Summer 1971

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Recommended Citation

Everett, Donald Edward, "Laser induced optical modulation in zinc selenide" (1971). *Master's Theses.* Paper 339.

LASER INDUCED OPTICAL MODULATION IN ZINC SELENIDE

BY

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A THESIS
SUBMITTED TO THE GRADUATE FACULTY
OF THE UNIVERSITY OF RICHMOND
IN CANDIDACY
FOR THE DEGREE OF
MASTER OF SCIENCE IN PHYSICS

AUGUST 1971

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III. INTRODUCTION

In the growth and analysis of crystals, there is much need for a non-destructive impurity and/or defect test. It must be one of simplicity and accuracy. This is one potential of the work reported in this paper on Light Induced Modulation and Absorption in Zinc Selenide. In solid state physics, intense optical excitation of certain translucent crystals, as in the II-VI semiconductor category, has been found to change the transmission of visible light. In 1967, E. J. Conway[1], at NASA-Langley, first observed and reported laser modulation of optical absorption in cadium sulfide. Later, in 1969, work was begun at Langley using zinc selenide by R. W. Major, whose work led to the investigations reported here.

In the work of Conway, light induced modulation of absorption, or, as he called it, LIMA, consists of a monochromatic primary light beam being modulated in a cadium sulfide crystal by a second more intense light beam, such as a laser. In his spectral experiments, he found cadium sulfide to have two LIMA maxima. That is, for two wavelengths the change in the coefficient of absorption has increased values. These were observed at approximately 800 nanometers and 1400 nanometers, which correspond very closely with known maxima of photoconductivity data in cadium sulfide. Conway also noted that α in cadium sulfide depended linearly with the laser intensity in the bleached range, 650 nanometers, but was not linear in the increased absorption region around 740 nanometers. This is thought to be due the transition from monomolecular to bimolecular recombination kinetics. From Kittel[2], the relationship for transmitted light intensity, I, is given in terms of the incident light, I_0, multiplied by the exponential of the optical absorption coefficient, α, times the distance, x, into the crystal, for which the value of I is wished. This is the classic equation $I = I_0 e^{-\alpha x}$.

The experiments reported here with zinc selenide have a two-fold purpose. First, by using basically the same experimental set-up as Conway did, we are attempting to duplicate this LIMA using zinc selenide instead of cadium sulfide. Unlike his set-up, primarily one laser chopping frequency was used. Also, only one laser wavelength, 632.8 nanometers, was available, where Conway used lasers of wavelengths 647.1 nanometers and 530.8 nanometers. Another main difference is that in earlier works by Conway, laser pulse duration was of the order of 40 milliseconds, whereas the present duration is approximately 2.5 milliseconds. It was observed that the crystal became saturated after approximately 2 milliseconds, therefore, the wasted saturation time was reduced.

The second objective, once LIMA was produced,was to attempt to investigate further and explain the electron redistribution processes over possible defect levels caused by laser excitation in the band gap. Since the band gap of zinc selenide is approximately 2.7 e.v. and the laser energy is 1.96 e.v., then it is not possible to generate direct electron transition from the valence band to the conduction band. In order to perform this direct process, the photon energy would have to be that of the band gap. This almost necessitates the discussion of impurities or defects in the sample to explain the optical modulations found in zinc selenide, since there is clearly photon absorption by some process. Such defect levels in the band gap would make possible laser absorption by redistributing the electrons over these intermediate levels. This, in turn, supplies the conduction band with "free" electrons. The question arises; how do these electrons and holes recombine in order to establish equilibrium both during laser illumination and after laser cutoff? One simple candidate is bimolecular recombination. By this method, illumination of the crystal results in the excitation of electrons from the valance band to the impurity level, where it is possible for an electron from the conduction band to be captured by impurity traps such as positive impurity ions. Now the electron has two alternatives. It can make a transition back to the valence band and recombine with a hole, which would be the same as a capture of a hole by the impurity trap. Alternatively, the electron, through thermal excitation which, at room temperature, is small compared to the band gap, can transfer again to the conduction band. This is improbable since the thermal energy is of the order of .026 e.v.. The second absorption of a photon by this same electron would have more than sufficient energy for the transition, but the probability of this occurring is small, also. The second alternative would be the excitation of an electron from the valence band directly to the defect level between the bands. The preceding types of electron and hole transfers are for a semiconductor with one type of trap. This is the simplest case. Some defect centers, such as copper impurity atoms, may be neutral, singly, doubly or triply, negatively charged.[3] These situations greatly increase the potential complexity of the problem, since with each type of center there will be associated a correspondingly different energy level in the forbidden band. This, in turn, greatly increases the possible number of excitation and recombination processes which must be considered.

In the area of photoconductivity, the illumination of a sample causes an increase in the number of mobile charge carriers in the crystal. This is done by the photon being absorbed by the crystal by raising an electron to the conduction band. The electron-hole pair created by this excitation will later recombine but will be influenced greatly by the presence of traps. A trap is usually an impurity in the crystal which is capable of capturing an electron or hole for a period of time.

Kittel's[2] relationship for the rate of change of the electron concentration may be explained as follows. Let N be the number of electron trap levels per unit volume of a certain crystal. The relation may be simplified by saying that the recombination coefficient A is the same for electron-hole recombination as for electron-trap capture. Letting n be the electron concentration in the conduction band, and L be the number of photons absorbed per unit volume of sample per unit time, one has the equation: $dn/dt = L - An(n+N)$. This relation does not take into account possible thermal ionization of carriers from traps to the conduction band. For a steady state situation, $dn/dt = 0$, the relation reduces to $n_o(n_o+N) = L/A$. There are two cases to which this may be reduced. The first one is where the electron concentration, n_o, is much less than the trap concentration, N. Therefore, the limit $n_o \ll N$ results in $n_o = L/AN$. This would suggest that there exists a linear relationship between the initial part of the laser rise time and the corresponding change in LIMA. The next case is at a higher level of illumination where $n_o \gg N$. Now the relation may be simplified to $n_o = (L/A)^{1/2}$. This corresponds to where the laser has reached a higher illumination level. Thus the change of optical modulation varies as the square root of laser intensity. The decay of the system may be predicted by solving the general equation where $L = 0$. The solution is $\log((n+N)/n) - \log((n_o+N)/n_o) = NAt$.

Since optical saturation was found by Conway to occur in considerably less time than 40ms., then one need not look at the entire signal. Therefore, to obtain better resolution, the time base was shortened to 10ms., 5ms., and 2ms., while maintaining the "laser-on" time at about 2.5ms. The laser rise time is of the order of 40µs. These shorter time bases give a better chance to look closer at the rise, saturation, and decay. The time base is an important factor because the time required to recover a desired signal using this detection system is directly proportional to the duration of the signal. Therefore, by reducing the initial signal to one of shorter duration, without losing the desired points of interest, one can examine the same data but with less time required to obtain it.

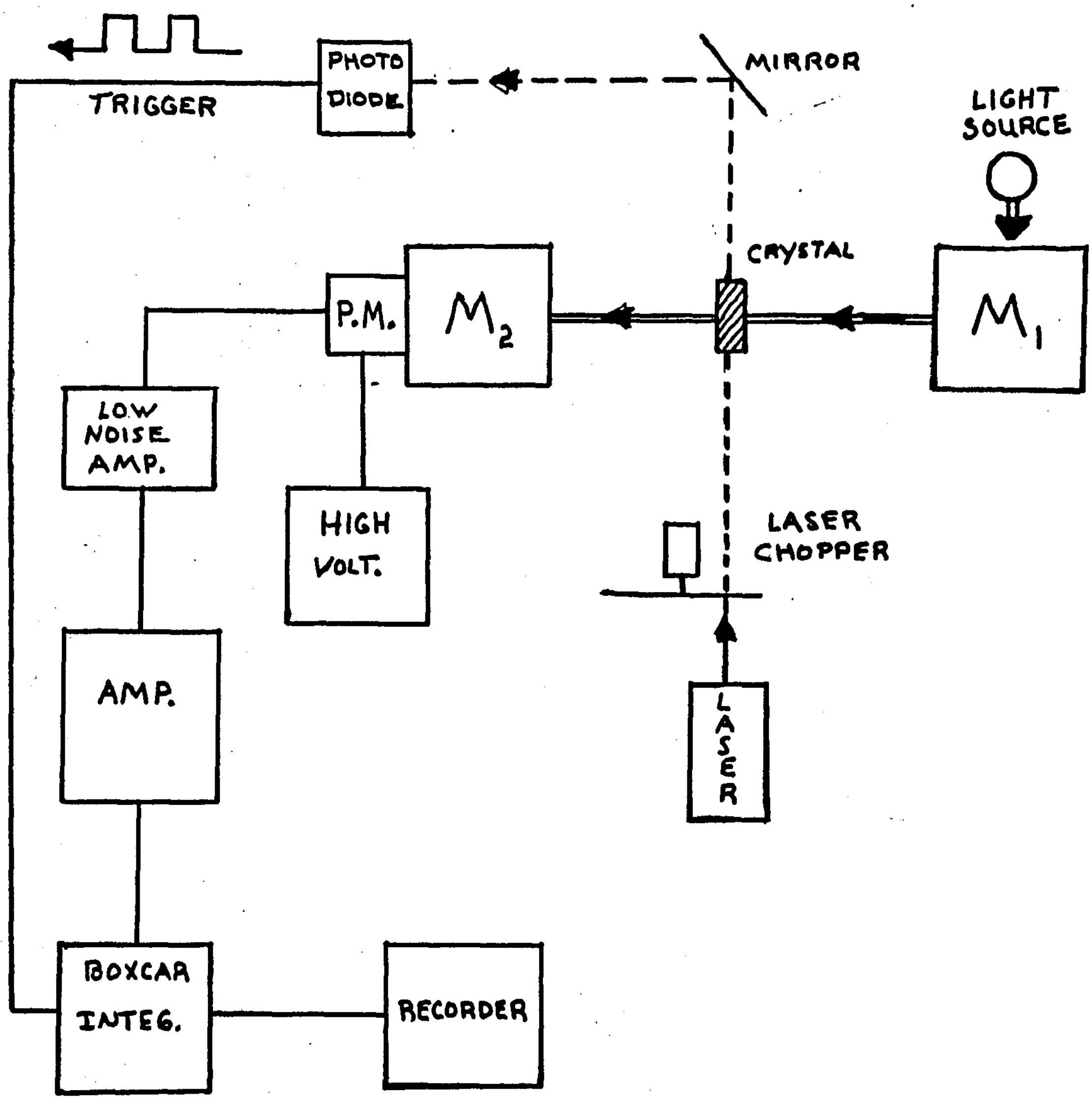
IV. EXPERIMENTAL DESIGN, INSTRUMENTS, SCHEMATIC

The experimental apparatus may be divided into three basic systems. They are the transmission, excitation, and detection systems. Refer to figure I for the experimental setup diagram.

The transmission system is made up of the primary light source, source monochromator, and collecting lenses before and after the crystal. The primary light source is a tungsten filament type drawing about three amperes. The source monochromator is of the grating type made by Bausch and Lomb. The lenses are used to focus primary light on the crystal and from there onto the receiving monochromator.

The excitation system is composed of the laser, light chopper, and the zinc selenide crystal. The laser is a 6mw. He-Ne C-W unit made by Spectraphysics. Its wavelength is 6328Å. The laser beam is chopped at approximately 57 Hertz by a mechanical chopper consisting of a disk with two slots cut out, mounted on a shaft of an electric motor. In later data runs, the chopper frequency was increased to 114 Hertz by the addition of two more slots. The zinc selenide crystal is the vehicle in which the modulation occurs. The sample used has a purity of 99.99%. It is a quarter inch square and one sixteenth inch thick.

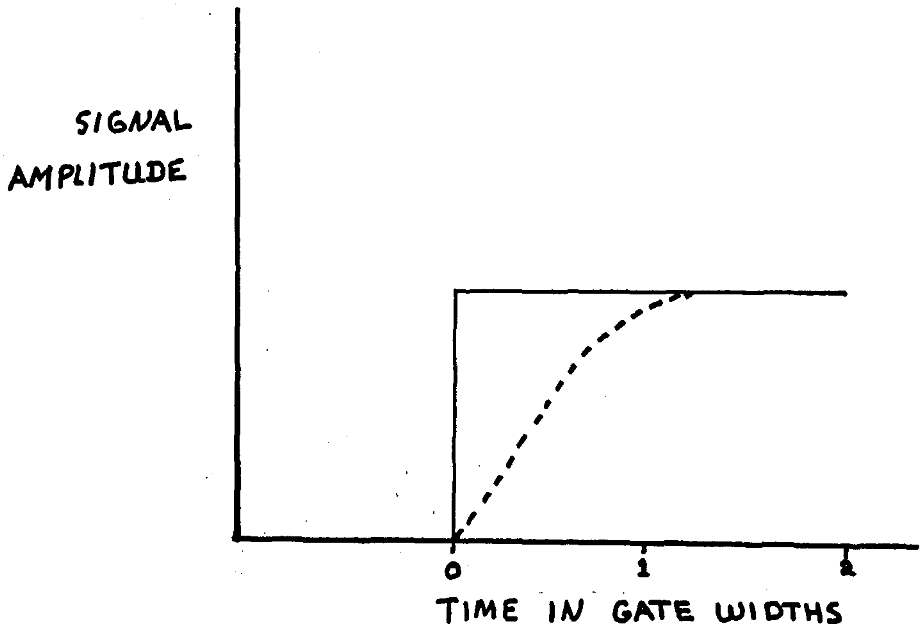
Figure I. EXPERIMENTAL SETUP



The detection system is made up of the receiving monochromator, photomultiplier, D.C. voltmeter, photodiode, low noise amplifier, box-car integrator, and chart recorder. The receiving monochromator is also of the grating type, adjusted to the primary light wavelength. This particular one is made by American Instrument Company. The photomultiplier tube is a RCA IP-28 which has a S-5 spectral response curve, thus having its peak intensity at 4500-5500 Å, the range of primary interest. This unit is mounted on the receiving monochromator in a light tight metal box. Due to the low signal magnitude, on the order of 10^{-3}V, the signal must be amplified so that the integrator will sense it, since the input sensitivity of the CW-1 is on the order of 1 volt. The unit used is a low noise, solid state amplifier with a maximum gain of 10^4. It also has low and high frequency cut-off circuits. With this amplifier just the signal within the appropriate band will be amplified. From the amplifier the signal goes to the boxcar integrator. The P.A.R. model CW-1 boxcar integrator utilizes a sampling and averaging technique to extract synchronous waveforms from noise. Since the signal which enters the CW-1 is a combination of the true waveform and, hopefully, random non-synchronous noise, all signals which are notsynchronous with the signal will be averaged out over a period of time. The length of time required to obtain a good signal to noise ratio on the recorder will vary inversely with the signal to noise ratio of the signal fed to the integrator. In other words, the greater the signal to noise ratio, the less integrator scan time required. If one takes the output of the integrator to a recorder, the trace will be that of the true waveform without much of the noise. In order for the integrator to interpret properly the input signal, the integrator must be synchronized with the laser pulse. This is done by a circuit which involves a diode upon which the laser beam, which has transversed the crystal, has been focused using a small spherical mirror. Each time the laser is "on", it energizes the diode which, in turn, sends a triggering signal to the integrator. This unit, as well as the chopper, was designed and built by the author.

In the setup there are a few areas where problems do arise. First of all, in order for LIMA to occur, the laser light and primary light must intersect in the same volume element in the crystal. Therefore, the alignment and focusing of the primary light on the sample is critical. Likewise, the alignment of the laser must be such that the beam is incident normally on the crystal edge and transverses the entire depth uniformly. Also, the D.C. power for the primary light must be constant with no fluctuations. Since the magnitude of the signal voltage is so small, on the order of a few thousandths of a volt, this presents another problem. With such a small signal any electronic noise, capacitance, or ground loops, will overshadow it easily. This has been a point of much concern. Even though the noise is not synchronous with the signal, it may contain spikes which can overdrive the amplifier. Another experiment limitation is imposed by the boxcar integrator itself. The instrument requires a minimum of one gatewidth to respond fully to a simple step function. For the data taken in earlier phases of this experiment, the gatewidth was approximately .9 milliseconds. As an illustration, from figure II, the dotted line represents the signal reproduced by the integrator. The solid line is the input to the integrator. The laser pulse rise time is of the order of 40 nanoseconds, which, of course, is a step function as seen by the integrator. But the modulation resulting from this pulse does not display such a rapid measured rise rate. Since longer scanning times are required when using narrower gates, it is rather difficult to shrink the gate much further without decreasing the time base. In later data, this was done. The time base was reduced to as short as 2 milliseconds and the gate width reduced accordingly to .3 milliseconds. This was done mainly to study the rise characteristics of LIMA with better time resolution.

Figure II. REPRODUCTION OF A STEP FUNCTION THROUGH THE BOXCAR INTEGRATOR RELATIVE TO THE GATE WIDTH



V. RESULTS

LIMA measurements have been concentrated on the overall signal behavior extending to about four times the laser pulse duration. The laser pulse duration is 2.5 milliseconds and the longest time base is 10 milliseconds. A few data runs have been made using shorter time bases, as short as 2 milliseconds, when studying the excitation kinetics. The modulations were found to be relatively small, approximately 5 parts per thousand, but reproducible. LIMA pulse shapes were measured at light wavelengths of 4800, 4900, 4930, 5000, and 5100 Å. Referring to figure III, one can see that the signal has values both positive and negative. In other words, there is a polarity reversal in their decay. This change from positive to negative was also evident in later runs with shorter gate widths and therefore, better resolution. Also, it must be noted that, in all cases, saturation is reached after the laser pulse has terminated. Referring to figure IV, which is a plot of LIMA for two separate runs of 4800 Å, one can see that the two curves are slightly different. Both runs were made with the same experimental setup and the same integrator characteristics. Therefore, the difference must be due to variations in the optical geometry. For example, in one run,

Figure III. LOW RESOLUTION LIMA EFFECT AT 57 HERTZ, .9 MS. GATE WIDTH, 10 MS. TIME BASE

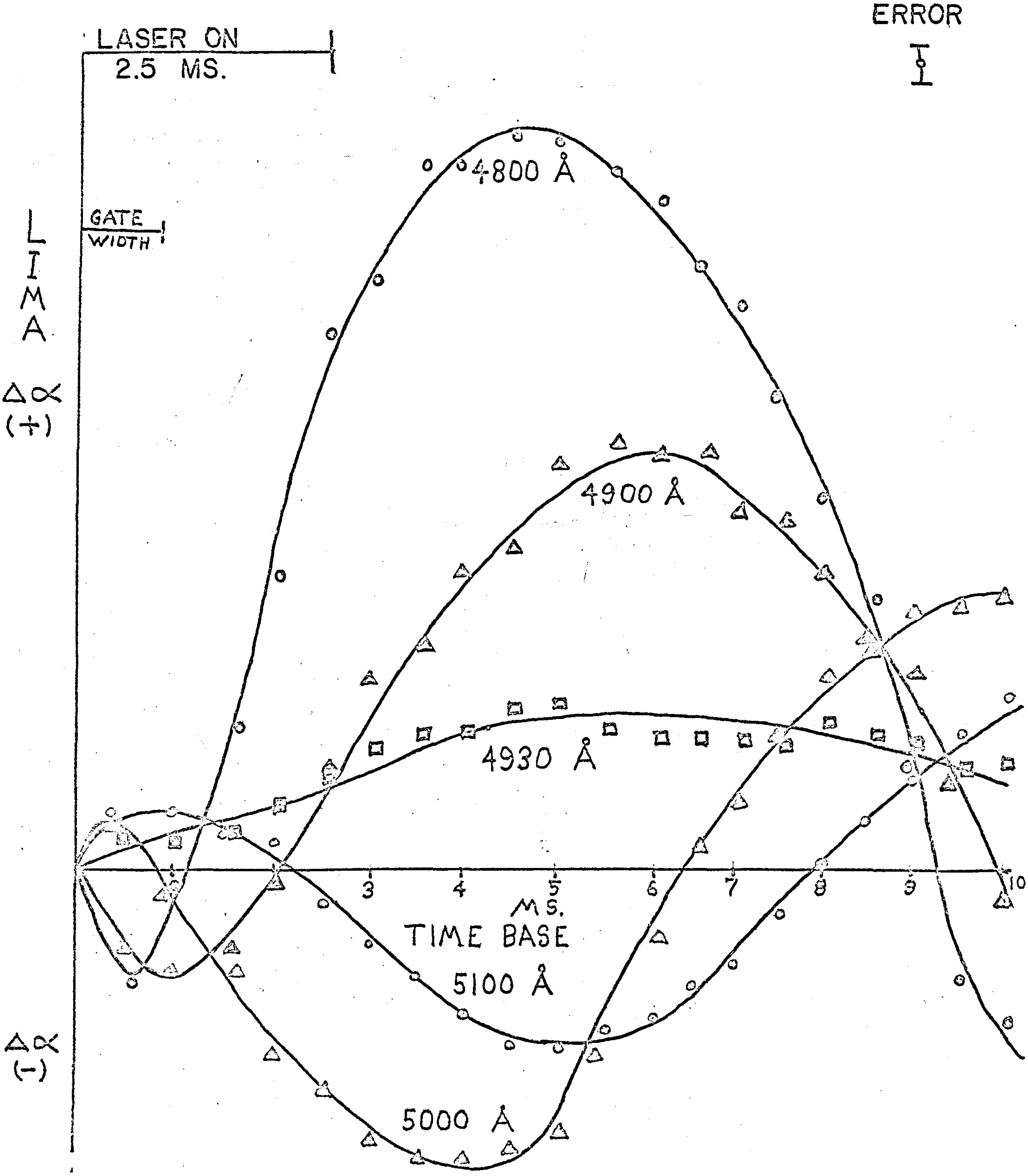
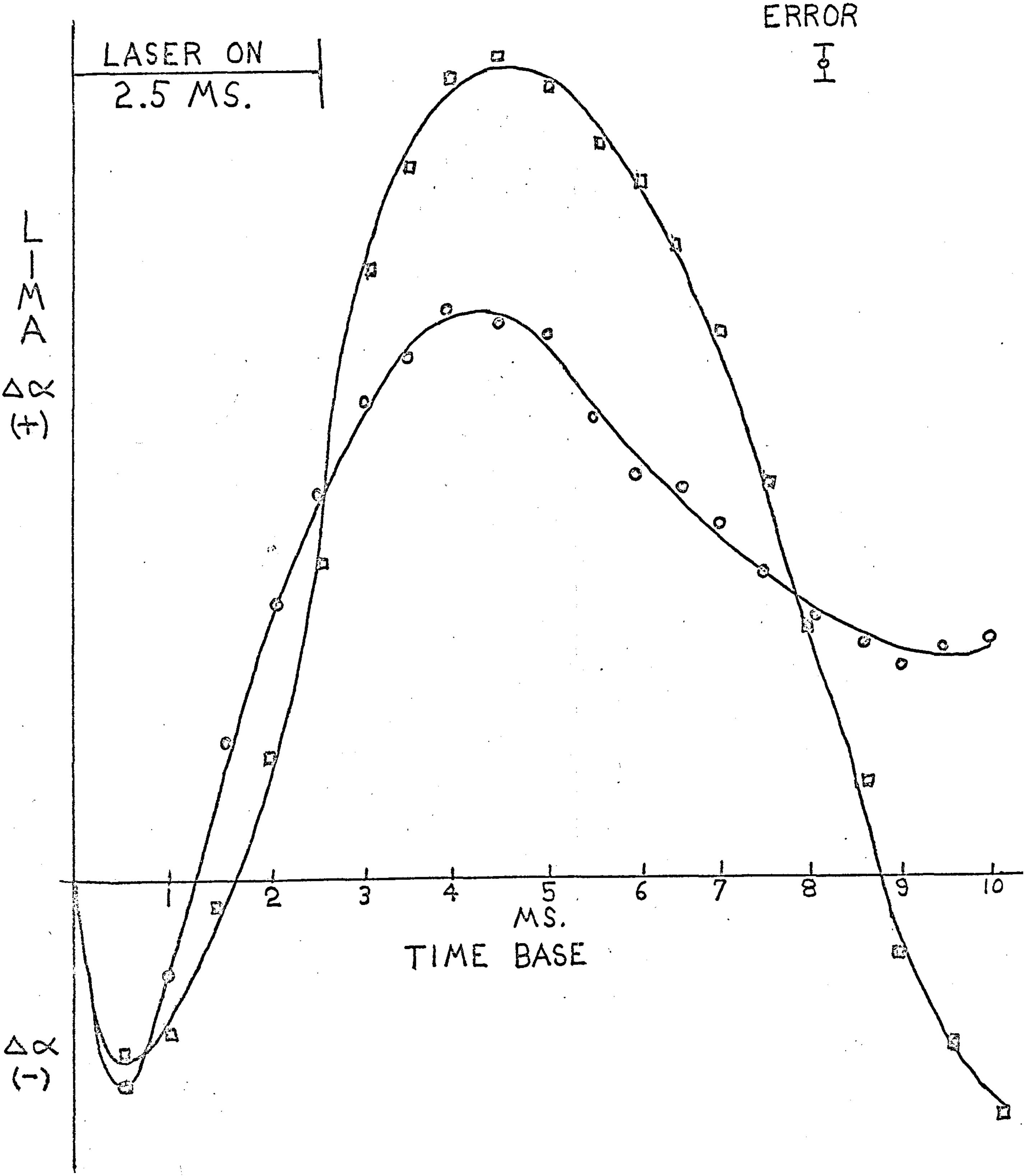


Figure IV. COMPARISON PLOT OF OBSERVED LIMA AT 4800 Å



the laser beam may have been a little off center and, therefore, the relative intensity of the beam was reduced and thus the LIMA effect itself is altered.

The normal procedure was to make an initial run having both laser and primary light incident on the crystal. Then a "background" run was made without the laser incident on the sample. The two records were compared and the resultant difference was the modulation. The difference was computed by taking selected values at .25 ms. intervals for both "foreground" and "background", and then subtracting the corresponding values of the "background" from the "foreground". This "background" run was found necessary in order to facilitate removal of any synchronous noise. More often, a slight D.C. drift was evident in this "background" run and had to be taken into account. This D.C. drift was probably caused by the second stage amplifier. The synchronous noise is the resultant effect of any electrical pulse or mechanical vibration synchronized with the laser pulse. In most cases, the correction via subtraction of "background" was small, on the order of 10% of signal magnitude.

This method was used for each of the five wavelengths concerned. It was found that the dominant amplitude of the signal reverses polarity somewhere between 4900 and 5000 Å. This is the prime reason additional measurements were made at 4930 Å.

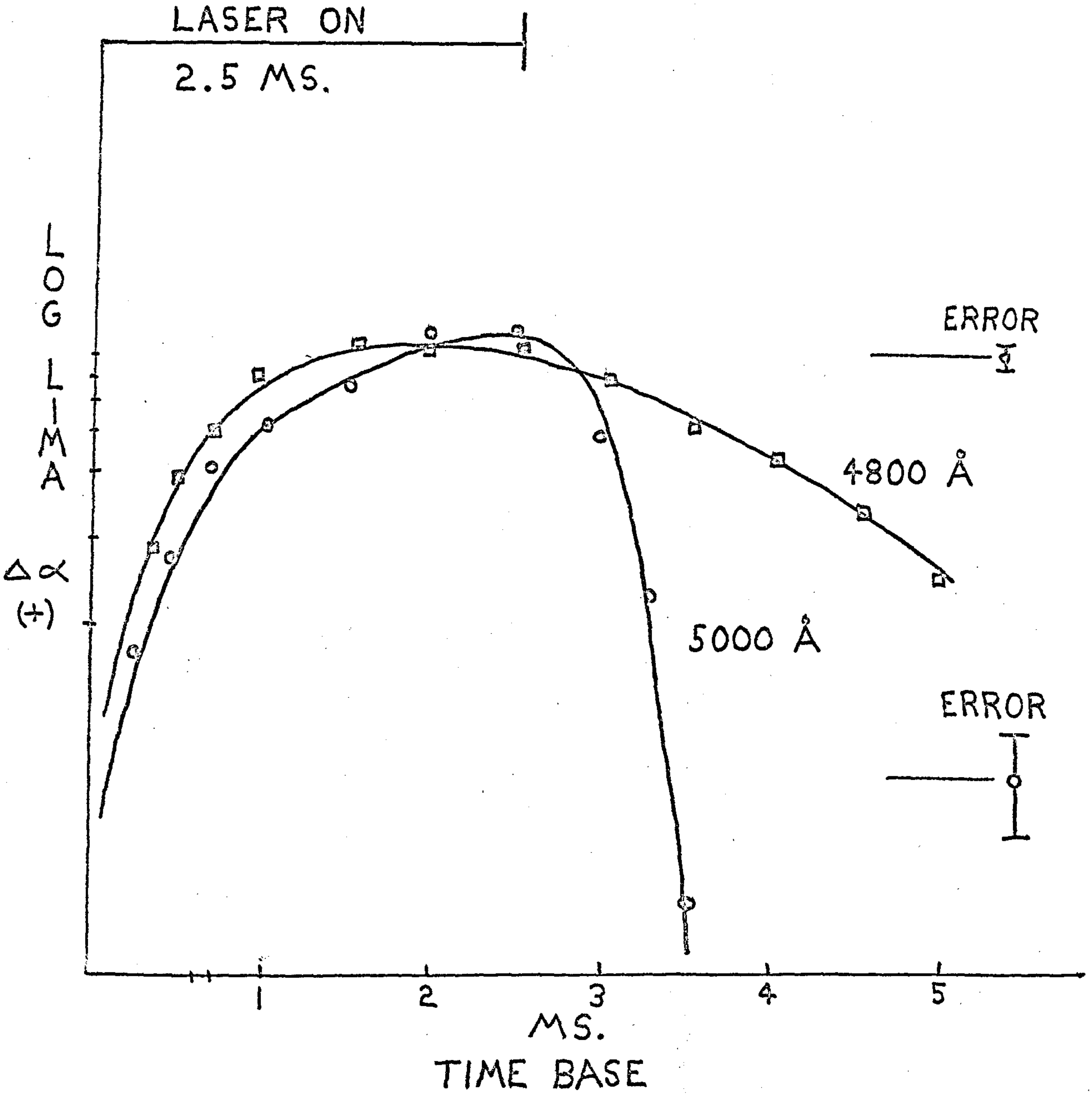
VI. CONCLUSIONS

The data obtained thus far have been somewhat noisy, but certain basic characteristics of the LIMA effect in zinc selenide are evident. With data teken using a .9 millisecond gate on the integrator, LIMA saturation does not appear to be reached until after laser shutoff. It is felt that due to the relatively wide gate width used, approximately one tenth of the time base, error in waveform reproduction has been introduced. But even though there is some error involved, the waveforms are sufficient enough to make some quantitative statements about them. First of all, and most important, LIMA does occur. This is rather important because of the very low laser power used, about 5 milliwatts. In Conway's work, LIMA was obtained with a 6 watt laser. Thus, the present modulation is being done with approximately one thousandth the laser intensity of previous work. For all wavelengths used, the decay always swings across the point of zero modulation to the opposite side. That is, one waveform has both positive and negative values. These points of changing from positive to negative, and vice versa, are different, depending upon the wavelength of the primary light. Another interesting point is the evidence that around 4900-5000 Å, there is a change from the bulk of a signal being of positive value to that of the bulk being negative in value.

In later work, shorter time base and gate widths were used. The results were impressive. As mentioned earlier, it is necessary that one gate width be passed before the maximum value of a step function is reproduced by the integrator, as shown in figure II. The work was done using a gate width of .6 and .7 milliseconds and a time base of 5 milliseconds. Referring to figure V, one can see the resolution is greatly improved. The rise times are comparable for both wavelengths but the decay is much faster at the higher wavelength. While the decay has been omitted, a cleaner "rise" signal has been obtained. It must be noted that in the initial part of the signal, the first millisecond or so, there is no sign change. Also, both waveforms are mostly of the same sign, unlike the previous 5000 Å run which used a .9 millisecond gate and 10 millisecond time base. This previous run had the greater part of its signal of negative polarity.

The lower resolution suggested in the earlier data may be caused by several situations. As mentioned above, it is due in part to the narrower gates used on the later runs. Also, the earlier data used a wider slit width on the receiving monochromator, approximately twice as wide as later runs. This would decrease resolution. A third point is that the later waveform is not exactly a duplicate of the earlier one in any case because in earlier runs the laser pulse

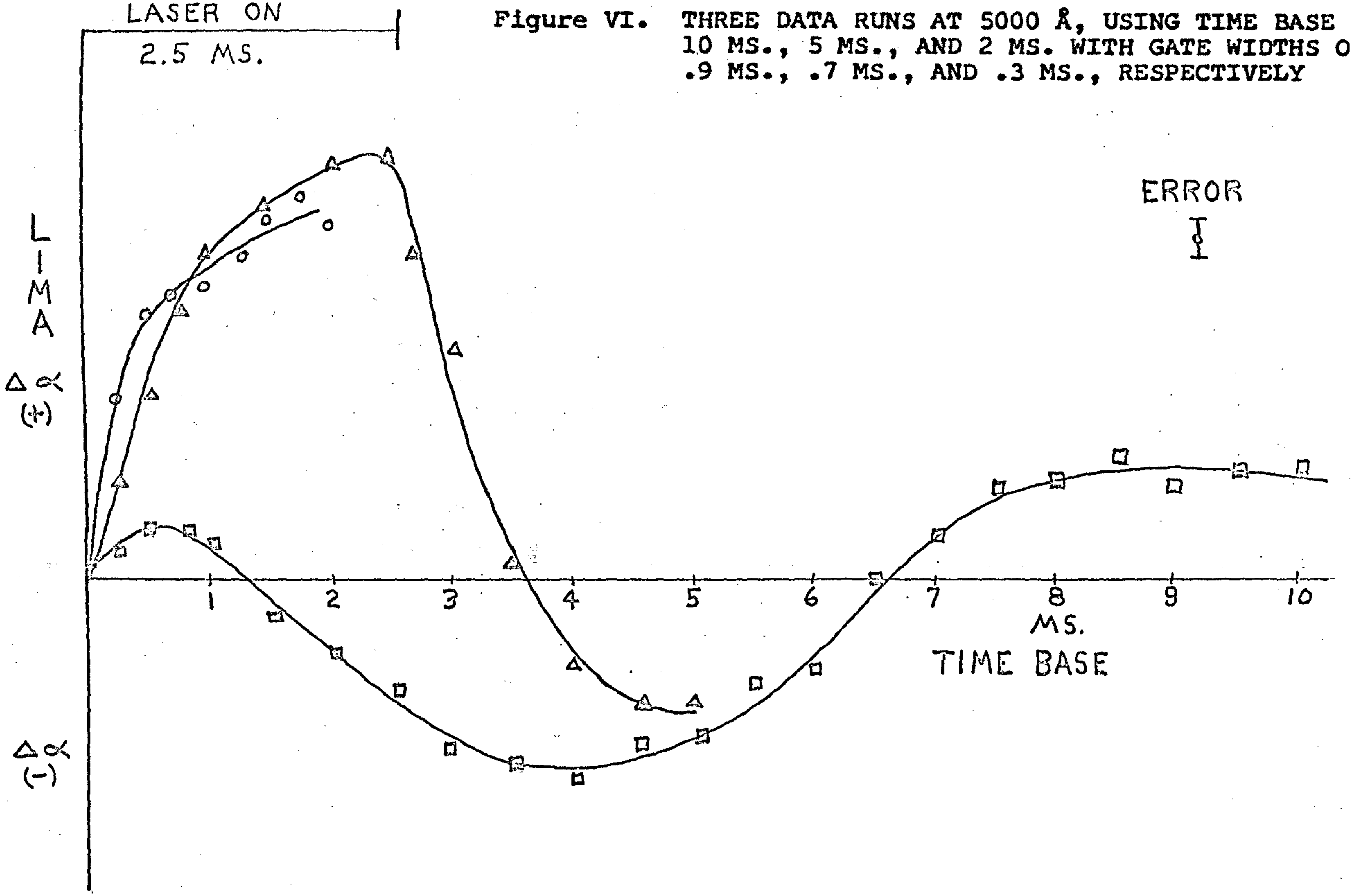
Figure V. SEMI-LOG PLOTS OF 4800 Å AND 5000 Å, WITH GATE WIDTHS OF .6 MS. AND .7 MS., RESPECTIVELY, HAVING A 5 MS. TIME BASE



frequency was approximately 57 Hertz. The frequency used in the later runs was twice this or 114 Hertz. This decreased the time between laser pulses. Therefore, in later runs at 114 Hertz, the laser pulse came when the crystal was at a relatively higher excitation level, as compared to the earlier runs at 57 Hertz. This idea would explain the initial sign change of the signal on the earlier data. Since the signal decayed to a value negative compared to the positive direction of the excitation, the excitation rise would not start at the expected zero value, but would have initially a negative value. This would explain the initial swing to a negative value. In later data a 2 millisecond time base was used on a 5000 Å data run, mainly to study the excitation rise. The result is plotted on figure VI, along with two other data sets at 5000 Å using 10 and 5 milliseconds. The initial part of the 2 and 5 millisecond runs seems to compare favorably, but they appear unlike the 10 millisecond run. Also, it must be noted that the last millisecond of the 5 millisecond run compares nicely with the corresponding waveform of the 10 millisecond data.

Of interest in examining results of this experiment is the corresponding work with cadium sulfide and zinc selenide in the field of photocurrents. Recent work has been done by Stringfellow and Bube[3] on zinc selenide using high purity samples and other samples which have been doped with copper. In crystals with copper as an impurity, they found

Figure VI. THREE DATA RUNS AT 5000 Å, USING TIME BASE OF 10 MS., 5 MS., AND 2 MS. WITH GATE WIDTHS OF .9 MS., .7 MS., AND .3 MS., RESPECTIVELY



a shoulder in their absorption spectra at 2.4-2.5 ev., which corresponds to a relative maximum in the zinc selenide LIMA data, when LIMA versus photon energy is plotted, as in figure VII. With this in mind, it is suspected that the sample may have copper impurities in it. This would be a logical mechanism in the optical absorption, since in pure zinc selenide, with the photon energies used, direct electron excitation from valence band to conduction band is not possible. Figure VIII shows the energy levels of a copper doped zinc selenide crystal. This summarizes results obtained by Stringfellow and Bube.[3] These impurity levels were found to be responsible for red and green luminescence emission. There are two impurity levels responsible for these emissions. The Cu^{x}_{zn} center, which is a ion of +2 charge, is 2.34 ev. below the conduction band and therefore gives rise to the green luminescence. The Cu'_{zn} center, having a charge of +1, is responsible for two red bands. The level is 1.97 ev. below the conduction band. This accounts for one red band. The second red emission, 1.95 ev., is from a shallow level near the conduction band. Stringfellow and Bube[3] found that the Cu'_{zn} center is the dominant acceptor, and that this level has a capture cross section for electrons 10^3 that of the Cu^{x}_{zn} center.

Future studies should involve, first of all, testing of the zinc selenide crystal used in this experiment. The results of its testing should indicate the crystal's purity, especially in regard to copper, and if impurities exist,

Figure VII. COMPARISON PLOTS OF THE ABSORPTION COEFFICIENT WITH LIMA FOR A SPECTRA OF PHOTON ENERGIES

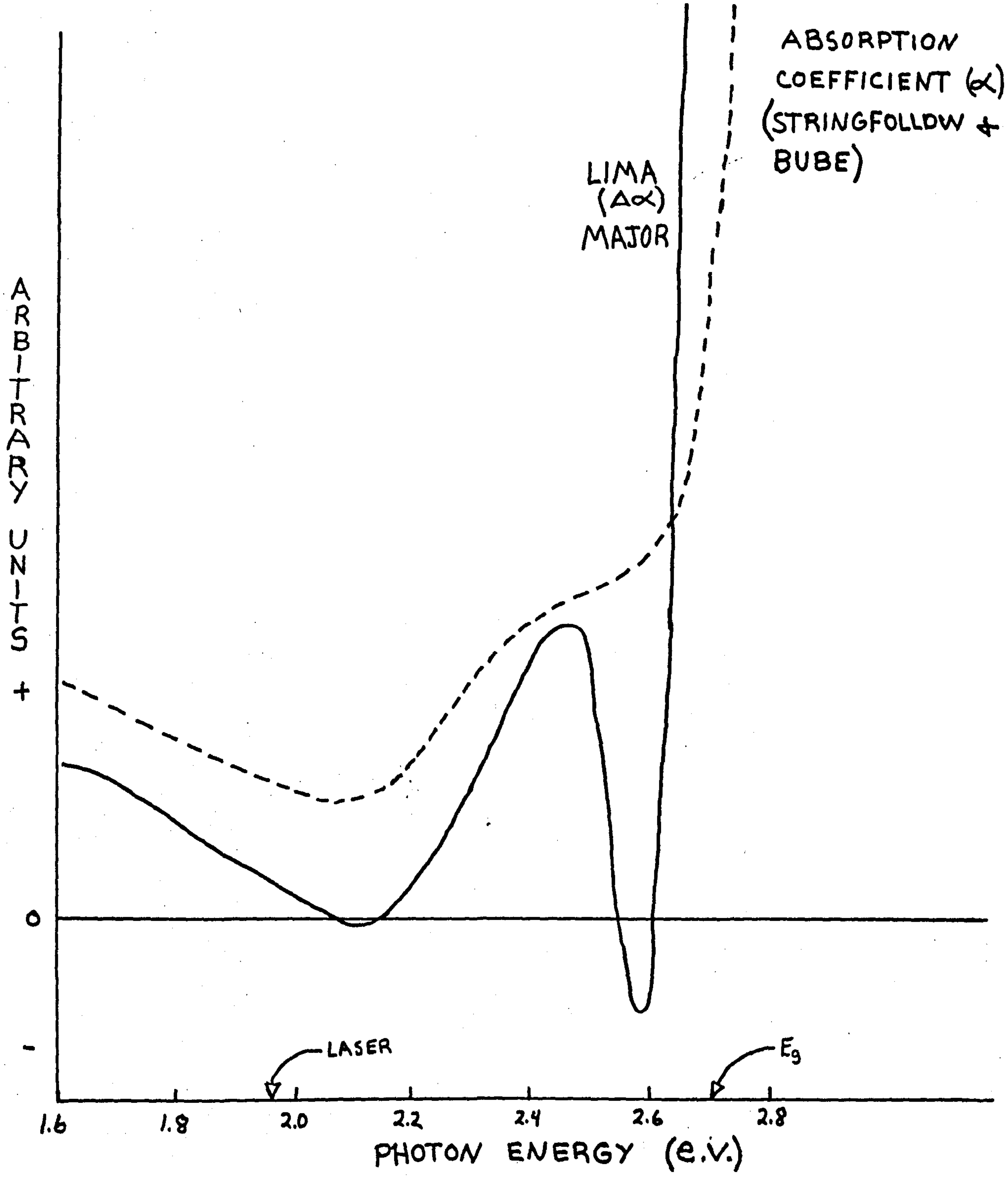
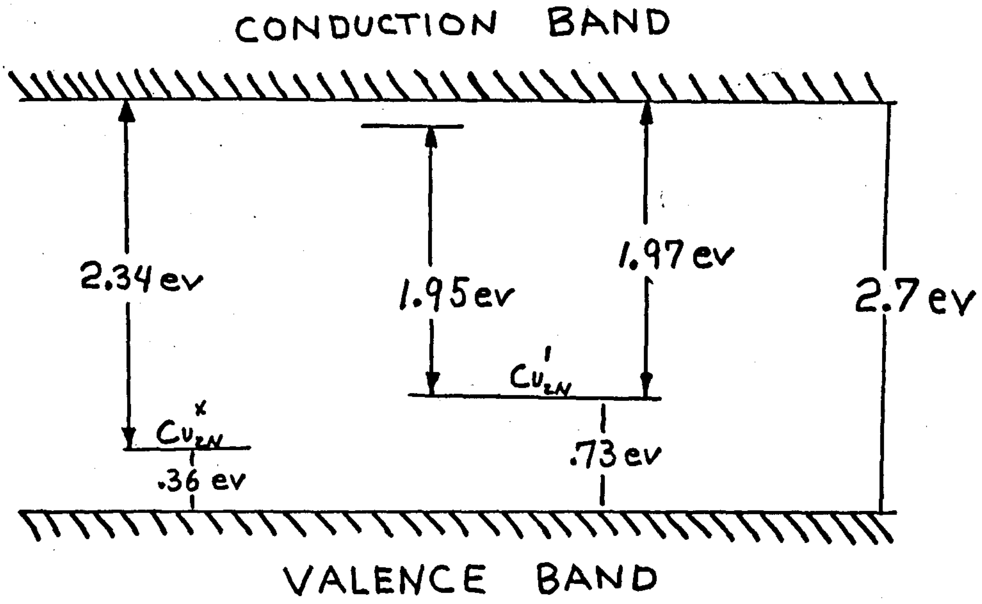


Figure VIII. MULTIVALENT COPPER-IMPURITY MODEL: ZnSe:Cu
STRINGFELLOW & BUBE



$Cu'_{ZN} = Cu^{+} \Rightarrow$ RED

$Cu^{x}_{ZN} = Cu^{+2} \Rightarrow$ GREEN their type and concentration. Additional data are needed to better delineate the kinetics of the decay. Thus far, there are strong indications that the period of crystal decay may last as long as 20 milliseconds. When using the same primary wavelength, but different chopper frequencies, the initiation of the next laser pulse, before decay is complete, causes different LIMA pulse shapes to be observed. This indicates that there is an optimum laser pulse frequency for obtaining the greatest LIMA magnitude. Thus, new data should be produced at selected primary wavelengths, for a range of chopper frequencies. The resulting plot of wavelength versus chopper frequency of maximum LIMA would be most interesting for future LIMA studies in order to obtain the largest LIMA effect for any desired wavelength.

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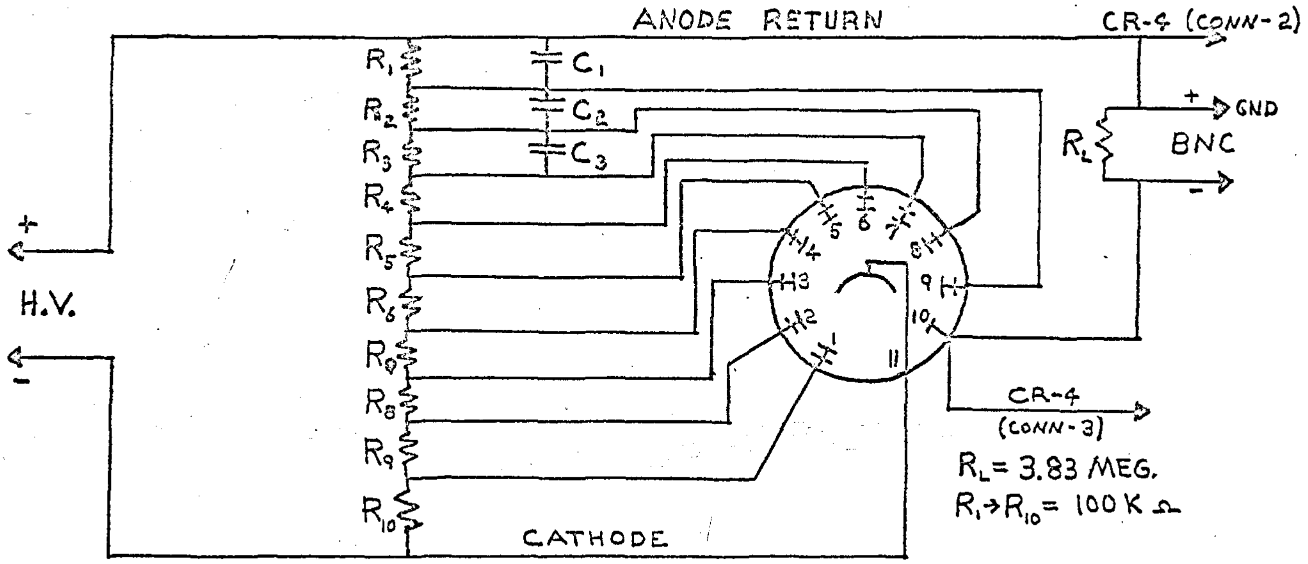
VIII. ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. R. Wayne Major for his counsel, guidance and encouragement during this investigation, and also to Herbert M. Berman for his assistance.

IX. APPENDIX



PHOTOMULTIPLIER CIRCUIT — RCA 1P28 TUBE

R_L = 3.83 MEG.

$R_1 \rightarrow R_{10}$ = 100 K Ω

PHOTODIODE CIRCUIT