energy transfer from green-Cu centers acting as the energy donors.

ii) the Cu ions act as the sensitizers of the rare earth luminescence.

iii) alkali ions act as charge compensators for trivalent rare earth ions.

The correlation between the kind of luminescence center created and the samples and amount of activator and/or coactivator which are incorporated in ZnS type crystals have been the subject of many research articles. Van Gool [11] has investigated this problem systematically and thoroughly, summarized the results, and presented a figure which expresses this correlation.

Shionoya and Fujiwara [12] undertook investigation on the nature of the luminescence transitions in ZnS, temperature dependence of emission, shift
of emission peak, and the change of the half-width of spectrum with temperature. The results were analyzed from theoretical viewpoint, with the use of the theory on the configurational coordinate model of localized center. From experimental analysis the shift of the emission peak towards higher energies occurs with an increase in temperature for the SA, 'R-Cu' and 'R-Cu, In' luminescences, while it is towards lower energies for the 'B-Cu' and 'G-Cu' luminescences. The half-widths of the SA, 'R-Cu' and 'R-Cu, In' luminescences increase markedly with increasing temperature in a range above liquid nitrogen temperature, and change almost linearly versus the square root of temperature, while the half-widths of the 'G-Cu' and 'B-Cu' luminescences increase only slightly with increasing temperature.

Larach [13] found that the luminescence of rare earth ions in ZnS is sensitized by the addition of alkali metal ions, and proposed that alkali metals act as charge compensators. Addition of alkali metal ions to sulphide phosphors containing rare earths tend to decrease the band emission while intensifying the sharp line f - f transitions of rare earth ions. Also very selective intensification of certain f - f transitions of the rare earth ions can occur.

Szczurek and Lozykowski [66] found the lines characteristic of the 4f-4f transition of rare earth tripositive ions in the electroluminescence of ZnSe thin films. They found very sharp emission lines for ZnSe:SmF$_3$ and ZnSe:ErF$_3$ well resolved even at room temperature. The emission lines of all rare earth (RE$^{3+}$) ions increase with temperature, probably because at low
temperatures the non-radiative transitions are less competitive. Their ZnSe:ErF$_3$ thin film device displayed strong electroluminescence, where not active in photoluminescence excited by mercury arc lamp or Nitrogen laser at room temperature and 77 K, that means the energy transfer from excited ZnSe lattice to the RE$^{3+}$ ions is taking place in monocrystalline ZnSe:RE$^{3+}$. The reason for this is the differences in configurations of electroluminescent RE$^{3+}$ sites in ZnSe thin films and photoluminescent ones in monocrystalline ZnSe. The low crystallinity of the ZnSe thin films may cause the energy transfer from the lattice to the luminescent centers to be ineffective.

In recent studies on the luminescence of trivalent rare earth ions in inorganic solids, it was found that the luminescence intensities of various rare earth ions are sometimes enhanced or quenched by the coexistence of other kinds of rare earth ions [40-42]. It has been concluded that these phenomena take place as a result of the non-radiative transfer of excitation energy between rare earth ions.

When an ion in a crystal lattice is excited, it may lose its excitation energy in several ways. It may make a radiative transition to a lower state. The transition probability for this is determined by the electronic structure of the ion and by the magnitude and symmetry of the crystalline field in which the ion finds itself. The ion can also transfer the energy directly to the crystal lattice. If the decay is exponential, it can be expressed by a single constant, the mean fluorescence lifetime.
Once energy has been transferred from the host lattice to the 4f\textsuperscript{n} electron configuration, the luminescence generally decays exponentially. This is characteristic of rare earth ions [48]. The decay time constant may be the radiative lifetime of the metastable level or may be shortened due to non-radiative decay induced by interaction with the lattice [50]. However, non-exponential decays have been observed [49].

The lattice emission decays very rapidly and is easily distinguished from the slow rare-earth emission decay. Trivalent rare-earth ions occupy several different sites in ZnS and CdS [50] presumably corresponding to near-neighbor association with various charge-compensating centers (acceptor defects). The differing crystal fields will cause different decay rates.

Two widely-differing time constants may be observed for different levels of a single rare-earth ion or the time constant associated with energy transfer from lattice to the rare earth ion differs from the subsequent transitions within the 4f\textsuperscript{n} configuration. There is no apparent correlation of metastable level lifetime with energy interval to the next lowest-level of the 4f\textsuperscript{n} configuration. Lifetimes of a given rare-earth level in ZnS lattice, when compared with the long lifetime observed in few cases argue strongly for the absence of non-radiative decay modes, once the energy has been transferred to the rare earth ion. The brightness of the short lifetime materials with ZnS indicate efficient radiative recombination [61].
**Luminescence decay curve**

A luminescence-decay curve is obtained by varying the delay between the excitation flash and the detector activation pulse and by plotting the output counts on a log scale. In most cases this results in a straight line, the slope of which determines the life time $\tau$ in the expression $I = I_0 \exp(-t/\tau)$.

When no straight line results, it is an indication of multi-exponential decay, and the results can be represented by the superposition of two or more exponential decays with different lifetimes.

Barasch and Dieke [48], from experimental observations, report that the decay time decreases with increasing temperature, which can be explained by interaction with the vibrating lattice.

In general, one can write the observed relaxation time $\tau$ as

$$1/\tau = (1/\tau_0) + (1/\tau_1)$$

where $\tau_0$ is the radiative lifetime and $\tau_1$ is the lifetime due to radiationless transitions. In principle, $\tau_0$ can be determined from absorption measurements together with the relative intensities of fluorescent lines. If $\tau_1 \ll \tau_0$, the observed relaxation time is almost entirely due to the ion-lattice interaction.

The relaxation time for radiationless transitions depends on the ion and the lattice. The energy transfer depends on the phonon spectrum of the
lattice. When the excitation can be used to excite one phonon, the transfer is very probable and the relaxation time is shorter. This is the case for the transfer between the different Stark components of one electronic level and has the result that, at low temperatures when the thermal equilibrium precludes repopulation of the higher Stark components, fluorescence always takes place only from the lowest Stark level.

Theories of the energy transfer mechanism [72] agree that multiphonon processes become increasingly improbable as the number of phonons that has to be excited increases.

A luminescence decay curve with corresponding log plot [62].
**Excited state lifetime measurements**

The measurement of excited state lifetimes has become a pervasive and invaluable tool in the realms of experimental and theoretical spectroscopy, solid state physics, energy transfer and other fields of science. It is used to make transition state assignments, to obtain energy-transfer parameters and to calculate laser thresholds for luminescent substances [62].

There is a great wealth of information in the literature that is applicable to lifetime measurements.

An elegant mathematical approach will be introduced in this chapter.

We begin by describing the more common possible states of a sample following excitation.

\[
D + h\nu \rightarrow ^*D
\]

\[
^*D \rightarrow _r^k D + h\nu
\]

\[
^*D \rightarrow _q^k D + \Delta
\]

\[
^*D \rightarrow _p^k \text{products}
\]

\[
^*D + Q \rightarrow _{2a}^k D + Q + \Delta
\]

\[
\rightarrow _{2b}^k D^\pm + Q^\pm
\]

\[
\rightarrow _{2c}^k D + ^*Q
\]

and \(k_2 = k_{2a} + k_{2b} + k_{2c}\)

where \(D\) and \(^*D\) are the ground and excited-state forms of the sample under study. \(Q\) is a deactivator or quencher which can, on close interaction
with the excited donor \(^\ast\)D, deactivate by a catalytic step, an excited state electron transfer, or an energy transfer. \(D^\pm\) and \(Q^\pm\) are the oxidized and reduced forms of the donor and quencher respectively. In the above rate equation, for each process- 'I' is the rate of excited state generation and \(k_r\) is the radiative rate constant for emission of a photon from the excited state, \(k_q\) is the rate constant for intramolecular excited state deactivation; \(k_p\) is the rate constant for direct excited state decomposition; and \(k_2\) is the bimolecular rate constant for all bimolecular excited state deactivations.

Within the model of the above equation, the rate of production of excited state \(^\ast\)D, \(d[^\ast\)D]/dt, is given by

\[
d[^\ast\)D]/dt = I - k[^\ast\)D]
\]

\[
k = k_r + k_q + k_p + k_2[Q]
\]

where \(k\) has the units of a first-order rate constant. Both \(I\) and \(Q\) may vary during the course of the experiment. In general, during an excited state measurement, \([Q]\) remains virtually constant so that \(k\) can be treated as a constant. Under conditions where the bimolecular term is nonzero but essentially constant, the system is referred to as pseudo-first order. In all subsequent discussions, \(k\) is assumed to be time independent.

The majority of lifetime measurements involve first-order or pseudo first-order kinetic processes. A first-order system is one that, in the absence of external perturbations, satisfies

\[
d[^\ast\)D] / dt = -k[^\ast\)D]
\]

the equation for an excited state.
If no \(^*D\) is added to the system during the decay, the time dependence of \([*D]\) can be written as

\[
\ln([*D]) = \ln([*D]_0) - kt
\]

\[
\log([*D]) = \log([*D]_0) - 2.303kt
\]

or

\[
[*D] = [*D]_0 \exp(-kt)
\]

where \([*D]_0\) is the initial \([*D]\).

The above system is approximated by a sample excited by a pulsed light whose width is shorter than the excited-state lifetime.

This is the standard method of analyzing kinetic data. A \(\ln([*D])\)-versus-time plot is linear with a slope of \(-k\) and an intercept of \(\ln([*D]_0)\).

A common kinetic problem arises when several transitions with different lifetimes occur simultaneously and independently. Such transitions from different metastable levels exhibit very complex multicomponent kinetics.

For a delta function (pulse excitation), the detector response is

\[
D(t) = \sum_{i=1}^{N} K_i \exp(-t/\tau_i)
\]

and \(\tau_i = 1/k_i\)

where \(N\) is the number of emitting components.

For the \(i\)th component, \(\tau_i\) is the lifetime and \(K_i\) is the pre-exponential factor contributing to the signal at zero time. It is assumed that the
emission spectrum of each component is independent of time following the excitation.

In general, the log plots of \( D(t) \) versus \( t \) are concave upwards for a multicomponent decay.

If only two components are present and their lifetimes differ significantly, it is possible to obtain the \( \tau_i \) and \( K_i \) by the method of component stripping [63]. In the component stripping technique, let the longlived component be represented as component 1. A \( \ln[D(t)] \)-versus-\( t \) plot is made. At very long times this curve will be linear with a slope of \(-1/\tau_1\) and an intercept of \( \ln[K_1] \). Using this \( K_1 \) and \( \tau_1 \), the contribution of the slow component is subtracted from \( D(t) \) to yield

\[
D(t)' = D(t) - K_1 \exp(-t/\tau_1)
\]

where \( D(t)' \) approximates the pure decay curve for the short-lived component which is then reduced just as any normal single-exponential decay curve.

The component-stripping method works best if the \( \tau \)'s are well separated and the disparity between the \( K \)'s is not large.

The problem of extracting kinetic information \( D(t) \), when the excitation pulse duration \( E(t) \) is comparable to the sample's impulse response \( i(t) \), is solved by 'deconvolution'. Once obtained, \( i(t) \) can be fit to any kinetic model using the least squares method.
A demonstration of component stripping technique [62].

Most deconvolution methods strive to obtain the best kinetic parameters in an assumed $i(t)$ that is a single-exponential or a sum of two or three exponentials.

A simple approach to the deconvolution of single exponentials is to take the measured $E(t)$ and compute a series of $D(t)$ curves for different assumed $\tau$'s. Then, by some form of curve matching, the observed decay is compared to these synthetic curves. The $\tau$ giving the closest visual match is assumed to be the correct lifetime.

The matching approach is rapid and simple. It lacks high accuracy and the ability to model more complex kinetics.
A popular deconvolution technique involves the moments methods which avoid some of the computational complexities of the non-linear least squares.

The moments methods take into account the shapes of $E(t)$ and $D(t)$ from their statistical moments:

$$\mu_k = \int_0^\infty t^k D(t) \, dt$$
$$m_k = \int_0^\infty t^k E(t) \, dt$$

where $\mu_k$ and $m_k$ are the $k^{th}$ moments of the decay and excitation respectively.

The simplest moments method for evaluating $\tau$ is to evaluate the center of gravity of $E(t)$ and $D(t)$ from,

$$C_F = \frac{m_1}{m_0}$$
$$C_D = \frac{\mu_1}{\mu_0}$$

where $C_F$ and $C_D$ are the centers of gravity of $E(t)$ and $D(t)$ respectively. Then,

$$\tau = C_D - C_F$$

The longer $\tau$, the more $D(t)$ is shifted to longer times and the later the occurrence of the center of gravity. Given the properties of the center of gravity, it is not necessary to carry out integration. The centers of gravity are found in the following way:

Each curve is cut out and suspended by a string from an outside point. The suspending string points to the center of gravity. By repeating this
process at two or more attachment points, the centers of gravity can be obtained by triangulation. \(C_D\) and \(C_F\) can be read off and used to determine \(\tau\).

If the sample impulse response is a sum of exponentials, rather than a single exponential, the methods of moments can be generalized. For an impulse response given by

\[i(t) = \sum_{i=1}^{N} K_i \exp\left(-t/\tau_i\right)\]

we can define \(G_s\) by \(G_s = \sum_{i=1}^{N} K_i \tau_i^s\)

then, it can then shown that [77],

\[
\begin{align*}
\mu_0 &= G_1 m_0, \quad \mu_1 = G_1 m_1 + G_2 m_0 \\
\mu_2 / 2! &= G_1 (m_2 / 2!) + G_2 m_1 + G_3 m_0 \\
&\vdots \\
\mu_k / k! &= \sum_{s=1}^{k} \left( m_{k+1-s} / (k+1-s)! \right) G_s 
\end{align*}
\]

This is a linear set of equations in the \(G\)'s. If there are \(N\) exponentials, then with \(2N\) equations, one can solve for \(G_1, G_2, \ldots, G_{2N}\).

It can then be shown that the desired \(\tau_1, \tau_2, \ldots, \tau_N\) lifetimes are the roots of the polynomial equation
Solution of this polynomial equation yields the N values of \( \tau \). These \( \tau \)'s are substituted into the following equations:

\[
1 \quad \tau \quad \tau^2 \quad \ldots \quad \tau^N \\
G_1 \quad G_2 \quad G_3 \quad \ldots \quad G_{N+1} \\
\vdots \\
G_N \quad G_{N+1} \quad G_{N+2} \quad \ldots \quad G_{2N}
\]

where the summations run from 1 to N. Solution of these N linear equations yields the value of \( K_i \).
IV. EXPERIMENTAL RESULTS:

This investigation was undertaken to elucidate the nature of luminescence transitions in ZnS-type crystals, especially those doped with rare earth impurities and thereby decide the type of transition responsible for typical luminescence. With this purpose in mind, the emission spectra from ZnS:Pr and ZnS:Nd samples were measured in a temperature range down to liquid helium temperature, paying attention to the shift of emission peak and change of the half-width of emission lines with temperature.

The photoluminescence study on crystals contained 0.00346 and 0.01867 mol% Pr$^{3+}$ in ZnS respectively; 0.00338, 0.01806, 0.018236 and 0.08848 mol% Nd$^{3+}$ in ZnS respectively and also a mixed-doped crystal containing 0.01106 mol% Pr and 0.00338 mol% Nd. The crystals had the dimension of about 10 x 2 mm and were provided by Alaya [64].

Emission and excitation spectra measurements were accomplished by exciting the samples with a light beam from an Argon ion Laser (Laser Ionics model 553A) filtered through a laser filter monochromator (Photo Physics). The luminescence spectra were recorded by a 1 M monochromator (Jarrell-Ash 490 U) and detected by a cooled (250 K) (Pacific Instruments model 3461) photomultiplier tube (Hamamatsu R928). The signals from the detector were preamplified (Ortec 474) and passed through the single-photon-counting system (fig.7). The spectra were then accumulated and displayed in the Multichannel Analyzer (Ortec 7100). The Multichannel analyser outputs the spectral data to an
IBM-PC for normalization, instrument response correction and for plotting (HP 7470A) the spectrum.

For low temperature measurements, a liquid helium cryostat (Oxford Instruments model MD3) was used. Temperature control was accomplished by a (Oxford Instruments model 3120) temperature controller with a rhodium iron resistance wire sensor. The temperature control was within 10% (1.2 K).

Absorption measurements were made at room temperature using HP 8451 Diode array spectrophotometer.

a ) Measurement of spectral response:

Monochromator was used for scanning the spectral region of interest, synchronously with memory channel sweep of the MCA, in the MCS mode. The output of the photomultiplier followed by timing filter amplifier (Ortec 474) and Constant-Fraction Discriminator Ortec 583) was directly connected to the MCA in order to accumulate the spectrum.

During most of the measurements, monochromator slits were set to 100 μm and the scissor-tail shutter adjusted to ensure that the maximum photon count was less than one million counts as monitored through a Quantum Photometer (PRA 1140A) as well as a digital counter.
When a stepping motor was used for scanning, the monochromator drive gear was set to 1250 °A/min and a computer program, 'MT-CNTL', to initiate stepping motor scanning was used. The counting time per channel in the multichannel analyzer, for the MCS mode, was set to 200 msecs.

Emission spectra were recorded by both direct and ratiometric methods. The measurement technique has been already described.

b) Decay measurements:

The monochromator was set for one of the emission peaks and aligned to optimize the detection. Entrance slits were reduced or deliberately defocussed so that the detection was in a single-photon-counting mode (photon count <10% of excitation repetition rate, that means for 25 KHz frequency the count was reduced to 2580-3050 counts). The same frequency generator was used to produce a start signal at the instant of source excitation. This start signal is used to trigger the voltage ramp of a time-to-amplitude converter (Ortec 457). The Photomultiplier output, at the detection of the first photon, is used as the stop signal for the TAC. The TAC output pulses are proportional to the elapsed time between start (source pulse) and stop (photon emission) signals. These pulses are accumulated in the multichannel analyzer and are sorted according to their voltage (hence, time) and stored as counts.

The decay data were recorded in the pulse height analysis (PHA) mode in MCA. Depending upon the emission intensity, i.e., the number of counts in
each channel of the MCA, the counting/recording time was in the range of 200 - 400 secs.

Whenever needed during lifetime measurements, ORIEL color glass filters (long pass) were used. These filters have 50 % transmission characteristic and block shorter wavelengths.

Throughout the interpretation, observed data was compared with the free ion spectra [31,32] and used to identify the energy levels and determine the transitions.

A set of computer programs were developed, and used to arrange all of the 1024 data points in a linear array for reconstructing the spectrum and for further plotting, before a meaningful data/spectral analysis and interpretation was made.

In this chapter, we have included the observed absorption and emission spectra, decay spectra and the transition assignments made as a result of our interpretation.
We excited the sample by each line from argon-ion laser, directly the rare earth ions, the level to which the excitation was done for both ZnS:Pr and ZnS:Nd are tabulated below:

<table>
<thead>
<tr>
<th>Wavelength ((\lambda))</th>
<th>level in ZnS:Pr</th>
<th>level in ZnS:Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>457.9 nm</td>
<td>(3p_1, 3p_2)</td>
<td>(4G_{11/2}, 2p_{1/2})</td>
</tr>
<tr>
<td>476.5 nm</td>
<td>(3p_1)</td>
<td>(4G_{9/2}, 2D_{3/2})</td>
</tr>
<tr>
<td>488.0 nm</td>
<td>(3p_0)</td>
<td>(4G_{9/2})</td>
</tr>
<tr>
<td>496.5 nm</td>
<td>(1D_{2}, 3p_0)</td>
<td>(2G_{9/2})</td>
</tr>
<tr>
<td>514.5 nm</td>
<td>(1D_{2}, 3p_0)</td>
<td>(2G_{9/2})</td>
</tr>
</tbody>
</table>

Unlike Anderson’s model of recombination and resonance energy transfer after intense UV excitation, our investigation and interpretation is simple and direct rare earth ion excitation below ZnS band gap (3.7 eV).
1. ZnS:Nd$^{3+}$

The spectra of ZnS:Nd$^{3+}$ at room temperature for the excitation wavelength 476.5 nm is presented here. The transitions involved are those occurring from the excited states $^4G_{7/2}$, $^2G_{7/2}$, $^4G_{5/2}$ and $^4F_{3/2}$ to the ground state $^4I_{9/2}$ as well as transition between the excited states $^2G_{9/2}$, $^4F_{9/2}$ and $^2S_{3/2}$ to $^4I_{11/2}$. The line assignments here and further in this work are those after Carlson and Dieke [70] unless otherwise stated.

The groups of lines resolved and their assigned transitions are listed in Table I and the absorption spectral lines and the transition assignments in Table II.
Table I

Spectral position of the observed lines in the photoluminescence spectrum of ZnS : Nd$^{3+}$

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed line (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4G_{7/2} \rightarrow ^4I_{9/2}$</td>
<td>530.63</td>
</tr>
<tr>
<td>$^2G_{9/2} \rightarrow ^4I_{11/2}$</td>
<td>550.18</td>
</tr>
<tr>
<td>$^2G_{7/2} \rightarrow ^4I_{9/2}$</td>
<td>574.37</td>
</tr>
<tr>
<td>$^4G_{5/2} \rightarrow ^4I_{9/2}$</td>
<td>605.04</td>
</tr>
<tr>
<td>$^4F_{9/2} \rightarrow ^4I_{11/2}$</td>
<td>788.53</td>
</tr>
<tr>
<td>$^2H_{9/2}, ^4F_{5/2} \rightarrow ^4I_{9/2}$</td>
<td>827.01</td>
</tr>
<tr>
<td>$^4F_{3/2} \rightarrow ^4I_{9/2}$</td>
<td>860.47</td>
</tr>
<tr>
<td>$^4G_{5/2}, ^2G_{7/2} \rightarrow ^4I_{15/2}$</td>
<td>905.65</td>
</tr>
<tr>
<td>$^2S_{3/2} \rightarrow ^4I_{13/2}, ^2H_{11/2} \rightarrow ^4I_{15/2}$</td>
<td>1030.58</td>
</tr>
</tbody>
</table>
Absorption spectrum of ZnS:Nd$^{3+}$ at room temperature

Rare earth concentration : 0.5 wt. % Nd
<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>0.26387</td>
</tr>
<tr>
<td>474</td>
<td>0.22421</td>
</tr>
<tr>
<td>514</td>
<td>0.46889</td>
</tr>
<tr>
<td>526</td>
<td>0.80684</td>
</tr>
<tr>
<td>584</td>
<td>2.24180</td>
</tr>
<tr>
<td>628</td>
<td>0.11575</td>
</tr>
<tr>
<td>656</td>
<td>0.10681</td>
</tr>
<tr>
<td>682</td>
<td>0.17076</td>
</tr>
<tr>
<td>748</td>
<td>1.17356</td>
</tr>
<tr>
<td>804</td>
<td>1.64225</td>
</tr>
</tbody>
</table>

Absorption spectrum of ZnS:Nd$^{3+}$ at room temperature

Rare earth concentration: 2.7 wt. % Nd
Table II

Absorption spectra of ZnS:Nd$^{3+}$

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed line (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4I_{9/2}$ $\rightarrow$ $^2D_{3/2}$</td>
<td>474.00</td>
</tr>
<tr>
<td>$^4I_{9/2}$ $\rightarrow$ $^2G_{9/2}$</td>
<td>514.00</td>
</tr>
<tr>
<td>$^4I_{9/2}$ $\rightarrow$ $^4G_{7/2}$</td>
<td>526.00</td>
</tr>
<tr>
<td>$^4I_{9/2}$ $\rightarrow$ $^4G_{5/2}$</td>
<td>584.00</td>
</tr>
<tr>
<td>$^4I_{9/2}$ $\rightarrow$ $^4F_{9/2}$</td>
<td>682.00</td>
</tr>
<tr>
<td>$^4I_{9/2}$ $\rightarrow$ $^2S_{3/2}$, $^4F_{7/2}$</td>
<td>748.00</td>
</tr>
<tr>
<td>$^4I_{9/2}$ $\rightarrow$ $^4F_{5/2}$, $^2H_{9/2}$</td>
<td>804.00</td>
</tr>
</tbody>
</table>
2 ZnS : Pr$^{3+}$

The luminescence emission spectra of ZnS:Pr$^{3+}$ at room temperature, and for the excitation wavelength 476.5 nm is presented here. The transitions involved are those occurring from the excited states $^3P_1$, $^3P_0$ and $^1D_2$ to the ground state $^3H_4$ as well as transition between excited states $^3P_1 \rightarrow ^3H_5$, $^3P_0 \rightarrow ^3H_6$ and $^3P_0 \rightarrow ^3F_2$, $^3F_4$. The line assignments are based on the work after Esterowitz [31].

When the sample was cooled down, the lines became more sharp and more intense. The groups of lines observed and resolved are listed in Table III and Table IV.
Luminescence emission spectra of ZnS:Pr$^{3+}$.
Table III

Spectral position of the lines in the photoluminescence of ZnS:Pr$^{3+}$

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed line (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3P_0 \rightarrow ^3H_4$</td>
<td>494.61</td>
</tr>
<tr>
<td>$^3P_1 \rightarrow ^3H_5$</td>
<td>532.26</td>
</tr>
<tr>
<td>$^3P_0 \rightarrow ^3H_6$, $^1D_2 \rightarrow ^3H_4$</td>
<td>619.97</td>
</tr>
<tr>
<td>$^3P_0 \rightarrow ^3F_2$</td>
<td>651.34</td>
</tr>
<tr>
<td>$^3P_0 \rightarrow ^3F_4$</td>
<td>737.98</td>
</tr>
<tr>
<td>$^3P_0 \rightarrow ^1G_4$</td>
<td>906.57</td>
</tr>
<tr>
<td>$^1D_2 \rightarrow ^3F_3$</td>
<td>984.71</td>
</tr>
</tbody>
</table>
Wavelength Intensity
(nm)

448 1.20429
472 0.76234
486 0.86301
594 0.34097
656 0.11369
808 0.10335

Absorption spectrum of ZnS:Pr$^{3+}$ at room temperature

Rare earth concentration: 2.7 wt. % Pr
Table IV

Absorption spectra of ZnS:Pr$^{3+}$ at room temperature.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed line (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3H_4 \rightarrow ^3P_2$</td>
<td>448.00</td>
</tr>
<tr>
<td>$^3H_4 \rightarrow ^3P_1$</td>
<td>472.00</td>
</tr>
<tr>
<td>$^3H_4 \rightarrow ^3P_0$</td>
<td>486.00</td>
</tr>
<tr>
<td>$^3H_4 \rightarrow ^1D_2$, $^3H_6 \rightarrow ^3P_1$</td>
<td>594.00</td>
</tr>
<tr>
<td>$^3H_5 \rightarrow ^1D_2$</td>
<td>656.00</td>
</tr>
<tr>
<td>$^3H_6 \rightarrow ^1D_2$</td>
<td>808.00</td>
</tr>
</tbody>
</table>
The spectra of mixed-dopant crystal ZnS:Nd:Pr at room and liquid nitrogen temperatures for the excitation wavelength 476.5 nm are presented here. The transitions involved are those occurring from the excited states of $^2G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}$, $^4F_{9/2}$, and $^4F_{5/2}$ to the ground state $^4I_{9/2}$ as well as transitions between excited states $^4G_{7/2}$, $^2G_{7/2}$ to $^4I_{11/2}$ due to Nd$^{3+}$ ions. Also transitions from $^3P_1$, $^3P_0$, and $^1D_2$ to ground level $^3H_4$ as well as $^1D_2 \rightarrow ^3F_2$, $^3F_4$ and $^3P_0 \rightarrow ^1G_4$ transitions due to Pr$^{3+}$ ions.

The emission intensity of each transitions due to Pr$^{3+}$ ions are stronger than those due to Nd$^{3+}$ ions in the visible range.

The groups of lines resolved are listed in Table V and the absorption data are listed in Table VI.
Luminescence emission spectra of ZnS: Nd: Pr
Table V

Spectral position of the lines in the photoluminescence spectrum of ZnS:Nd:Pr

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed line (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3p_0 \rightarrow ^3H_4$</td>
<td>493.49</td>
</tr>
<tr>
<td>$^3p_1 \rightarrow ^3H_5$ : $^4G_{7/2} \rightarrow ^4I_{9/2}$</td>
<td>530.55</td>
</tr>
<tr>
<td>$^3p_1 \rightarrow ^3H_6$ : $^2G_{7/2} \rightarrow ^4I_{9/2}$</td>
<td>578.83</td>
</tr>
<tr>
<td>$^3p_0 \rightarrow ^3H_6$ : $^1D_2 \rightarrow ^3H_4$</td>
<td>616.75</td>
</tr>
<tr>
<td>$^3p_0 \rightarrow ^3F_2$</td>
<td>645.75</td>
</tr>
<tr>
<td>$^3p_0 \rightarrow ^3F_4$</td>
<td>730.53</td>
</tr>
<tr>
<td>$^4F_{9/2} \rightarrow ^4I_{11/2}$</td>
<td>788.85</td>
</tr>
<tr>
<td>$^2H_{9/2}$ : $^4F_{5/2} \rightarrow ^4I_{9/2}$ : $^1D_2 \rightarrow ^3H_6$</td>
<td>813.63</td>
</tr>
<tr>
<td>$^4G_{5/2}$ : $^2G_{7/2} \rightarrow ^4I_{15/2}$ : $^3P_0 \rightarrow ^1G_4$</td>
<td>906.92</td>
</tr>
<tr>
<td>$^2S_{3/2} \rightarrow ^4I_{13/2}$ : $^1D_2 \rightarrow ^3F_3$</td>
<td>1031.24</td>
</tr>
</tbody>
</table>
Wavelength | Intensity (nm)
---|---
448 | 1.02943
472 | 0.67964
486 | 0.73282
514 | 0.22259
526 | 0.32350
584 | 0.98367
624 | 0.10245
672 | 0.11678
684 | 0.10123
748 | 0.40889
804 | 0.57372

Absorption spectrum of ZnS:Nd\(^{3+}\) at room temperature

Rare earth concentration: 0.5 wt. % Nd
1.6 wt. % Pr
Table VI

Absorption spectra of ZnS:Nd:Pr

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed line (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\text{H}_4 \rightarrow ^3\text{P}_2$</td>
<td>448.00</td>
</tr>
<tr>
<td>$^3\text{H}_4 \rightarrow ^3\text{P}_1$</td>
<td>472.00</td>
</tr>
<tr>
<td>$^3\text{H}_4 \rightarrow ^3\text{P}_0$</td>
<td>486.00</td>
</tr>
<tr>
<td>$^4\text{I}<em>{9/2} \rightarrow ^2\text{G}</em>{9/2}$</td>
<td>514.00</td>
</tr>
<tr>
<td>$^4\text{I}<em>{9/2} \rightarrow ^4\text{G}</em>{7/2}$</td>
<td>526.00</td>
</tr>
<tr>
<td>$^4\text{I}<em>{9/2} \rightarrow ^4\text{G}</em>{5/2}, ^3\text{H}_4 \rightarrow ^1\text{D}_2$</td>
<td>584.00</td>
</tr>
<tr>
<td>$^4\text{I}<em>{9/2} \rightarrow ^2\text{S}</em>{3/2}, ^4\text{F}_{7/2}$</td>
<td>748.00</td>
</tr>
<tr>
<td>$^4\text{I}<em>{9/2} \rightarrow ^4\text{F}</em>{5/2}, ^2\text{H}_{9/2}, ^3\text{H}_6 \rightarrow ^1\text{D}_2$</td>
<td>804.00</td>
</tr>
</tbody>
</table>
Empirical Energy levels of Pr\(^{3+}\) (\(f^2\))
Empirical Energy levels of Nd$^{3+}$ ($f^3$)
V. CONCLUSIONS

The most important luminescence equipment - the photoluminescence (electroluminescence) lifetime and time resolving spectroscopy systems - was designed and built using the time-correlated single-photon counting technique (fig. 7). This technique has been described in a variety of useful articles [18-23, 34-37] and is generally accepted as the best technique for acquiring meaningful lifetime data.

The time-correlated single-photon counting (TCSPC) technique has as its basis the timing of individual emission photons relative to a zero-time determined by the onset of the excitation pulse. By using a repetitive laser beam operating at a high frequency it is possible to rapidly record a histogram representing the probability of photon emission as a function of time after excitation.

The excitation light source consists of CW argon ion laser with acousto-optic modulator outside the cavity. The light pulses can have repetition rates from dc to 10 MHz with rise and decay times of 3 nsec.

By keeping the emission counts to a few percent of the excitation repetition rate, bias towards early events is avoided. A luminescence decay curve is obtained which is distorted only by the finite width of the instrument response function.
In TCSPC the sample is repetitively excited with a pulsed source (Laser). The source is optically monitored (or electrically triggered) to produce a start signal at the instant of source excitation. This start signal is used to trigger the voltage ramp of a time-to-amplitude converter (TAC). The voltage ramp of the TAC is stopped when a photon emitted from the sample is detected. The TAC output pulses are proportional to the elapsed time between start (source pulse) and stop (photon emission) signals. These pulses are digitized by an analog-to-digital converter (ADC) of the multichannel analyser (MCA) and are sorted according to their voltage (hence, time) and stored as counts. Because the probability of detecting a single photon at a certain time after excitation is directly proportional to the intensity of the total sample emission at that same time, the counts in the MCA will be distributed among the various time channels in the same way as a conventional profile of emission intensity versus time. The TCSPC technique generates decay data of exceptional precision; the decay curve is displayed on the screen of the multichannel analyzer and plotted by a digital plotter (HP 7470 A) interfaced to an IBM-PC.

The time-correlated single-photon counting (TCSPC) technique has several advantages over alternative techniques for lifetime measurements, all of which use analog detection. This is because it offers a combination of single-photon sensitivity, the precision of a mainly digital technique, a wide dynamic range, and a time resolution that still surpasses the capabilities of the fastest photomultipliers.
In our present study, we used the time-correlated single-photon counting technique and a computer-controlled SPC system to record the photoluminescence emission spectra (in MCS mode) and the lifetime data (in PHA mode) of rare-earth doped (Pr and Nd) zinc sulphide crystals.

In this thesis, we present our experimental findings, the sharp line emissions characteristic of the f-f transition of rare earth ions.

1. In the samples of ZnS:Pr, we observed transitions from excited states $^3P_1$, $^3P_0$ and $^1D_2$ to ground state $^3H_4$ and the transition $^3P_1 \rightarrow ^3H_5$, $^3P_0 \rightarrow ^3H_6$, $^3P_0 \rightarrow ^3F_2$, $^3F_4$ for the direct excitation to $^3P_1$ and $^3P_0$ levels. This is in very good agreement with the electroluminescence study in ZnS:PrF$_3$ by Chase and Krupka [68]. The observed PL emission lines are compared in Table 1 (p 90).

2. The excitation spectrum of ZnS:Nd-Li investigated by Larach[13] is in very good agreement with our room-temperature absorption spectra of ZnS:Nd. The lines and the transition assignments are compared as shown in Table 2 (p 91).

3. In the samples of ZnS:Nd, we observed transitions from excited states $^4G_{7/2}$, $^2G_{7/2}$, $^4G_{5/2}$ and $^4F_{3/2}$ to the ground state $^4I_{9/2}$ as well as transitions between the excited states $^2G_{9/2}$, $^4F_{9/2}$ and $^2S_{3/2}$ to $^4I_{11/2}$ for the direct excitation to $^2G_{9/2}$, $^4G_{9/2}$ and between $^2P_{1/2}$ levels. Our emission spectrum is...
in very good agreement with the EL spectrum of ZnS:NdF₃ by Chase [68].

The comparison is given in Table 3 (p 92). Comparison of our absorption spectra with Anderson [3] is listed in Table 4 (p 93), which highlights the precision of our apparatus.

4. At low temperature the emission lines are sharp and intense. The possible explanation for this is, at low temperatures impurity centers are less coupled with lattice vibrations than at room temperatures. As a result it is expected that spectral bands are narrower at low temperatures and spectral resolution is better. There are observable temperature shifts of peaks which account for the variation of the forbidden-energy gap in the crystal. These temperature shifts are related to the occupancy and the widths of bands in the excited states [72,73].

5. We observed in our emission spectra the effect of concentration of the rare earth in ZnS lattice as either enhancing or quenching the emission intensity. The possible reasoning can be that, if the concentration of the activator becomes so high that the probability of energy transfer exceeds that from emission, then the excitation energy starts migrating through the lattice. The host lattice is not perfect that contains all kinds of sites where the excitation energy may be scattered or lost at the surface in some way. The efficiency then decreases, in spite of the increase of the activator concentration [60]. Thus, at higher concentrations, interactions between close neighbors quench the fluorescence and account for weaker fluorescence [48].
6. In the samples of Pr\(^{3+}\), the lifetimes are relatively short, whereas the fluorescence is quite bright. This suggests high radiation-transition probabilities. The relaxation times at 77 K are longer than at 4 K. A possible interpretation is by reabsorption of the resonance radiation. At 77 K, both the ground state and the first Stark level of \(^3\)H\(_{4}\), 79 cm\(^{-1}\) above the ground state absorb. This means that a greater fraction of the total luminescence is reabsorbed and therefore results in a longer relaxation time. The lifetime decreases from 77 K to 300 K, which may be due to higher interaction of the ion with the strongly-vibrating lattice. Barasch observed [48] in LaCl\(_3\) (for 1% concentration of Pr\(^{3+}\)) lifetimes of 13.4, 16.7 and 10.2 microseconds at 4, 77 and 300 degree kelvin respectively using 488 nm excitation and detection at 644 nm. By a single-component decay approximation, we observed in samples of ZnS:Pr\(^{3+}\) a decay time of 5.079034 \(\mu\)sec, for the 476.5 nm excitation at 3.6 K. Even though fluorescence has been observed in samples of Nd\(^{3+}\), it is too weak and short-lived for its lifetime to be measured.
Electroluminescence emission spectra of ZnS:PrF$_3$ by Chase [68]
Table 1

Comparison of EL and PL spectra of ZnS:Pr

<table>
<thead>
<tr>
<th>λ in nm</th>
<th>EL lines by Chase (ZnS:PrF₃)</th>
<th>λ in nm</th>
<th>PL lines of ours (ZnS:Pr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>493.7,502</td>
<td>(^3\text{P}_0\to^3\text{H}_4)</td>
<td>494.6</td>
<td>(^3\text{P}_0\to^3\text{H}_4)</td>
</tr>
<tr>
<td>536</td>
<td>(^3\text{P}_0\to^3\text{H}_5)</td>
<td>532.2</td>
<td>(^3\text{P}_1\to^3\text{H}_5)</td>
</tr>
<tr>
<td></td>
<td>(^3\text{P}_0\to^3\text{H}_6)</td>
<td>619.9</td>
<td>(^3\text{P}_0\to^3\text{H}_6,^1\text{D}_2\to^3\text{H}_4)</td>
</tr>
<tr>
<td>651.3,656</td>
<td>(^3\text{P}_0\to^3\text{F}_2)</td>
<td>651.3</td>
<td>(^3\text{P}_0\to^3\text{F}_2)</td>
</tr>
<tr>
<td>717.5,741</td>
<td>(^3\text{P}_0\to^3\text{F}_4)</td>
<td>737.9</td>
<td>(^3\text{P}_0\to^3\text{F}_4)</td>
</tr>
<tr>
<td>856,986.5</td>
<td>(^1\text{D}_2\to^3\text{F}_2)</td>
<td>984.7</td>
<td>(^1\text{D}_2\to^3\text{F}_2)</td>
</tr>
</tbody>
</table>
Excitation spectra of ZnS:Nd-Li by Larach [13]
## Table 2

Comparison of Excitation and absorption spectra of ZnS:Nd

<table>
<thead>
<tr>
<th>Transition</th>
<th>Spectral line (nm)</th>
<th>in Excitation spectrum</th>
<th>in our absorption spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ZnS:Nd:Li</td>
<td>ZnS:Nd</td>
</tr>
<tr>
<td>$^2D_{3/2} \leftarrow ^4I_{9/2}$</td>
<td>474</td>
<td>480</td>
<td></td>
</tr>
<tr>
<td>$^2G_{9/2} \leftarrow ^4I_{9/2}$</td>
<td>514</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4G_{7/2} \leftarrow ^4I_{9/2}$</td>
<td>526</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4G_{5/2} \leftarrow ^4I_{9/2}$</td>
<td>584</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>670</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4F_{9/2} \leftarrow ^4I_{9/2}$</td>
<td>682</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>710</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^2S_{3/2}, ^4F_{7/2} \leftarrow ^4I_{9/2}$</td>
<td>748</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4F_{5/2}, ^2H_{9/2} \leftarrow ^4I_{9/2}$</td>
<td>804</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3

Comparison of EL and PL spectra of ZnS:Nd

<table>
<thead>
<tr>
<th>λ in nm</th>
<th>EL lines by Chase (ZnS:NdF₃)</th>
<th>λ in nm</th>
<th>PL lines of our spectra (ZnS:Nd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>540</td>
<td>$^{4}G_{7/2} \rightarrow ^{4}I_{9/2}$</td>
<td>530.63</td>
<td>$^{4}G_{7/2} \rightarrow ^{4}I_{9/2}$</td>
</tr>
<tr>
<td>600</td>
<td>$^{4}G_{5/2} \rightarrow ^{4}I_{9/2}$</td>
<td>550.18</td>
<td>$^{2}G_{9/2} \rightarrow ^{4}I_{11/2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>574.37</td>
<td>$^{2}G_{7/2} \rightarrow ^{4}I_{9/2}$</td>
</tr>
<tr>
<td>814,818.5</td>
<td>$^{4}F_{5/2} \rightarrow ^{4}I_{9/2}$</td>
<td>827.01</td>
<td>$^{2}H_{9/2}, ^{4}F_{5/2} \rightarrow ^{4}I_{9/2}$</td>
</tr>
<tr>
<td>888,5894</td>
<td>$^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$</td>
<td>860.47, 905.6</td>
<td>$^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$</td>
</tr>
</tbody>
</table>
| 1070    | $^{4}F_{3/2} \rightarrow ^{4}I_{11/2}$ | 1030.58 | $^{2}S_{3/2} \rightarrow ^{4}I_{13/2}$;
|         |                               |         | $^{4}F_{3/2} \rightarrow ^{4}I_{11/2}$ |
Table 4
Comparison of ZnS:Nd³⁺ lines observed in absorption

<table>
<thead>
<tr>
<th>λ in nm by Anderson</th>
<th>λ in nm observed in our spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>474.00</td>
<td>⁴I₉/₂ → ²D₃/₂</td>
</tr>
<tr>
<td>514.00</td>
<td>⁴I₉/₂ → ²G₉/₂</td>
</tr>
<tr>
<td>530</td>
<td>⁴I₉/₂ → ⁴G₇/₂</td>
</tr>
<tr>
<td>526.00</td>
<td>⁴I₉/₂ → ⁴G₇/₂</td>
</tr>
<tr>
<td>590</td>
<td>⁴I₉/₂ → ²G₇/₂, ⁴G₅/₂</td>
</tr>
<tr>
<td>584.00</td>
<td>⁴I₉/₂ → ⁴G₅/₂</td>
</tr>
<tr>
<td>682.00</td>
<td>⁴I₉/₂ → ⁴F₉/₂</td>
</tr>
<tr>
<td>754</td>
<td>⁴I₉/₂ → ⁴S₃/₂, ⁴F₇/₂</td>
</tr>
<tr>
<td>748.00</td>
<td>²I₉/₂ → ²S₃/₂, ⁴F₇/₂</td>
</tr>
<tr>
<td>808</td>
<td>⁴I₉/₂ → ²H₉/₂, ⁴F₅/₂</td>
</tr>
<tr>
<td>804.00</td>
<td>²I₉/₂ → ²H₉/₂, ⁴F₅/₂</td>
</tr>
<tr>
<td>884</td>
<td>⁴I₉/₂ → ⁴F₃/₂</td>
</tr>
</tbody>
</table>
Decay spectrum of ZnS:Pr$^{3+}$

Excitation wavelength : 476.50 nm
Detection wavelength : 615.98 nm
Temperature : 3.6 K
Excitation repetition rate (PRR) : 25 KHz
Excitation duration (PD) : 5 μsec
Decay time $\tau$ by deconvolution : 5.079034 μsec
Lifetime decay spectra of ZnS:Pr^{3+}

Excitation:
Duration 5 usec

Decay Time:
\[ T = 5.079034 \text{ usec} \]
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APPENDIX - A

SPC INSTRUMENTS
A brief description of the basic equipment used for single photon counting is explained in this appendix.

Excitation source
Detector
Scanning system
Single-photon timing electronics system
Data recording
Data analysis & plotting
Low temperature measurement system

**Excitation source:**

1. **Argon ion Laser**

Laser Ionics, Inc model 553A Argon ion laser, is a specialized electron tube consisting of mainly two elements, namely the optical laser head and the dc power supply. The major components of the optical head are the tungsten bore plasma tube, the magnetic field solenoid, and the thermally isolated quartz rod resonator containing the laser optics/mirrors. The power supply is a series-pass design providing the necessary voltages, monitoring and safety circuits to insure complete, safe operation of the laser system.

This laser operates in the continuous wave (CW) mode and has emission lines at 457.9nm, 476.5nm, 488nm and 496.5nm, 514.5nm. The total power output is 7 Watts and has 2.25 watts power for 514.5nm line and 2 watts in
488nm line. For decay measurements, the excitation must be pulsed with the possibility of adjusting the duration of the pulse. Hence, the CW output of the Argon ion laser is chopped/pulsed using an acousto-optic modulator outside the cavity.

The unit operates from a 220 VAC/3 phase/60 A supply and is water cooled at 4 GPM-50 psi. With UV optics, this laser can be used as a UV laser.

2. Acousto-optic light modulator

The acousto-optic light modulator (AOM), Intra Action model AOM-125 is used to intensity-modulate the laser light optical frequency by the applied acoustic frequency. This unit is a Bragg-type diffraction modulator and hence by adjusting the angle of incidence of the laser beam on the LiNbO3 crystal will yield both zero order (undiffracted) and the first order (diffracted) output beams.

The Intra Action model ME-125 signal processor provides the drive power to the AOM-125 acousto-optic modulator. In amplitude modulation mode, the 125 MHz carrier can be modulated from dc to video frequencies. This processor is designed to accept an analog input signal of 0 to +1 Volt and provide 100% amplitude modulation of output power of 3 watts. Usually the acoustic frequency is provided by a pulse generator, like the HP 8013 B.
3. **Nitrogen Gas Laser**

The AVCO model C950 nitrogen gas laser is a continuous gas flow type pulsed laser. The system basically consists of a cross-field discharge channel, a high voltage pulse generator to excite gas within the channel, and a lower-voltage trigger generator to provide controlled triggers to the high-voltage pulse generator.

This laser has an emission line at 337.1nm in the UV spectrum when operated with nitrogen gas alone and another line at 540.1nm in the visible spectrum when operated with nitrogen and neon. The laser requires a continuous throughput of gas for proper operation. This is accomplished in practice by supplying a reasonably pure grade of nitrogen (e.g., Matheson) gas to the laser from standard pressurized cylinders (with regulators) and exhausting the expended gas to the atmosphere via a small vacuum pump.

The laser operates between 1 pps to 100 pps with 10 nsec pulse width, with peak output power of 147 KW at 1pps and 131 KW at 100 pps. The unit is powered by 110-120 VAC, 60 Hz line.

4. **Laser Filter Monochromator**

Usually in laser optics experiments, the excitation source has to be monochromatic. Even though the Ar-ion laser has predominant emission at 488nm and 514.5nm, it will also contain the plasma lines in its radiation,
and hence, the output needs to be purified. An Applied Photo Physics model 2300 continuously tunable filter monochromator is inserted in the laser beam path. This filter has exceptionally high transmission characteristics (- 75%). Its output beam will have a bandwidth of less than 1 nm.

Detector

1. Photomultiplier tube (PMT)

The photomultiplier tube is a photosensitive detector of radiant energy in the ultraviolet, visible and near infrared regions of the electromagnetic spectrum. This is a device consisting of a photosensitive cathode followed by focusing electrodes, set of dynodes or the electron multipliers and a collector/anode.

When light enters the photocathode, it emits photoelectrons or photons into the vacuum inside the tube. These photoelectrons are then directed by the focusing electrode voltages towards the electron multiplier where electrons are multiplied by the process of secondary emission. The multiplied electrons are collected by the anode as an output signal.

The photocathode converts energy of incident light into electrons. The conversion efficiency (photocathode sensitivity) varies with the wavelength of incident light.
2. Power meter

The Newport corporation model 815 digital Power meter is a precision instrument for accurate measurement of total power or power density of lasers and other sources. It operates in the wavelength range of 400 - 1060 nm. It has a 3½ digit LCD display directly indicating the power of the incident light.

This unit consists of a battery powered display module and a calibrated photosensor head with a detachable O.D.3 neutral density filter. The detector head has a planar diffused silicon PIN diode with a glass diffuser at front end. The spectral response of the detector is 400 nm - 1060 nm on an 1 cm² active area. The maximum continuous input is 2 Watts/cm². The output power can be read in 0.002, 0.02, 0.2 and 2 watt ranges.

3. PRA Quantum photometer

The PRA model 1140 A quantum photometer combines the features and capabilities of a low-level photon counting system with the intermediate and high-level light measurement capacity of a wide-range electrometer.

In combination with the photomultiplier tube, this instrument is a simple, direct-reading type, light intensity measuring device. It can deliver high voltage to the PM tubes and has an input amplifier and discriminator. The output is displayed on the front panel analog meter and the current sensitivity range and the time constant can be set/controlled by the
decade switches.

**Scanning system**

1. Jarrell Ash model 78-490 0.75 M scanning spectrometer is a diffraction grating type scanning spectro photometer. This instrument is provided with an 1180 grooves/mm grating. The instrument is calibrated such that the five digit wavelength counter will read directly in angstroms from 0 to 16,000 Å.

A dc motor drives the scanning system, through the gear assembly, either in forward or reverse direction for scanning towards increasing(+) or decreasing(-) wavelengths. Variable scan speed is available by proper choice of scan speed -/ +Å/min by the gear setting. Scanning is also accomplished by computer controlled stepping motor. The entrance/exit -dual slit assembly can be adjusted from 0 -400 μm to allow any desired intensity of light through the system before detection. The detector photomultiplier is mounted at the exit slit of this unit.

2. The MODULYNX motor controller is a computer-controlled motion control device. The driver card delivers power to the SLO-SYN stepping motor and microcomputer-based indexer card controls the direction, distance, acceleration, running speed and deceleration of the stepping motor.

The indexer card can be digitally programmed and controlled by instructions from an IBM-PC.
Data recording

An ORTEC 7100 multichannel analyzer is used to record both the spectrum and the decay data. This digital data recording is in comparison to the conventional strip-chart recording technique.

The Multichannel analyzer (MCA) is basically composed of an analog-to-digital converter (ADC), the memory, the CRT display and the overall control, analysis and I/O function capabilities. Analog pulses (normally 0 to 10 Volts positive) are digitized by the ADC and select a memory location (or channel number) proportional to the input signal voltage. A spectrum of the number of pulses vs voltage is obtained when a count is added to the appropriate memory location as each input pulse is digitized.

The multichannel analyser is used in two modes, namely pulse-height analysis (PHA) mode and multichannel scaling (MCS) mode. The pulse height analysis mode is used to accumulate the decay spectrum, while the multichannel scaling mode is used to record a scanning wavelength spectrum. The advantage of either mode is online display of spectrum accumulation and also the special features of scale expansion, range selection and feature of numeric operations on data (ADD or SUB, SMOOTH).

Data analysis & plotting

1. an IBM PC is used to analyse the recorded data and for further
reconstruction using graphics software. The asynchronous communication ports/commands are used to control the stepping motor controller as well as to remotely control the multichannel analyzer.

Several programs have been written exclusively for the present experimental setup, and are used for constructing graphs from the recorded data.

2. a Line printer is used to print out the text content or the listing of the control programs and for any other edit options for programs.

3. an HP 7470A plotter is used for plotting the graph. Along with scale expansion/reduction, this plotter also provides the text information that can be used for labelling.

Single -Photon Counting (SPC) Instruments

1. NIM Bin & Power Supply

Most electronic instruments used in SPC instrumentation are Standard Nuclear Instruments modules (NIM) and derive their voltage through the connection on the rear panel from NIM power supply. This NIM power supply is a standard 19" rack mounting type crate with number of power outlets (generally 12) for insertion of plug-in modules. The NIM power supply outputs are regulated, shortcircuit protected, current-limited and thermally protected.
The power supply and the crate that is to hold the plug-in modules is called the NIM BIN. Sockets at each module position always provide both positive and negative 12 V, 24 V and 6 Volts.

2. Preamplifiers

ORTEC model 9301/9301S fast preamplifiers feature very low noise and fast rise time to facilitate precise timing measurements. Their compact size and light weight permits use in close proximity to the detector.

The power for this unit, +12 Volts @ 30 mA and -12 Volts @ 30 mA is derived from the NIM BIN power supply. Both input and output impedances are 50 ohms. The risetime of the output pulse is <1.5 nsec and the voltage gain is 10. The output is connected to the timing filter amplifier through a 50 ohm coaxial cable to avoid/minimize pulse reflections and stray noise.

3. Timing filter amplifier

The ORTEC 474 Timing filter amplifier (TFA) is a NIM standard module for use where a wide band, fast, variable RC filter, high gain amplifier is needed. Features of 474 include a wide gain control range as well as separately selectable RC integrate and differentiate time constants in the nanosecond region. The gain can be set at any value from x2 through x250, using six coarse gain settings and a fine gain control. The gain factors are selected to provide range overlap and to assure continuously adjustable gain control throughout the full range.
Two 6-position switches permit separate selection of RC-integrate and RC-differentiate time constants. The integrate time constant can be selected from 10 nsec (switch position at OUT) through 500 nsec. The differentiate time constant can be selected from 20 nsec through 500 nsec (150 μsec at position OUT). Thus, the input pulses can be reshaped to provide a consistent rise time and decay time.

Input signals may be either positive or negative, unipolar or bipolar, with either positive or negative lobe leading. The acceptable amplitude range for the linear input, to retain its linearity, is 0 to 1 Volt. The linear output pulses can be either unipolar or bipolar, depending on the type of input pulses that are furnished to the 474. When the front panel toggle switch selects INVERT, the output is the opposite polarity to the input; when the toggle switch selects NONINVERT, the polarities are the same.

4. Constant fraction discriminator (CFD)

ORTEC model 583 constant-fraction differential discriminator generates NIM fast negative output pulses for input pulses in the range 0 to -10 Volts, based on the constant-fraction time derivation. It provides excellent timing characteristics for a wide dynamic range of input signal amplitudes. In the constant-fraction technique, an input signal is delayed and a fraction of the undelayed pulse is subtracted from it. A bipolar signal is generated, and its zero crossing is detected and used to produce an output logic pulse. The constant fraction shaping delay is controlled by the length of the cable that is connected externally between the two delay connectors on the
This instrument can be operated as an integral discriminator or as a single channel analyzer. When operated as an integral discriminator (INT mode), each input pulse that exceeds the adjusted lower level threshold, set on the front panel LLD, causes a set of timing output signals to be generated. When operated in DIFFERENTIAL mode, the input signal must exceed the lower level threshold and must not exceed the upper level threshold.

Schematic representation of constant fraction timing discrimination. Timing is from a position on the leading edge that is always a fixed fraction \( f \) of the input pulse height. Input pulse not shown. (a) Input pulse (amplitude \(-V_t\)) inverted and delayed by time \( \delta \). (b) Undelayed input pulse attenuated to maximum amplitude \(-fV_t\). (c) Zero-crossing pulse (sum of (a) and (b)).

To ensure proper operation in the DIFFERENTIAL mode, the LLD level should always be lower than the ULD setting.

Other features of the CFD includes a slow rise time reject function, which inhibits the discriminator to input signals that would cause leading edge timing. The unit accepts negative input signals from 0 to -10 Volts. An
upper level output pulse is generated when the internal ULD circuit is triggered by an input signal. The output is a fast negative logic pulse and is generated in either the differential or the integral mode.

During decay measurements, usually the output of CFD is often used as the START pulse of the time-to-amplitude converter.

5. Gate & delay generator

The ORTEC 416 A Gate & delay generator accepts either polarity of logic pulses, provides an adjusted delay for each input pulse, and generates output pulses with both polarities that have an adjusted amplitude and width. The logic pulse delay is adjustable from 0.1 through 110 µsec in three overlapping ranges. The amplitude of both polarities of output pulses is adjustable within the range of 2 to 10 Volts. The output pulse width can be adjusted within the range of 400 nsec through 4 µsec.

The front panel DELAY potentiometer with direct reading duo-dial facilitates continuous adjustment within the range selected by the locking 3-position toggle switch, which selects the range for delay control. The inner concentric single-turn control adjusts the output pulse amplitude from 2 to 10 Volts, and the outer concentric single-turn control adjusts the output pulse width from 400 nsec to 4 µsec. Front panel POS input accepts positive input logic pulses in the range 2-12 Volts; 100 nsec minimum width. Similarly, the NEG input accepts fast negative logic input pulses; -250 mV minimum into 50 ohms; 5 nsec minimum width.
DLY'D MARKER output provides a fast negative logic pulse at the end of the delay time whose amplitude is -0.6 Volts, < 25 nsec wide. The output pulse, usually after discrimination, is used as the STOP pulse for the TAC.

6. 100 MHz discriminator

The ORTEC 436 fast discriminator is used as a timing trigger or pulse shaper with any input signal shape from dc to 100 MHz. An optional PROMPT or DELAYED RESET provides the equivalent of pulse stretchinh when analyzing pulses of various widths. It generates only one signal for each input pulse, regardless of the input pulse width.

Usually, the input is derived from a gate & delay generator when used for SPC measurements, and this unit produces two identical, isolated, fast, negative logic outputs for use as the STOP pulse of the TAC. The discriminator level is adjustable from 50 mV through 500 mVolts.

7. Time-to-amplitude Converter (TAC)

The ORTEC 457 Time to pulse height converter or simply the time to amplitude converter, measures the time interval between pulses to its START and STOP inputs and generates an analog output pulse proportional to the measured time. A biased amplifier is also included in the 457 to simplify spectral expansion and selection of any region of interest within its selected range.
Start-to-stop time conversion is accomplished only after a valid start has been identified and after a stop pulse arrives within the selected time range. The start input is disabled during the 'busy' interval to prohibit pileup; the stop input is disabled after the first accepted stop signal.

Time ranges are switch-selected for time scales from 50 nsec to 80 µsec. The strobed analog time signal is then furnished to a linear biased amplifier, where any low portion of the selected full range can be biased off and the remainder expanded by post gain. The gain is continuously adjustable from 0.5 to 15 using switch-selectable coarse and fine gain controls. The analog outputs are dc-coupled and have a full range that is linear from 0 to 10 Volts. The output is connected to the multichannel analyzer (MCA).

The unit provides both POS and NEG output pulses whose amplitude will be in the range 0 to +10 and -10 Volts respectively. TRUE START is a positive logic timing output to indicate the interval from an accepted start input signal until its strobed output occurs.
8. Single channel analyzer (SCA)

The ORTEC 550 single channel analyzer has an exceptionally wide dynamic range, high stability and resolution. This unit accepts either positive unipolar or bipolar input pulses. It examines the amplitude of each input pulse and generates appropriate positive logic output pulses.

The SCA has a 3-position locking toggle switch on the front panel to select different modes of operation. In the INTEGRAL mode, it provides an output signal if the input pulse amplitude exceeds the adjusted lower-level threshold in the range 0 to +10 Volts. In the NORMAL mode, it provides an output pulse if the input pulse amplitude exceeds the lower-level threshold, but does not exceed the upper-level threshold. In this mode, each threshold is adjusted independently in the range of 0 to +10 Volts. The ULD level must be set higher than the LLD level to permit the SCA output to be generated.

In the WINDOW mode, the SCA provides an output pulse if the input pulse amplitude exceeds the lower-level threshold by an amount that is less than the adjusted window width. The range of the LLD is 0 to +10 Volts and the range of the window is adjusted from 0 to +1 volts above the LLD level.

During time-resolved measurements (TRES), SCA is used between the TAC and the multichannel analyzer.
9. Time calibrator

The ORTEC 462 time calibrator generates logic signals at precise time intervals that can be used to test and calibrate the TAC. Each output consists of a pair of START and STOP pulses for the TAC. Each pair of pulses is exactly \( N \) integral time intervals apart, where \( N = \text{multiple of 2 of the selected period} \) (set on 462). The period selection consists of 11 binary steps from 10 nsec to 10.24 \( \mu \)sec. The time-spectrum that can be obtained from the TAC consists of a series of sharp peaks at multiples of the selected period within the range.

10. Liquid Helium Cryostat

The OXFORD Instrument MD3 modular dewar, bath type cryostat, is essentially a reservoir of coolant, usually liquid nitrogen for temperatures above 77 K, liquid helium for temperatures down to 4.2 K and pumped helium for the 1.5 - 4.2 K range. This is a high vacuum insulated cryogenic vessel. The sample space is at the center of the cryostat. Monitoring the liquid levels and variable temperature-tails are accomplished by temperature-controller and level-meter.
APPENDIX - B

COMPUTER PROGRAMS
PROGRAM "DRIVECON"

This program is to define M pulses for the stepping motor and time per channel for the multichannel analyzer.

10 print "COMPUTER INITIATED SCAN DEFINITION"
20 print " the gear setting in 0A/min = "
30 input G
40 M=(250/G)
50 print " the range to be scanned in 0A = "
60 input Y
70 Z=Y*M*200
80 print " ## the value of M to be defined ## = ";Z
90 S=(Y/G)*(60/1024)
100 print " the sweep time T in secs. for T/CH in MCA = ";S
110 B=Z/(S*1024)
120 print " ## motor base speed to be defined in MT-CNTL ## = ";B
130 REM this routine gives the stop wavelength
140 print " the start wavelength in 0A = "
150 input W
160 print " the T/CH defined in secs for MCA = ";
170 input T
180 print " the base speed possible/defined = ";
190 input K
200 D=Z/K
210 print " the scan time in secs. = ";D
220 \( H = \frac{Y \cdot 1024}{T} \)

230 print " the actual stop wavelength in MCA =";H

240 \( X = \frac{H}{1024} \)

250 print " time per channel ( step ) while plotting = ";X

260 \( STP = (A + H) \)

270 print " actual STOP wavelength in MCA = ";STP

280 print " are the parameters O.K.? (1=yes,0=no) ";

290 input C

300 if C=1 then go to 310 else 320

310 go to 90

320 end
PROGRAM "MT-CNTL"

This program is to scan wavelength region by the stepping motor synchronously with memory channel sweep of the analyzer.

10 PRINT "COMPUTER INITIATED MULTICHANNEL SCALING"
20 REM This program is meant for direct spectrum recording
30 OPEN " com1 :300,n,8,2,cs0,ds0,cd0 " AS #1
40 OPEN " com2:9600,n,8,1 " AS #2
50 B$=""
60 LF$=CHR$(10)
80 PRINT #2,"D.G1000000.E."
90 PRINT #1,CHR$(7)"R"
100 FOR X=0 TO 500:NEXT X
110 PRINT #1,"V"
120 FOR X=0 TO 2000000:NEXT X
130 END

Specific description of some characters:

30 OPEN " com1 :300,n,8,2,cs0,ds0,cd0 " AS #1
   -- This line opens a communications file.
   Valid only with asynchronous communications adapter.
   Format:OPEN "COM [1-9];[speed],[parity],[data],[stop],[RS ]
   [CS(n)], [DS(n)], [CD(n)], [LF] AS [# 1]
Opens I/O link between MCA and IBM PC.

```
40 OPEN " com2:9600,n,8,1" AS #2
```

This line allows I/O to a file or a device

Format: `OPEN "COM2:[baud rate],[parity],[data],[stop] AS [# 2]`

Opens a communication link with Modulynx Motion controller IOD009 card.

```
```

This line defines motion parameters and motion execution commands.

Motion parameters defining:

- `An` - to select acceleration/deceleration
- `Bn` - to select base speed
- `Hn` - to select high speed
- `Mn` - to select the distance/range to be moved
- `U` - U axis selection/installed
- `D` - to apply power to motor windings
- `E` - to remove power from motor windings

```
80 PRINT #2 ," D.G1000000.E. " LF$
```

`Gn` - to index the motor n times (this command executes a move operation according to the previously programme base speed, acceleration, high speed and move distance mode. The n portion of the command specifies the number of times the G instruction
will be performed).

90 PRINT #1, CHR$(7) " R "
    " R " --> this is a Serial Remote Control command for the MCA in
    ASCII character form to 'RUN' a pre-selected operation.

100 FOR X=0 TO 500:NEXT X
    --> this is a DO LOOP type command to account for the time/
    operational delay.

110 PRINT #1, " V "
    " V " --> this is a Serial Remote Control command for the MCA in
    ASCII form for 'MCS'.

PROGRAM " RM - CNTL "

This program is to record the emission spectrum by ratiometric method of measurement.

10 PRINT " COMPUTER INITIATED MULTICHANNEL SCALING "
20 REM This program is meant for ratiometric method of recording
30 REM the spectrum using Modulynx Stepper Motor /drive
40 OPEN " COM1:300,n,8,2,cs0,ds0,cd0 " AS # 1
50 OPEN " COM2:9600,N,8,1 " AS # 2
60 LF$=CHR$(10)
80 PRINT#2, "E.ENP.1.KYLO.KYL1.KYLO.KYWO.D.J400.E..M**1024."",LF$
90 PRINT #1, CHR$(7) " R "
100 FOR X=0 TO 500:NEXT X
110 PRINT #1," V "
120 A$=INKEY$:IF A$=" " THEN GOTO 120
130 PRINT #2, A$ " . " LF$
140 A$=INKEY$:IF A$=" " THEN GOTO 140
150 PRINT #2,A$ " . " LF$
160 END

Specific description of some characters /commands :

80 PRINT #2," E.ENP.1.KYLO.KYL1.KYLO.KYWO.D.J400.E..M**1024."",LF$

--> This line allows the user to program the Modulynx motion
controller computer and to record the spectrum in an excitation intensity fluctuation compensated mode. 

Programming parameters being:

**ENP.1** - to clear and Enter New Program until $. 
- the ENP command will clear the program which is in RAM and allow entry of a new program. The $ character indicates completion of the new program.

**KYLn** - to load IOD009 Output Y with n 
- this command controls the programmable outputs the IOD009 card. The n value turns the output on or off as below; 
  
  \[ n = 0 \text{ Relay off} \quad n = 1 \text{ Relay on} \]

**KYWn** - command for Wait for Input Y 
- this command is a wait command that is associated with input Y of the IOD009 card. This command tells the card to hold further program execution until the specified input is in a specific state. The n values used with this command has the significance as;  
  
  \[ n = 0 \text{ Input off} \quad n = 1 \text{ Input on} \]

**Jn** - command for manual motion execution, Jog plus n times 
- this command causes the appropriate axis to be driven one pulse in the appropriate direction the number of times specified (n).

**M"n** - to execute program memory from present position to End n times.
220 FOR X=0 TO 1000: NEXT X
230 PRINT "#1," A "
240 FOR X=0 TO 2000: NEXT X
250 PRINT "#1," C "CHR$(3)
260 END

Programming parameters being:

80 PRINT "#1," I "
    --> this is a Serial Remote Control command for the MCA in ASCII form to perform I/O operation.

90 A$ = INPUT$(1, #1)
100 IF A$ = CHR$(254) THEN GOTO 90
110 IF A$ = CHR$(22) THEN GOTO 90
120 IF A$ = CHR$(0) THEN GOTO 90
130 IF A$ = CHR$(4) THEN GOTO 170
140 PRINT #3, A$;
150 GOTO 90
    --> this is a DO LOOP type command to for the elimination of non-printable and linefeed, carriage return and any other non-data characters before data transfer.

210 PRINT "#1," O " ." ."
220 FOR X=0 TO 1000: NEXT X
230 PRINT #1, " A ",
240 FOR X=0 TO 2000:NEXT X
250 PRINT #1," C " CHR$(3)
   --> this is a Serial Remote Control command to erase the spectrum on
       the MCA screen, and to reset the MCA for next operation, once the
data is transferred.

30 OPEN " b : spectrum .prn " FOR OUTPUT AS #3
   - this statement opens the file named 'spectrum .prn ' for sequential
      output from the default drive (b:).

Note: the above program is used when the data transfer rate is slow, i.e.,
      BAUD RATE  300.
PROGRAM "FAST PASS"

This program is to transfer data from the MCA to an IBM-PC at higher baud rates, say 1200 bps.

10 PRINT " MCA - IBM DATA TRANSFER "
20 OPEN "COM1:1200,n,8,2,cs0,ds0,cd0 " AS #1
30 OPEN "b:test.prn " FOR OUTPUT AS #3
40 B$=" "
50 LF$=CHR$(10)
60 PRINT #1,CHR$(7)" R"
70 FOR X =0 TO 500:NEXT X
80 PRINT #1," I"
90 A$=INPUT$(1,"#1)
100 PRINT #3,A$;
110 GOTO 90
120 CLOSE #3
130 PRINT " THE REAL END "
140 END

Note: The above transferred data contains non-printable character sets, line feed, carriage return etc., which must be deleted from data file. Along with 1024 data points, -the MCA transfers the corresponding channel numbers for each data points, which are not attempted to be eliminated at this stage.
PROGRAM "RECONST"

This program deletes the non-printable characters when the data from the MCA is transferred to an IBM-PC at a higher baud rate.

10 OPEN "a: test.prn" FOR INPUT AS # 1
20 OPEN "b: spectrum.prn" FOR OUTPUT AS # 3
30 B$ = ""
40 LF$ = CHR$(10)
50 A$ = INPUT$(1, #1)
60 IF A$ = CHR$(254) THEN GOTO 50
70 IF A$ = CHR$(22) THEN GOTO 50
80 IF A$ = CHR$(0) THEN GOTO 50
90 IF A$ = CHR$(4) THEN GOTO 120
100 PRINT #3, A$;
110 GOTO 50
120 CLOSE #3
130 END
PROGRAM " LNAR "

This program deletes the channel numbers from the file and rearranges the 1024 data points that are in a matrix form (128 x 8) into a linear array for plotting convenience.

10 PRINT " LINEAR DATA PROGRAM "
20 REM -this routine reads the data file
30 DIM A(128,8), A1(1024)
40 OPEN " b: spectrum.prn " FOR INPUT AS #1
50 REM -the lines 60 - 80 are to eliminate non data characters
60 FOR X=1 TO 3
70 LINE INPUT #1,A$
80 NEXT X
90 FOR R =0 TO 127
100 C =0
110 REM - variable x deletes the channel numbers
120 INPUT #1,X,A(R,C),A(R,C+1),A(R,C+2),A(R,C+3),A(R,C+4),A(R,C+5),
A(R,C+6),A(R,C+7)
130 NEXT R
140 PRINT " ** end of reading data from file ** "
150 CLOSE #1
160 REM - this routine flips the data into a linear array
170 Q =0
180 FOR R =0 TO 127
190 FOR C =0 TO 7
200 A1(Q) = A(R,C)
210 Q = Q + 1 : NEXT C
220 NEXT R
230 PRINT " ** end of data arrangement in a linear array ** "
240 REM - this routine finds the lowest & highest number in the array
250 LOWNUM = 999999!
260 HIGHNUM = 0.0000001
270 FOR R = 0 TO 1023
280 IF A1(R) < LOWNUM THEN LOWNUM = A1(R) : L = R
290 IF A1(R) > HIGHNUM THEN HIGHNUM = A1(R) : N = R
300 NEXT R
310 PRINT " lownum = " LOWNUM ; " Channel number = "; L
320 PRINT " highnum = " HIGHNUM ; " Channel number = "; N
330 REM - this routine will the linear data to a disk
340 OPEN " b:LNAR.DIF " FOR OUTPUT AS #2
350 INPUT " sample interval "; Y
360 R = 0
370 FOR C = 0 TO Y
380 PRINT #2, A1(R);
390 R = R + 1
400 IF R = 1024 THEN END
410 NEXT C
420 PRINT #2, " "
430 GOTO 370
440 END
**PROGRAM " DECONVOLUTION "**

This program is used to compute the single and/or multiple exponential decay time constants (τ).

10 PRINT " ** DECAY DECONVOLUTION ** "
20 DIM A(128,8), A1(1024), A2(1024), R(1024)
30 OPEN " b:spectrum.prn " FOR INPUT AS #1
40 REM - the lines 50-70 eliminate non data characters
50 FOR X=1 TO 3
60 LINE INPUT #1, A$
70 NEXT X
80 FOR R=0 TO 127
90 C=0
100 REM - variable x eliminates the channel numbers
110 INPUT #1, X, A(R,C), A(R,C+1), A(R,C+2), A(R,C+3), A(R,C+4), A(R,C+5),
     A(R,C+6), A(R,C+7)
120 NEXT R
130 PRINT " ** end of reading data from file ** "
140 CLOSE #1
150 REM - this routine flips the data into a linear array
160 Q=0
170 FOR R=0 TO 127
180 FOR C=0 TO 7
190 A1(Q) = A(R,C)
200 Q=Q+1 : NEXT C
210 NEXT R
220 PRINT " ** end of data arrangement in a linear array ** 
230 REM-this routine finds the lowest & highest numbers in the array
240 PRINT " Time/channel = ";
250 INPUT W
260 LOWNUM =999999!
270 HIGHNUM =0.0000001
280 FOR R=0 TO 1023
290 IF A1(R) < LOWNUM THEN LOWNUM =A1(R):F=R
300 IF A1(R) > HIGHNUM THEN HIGHNUM =A1(R):D=R
310 NEXT R
320 PRINT " lownum = "LOWNUM; " Channel number = ";F
330 PRINT " highnum = "HIGHNUM; " Channel number = ";D
340 REM-this routine computes the decay
350 PRINT " Number of channels on time axis from = ";
360 INPUT P
370 IF P=0 THEN GOTO 670
380 PRINT " Number of channels on time axis to = ";
390 INPUT S
400 N=ABS(S-P)
410 PRINT " Number of known points = ";N
420 Z=(N*W)
430 PRINT " Duration on time axis = "Z
440 J=0
450 K=0
460 L=0
470 M=0
480 G=0
490 FOR R=1 TO N
500 A1(R)=LOG(A1(R))
510 J=J*R
520 K=K*A1(R)
530 L=L*R*R
540 M=M*A1(R)*A1(R)
550 G=G*R*A1(R)
560 NEXT R
570 REM-computation of coefficient of equation
580 B = (N*G-K*J)/(N*L-J*J)
590 A = (K-B*J)/N
600 PRINT
610 PRINT " F(R) = EXP(A)*e^CSNG(B)*R"
620 PRINT " Coefficients of computation :"
630 B=ABS(B)
640 PRINT " exponential component = \";B
650 T= W/B
660 PRINT " Decay time constant T in seconds = \";ABS(T)
670 END
APPENDIX - C

EXPERIMENTAL PROCEDURES
EXPERIMENTAL PROCEDURES

1. Laser

2. Monochromator

3. Multichannel analyzer

4. Optical alignment

5. NIM bin modules

6. Computer software
   - stepper motor control
   - data transfer
   - data analysis

7. Plotting

8. Low temperature measurements
   - vacuum system
   - liquid helium cryostat
   - temperature controller
1 Argon ion Laser:

Laser is used as the excitation source.

1.1 Before turning ON laser power supply circuit breaker:

a. open the laser cooling water valve.
b. switch ON the cooling water booster pump.
c. switch ON the 3 phase power supply transformer
d. switch ON the start timing & indicator unit

This turns ON the laser safety/operation indicator GREEN lamp.
e. open the front shutter of the laser head
f. adjust the current limit control knob fully counter clockwise
g. adjust the tube current (servo) fully clockwise
h. turn the interlock key of the power supply unit clockwise.

1.2 Turn ON the circuit breaker and observe that all 3 phase indicators are lit.

1.3 After about 100 seconds, the START button will be lit (red), in the power supply unit, indicating that the system is ready to start. At this instant, the operation lamp will flip to YELLOW lamp.

Push the START button, while observing the current meter.

Note: when the plasma ignites the current will increase to approximately 20 amps. At this instant, the operation indicator will flip to RED lamp.

1.4 Adjust the current control clockwise so the current meter reads about 25 amps.

CAUTION: Laser operating current setting should never exceed 33 amps which is the maximum.
- Power Supply Front Panel

- Power Supply Rear Panel

Argon Ion Laser power supply
Note: Emission lines 488 nm and 496.5 nm emit appreciable power even at 22-26 amps. Current setting of 27-30 amps is needed most of the time to get lines 457.9 nm and 514.5 nm. Allow 30 minutes for system warm-up and steady laser output. Note: If only the plasma discharge is seen and there is no lasing, increase the tube current to 25-28 amps and adjust the mirrors on micrometer scale as described in the manual.

1.5 Turn the SERVO control knob counter-clockwise, to reduce the tube current to get the required optical output.

Note: this will engage the optical feedback circuit for the servo mode of current control.

1.6 Read the output power directly from the output power indicator on the power supply unit, using range switch, or from external power meter inserted in the beam path.
2. **Monochromator**

Monochromator is used to scan the wavelength region of interest.

2.1 Read the wavelength as 4 digit value on the mechanical counter (eg., 6328 or 5145).

2.2 Turn on the scan dc motor to advance forward or reverse to reach the desired start wavelength.

2.3 Depending on the range to be scanned and the time of recording in the multichannel analyzer, select the gear setting (eg., 0.25 A/min - 2500 A/min)

2.4 Open the entrance slit cover.

2.5 Adjust the slit width by turning the micrometer to set slit width in the range 1-400µm.

Note: For photoluminescence experiments, as the intensity is high, the usual setting is 100 µm. For electroluminescence, as the intensity is low, slits are fully open.

2.6 Adjust the slide/scissor tail shutter so as to allow appreciable detection of photons by the cooled photomultiplier.

Note: The detector photomultiplier is mounted at the exit slit of the monochromator and the amount of detected photons is read through a Quantum Photometer (PRA 1140A).

Scanning is accomplished by manual as well as by computer-controlled operations.
Jarrell-Ash Scanning Spectrometer

1. Direction of scan select
2. Limit of scan indicator
3. Scan speed gear select
4. Wavelength counter
5. Entrance / exit slit
6. Focus tail shutter
A. **Manual scan**:

1. Set up the recording/sweep time per channel in the multichannel analyzer.
   - Press SETUP key first and then press MCS soft key.
   - Press CONT key till the reverse video setting block is T/CH.
   - Press the numeric keys to enter the time and press \( x10 \) or \( \div10 \) soft key to get usec or msec.
   - Press CANCEL to terminate setting operation.

2. At this instant, gear setting, start wavelength setting and range being scanned are all known.
   - Turn ON the scan motor for forward motion and at the same instant of time, press RUN key and then MCS soft key of the analyzer.

3. STOP the scan motor once the desired range scan is completed or immediately after automatic stop of MCS mode of recording of the analyzer.

   Note: Multichannel analyser is used in multichannel scaling mode and spectral information/intensity value recorded in 1024 channels in one sweep.

4. Turn the scan motor for reverse motion to return back to the start wavelength.
B. Computer-controlled stepping motor scan:

1. After booting the IBM-PC, when you see D:\ prompt, type in `cd speccont < cr >` and then type `basica < cr >`. Press function key F3 to load the desired file.

2. Type in `DRIVECON < cr >` when the prompt is LOAD ‘’

Note: This program helps to determine the gear setting and T/CH in multichannel analyser and parameters for stepping motor control program for the desired range to be scanned.

3. Having known the parameters to be defined, load the motor control program. Press F3 to load file "MT-CNTL ". EDIT line 70 to define base speed and number of advancing pulses for the MT-CNTL program.

Note: Refer to the detailed information of stepping motor program to alter the base speed and number of M pulses.

4. Turn ON the stepping motor controller computer.

Note: Whenever the motor controller switch is Turned ON, a high frequency sound from the motor will be heard and the scan drive shaft will give a feeling like the scanning system is locked.

5. Ensure that the computer communication control unit is switched to position 3, else turn it to position 3.

6. Verify the gear setting and change as needed.

Note: This is done based on the output of DRIVECON program (eg., 1250 A/min)

7. Press F2 to RUN the program.
8. Once the recording is completed, disable the multichannel analyzer from its serial remote control loop from IBM-PC by depressing the RESET button at the rear of MCA.

Note: The program "MT-CNTL" will clear the analyser screen as well as disable the remote control. However if scale expansion is needed to observe/read the peaks on MCA screen, manual RESET is recommended.

The power to the stepping motor will be switched-off automatically after advancing M number of pulses, as is defined in the MT-CNTL program.

At this instance, there will be no high frequency sound from the motor and the motor shaft is unlocked/free to rotate by hand or by dc motor in either direction.

9. Turn the dc scan motor ON for reverse motion to get back to the start wavelength.

Note: The features of returning back to the start wavelength can be incorporated in MT-CNTL program.
Flowchart showing spectrum recording program execution
3. Multichannel analyzer (MCA)

The user is strongly recommended to read the ORTEC 7100 Multichannel Analyzer manual before using the instrument, as the instruction manual familiarizes the user with all of the operating, programming and interfacing procedures for the precision instrument.

The manual is a first-time learning guide and a significant aid/as reference material from time-to-time.

3.1 Pulse height analysis mode (PIIA):

1. Turn ON the MCA. The amber lever switch should light-up and within a few seconds self-test information will be displayed on the screen.
2. Adjust the display intensity control (mounted on the rear panel) as desired for comfortable viewing.

Note: Intensity has to be a bare minimum while recording electro luminescence spectrum.

3. After power is applied, the MCA's computer performs a series of hardware and firmware tests during the brief warmup period. Upon the completion of each test, a message will appear on the display the results of the test.

Note: If any of the tests should result in an error, a series of beeps will alert the error to the user.
EG & G Ortec model 7100 Multichannel analyzer
If the tests run successfully, and the display for each test is O.K., press CONT key to exit from the self-test and to continue for normal operation.

4. Mode selection is a means by which one can select any one of the operating modes for set up and execution.

Press SETUP key.

On the right hand top corner there will be the indication of available modes of operation like PHA, MCS and I/O for the soft keys.

5. Press PHA soft key.

6. Once the soft key is pressed, the first parameter in the command line changes to PHA.

Note: Before data collection or analysis can produce any useful results, the analog-to-digital converter (ADC) must be properly set up and adjusted prior to use.

Press CONT key to setup or skip the subsequent parameters in the command line.

7. Press TERM key or CANCEL key to terminate the setup sequence.

8. Skip steps 6 and 7 if there is no change in the setup sequence.

9. Press RUN key to execute the operation.

10. Press TERM key at any time during execution, if necessary.

If the execution is desired from a computer program, using serial remote control, use the following sequence.

1. Once the IBM-PC is booted, change the root directory by entering (typing in)
Note: The computer accepts both lower and upper case letters.

2. Press F3 to load the program.

3. Type CC-PHA < cr >

Note: See the program CC-PHA for details and necessary modifications to suit the desired experiment.

4. Ensure the computer communication control in position 3.

5. Press F2 to run the program.

6. If LT or RT was selected, by pressing the numeric keys, the selected parameter value will be in seconds. Operation automatically stops as soon as the preset count value is reached.

   If none was selected, press TERM key or CANCEL key to abort the operation, whenever desired.

7. To disable the serial remote control from the computer depress the RESET button.

3.2 Multichannel Scaling Mode ( MCS ) :

The MCS mode allows recording of the spectral/wavelength region being scanned.

1. Press SETUP key

   Note: As mentioned earlier, first three soft keys will appear (PHA, MCS and I/O) and the command line displays the first parameter in reverse video.

2. Press MCS soft key.
3. Press CONT key to choose the subsequent parameters to be defined or skipped.
   eg., select ADD or SUB, memory group, sweep numbers etc.,

4. Select T/CH (time per channel)
   Note: This determines the dwell time (the allotted time during which collected data is being stored in any given channel).
   Press desired numeric key to enter T/CH value to set the time (eg., 200 or 100 or 400).

5. Press the desired x10 or ÷10 soft key to multiply or divide the dwell time by 10 to get msec or usec.

6. Press TERM or CANCEL key to exit from setup operation.

7. Press RUN key to execute the operation.
   Note: Since spectral recording in MCS mode is done with synchronized wavelength scan, the monochromator dc motor or the computer controlled stepping motor is turned ON at the instant, the MCA RUN key is pressed.

8. Normally the recorded spectrum will contain background and several other noise content associated with electronic systems and needs to be smoothed.
   Press OPTIONS key and then the SMTH soft key.

9. When the display in the command line is 'smooth ready' press SMTH soft key any number of times (eg., 5 or 10) till the spectrum seems smooth or Press RUN - PROGRAM 1 keys.
   Note: PROGRAM 1 can be written easily which smooths the recorded spectra 10 times. The smoothing operation can be incorporated in the main MT-CNTL program also.
10. Press TERM or CANCEL key to terminate the option operation.

Since the spectral recording is done in multichannel scaling mode (MCS) synchronized with the stepping motor wavelength scan, computer-initiated MCS is a integral part of the MT-CNTL program.

4. Optical alignment

4.1 Excitation source

1. Using the mirror mount or set of parallel mirrors, raise the laser beam height to 10.25" from 4.35" and adjust mirror such that the beam is parallel to the optical table.
2. Using a lens of focal length $f=15$ cms reduce the beam spread.
3. Insert the Laser filter monochromator (Photo physics) in the beam path and adjust the beam to pass through the inlet aperture.
4. Rotate the wavelength select/tuning micrometer to get the filtered laser beam from plasma lines.
5. Rotate the horizontal as well as vertical positioning knobs to optimize the output beam.
6. Using another mirror, deflect the laser beam by approximately 90 degrees to focus on to the sample.
7. Using a lens of focal length $f=50$ mms, focus the beam to a small spot on the sample.
8. Insert a pin-hole or a diaphragm between the lens and the sample to maintain the excitation spot at the same location.
Note: For room temperature measurements, the sample can be mounted on an open sample mount. But, for low temperature measurements the sample is mounted on the sample holder of a liquid helium cryostat.

9. For decay measurements, the beam has to be a pulsed source. An Ar-ion laser is used as a continuous (CW) and as a pulsed excitation source. To achieve a pulsed mode from CW laser, an acousto-optic modulator is used.

Insert the acousto-optic modulator (AOM), in the laser beam path after laser filter monochromator and the lens with f=15 cms.

10. Adjust the horizontal and vertical positioning screws such that the laser beam is focussed on AOM and is passing through the central portion of AOM.

11. Connect the AOM to the signal processor (modulator/driver)

Apply 1 volt peak-to-peak 20-25 KHz pulse, derived from a pulse generator (eg., HP 8013 B).

eg., square wave pulse with duration 5 µsec & repetition rate 40 µsec.

12. Turn ON the AOM signal processor. Rotate the amplitude control clockwise and turn it back fully counter clockwise.

Note: The AOM operates in an intensity (amplitude) modulation mode.

13. Since AOM is a Bragg type diffraction modulator, adjust the angle of the AOM mount w.r.t. the laser beam such that multiple modes like first-order and second-order modes of the incident beam are available.
Schematic representation of splitting the continuous wave (CW) laser beam into diffracted and undiffracted beams
Optimize the beam focus on AOM and position and angle of AOM such that higher/maximum energy is available in the diffracted beam (pulsed).

14. Insert a diaphragm to block the zero order beam, which is cw and adjust to pass only the first-order beam.

Note: The rest of the procedure to focus the laser beam to a spot on the sample is the same.

4.2 Sample position

1. For room temperature measurements, mount the sample on the brass sample holder with the glue.

2. Insert the sample holder on a X-Y positioner.

   Adjust the height such that the focused laser spot is on the sample, which is nothing but the height of the sample being 10.25".

3. Adjust the horizontal positioning knob such that the sample is in axis with the entrance slit of the monochromator.

4. For low temperature measurements, samples are mounted on a sample holder which goes into a liquid helium cryostat.

   On either side of the sample holder 2-3 samples are mounted with the glue.

   Rotate the sample holder to the position such that, the sample surface makes a 45 degree to the excitation beam.

5. Rotate the brass 'height adjust' knob to lower or raise the desired sample to the excitation spot.

Note: Since the cryostat is fixed on the optical table the sample holder
center in-line with axis of entrance slit, there is no need or concern about horizontal position adjustment.

4.3 Optimization of luminescence detection

1. Insert a lens of focal length \( f = 15 \) cms mounted on a X-Y positioner and on the horizontal rail in-line with the entrance slit.

2. Open the monochromator entrance slit cover plate.
   Set the slit width to any value between 1-400 um.
   eg., 100 um for photoluminescence experiments.

3. Move the lens on the horizontal rail so as to focus the image of the luminescence sample to the actual/reduced size of the sample.

4. Adjust the X-Y position control knobs so as to adjust the height and the position in-line with slit axis to optimize the detected signals.

Note: The optimum value of detected signal can be seen /verified using a Quantum photometer (PRA 1140 A).

5. SPC instruments & NIM bin modules

5.1 Spectrum recording

ORTEC 9301/9301S fast preamplifier is connected to the photomultiplier tube (R928), the output of which is connected to the input of a Timing-filter amplifier (TFA) through a 50 ohm cable.
The filtered and shaped output pulses from TFA are connected to constant-fraction discriminator (CFD), the true output of which is directly connected to the ADC input of the multichannel analyzer (MCA).

5.1.1 Adjustments on Timing filter amplifier

ORTEC 474 Timing filter amplifier, is a NIM standard module for use as a wide band, fast, variable RC filter amplifier with variable gains as needed.

1. Plug IN the NIM bin cooling fan.
2. Turn ON the NIM bin Power supply.

Note: The NIM bin power supply provides power to 12 plug-in modules simultaneously. Hence, once it is ON all modules in the Bin will have the power ON, no matter whether the particular instrument is used or not.

3. Ensure the following setting, if not set it before any recording is made.

   INVERT/NON-INVERT toggle switch in position NON-INVERT
   DIFFERENTIATE/INTEGRATE selector in position OUT

Note: This OUT position will provide pass band, typically, 1 KHz to 35 MHz.

4. Set the coarse gain control to x10 or x20, based on the need of amplification.

Note: The 6 position coarse gain and fine gain control (continuously variable) together, provide variation in gain between x2 to x250.
In most of the experiments, the coarse gain setting x20 and the fine gain setting fully clockwise, doesn't need to be changed.

5.1.2 Adjustments on Constant-fraction discriminator

ORTEC 583 constant-fraction discriminator provides accurate timing pulses, for a wide dynamic range of input signals in the range 0 to -10 volts and generates fast negative output pulses.

1. When CFD is operated as an integral discriminator (INT mode), each input pulse exceeds the adjusted lower level threshold set on the LLD control.

Set the LLD level (threshold) depending on the experiment and the amount of dark counts by the cooled PMT at the instant of recording. eg., 1.06 on micrometer control knob when PMT is operating at -20°C or below.

2. When differential (DIFF) mode is selected, the input signal must exceed the lower level threshold and must not exceed the upper level threshold; in order to generate timing output pulses.

Note: Each of the thresholds have a range of -30mV to -5 Volts.

Set the ULD (upper level threshold)

eg., 4.76 on micrometer knob.

3. Ensure that the SRT/CF toggle switch is in position SRT.

Note: A slow rise-time (SRT) timing mode can be employed, to ensure that the leading edge time walk is not introduced by either the lower or upper level discriminator.
In SRT mode an input signal that does not cross the lower-level threshold before constant-fraction zero crossing time, will not produce a timing output pulse.

5.1.3. Settings for the PMT thermo-electric temperature controller

To keep the dark counts to a minimum value, it is necessary that photomultiplier tubes are cooled to -20 or -30 °C. A Pacific instruments thermo-electric PMT temperature controller is used.

1. Open the PMT cooling water valve & adjust the flow rate for a streak flow.

2. Turn ON the PMT high voltage power supply and apply at least 200 - 250 Volts to the photocathode.

3. Turn ON the temperature controller and set the temperature control at approximately 10 o'clock.

Note: The current supplied to the thermo-electric elements is controlled using the front panel temperature control. The current will be at minimum with the knob turned fully clockwise and at maximum when turned fully counter clockwise.

When the unit is first turned ON, since the PMT housing is warm, the thermo-electric elements will draw maximum current.

4. When the power switch is turned ON, the amber ON indicator of the switch will illuminate. The RED OVERLOAD indicator will also illuminate.

Depress the RESET button to start the temperature controller power supply.
Note: At this instant, the OVERLOAD indicator will extinguish.

5. After about half an hour or hour of operation, equilibrium will be established and the temperature indication will read approximately 0 °C.

Slowly rotate the temperature control counter clockwise to achieve colder temperatures.

A visual indication of temperature regulator performance and the current temperature is obtained with the front panel meter.

Note: with each setting of temperature in counter clockwise direction, colder temperatures are achieved.

eg., -20 °C or below within an hour.

CAUTION: For best long-term operation and maximum cooling, do not operate the system with the temperature control fully counter clockwise.

5.1.4. Setting of the PMT high voltage power supply

The PACIFIC instruments Model 204 is a high voltage power supply which provides regulated dc voltages to the PMT. This unit provides calibrated voltage steps of 100, 10 and 1 volts.

1. Turn ON the power supply.

2. Rotate the step voltage selector knobs to set any voltage desired.

Output voltage is the sum of the switch settings.

eg., voltage setting of 200-250 volts during PMT cooling and 1250 V - 1350 Volts during the emission/decay measurements.
3. A front panel meter displays the output voltage.
   Ensure the voltage selected through the panel meter.
   CAUTION: This instrument should always be turned OFF, the high
   voltage controls turned to OFF position when not in use.

5.1.5. Reading detection intensity through counter

The CANBERRA model 2071A dual counter-timer is used as an
event counter with a preset time.
1. Turn ON the counter.
2. Set 0.01 SEC/COUNT B/ 0.01 MIN switch to position COUNT B.
3. Set the thumb wheel switches to PRESET time positions.
4. Depress RESET button to reset both the counters to zero.
5. Depress the START/STOP switch to START which will start
   accumulation. When the preset is reached, channel A will contain
   the total counts accumulated and channel B will contain the time
during which the counts in channel A were accumulated.
   Note: The time shown will equal the preset time.
6. To display the contents of either channel, move the DISPLAY
   SELECT switch to either A or B.
   Note: Only one channel will be displayed at a time.
   The display will also show either CNT (counts) or SEC or MIN
   (the preset time).
5.2 Decay measurements

Single-photon counting technique is adopted for recording the decay lifetime of samples. The PMT output pulses are amplified by a factor x10 by ORTEC 9301/9301S preamplifier, filtered and shaped by timing filter amplifier (TFA Ortec 457) and timed by the CFD. The time-to-pulse height converter (TPHC) or the time-to-amplitude converter (TAC) measures the time interval between pulses to its start and stop inputs and generates an analog output pulse proportional to the measured time. The output of CFD is connected to the start input of the TAC.

Either HP 8013B pulse generator or another cooled PMT is used to derive the reference/stop pulse for the TAC; through ORTEC 416A gate & delay generator and ORTEC 436 100 MHz discriminator. As the procedures for adjusting the timing filter amplifier, constant-fraction discriminator are the same, they are not repeated here.

5.2.1. Adjustments on Gate & Delay generator

ORTEC 416A Gate & Delay generator accepts both positive and negative logic pulses, provides an adjusted delay for each input pulse, and generates output pulses with both polarities that have an adjusted amplitude and width. i) the logic pulse delay is adjustable from 0.1 μsec through 110 μsec,
in three overlapping ranges.

ii) the amplitude of both polarities of output pulses is adjustable within the range of 2 to 10 Volts.

iii) the output pulse width can be adjusted within the range of 400 nsec to 4 μsec.

1. Front panel POS input BNC connector accepts positive logic pulses of amplitudes in the range 2-12 Volts; 100 nsec minimum width and NEG input BNC connector, negative logic pulses from -250 mV to 12 Volts, 5 nsec minimum pulse width. Connect the input BNC connector to either POS input or NEG input depending on the type of input pulse.

   e.g., NEG input if derived from a reference PMT or either POS or NEG input when HP 8013B is used.

2. Set the AMPLITUDE such that the output pulse amplitude is in the range 2-10 volts.

3. Adjust the pulse width within the limits of 400 nsec to 4 μsec.

4. Select the 3 position locking toggle switch that selects the range for the delay control adjustment.

   1.1 μsec .....for range 0.1 through 1.1 μsec
   11 μsec ......for range 1 through 11 μsec
   110 μsec .....for range 10 through 110 μsec

5. Output is derived from the delayed marker BNC; which provides a fast negative NIM standard logic pulse at the
Delayed Marker pulse (to TAC stop input)

Gate input (from HP 8013B)

Pulse repetition rate: 25 KHz

Adjustment of delayed trigger pulse on delay generator (ORTEC 416A), compatible with TAC for decay measurements
end of the delay time, as the logic trigger pulse for the TAC, with fixed parameters

- output amplitude: -600 mV
- rise time: \(<10\) nsec
- width: \(<25\) nsec

5.2.2. Adjustments on 100 MHz discriminator

A 100 MHz discriminator (ORTEC 436) is used to shape the reference PMT output pulses from dc to 100 MHz. It generates only one signal for each input pulse, regardless of input pulse width.

i) this unit accepts input signals greater than adjusted threshold.

ii) discriminator level is adjusted in the range of 50 - 500 mVolts in 1000 steps.

1. Set the DISCRIMINATOR level.
   e.g., typically 7.0 on discriminator micrometer knob for minimum dark count.

2. Connect the 9301/9301S preamplifier output to the input BNC.

3. Slide the RESET two-position switch to either PROMPT or DELAY'D to define the input conditions to the discriminator (whether the input pulse needs to be stretched or not).

4. Output pulse is derived from either of the OUT 1 or OUT 2 BNC connectors, which are TAC compatible.
5.2.3. Adjustments on Time-to-amplitude Converter

The ORTEC 457 time-to-converter (TAC) measures the time interval between pulses to its start and stop inputs and generates an analog output pulse proportional to the measured time.

Start-to-stop time conversion is accomplished only after a valid start has been identified and after a stop pulse arrives within the selected time range.

Time ranges are switch selectable between 50 nsec to 80 μsec.

A strobe output pulse is obtained from stop input pulse. This strobed analog time signal is then furnished to a linear amplifier, where any low portion of the selected full range may be biased off and the remainder expanded by the post gain.

The gain factor is continuously variable in the range x0.5 to 1.5 in fine control and in coarse steps of x2.

1. Connect the delayed marker output from 100 MHz discriminator to the STOP input BNC connector.

2. Connect the OUTPUT from constant-fraction discriminator to the START input BNC connector.

Note: both start and stop pulses are fast negative logic pulses.

3. Slide the GATE switch to ANTICOINCIDENCE position.

4. Slide the STROBE switch to INT position.

Note: steps 3 & 4 can be skipped depending on setting.

5. Two of the front panel controls, TIME RANGE and MULTIPLIER determine the full scale time limit for time conversion.

Select the RANGE and MULTIPLIER as desired.
Note: The manual gives various combinations of switch position for different times.

No output pulse is furnished unless a stop signal is accepted within the selected full-range time. A stop signal is not effective unless it is preceded by a true start signal.

5.2.4. Adjustments on single-channel analyzer

ORTEC model 550 single channel analyzer (SCA) accepts either positive unipolar or bi-polar input and examines the amplitude of each input pulse and generates an appropriate positive logic output pulse which is equal to the difference between lower-level threshold (LLD) and the upper-level threshold (ULD) settings.

i) in the INTEGRAL mode, the SCA provides an output if the pulse amplitude exceeds the adjusted lower level threshold, set in the range 0 to +10 Volts.

ii) in the NORMAL mode, there will be an output if the input pulse amplitude exceeds the lower-level threshold, but does not exceed the upper level threshold.

Note: each threshold is adjusted independently in the range of 0 to +10 Volts, and the ULD level must be set higher than the LLD level to permit the SCA output to be generated.

iii) in the WINDOW mode, there will be an output if the input pulse amplitude exceeds the LLD threshold by an amount that is less than the adjusted window width.

Note: The range of LLD is 0 to +10 Volts and the range of the window
is adjusted from 0 to +1 Volt above the LLD level.

1. Connect the POS output of TAC to the dc INPUT BNC of the SCA.

2. Depending upon the need choose the mode of operation.
   Select and set the mode locking 3-position toggle key.

3. Set the LLD threshold level.

4. Set the ULD threshold level.

5. Connect the POS OUTPUT to the input BNC connector of the ORTEC 7100 multichannel analyzer.
6. Computer Software

'LUMINSPEC' -Recorder is an interactive program designed recording of emission spectra from any monochromator. This program is exclusively developed wherein the central computer IBM-PC interfaces with Modulynx Motion Controls computer/stepping motor for monochromator and Ortec 7100 Multichannel analyser.

This program is versatile and the user can modify certain commands and parameters to suit his experimental need and other instruments being incorporated.

'LUMINSPEC' -Analyzer is a program which enables the user work on the data obtained using the program LUMINSPEC-Recorder. This is a powerful analytical tool in working and computing on spectral data. This is also an essential component of the interface operation of different instruments and the computer.

'LUMINSPEC' -Plotter is a program designed to print and plot the data files and spectrum reconstructed from the data points. It enables the user to plot and view the spectra, prepared by this software in a variety of formats and over any wavelength range and intensity scales desired within the file.
6.1 MCA – IBM data transfer:

1. After the self boot of the computer, change the root directory by typing,
   
   CD SPECCONT < cr > and then BASICA < cr > or
   CD SPECCONT\BASICA < cr >.

2. Press F3 to load the desired file.
   
   Type in PASS < cr >

   Note: As soon as the file is loaded, the prompt O.K will appear.

3. Press F2 to run or execute the program.

   Note: The message -‘MCA-IBM DATA TRANSFER’ will be displayed on the computer monitor and the operating mode/command line on the screen of MCA flipped to I/O.

4. Within a few seconds, the data starts getting transferred the floppy disk in drive B.

   Note: The whirl and the indicator of disk drive B will be heard. As the data of 1024 channels takes about 1.2 minutes, at the end of data transfer a message indicating the end of program comes on monitor screen and the MCA I/O operation reverse video display will disappear.

5. Use the computer program to disable the serial remote control of the MCA or depress the RESET button.

6. Rename the data file in drive B.

   eg., Type in B: Rename spectrum.prn CdS-Ag-RT.Spec < cr >

   Note: Each time the data is transferred from the MCA will have the file name as 'spectrum.prn' as in the program and once transferred the
title must be changed, otherwise the data will be overwritten when used for next operation and the previous data file will be lost.

7. Type in DIR to see the directory of the files.

Note: This is recommended to ensure that transferred files have been renamed and no file named 'spectrum.prn' exists on the disk to avoid losing data files.

8. Change the disk drive back to D.

   Type in D: < cr >

9. Infront of prompt D:\specont\

   type in basica < cr >

10. Press F3 to load any file desired for the subsequent operation.

### 6.2 Data analysis

All the data from MCA (from 1024 channels) that are transferred to floppy disk in drive B of IBM-PC are in 128 rows and 8 columns along with additional three rows of non-data characters and one column of channel numbers. Whenever the data is transferred, it contains line feed, carriage return nul and many other non printing characters which must be removed before any further data analysis is done.
Flowchart showing data transfer program execution
1. After self boot of IBM-PC, change the disk drive to rename the file for data analysis.
   Type in B: < cr >
2. Type DIR < cr > to choose a file.
3. Rename the file
   eg., type RENAME CdS-Ag-Spec test.prn
4. Change the disk drive again to D
   Type in D: < cr >
5. Type in CD SPECCONT\BASICA < cr >
6. Press F3 to load the file RECONST.BAS

Note: This program is exclusively written to delete the non printing characters, line feed and carriage return characters.
7. Press F2 to RUN the program.

Note: The program RECONST reads the 'test.prn' file and deletes the non-printing characters and writes it back in drive B as the file 'spectrum.prn'.
8. For further analysis, only the data values, not the information of the channel numbers or any other letter character information is needed. And also the data needs to be arranged in a linear array than as a 128 x 8 matrix.

   To do that use the program LNAR.BAS.

   Press F3 and then LNAR < cr >
9. Press F2 to RUN the program.
10. The program first reads the data from the file 'spectrum.prn' from drive B. As the program is being executed the following
messages for successful operation will be displayed.

** end of reading data **

** end of data arrangement in a linear array **

Low Num = Channel Number =

High Num = Channel Number =

sample interval ?

Type in 1 (cr) as an answer for sample interval.

Note: This will write back the data values in a linear on the disk in

drive B as file LNAR.DIF

11. Type SYSTEM (cr)

Note: You will see the prompt as D:\SPECCONT\

12. Type B: (cr)

13. Rename the file LNAR.DIF

eg., type in Rename LNAR.DIF CdS-Agl.dif (cr)

14. Type DIR to ensure that no file with the following set names exist

and all are renamed.

test.prn

spectrum.prn

lnar.dif as otherwise, when the above sequence performed on

the new data file the previous data will be lost.

6.3 Use of programs PEAKFIND and DECONVOLUTION

These programs are RUN to find the emission peaks and the decay

lifetimes of luminescent samples, from the recorded data points.
7. Plotting

The recorded spectrum is reconstructed using SYMPHONY graphics software and plotted by HP 7470A plotter. The spectrum is constructed as a XY graph using the linearized data values and the x-coordinate values defined as the range of wavelength scanned.

**First to create the graph:**

1. After the self boot of IBM-PC, infront of prompt D:\
   Type in SYMPHONY < cr > to access symphony.
2. Next to several symphony installation messages, when the command line appears in reverse video high lighting SYMPHONY,
   then press < cr >
   Press < cr > once again when the prompt asks for it.
3. Press F9 key to retrieve the desired file.

**Note:** For the plotting convenience, already three plotting work sheets have been created.

- EASYPLOT.WRK for the range 480 - 800 nm
- LOWTEMP.WRK " 500 - 820 nm
- DYELASER.WRK " 560 - 880 nm

**Note:** The above wavelength range is regularly used.

4. Once the monitor screen is filled with pre-recorded data values, to plot the spectrum with specific data values
   Use arrow key -> to move to column B
5. Use the downward arrow key to be on the start wavelength row in column B.
6. Press F9 to import data values from drive B
   Press FIS < cr > which will import structured file.

7. Press DELETE computer key 5 times till beeps are heard.
   then type B: < cr >
   Note: All the files on floopy disk in drive B will appear on top
   command line of work sheet. Use <- -> arrow keys to select the
   specific linearized data file (eg. Cds-Ad1.dif) and < cr >. The
   symphony program prompts WAIT as it is reading data from file.

8. Once the new data values are in column B and the symphony
   prompt displays SHEET
   Press F10 to view the graph.
   Type in GP < cr > to preview the graph
9. Type < cr > to get back to command line.
10. Use <- -> arrow keys to alter any parameters like
    e.g., TITLE, X-AXIS, Y-AXIS, Y-SCALE in 2nd setting or any relevant
    parameters in 1st setting.
11. Use HOME key or <- arrow key to preview the graph with all the
    necessary details incorporated within.
12. Type in I < cr > to perform image save operation.
13. Usually the symphony comes with a choice of D drive to save the
    image. But it is desirable to save the graph on the floppy disk itself.
    Hence change the drive to B.
    Press DELETE key till beep is heard and type B: < cr >
14. Give a name to the graph generated.
    eg., Type Cds-Ag1.PIC < cr >
Start

Rename the desired file

Load & Run LNAR

reading data?

no

yes

write data in a linear array

EXIT basic and access SYMPHONY

Retrieve file WRK

Import linear data

Preview graph

Changes??

yes

no

Save

EXIT SYMPHONY

(as spectrum prn)

EASYPLOT.WRK
LOWTEMP.WRK
DYELASER.WRK

sample description
X-Y scales range, legends
15. Once the graph is saved press END <cr> or Q <cr> to quit creating graph.

16. Press F9 and type E <cr>, Y <cr>, E <cr> to exit from symphony.

   Note: After exit from symphony the prompt will be D:

Next to plot the graph:

17. Type in CD LOTUS\GRAPH <cr>

18. To select the graph for plotting, when the reverse is, SELECT press RETURN key.

19. Use the downward arrow key to choose the graph to be plotted and press spacebar, to indicate the choice.

20. Insert the paper and pen in the holder turn ON the plotter.

21. Turn the computer communication control to position 1.

22. The lotus graphics menu displays the file chosen for plotting.
   Use -> arrow key to move to GO.
   Press RETURN key to execute the plotting program.

23. Press SPACEBAR twice when the beep is heard to load picture file from floppy disk to plotter memory and then to execute.

24. Once the graph is plotted, press paper feed back on plotter and lift the paper hold arm.
Flowchart showing plotting program execution
8. **Low temperature measurements**: 

8.1 **Vacuum system**: 

1. Plug in the R2 rotary pump  
2. Open the 'roughing' valve  
3. Switch ON the thermocouple gauge indicator and select indication to select the gauge in cryostat outer jacket/main vacuum line.  
4. After about 5-10 minutes, read the vacuum indication when it is between 5-10 torr, close the roughing valve.  
5. Turn ON the fan and the diffusion pump and open the 'foreline' valve.  
6. Switch ON the Ionization gauge and open the 'hi-vacuum' valve.  
7. In about 3-5 minutes, once the oil is heated up, the vacuum level will change dramatically towards higher vacuum (eg, $10^{-4}$). The thermocouple gauge can no longer resolve the vacuum level. To read the vacuum, press the 'Filament' RED button on ionization gauge. 

Note: The filament red button trips-off and doesn't indicate any vacuum level if the vacuum is bad or not below $10^{-4}$.  

8. Keep the thermocouple gauge indicator ON, even though indications can not resolve higher vacuum, to indicate the leaks if any or vacuum ruptures. Note the increasing vacuum and change the indication range to $x10^{-5}$ or $10^{-6}$ suitably to read the value precisely.  

9. Fill the diffusion pump cold trap with liquid nitrogen to achieve vacuum below $5 \times 10^{-5}$. 
Note: Turn the range switch to 'Degauss' for a few seconds and the higher vacuum will be achieved rapidly.

Within about 15-20 minutes $1-2 \times 10^{-6}$ torr is reached.

10. Open the cryostat main jacket vacuum valve.

Note: If the vacuum in cryostat outer jacket is bad or lower than the pumping system, there will be a reduction in vacuum indication both in ionization gauge and in thermo couple gauge indicator (marginal).

Continue pumping until a very high vacuum is reached.

11. Close the cryostat vacuum valve.

8.2 Liquid helium cryostat:

To operate variable temperature tail.

8.2.1. Cool down

1. Start the gas flow pump.

2. Open the VC30 valve.

3. Open the needle valve.

Note: The coolant (liquid helium) will now start to flow through the exchange chamber and into the sample chamber. Within a few seconds, there will be a low indication of temperature (eg., 4.2 K) and the sample space being filled with liquid helium.

4. Read the temperature in the temperature controller.

5. Initially the flowrate will drop below 1 litre per hour, but will increase to 2 litres per hour as the temperature lowers.
OXFORD Instruments Liquid Helium Cryostat
Note: The pressure read on the VC30 gauge will be about 0.25 bar below atmospheric, when the flowrate is maximum.

6. Once the indicated temperature is 3.7 K or below, and sample space is being filled with liquid helium, the coolant flow can be reduced gradually by adjustment of the needle valve.

8.2.2. Temperature control

a) above 3.7 K

1. Fully open the VC30 valve and set the minimum flow for base temperature of about 3.7 K by adjusting the needle valve.
2. The cryostat needle valve can be left at this setting.
   Adjust the VC30 valve to set minimum flow at any desired higher temperature.
3. For automatic heater control, set the required temperature on the controller and switch to the 'AUTO' mode.

b) below 3.7 K

1. Close the VC30 valve and start the high throughput rotary pump.
2. Close the needle valve (rotate fully clockwise).
3. Open the valve to the sample space pumping line.
4. Temperature control below lambda point (boiling point) of liquid helium is obtained by throttling the flow of the high throughput pump.
Flow circuit for VC 30
Note: To read the actual temperature refer to the helium vapour pressure curves of the manual.

5. To refill the sample space, open the needle valve observe the pressure gauge on the pump. When the pressure is approximately 80 torr with a slight oscillation on the gauge, close the needle valve gradually, as the sample space will be full at this instant.

6. Close the needle valve fully clockwise and pump collected helium to base temperature (1.2 - 1.5 K).

8.2.3 Changing samples

Samples can be changed at low temperatures, provided there is a slight over pressure of exchange in the sample space. This prevents air and moisture from condensing in the cryostat.

1. Open the helium gas bottle main valve and the valve (purge line) mounted on the wall.

2. Set the reducer gas pressure to 2-3 psi.

3. Close the sample space pumping valve.

4. Open the helium purge valve, mounted on cryostat holding frame, to allow helium gas to flow through the sample chamber.

Note: Observe the increase of pressure in the sample space and close the helium purge valve when the pressure is atmospheric or well above 750-800 mm of Hg.

5. Adjust the purge valve for reduced continuous flow of helium gas for a steady over pressure.

6. Unscrew slightly the sample holder O-ring lock knob and remove
the sample holder and plug the sample space with a rubber cork in the O-ring seal, on top of the cryostat.

7. To re-insert the sample holder, remove the rubber cork insert the sample holder and tighten the sample space/O-ring by turning the black knob gently.

8. Close the purge valve completely and the valve on the wall.

9. Open the sample space vacuum valve and read the pressure which should be back to the original value (0.1-1 mm of Hg). If not, check for possible leaks after changing samples.

8.3 Temperature controller

Temperature controller is an instrument designed to measure the temperature of a system and to maintain it at some required temperature.

Measured temperature is compared with a required temperature and an error signal is generated proportional to the temperature difference. This forms the input to a controller. The controller regulates the power fed to a heater, or other means of varying the system temperature.

8.3.1 Measurement of temperature

1. Turn ON the temperature controller.

2. Press MEAS button.

3. The display will indicate the sensor temperature.
Note: If the sensor temperature is outside the working range of the instrument, the display will flash.

8.3.2 Setting a required temperature

1. Press the SET button. The display will indicate the set temperature.

2. Rotate the SET knob (clockwise or counter-clockwise) observe that it is possible to set a required temperature.

3. Release the ERROR switch and note that the error meter swings to the right when the set temperature is below the measured temperature and to the left when it is above.

Manual control, automatic control and setting PID controllers are explained in detail in the instrument manual. It is recommended that the user be familiar with the various controls and sequence of various setting.
Front panel controls of OXFORD instruments temperature controller
SYSTEM SHUT DOWN PROCEDURES

1. Argon Ion Laser

1.1 Adjust current control counter-clockwise for minimum (zero) current.
1.2 Adjust the SERVO control fully clockwise.
   Note: omit this step, if SERVO mode is not used.
1.3 Push the circuit-breaker to OFF position
   Note: At this instance all the 3φ indicator lamps are off and the safety/timing indicator flips to GREEN lamp.
1.4 Turn OFF the start timing/indicator unit
1.5 Close the front shutter of laser head
1.6 Switch OFF the 3φ buck-boost power transformer
1.7 Switch OFF the power to the booster water pump
1.8 IMPORTANT: Allow at least 10-15 minutes after shutdown of the system before closing the water supply.

2 Nitrogen Laser

2.1 Reduce the main HIGH VOLTAGE control to zero
2.2 Depress the MASTER STOP control
   Note: The MASTER STOP control may be depressed at any time
2.3 Set the MODE selector to TRIGGER OFF
2.4 Close the Nitrogen cylinder main valve and set the regulator to zero output.
2.5 Close the Nitrogen INPUT valve
2.6 Allow the channel pressure to drop to 0 mm. Hg.
2.7 Close the VACUUM valve
2.8 Turn OFF the power to the complete laser system.
2.9 Turn OFF the power to the vacuum pump and bleed the air
2.9.1 Slowly open the VENT valve to release the channel to atmosphere
2.9.2 Turn off the cooling water.

3 NIM Bin

3.1 Reduce the photomultiplier high voltage to zero and turn OFF the H.V. power supply.
3.2 Turn the PMT temperature controller to 10 o'clock position and turn OFF the Unit
3.3 Turn OFF the Nim Bin power supply
3.4 IMPORTANT: When stepping motor MODULYNX controller is not in use switch OFF the power to the controller.
   If the stepping motor is used, switch OFF the controller power supply.
3.5 Close the photomultiplier cooling water supply
3.6 Switch OFF the Nim Bin cooling fan

4. Vacuum system

4.1 Ensure that, the cryostat main vacuum/outer jacket valve is closed.
4.2 Close the HIGH VACUUM valve
4.3 Turn OFF the diffusion pump
4.4 Turn OFF the Ionization Gauge
4.5 Turn OFF the thermocouple gauge
4.6 After about 10-15 minutes, close the 'foreline' valve
4.7 Switch OFF the rotary pump
4.8 Open the air-bleeder
4.9 After another 10-15 minutes or when the diffusion pump is cooled down, turn OFF the fan.

IMPORTANT: The start-up and shut down procedure has to be strictly followed each time.

5. Liquid helium cryostat

At the end of an experiment, or at any time, it may be necessary that the system may be allowed to warm-up to room temperature by either leaving the helium and nitrogen to boil-off naturally or by back transferring the fluids into their respective storage vessels.

5.1 Set the temperature controller to room temperature and monitor the steady rise in temperature.
5.2 Ensure the over pressure relief valve functioning
5.3 To accelerate the warm-up of the system, helium or nitrogen gas is introduced into the system vacuum space.

Note: This should be done gradually, since it may produce violent boil-offs of the remaining fluids.
5.4 Either open or adjust the over-pressure relief valve

Note: It is absolutely essential that there are no trapped volumes of gas in the cryostat during warm-up.

5.5 Slightly over-pressure the sample chamber with helium or nitrogen gas to avoid contamination of sample chamber with atmosphere and moisture.
REFERENCES:

- for figures and operating instructions.

1. EG & G ORTEC Product Catalog (1983)
2. EG & G ORTEC Instrument Instruction Manual
4. Intra Action Corp., Instruction manual
6. AVCO Everett Research Lab., Instruction Manual
8. CANBERRA Operator’s Manual
9. The SUPERIOR ELECTRIC, Modulynx Motion Control,
   Instruction and Programming Manual
10. HP Operating Instructions
11. IBM-PC DOS/BASIC Manual