

THERMOLUMINESCENCE STUDIES OF F CENTERS
IN X-IRRADIATED POTASSIUM CHLORIDE

by

Susan Flanagan

Submitted as an Honors Paper
in the
Department of Physics

The University of North Carolina
at Greensboro
1969

TABLE OF CONTENTS

| | Page |
|----------------------------------------|------|
| I. Introduction | 1 |
| II. Theory | 3 |
| III. Experimental Equipment | 7 |
| IV. Procedure | 11 |
| V. Results | 12 |
| A. Growth of F Centers | 12 |
| B. Quenched Crystals | 16 |
| C. Activation Energy | 21 |
| D. Spectral Studies | 31 |
| E. Effect of Thickness | 36 |
| VI. Sources of Error | 36 |
| VII. Summary and Conclusions | 37 |
| Footnotes | 42 |
| Bibliography | 43 |

Approved by

G. T. Hogereth

Director

Examining Committee

Eugene E. McDowell

Richard T. Whitlock

G. T. Hogereth

Introduction

Solid State Physics is a comparatively new field in which much research has been conducted in the past few decades. The study of crystal defects is a topic of major concern in this field. Color centers are crystal defects which have been the subject of extensive research in an attempt to understand what they are, how they are formed, and how they are annihilated or transformed into other defects, as well as how they affect the properties of the crystal in which they are present. Historically, color center research was performed with the alkali halides because of their comparatively simple structure and because of the fact that they are easily obtainable in a reasonably pure state. The alkali halides (of which potassium chloride given the symbol KCl is an example) are compounds formed from ions in the first and seventh group of the periodic table which typically crystallize in the NaCl-type structure. "In this structure each cation (alkali metal ion) is surrounded by (or 'coordinated' with) six nearest-neighbor anions (halogen ions), and each anion by six nearest-neighbor cations. The cations and anions are each situated on the points of separate face-centered cubic lattices, and these two lattices are interleaved with each other."¹ Figure 1 is an example of the NaCl-type structure.

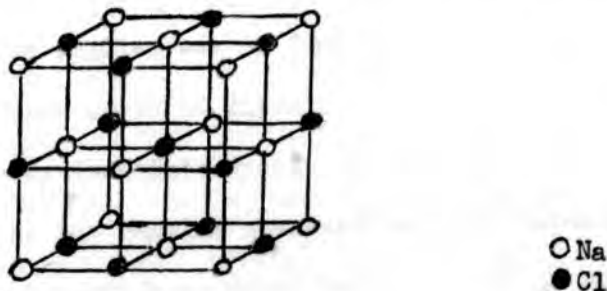


Figure 1

The main reason for undertaking thermoluminescence studies of F centers in x-irradiated potassium chloride was monetary. With a small department and relatively few funds for research equipment, a topic had to be chosen which could be pursued with a minimum of expensive new equipment. The technique of thermoluminescence for studying F centers was chosen because it is relatively new so there is much which has not been done with it, and also it requires relatively inexpensive experimental equipment. Since an x-ray machine was already being installed, x-irradiation was chosen as the mechanism for creating the color centers in the crystals. Potassium chloride was chosen as the crystal for this study because much of the previous research in this area has been done on potassium chloride and it was necessary to have some standard results with which to compare data, especially in the preliminary stages of getting the equipment set up and operating. Because of numerous difficulties associated with the lack of proper equipment such as inadequate means of employing liquid nitrogen for cooling the crystal chamber, and failure of the vacuum pump when the chamber was cooled to liquid nitrogen temperature (77°K), these studies are confined to room temperature. This fact is important since "it is known that the mechanisms of color-center formation at room temperature and at low temperature are quite different."²

The purpose of these studies was to find out more about F centers in crystals. These studies would be classified under pure research and therefore they have no immediate applications. It was hoped that they would reproduce the results obtained by other experimenters as well as lead to some new evidence which could be used to obtain a clearer understanding of the F center.

Theory

An F center is the simplest color center. The name comes from the German word for color, Farbe. "The center has been identified by electron spin resonance as an electron bound at a negative ion vacancy in agreement with a model suggested by de Boer. . . The distribution of the excess electron is largely on the positive metal ions adjacent to the vacant lattice site."³ Figure 2 is a schematic diagram of the F center.

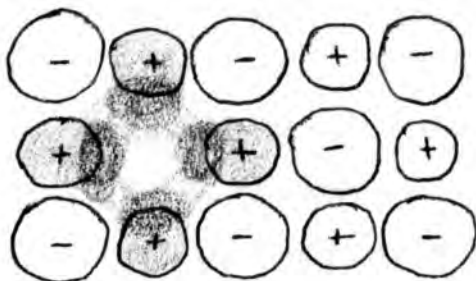


Figure 2

Color centers can be formed in a crystal in a variety of ways. Additive coloration or electrolytic coloration are two important techniques. "We can also produce F and V centers in alkali halide crystals by bombarding them with ionizing radiation such as x-rays or cathode rays (electrons). When an electron is knocked off a halogen ion, a hole-electron pair is created; each localizes at a vacancy and remains until either thermal or optical excitation allows them to recombine. Removal of an electron from an alkali ion produces the same result except that the hole moves first from the alkali to a halogen, and then to a vacancy. The radiation also produces new vacancies to accommodate the F and V centers, but this mechanism is still not properly understood and is the subject of considerable

speculation."⁴

"The most prominent absorption band produced by room temperature irradiation is, of course, the F band. . . The absolute magnitude of the coloration and even the shape of the curve of coloration vs. energy absorbed, depends upon the purity of the material and the x-ray intensity. The coloration is oftentimes described as taking place in two distinct 'stages'. In 'stage I' there is rapid coloration, whereas in 'stage II' there is a much slower coloration rate that suggests an approach to saturation."⁵ In reference to the "stages" of F center coloration, P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski state: "It is believed that F centers are formed in alkali halides by x rays by two distinct processes. In one of them negative-ion vacancies initially present in the crystal may trap electrons liberated by x rays. In the other one new vacancies are generated and these in turn may trap electrons and form additional F centers."⁶ S. C. Jain and F. C. Mehendru came to a similar conclusion as a result of their research. "F centers of the first type are formed by the vacancies present in the crystal prior to the irradiation and are distributed statistically. F centers of the second type are formed by the vacancies generated during the irradiation process."⁷ "The deliberate introduction of known distributions of vacancies by heat treatment and by deformation provide additional evidence that the initial vacancies in the as-received crystal are well distributed and that the vacancies generated by irradiation are localized."⁸ F_1 shall denote the F centers formed by vacancies originally present in the crystal and F_2 shall denote the centers formed by vacancies generated by irradiation.

Thermoluminescence is the process of emission of light from a crystal which is stimulated by the addition of heat to the crystal. The fact that trapped-electron centers can be destroyed or "bleached" by warming the crystal "is readily understandable in view of the fact that an electron trapped by a positively-charged defect comprises a system analogous to a hydrogen atom. As such it has various excited states into which it can be excited thermally or by absorption of light of the requisite energy. With the absorption of sufficient energy, the electron can be completely freed from the defect, paralleling the ionization of a hydrogen atom. If the free electron encounters a trapped positive hole during its migration through the crystal, it can fall into the hole and annihilate it."⁹

"A typical crystal energy-band diagram including the various excited states and trapping levels associated with luminescence centers and traps is shown in Figure 3.

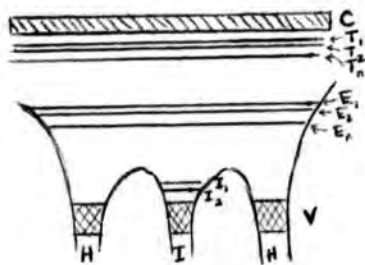


Figure 3

The impurity ion or defect is located at position I, the host crystal ions at H. The band V represents the (filled) valence band and the band C the (empty) conduction band of the host crystal. The levels I_1, I_2, \dots lying above the valence band are the normally filled upper impurity levels; E_1, E_2, \dots are the excited states of the center. The levels T_1, T_2, \dots are electron traps which

may be distributed in energy throughout the band gap. This somewhat idealistic model may be used to describe the various possible luminescence processes.

"Two main types of luminescence mechanisms may be distinguished. One is the localized or quasiatomic model of which KCl (T1) is a typical example. On this model both the luminescence transition and the trapping take place at the impurity site. In Figure 3 this would correspond to excitation from I or V to the E levels some of which are likely metastable (transitions to the ground state are forbidden). Thermoluminescence would then result upon warming the crystal since this would cause transitions of the trapped carriers into higher excited levels from which they could return to the ground state with emission of radiation."¹⁰

"Important information about color centers can be obtained by measuring the changes that occur when a colored crystal is gradually heated from some low temperature to a higher temperature. As the temperature is raised electrons and holes escape from their traps at an increasing rate. The freed charges can recombine with each other or with other defects, and often give out luminescence by this recombination. The resulting thermoluminescence or 'glow' reaches a maximum and then decreases to zero as the supply of trapped electrons or holes becomes exhausted. The plot of luminescence intensity vs. temperature, taken at a constant heating rate, is called the 'glow curve'. It may contain one or many glow peaks, depending upon whether there are one or several different kinds of traps. From the glow curve one can determine the trap depth; the deeper the trap, the higher the temperature of the glow peak."¹¹

According to J. A. Crawford, "thermoluminescence is an extremely useful technique for obtaining information about the defect and impurity energy levels in the band gap of semiconducting or insulating compounds."¹²

Experimental Equipment

The experimental equipment used for these thermoluminescence studies was relatively simple. The main components were a phototube with a high voltage supply, an electrometer and strip chart recorder for monitoring the output of the phototube, a soldering iron and Variac to adjust the heating rate, a thermocouple and chart recorder for determining the temperature of the crystal, and a potassium chloride crystal. Figure 4 is a schematic diagram of the experimental equipment showing the necessary connections.

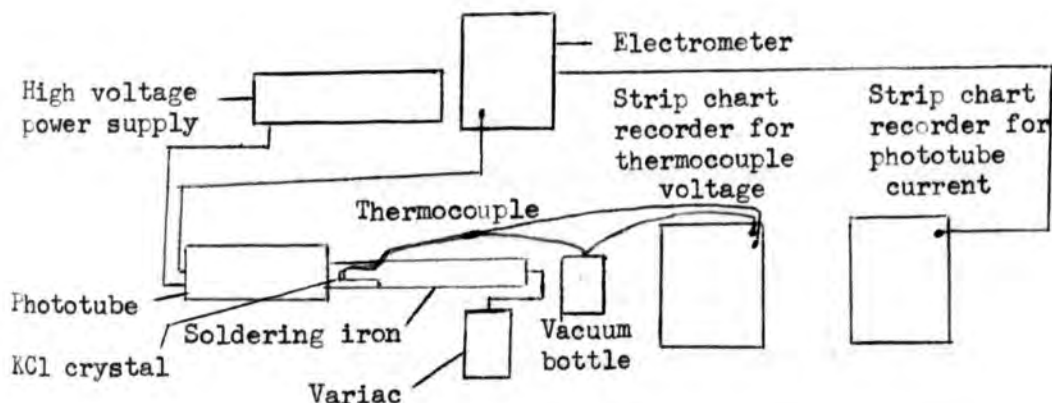


Figure 4

The phototube used for the first month of experimentation was the IP28. This has a spectral response between 2500 and 7000 Å. On February 28, 1969 a 6199 phototube was acquired and used for the rest of the experiments. The 6199 has a spectral response between 3000 and 7000 Å but a comparison of the relative sensitivity at a

given wavelength as given in Table 1 shows that the 6199 is more sensitive in the region of interest for these thermoluminescence studies which is 4000 to 6000 Å.

| Wavelength | IP28 | 6199 |
|------------|----------------------|-------|
| | Relative Sensitivity | |
| 3000 A | 90 % | 0 % |
| 3500 A | 100 % | 50 % |
| 4000 A | 85 % | 90 % |
| 4500 A | 70 % | 100 % |
| 5000 A | 50 % | 90 % |
| 5500 A | 30 % | 55 % |
| 6000 A | 10 % | 20 % |
| 6500 A | 3 % | 1 % |
| 7000 A | 0 % | 0 % |

Table 1

A high voltage regulated direct current power supply was used to provide the operating voltage for the phototube. A Keithley 600A Electrometer with sensitivity to 10^{-11} amps was employed for visual monitoring of the phototube output current and for determination of the scale on the strip chart recorder. A Varian G-14 strip chart recorder with speeds of one-half inch per minute and two inches per minute was utilized to obtain a permanent record of the luminescence vs. time as the crystal was being heated.

A 150 watt soldering iron was used for heating the crystal during the first month of experimentation. A variac provided a means of adjusting the heating rate. With this soldering iron, a

maximum of $16^{\circ}\text{C}/\text{min}$ heating rate was obtainable. In order to attain a greater heating rate, a 200 watt soldering iron was acquired and used for the rest of these studies. With this 200 watt soldering iron, a $22^{\circ}\text{C}/\text{min}$ heating rate was easily obtainable and higher heating rates were possible.

A copper-constantan thermocouple with reference junction at 0°C measured the temperature of the crystal during thermoluminescence. The thermocouple was connected to the end of the soldering iron on which the crystal was placed. A Varian G-14 strip chart recorder with speeds of one-half inch per minute and four inches per minute provided a record of the reading of the thermocouple in millivolts vs. time. This could be converted to the temperature of the crystal vs. time and could then be correlated with the record from the other strip chart recorder of the thermoluminescence vs. time to obtain the variation of thermoluminescence with temperature which is the "glow curve". When one of the Varian recorders broke down, the thermocouple voltage was switched to a Heath Servo-recorder with adjustable chart speeds.

The crystals used for the first month of experimentation were Harshaw crystals cleaved from one large potassium chloride crystal about $20\text{mm} \times 20\text{mm} \times 10\text{mm}$. There was a definite lack of uniformity of size, thickness, and smoothness. No attempt at individual identification of these crystals was made since it was assumed that their thermoluminescence responses would be similar. When some crystals were quenched by heating them in a crucible in a small Thermolyne furnace to 700°C and then cooling them quickly to room temperature on a piece of metal, individual identification of crystals

was made. Some Oak Ridge crystals were also used which were obtained by cleaving from one large potassium chloride crystal and these too were not individually identified until after quenching. On March 7, 1969 a shipment of highly pure potassium chloride crystals 10mm x 10mm x 2mm was received from Harshaw Crystal Solid State Division. These crystals were each cleaved into four smaller crystals and individually named "New Harshaw" followed by an appropriate number and were used most extensively in the rest of the thermoluminescence studies.

The x-ray machine which was used to color the crystals was from Philips Electronics Instruments. It was operated at 35 kilovolts and from five to twenty milliamps. There are three ports over which the crystal could be mounted. Crystals were colored on one side only. The x-rays used fall in the range of soft x-rays. "Soft x-rays have a broad energy spectrum, and since the absorption coefficient for photons of these energies is strongly dependent upon energy, the coloration is always most intense at the surface and has an approximate exponential dependence away from the surface. . . The amount of coloration that is obtained in a given material as a function of the x-ray exposure depends upon the particular alkali halide, the temperature at which the irradiation is performed, and upon the purity of the crystal."¹³

In an attempt to determine the wavelength of the luminescence given off by the crystals, a spectral study was conducted. The equipment necessary for this was the same as that required for the thermoluminescence studies with the addition of a monochromator equipped with a reversible micrometer drive which was placed between

the crystal and the phototube. The monochromator was a model F-11-20 ultraviolet-infrared monochromator put out by Oriel (now Orion) Optics Corporation. It has a calibrated wavelength range from 1900 to 15,000 angstroms and an adjustable slit of zero to two millimeters width. It is a quartz prism monochromator with in line configuration of the entrance and exit beams which make possible instillation into the optical path without disturbing its direction. The micrometer dial reading is related to the wavelength by a calibration table. The reversible micrometer drive was used to sweep the spectrum at a constant rate through the desired wavelength ranges. Because the addition of the monochromator moved the crystal further from the phototube thereby reducing the intensity of the thermoluminescence picked up by the phototube, and because the narrow slit further reduced the intensity, the dark current of the phototube had to be greatly reduced for any thermoluminescence effect to be seen. This was accomplished by packing the phototube with dry ice.

Procedure

The procedure for the thermoluminescence studies consisted of x-raying a crystal to create F centers, mounting the crystal on the soldering iron with the more intensely colored side facing the phototube, positioning the soldering iron close to the phototube and sealing out the stray background light, heating the crystal while recording temperature and luminescence intensity, and allowing the crystal to cool back to room temperature when the luminescence returned to zero.

For the spectral studies the procedure was essentially the same. The dark current of the phototube which was normally around 3×10^{-8}

amperes was first reduced, however, to the 10^{-10} amp range by packing dry ice around the tube. When the temperature attained the proper value for a luminescence peak, the micrometer drive was switched on and a spectral sweep of wavelengths was made, usually from 3900 to 8000 Å which covers the entire visible range.

Results

Growth of F Centers

The first thermoluminescence studies were conducted on various Harshaw crystals in order to obtain the two thermoluminescence peaks corresponding to the two types of F centers. The fact that there are two peaks was reported by S. C. Jain and P. C. Mehendru who concluded "that in undeformed KCl crystals, x irradiated at room temperature, there are two thermoluminescence peaks characteristic of the pure KCl. These peaks are at 135 and 190°C respectively, for the heating rate 40°C/min, and at 93 and 165°C for the heating rate 5°C/min."¹⁴ A heating rate of 16°C/min was used and the crystals had varying thicknesses instead of a uniform thickness of 0.5mm characteristic of the crystals used by Jain and Mehendru. The crystals were exposed to an x-ray intensity of 35 kilovolts and 20 milliamps for varying periods of time ranging from 2.5 minutes to six hours. In each case only one fairly broad peak was obtained, although a shoulder around 85°C was noticed which was attributed to background impurity. With increasing exposure time the peak grew in intensity and also shifted to higher temperatures. For 2.5 minutes the maximum intensity was 3.4 units and the peak occurred at 95°C whereas for six hours the maximum intensity was 21 units and the peak occurred at 181°C. Since this attempt at peak resolution failed, a similar study was conducted

on another group of Harshaw crystals exposed to an x-ray intensity of 35 kilovolts and 10 milliamps for periods of time ranging from 15 minutes to six hours. The same $16^{\circ}\text{C}/\text{min}$ heating rate (maximum for the 150 watt soldering iron) was used and similar results were obtained. Each luminescence curve had a small shoulder around 75°C and one broad peak which grew in intensity and shifted toward higher temperatures as the time of x-ray exposure was increased. For 15 minutes the maximum intensity was 4.6 units and the peak occurred at 118°C whereas for six hours the maximum intensity was 26 units and the peak occurred at 193°C . Both of these studies were conducted using the IP28 phototube which, as was pointed out earlier, has a decreased sensitivity in the wavelength region of interest in thermoluminescence studies.

With the acquisition of the 200 watt soldering iron, the 6199 phototube, and the pure crystals shipped from Harshaw, a final attempt at peak separation was made which was successful. A thorough study of the growth of F_1 and F_2 centers as a function of amount of x-ray exposure at an intensity of 35 kilovolts and 20 milliamps was carried out on New Harshaw 5. A $24^{\circ}\text{C}/\text{min}$ heating rate was used. The results of this study are shown in Figure 5 and Figure 6. The first set of peaks centering around 138°C corresponds to F_1 and the second set centering around 195°C corresponds to F_2 . The colors serve to distinguish the different luminescence curves and the numbers above the peaks refer to the amount of x-ray exposure in hours. It can be seen that the F_1 reaches its maximum growth in about four hours whereas the F_2 continues to grow although at a decreasing rate for long exposure times. Figure 6 shows the same

Figure 5

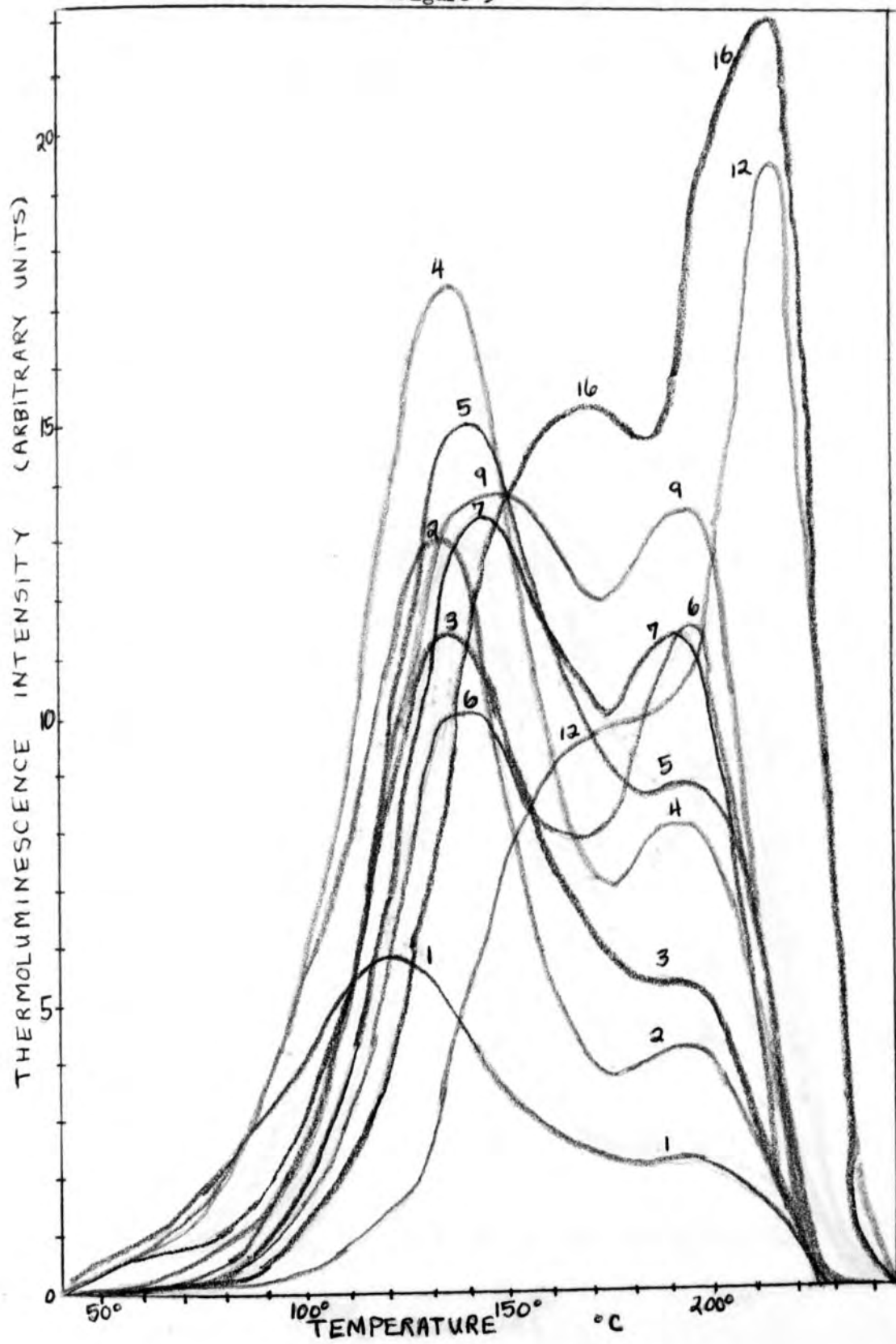
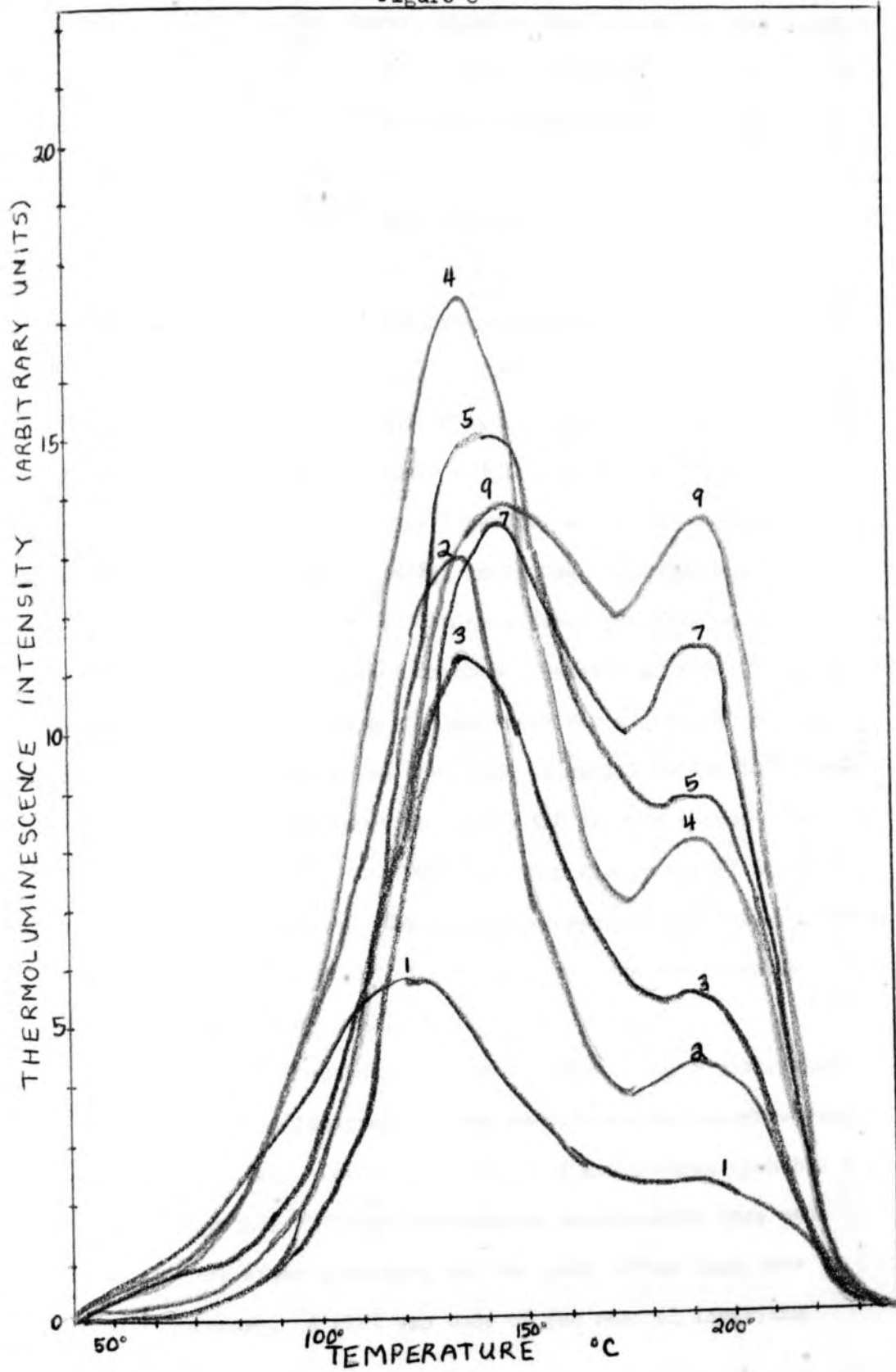


Figure 6



data as Figure 5 with the longer exposure time curves omitted so that a clearer picture of the growth of the F_2 intensity as a function of amount of x-ray exposure can be seen. These results are similar to those obtained by Jain and Mehendru.

Quenched Crystals

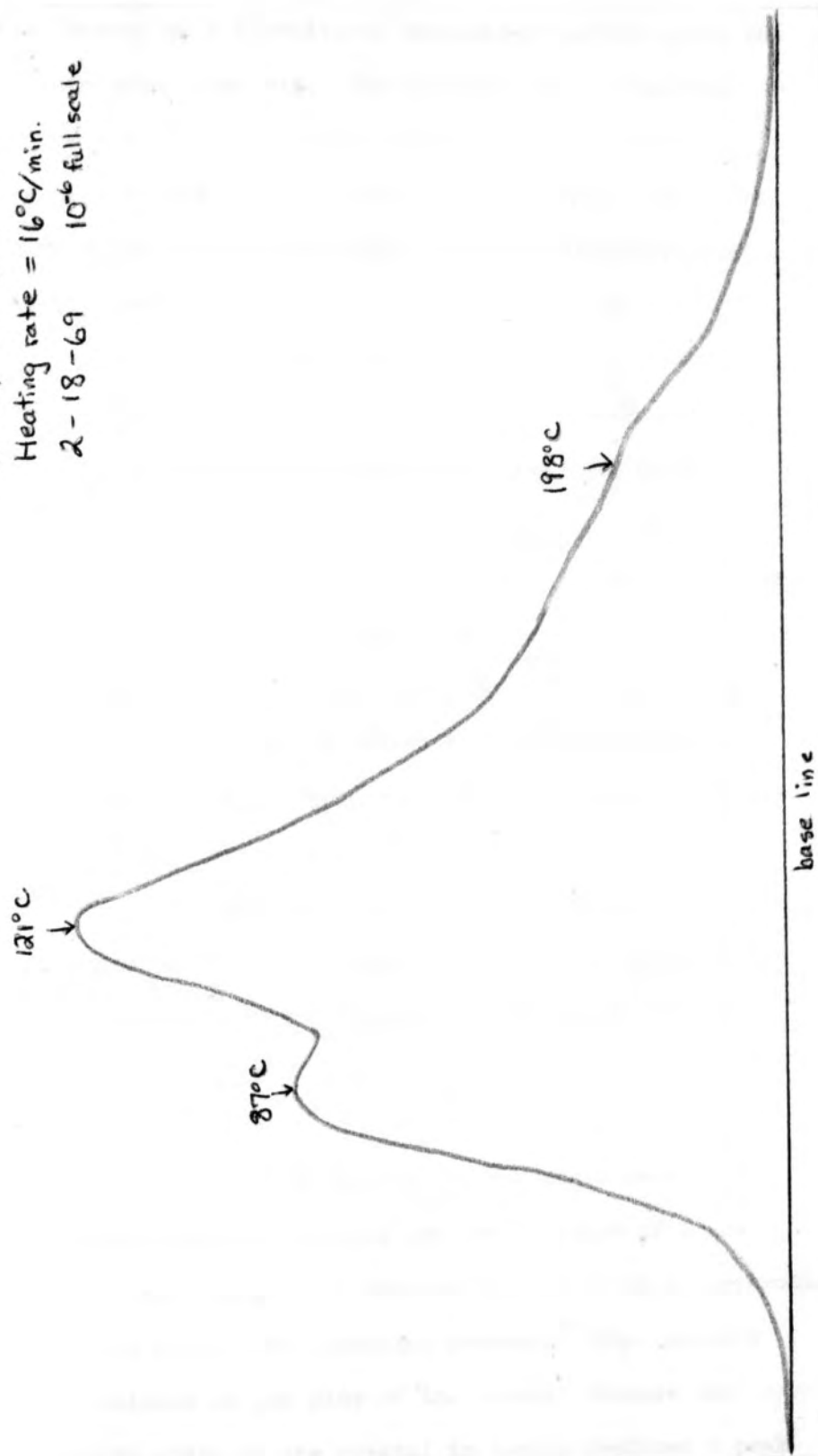
Another group of thermoluminescence studies were performed on quenched crystals. As explained previously, the process of quenching consisted of heating the crystals to 700°C in a crucible in the Thermolyne furnace and then rapidly cooling them to room temperature on a piece of metal. This process had the effect of greatly increasing the thermoluminescence intensity mainly of the peaks corresponding to impurities and F_1 . A typical luminescence curve for a 35 kilovolt, 5 milliamp, 30 minute x-ray exposure on an unquenched crystal would have a maximum intensity in the 10^{-7} scale on the electrometer whereas a similar curve for a quenched crystal as illustrated by Figure 7 has a maximum intensity in the 10^{-6} scale range. The quenching appeared to affect the F_2 to a lesser extent. A few crystals were heated to 700°C and then slowly cooled to room temperature in the furnace. The thermoluminescence for these crystals showed a decrease in intensity for the low temperature peaks as compared to a regular crystal.

An interesting effect observed in the first few crystals that were quenched was the decay of the enhanced thermoluminescence peak intensities with time. Oak Ridge Quenched 4 and Harshaw Quenched 5 are two such crystals. Thermoluminescence measurements were made on different days after quenching and the peak intensities were observed to decrease. A plot was made of the natural logarithm

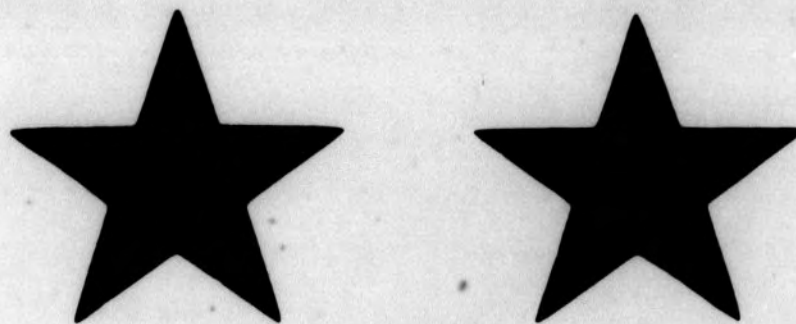
Figure 7

OAK RIDGE QUENCHED 4

35 kv, 5 ma, 30 min.
Heating rate = $16^{\circ}\text{C}/\text{min}$.
2-18-69 10^{16} full scale



CORRECTION



***PRECEDING IMAGE HAS BEEN
REFILMED
TO ASSURE LEGIBILITY OR TO
CORRECT A POSSIBLE ERROR***

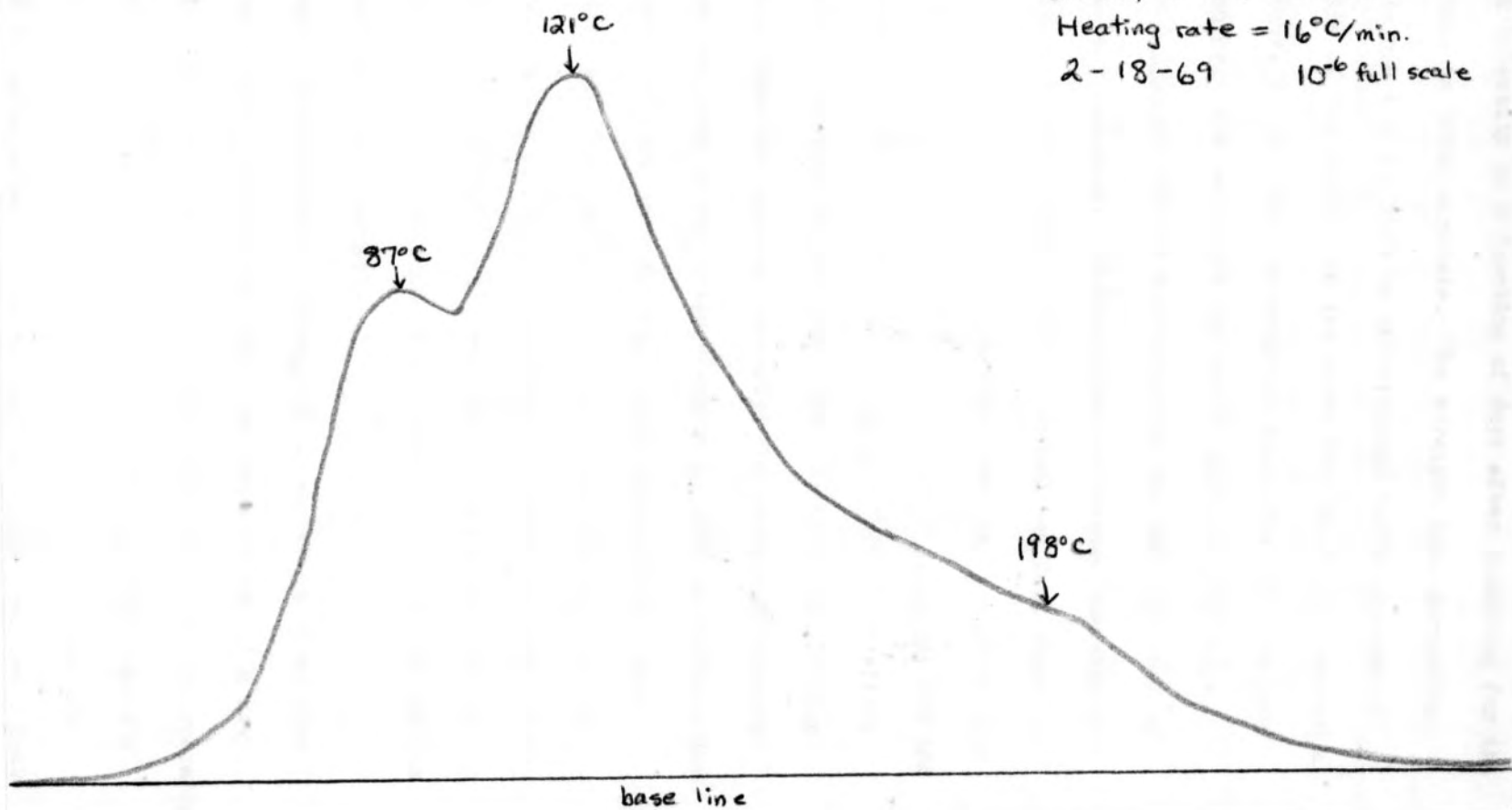
Figure 7

OAK RIDGE QUENCHED 4

35 kv, 5 ma, 30 min.

Heating rate = $16^{\circ}\text{C}/\text{min}$.

2-18-69 10^{-6} full scale



of the peak intensity as a function of days after quenching for the observed peaks in these crystals. The straight line connecting these points has a slope that is proportional to the inverse of the half-life of the decay. On the curve for Oak Ridge Quenched 4 shown in Figure 8, the decay essentially stopped within six days after quenching. The half-life for the F_1 is $T_{\frac{1}{2}} = .693/\text{slope} = .693/.200 = \underline{3.5 \text{ days}}$; and the half-life for the impurity peak is $T_{\frac{1}{2}} = .693/.214 = \underline{3.2 \text{ days}}$. On the curve for Harshaw Quenched 5 shown in Figure 9, the decay levels off around ten days after quenching. The half-life for the impurity peak is $T_{\frac{1}{2}} = .693/.23 = \underline{3.0 \text{ days}}$; the half-life for F_1 is $T_{\frac{1}{2}} = .693/.20 = \underline{3.5 \text{ days}}$; and the half-life for F_2 is $T_{\frac{1}{2}} = .693/.21 = \underline{3.3 \text{ days}}$. This decay effect appears to be a function of the time after quenching rather than the number of times the crystal is heated for thermoluminescence runs because two runs on Oak Ridge Quenched 4 taken on the same day showed no decay of peak intensities. These decay studies were conducted with the IP28 phototube. With the acquisition of the New Harshaw crystals and the 6199 phototube, a similar decay study was attempted. Unfortunately the results of this study did not provide enough good data to plot decay curves to see if the results observed earlier were repeatable.

One major complication in attempting to reproduce decay data with the New Harshaw quenched crystals was the addition of a new thermoluminescence peak around 65°C apparently due to the incorporation of some new impurity during the quenching process. This impurity was definitely localized on one side of the crystal because the exposure of opposite sides of the crystal to x-rays produced a peak

Figure 8
OAK RIDGE QUENCHED 4

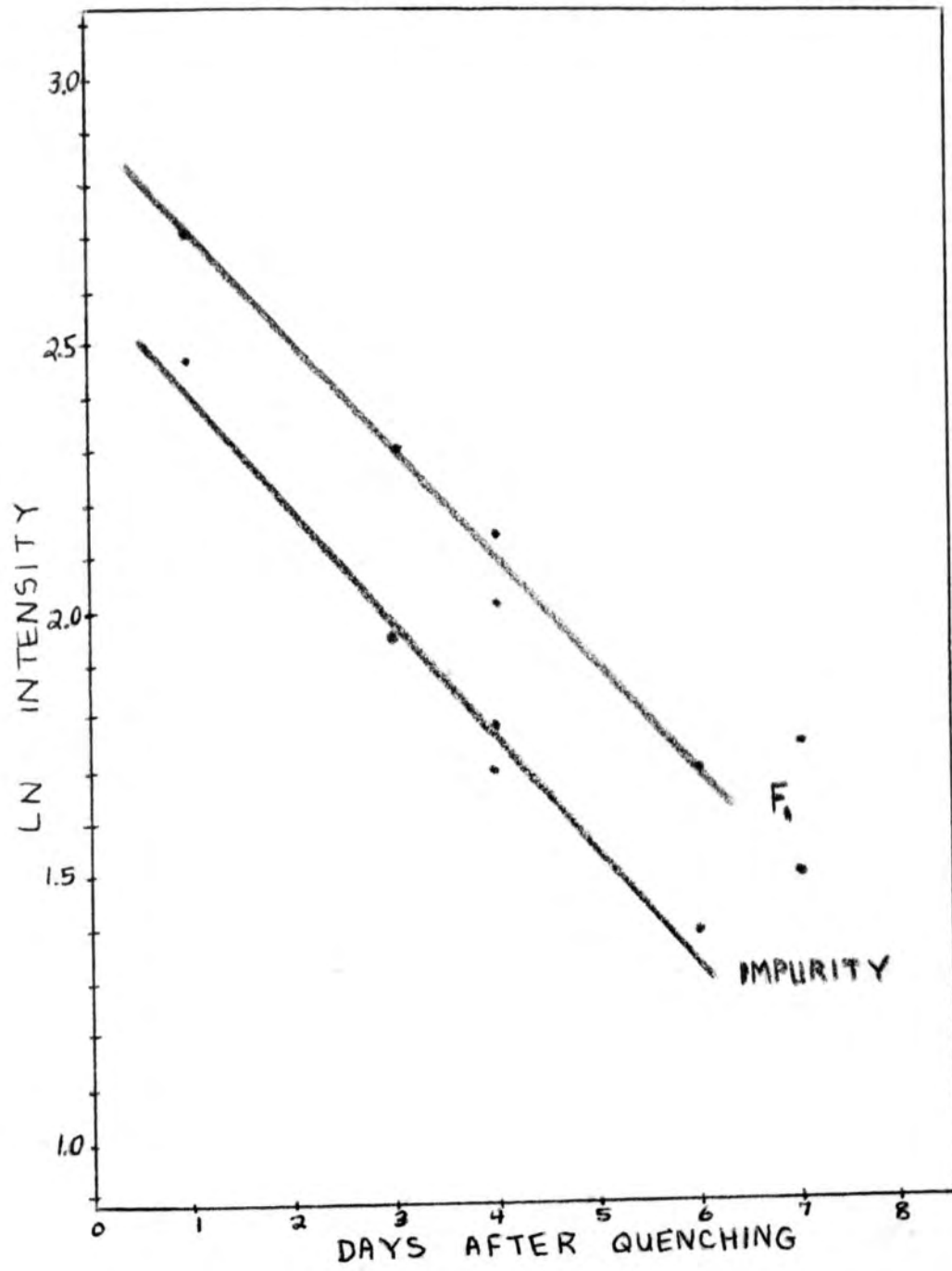
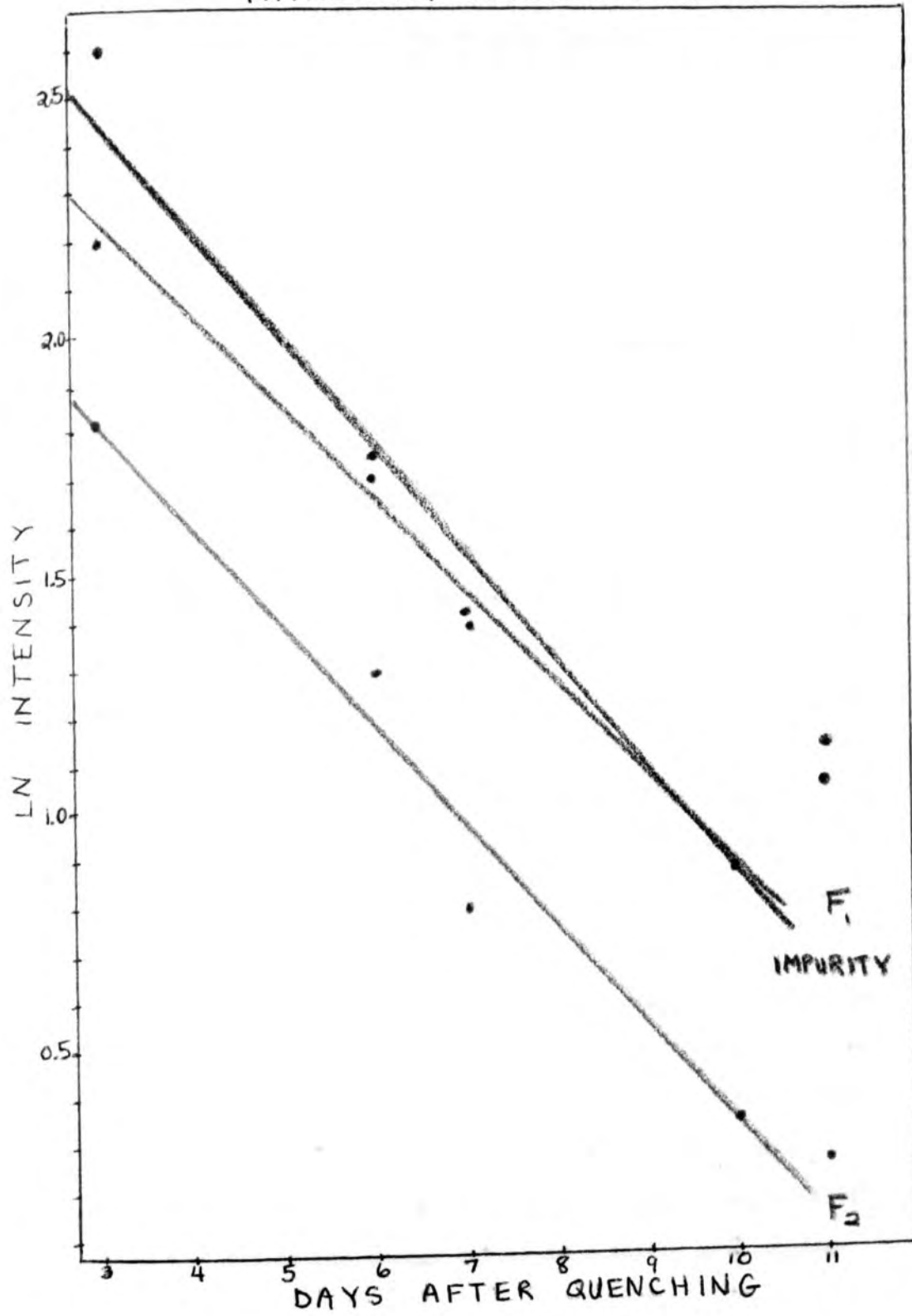


Figure 9
HARSHAW QUENCHED 5



on one side and a shoulder on the other side as shown in Figure 10 and Figure 11. In addition to New Harshaw Quenched 4, New Harshaw quenched 11 and New Harshaw Quenched 21 also exhibited this new low temperature one-sided impurity effect. This effect was not noticeable in the Oak Ridge Quenched crystals. The side of the crystals on which there is a definite peak around 65°C corresponds to the side which was exposed to the air during the quenching process, and the side on which there is only a shoulder around 65°C corresponds to the side which was against the metal during the quenching process.

Activation Energy

Valuable information about the structure of F centers can be obtained from a knowledge of the trap depth, that is the energy difference between the electron trapped in a negative ion vacancy forming an F center and an electron which has been freed from the F center. This energy difference is referred to as the activation energy E . "The most common method to determine E is what is called the initial-rise method, first advocated by Garlick and Gibson. This method is based on the fact that the rise of the low-temperature side of a glow peak is proportional to $\exp(-E/kT)$ for temperatures well below the peak temperature T_m ."¹⁵ Thus the intensity I of the thermoluminescence in this region is related to the temperature by the following equation: $\ln I = -E/kT + C$, where C is a constant and k is Boltzmann's constant. A plot of $\ln I$ vs. $1/T$ yields a straight line whose slope is $-E/k$ so the activation energy can be easily determined from the slope. This is not the most accurate means of determining the activation energy but it is a fairly good approximation.

Of course, it is not possible to have a single peak at 64°C and another at 90°C. The fact that there are two peaks at these temperatures is evidence of a phase transition. The first peak at 64°C is due to the melting of the polymer, and the second peak at 90°C is due to the melting of the crystalline regions. The fact that the second peak is at a higher temperature than the first peak is evidence of a phase transition. The fact that the second peak is at a higher temperature than the first peak is evidence of a phase transition.

Figure 10

NEW HARSHAW QUENCHED 4

35 kv, 10 ma, 10 min.
 Heating rate = 22°C/min.
 3-21-69 3×10^{-7} full scale

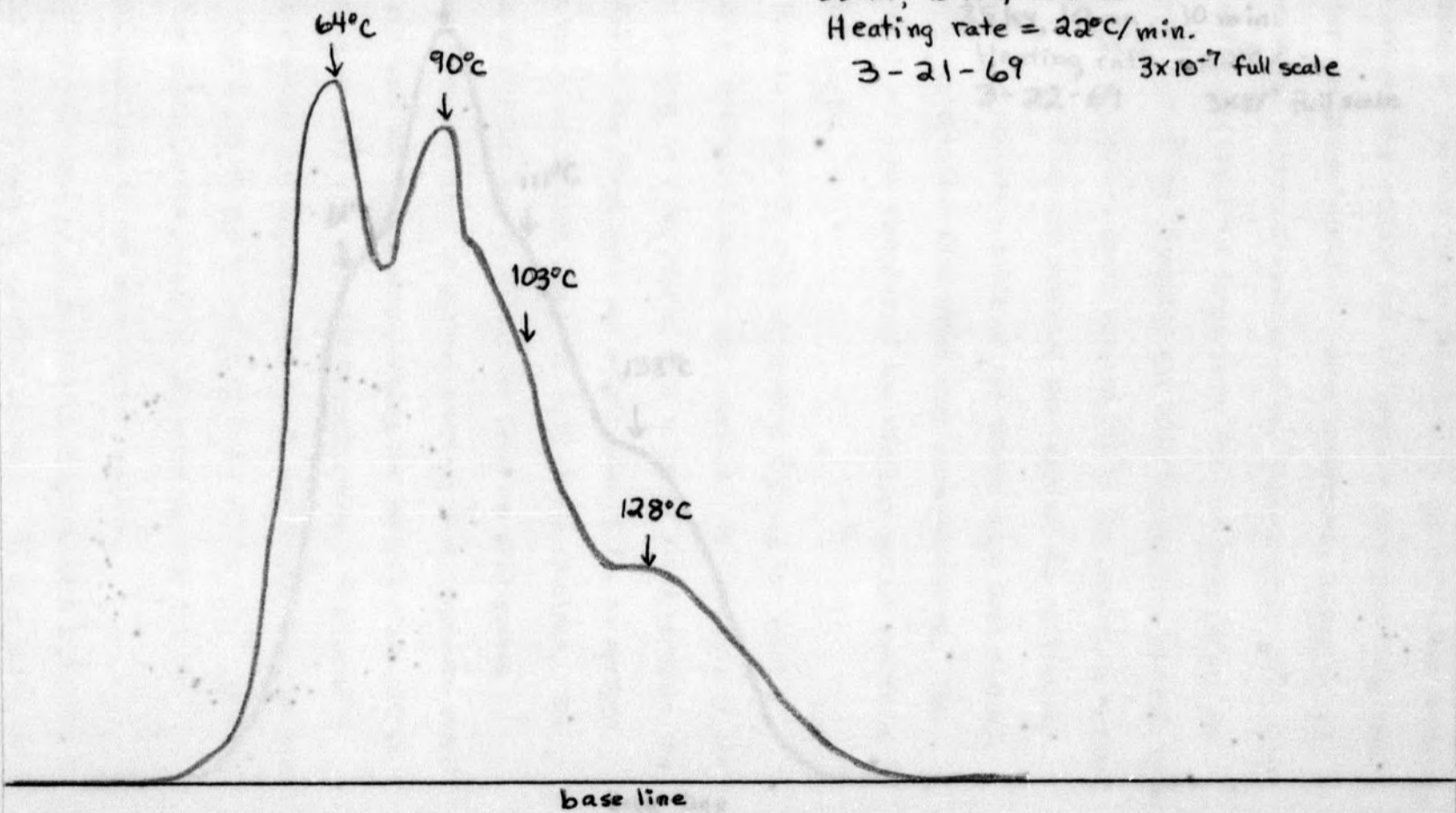
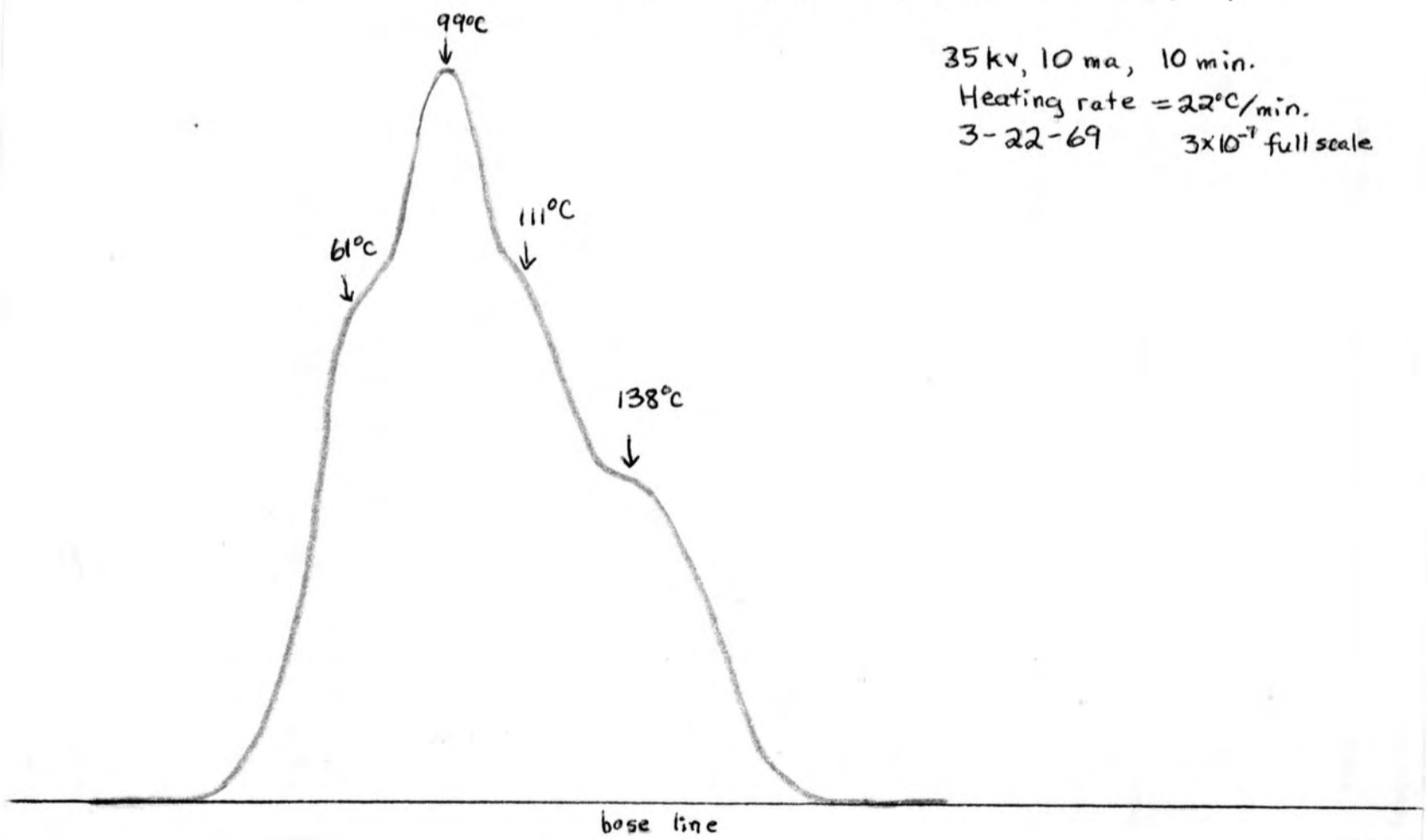


Figure 11

NEW HARSHAW QUENCHED 4

35 kv, 10 ma, 10 min.
Heating rate = 22°C/min.
3-22-69 3×10^{-7} full scale



In order to simplify the calculations of the activation energies, a Fortran program was written and the computer performed this task. The computer was given values of thermoluminescence intensity and the corresponding millivolt reading of the thermocouple. From this input data it calculated the temperature for each data point, the natural logarithm of the intensity and $1000/\text{Temperature}$, plotted these values on a graph, made a least squares fit to the points, determined the slope of that line, and computed the value of the activation energy. It also printed a table of the values which were plotted and the input data values from which they were calculated. The program itself and some examples of the computer output are shown in the next few pages.

New Harshaw 5 was the only unquenched crystal for which a calculation of activation energy was possible. On the basis of the assumption that up to a maximum of four hours of x-ray exposure the initial-rise of the first peak was mainly that of F_1 , an average value for the F_1 activation energy of 0.59 eV was obtained. The activation energy for the F_1 calculated from the glow curves corresponding to from five to sixteen hours of x-ray exposure where it is likely that the F_2 was complicating the initial-rise, had an average value of 0.82 eV. Jain and Mehendru made a very careful study of the activation energies for the F_1 and F_2 and obtained the values of $1.05 \pm .05$ eV for F_1 and $1.15 \pm .05$ eV for F_2 .¹⁶ Instead of using the initial-rise method to determine E, they fit the theoretical equations to the experimental results.

All other calculations of activation energies were performed on the initial impurity peak in quenched crystals. In many cases the

FORTRAN PROGRAM FOR COMPUTING
ACTIVATION ENERGIES

```

C      INITIAL-RISE METHOD FOR DETERMINING TRAP DEPTH          005
      DIMENSION THERM(61),YINT(20),XMV(20),T(20),XTEMP(20),YLNINT(20)
      CALL RANGE(-3.,3.,2.3,.02,0,0,'1000/TEMPERATURE0,16,'LN INTENSITY
10,12)
      READ(1,10) (THERM(I),I=1,61)
10  FORMAT(16F5.2)
      9  READ(1,50,END=100)
50  FORMAT(55H THIS STATEMENT WILL BE READ IN FOR EACH DATA SET      ) 0081
      READ(1,11) ND,(YINT(J),XMV(J),J=1,ND)
11  FORMAT(15/16F5.2)
      B=0.
      C=0.
      D=0.
      E=0.
      DO 30 J=1,ND
      DO 20 I=1,61
      IF(THERM(I)-XMV(J))20,21,25
20  CONTINUE
21  T(J)=(I-1)*5.+273.
      GO TO 26
25  A=(I-1)*5.
      T(J)=A-5.*(THERM(I)-XMV(J))/(THERM(I)-THERM(I-1))+273.
26  XT=1000./T(J)
      XTEMP(J)=XT
C      E#XSUM B#XSQSUM C#XYSUM D#YSUM
      E=E+XT
      B=B+XT*XT
      YL=ALOG(YINT(J))
      YLNINT(J)=YL
      C=C+XT*YL
      D=D+YL

```

CONTINUATION OF FORTRAN PROGRAM

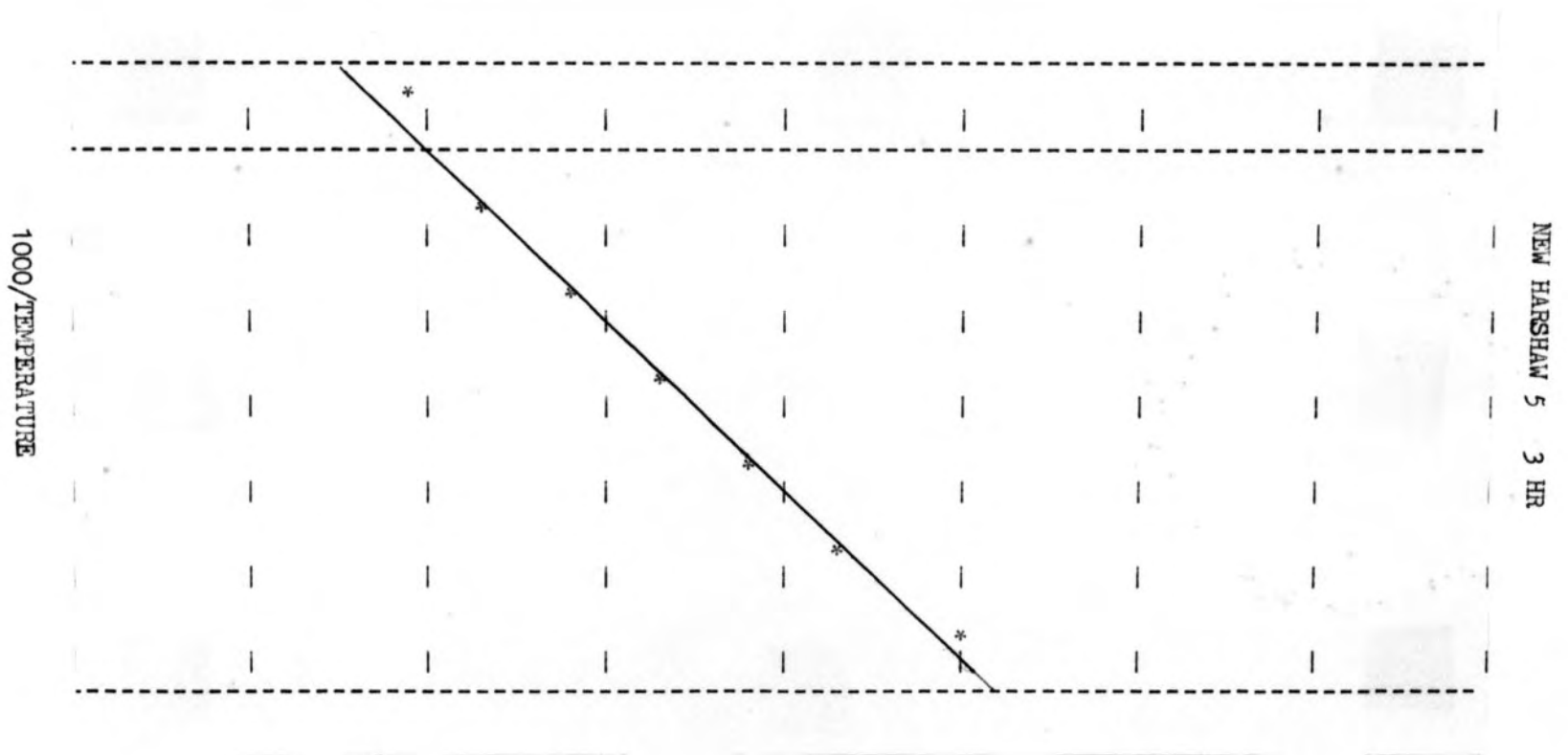
```
30 CONTINUE
   SLOPE=(D*E-ND*C)/(E*E-ND*B)
   ENERGY=SLOPE*0.158/1.6
   WRITE(3,40)
   WRITE(3,50)
   WRITE(3,60)
   WRITE(3,90)
   WRITE(3,70)(YLNINT(J),XTEMP(J),T(J),YINT(J),XMV(J),J=1,ND)
   WRITE(3,80)SLOPE,ENERGY
   CALL PLOT6(ND,YLNINT)
   GO TO 9
100 CONTINUE
   STOP
   40 FORMAT(////)
   60 FORMAT(//)
   90 FORMAT(82H LN INTENSITY    1000/TEMPERATURE    TEMPERATURE    INTE 042
   INSITY    MILLIVOLT READING)
   70 FORMAT(F12.3,F16.3,F16.1,F15.2,F16.2/)
   80 FORMAT(11H    SLOPE=,F7.2,10H    ENERGY=,F7.2,2HEV////)
   END
```

135 DEGREE PEAK IN NEW HARSHAW 5 3 HR 3-21-69

| LN INTENSITY | 1000/TEMPERATURE | TEMPERATURE | INTENSITY | MILLIVOLT READING |
|--------------|------------------|-------------|-----------|-------------------|
| -1.204 | 2.849 | 351.0 | 0.30 | 3.27 |
| -0.799 | 2.806 | 356.4 | 0.45 | 3.51 |
| -0.478 | 2.758 | 362.6 | 0.62 | 3.79 |
| -0.186 | 2.721 | 367.6 | 0.83 | 4.02 |
| 0.095 | 2.674 | 374.0 | 1.10 | 4.30 |
| 0.405 | 2.641 | 378.6 | 1.50 | 4.54 |
| 0.631 | 2.603 | 384.2 | 1.88 | 4.81 |

SLOPE= -7.37 ENERGY= -0.64EV

LN INTENSITY



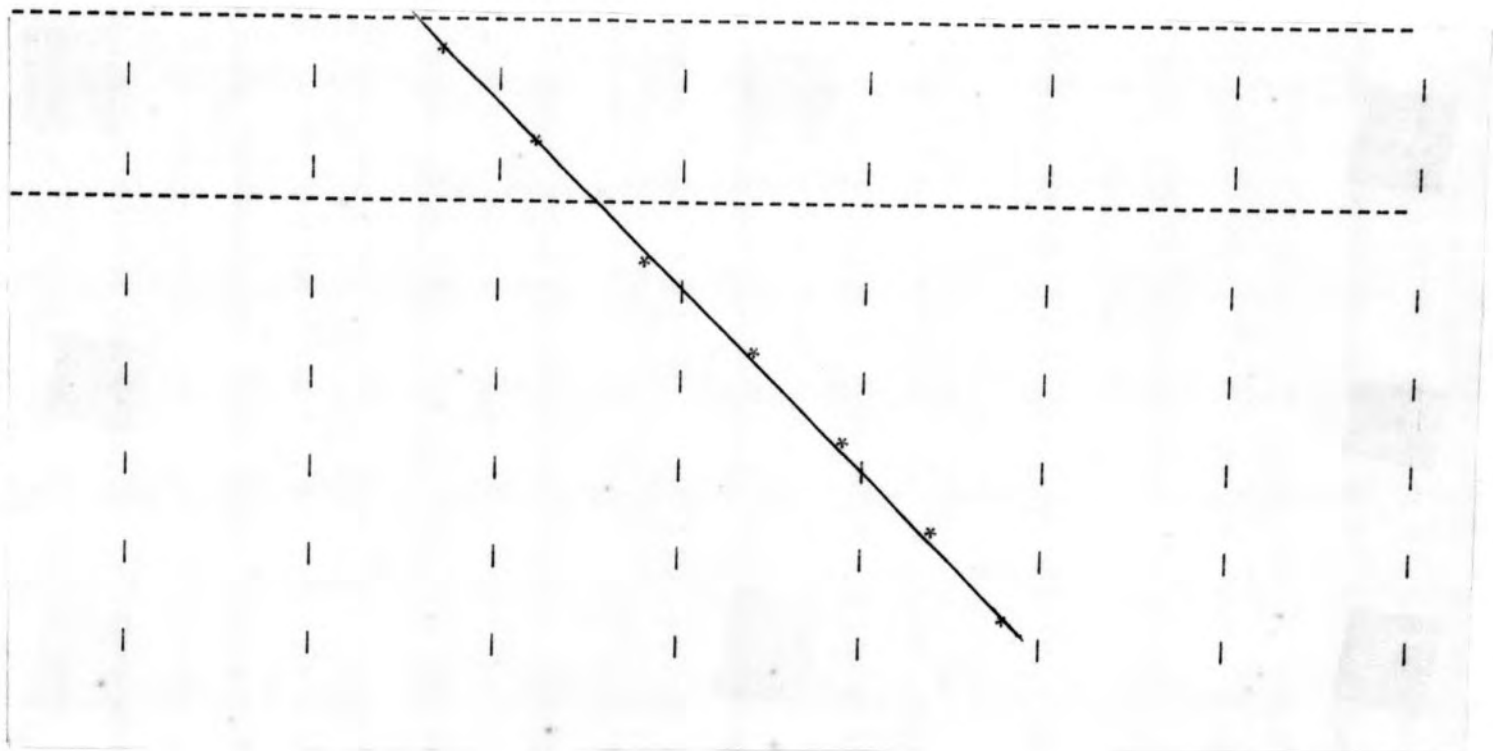
156 DEGREE PEAK IN NEW HARSHAW 5 9 HR 3-22-69

| LN INTENSITY | 1000/TEMPERATURE | TEMPERATURE | INTENSITY | MILLIVOLT READING |
|--------------|------------------|-------------|-----------|-------------------|
| -1.661 | 2.822 | 354.4 | 0.19 | 3.42 |
| -1.427 | 2.773 | 360.6 | 0.24 | 3.70 |
| -1.139 | 2.732 | 366.0 | 0.32 | 3.95 |
| -0.821 | 2.683 | 372.8 | 0.44 | 4.24 |
| -0.494 | 2.647 | 377.8 | 0.61 | 4.50 |
| -0.117 | 2.625 | 380.9 | 0.89 | 4.65 |
| 0.182 | 2.576 | 388.2 | 1.20 | 5.01 |

SLOPE= -7.75 ENERGY= -0.67EV

1000/TEMPERATURE

LN INTENSITY



NEW HARSHAW 5 9 HR

differences were so great that a meaningful average could not be obtained. Oak Ridge Quenched 4, New Harshaw Quenched 4, and New Harshaw Quenched 10 are three crystals for which this was the case. Two crystals, however, Oak Ridge Quenched 10 and New Harshaw Quenched 11 had average activation energies for the first impurity peak of 1.53 eV and 1.59 eV respectively. The average temperatures of these impurity peaks were 73°C and 62°C respectively.

Spectral Studies

The most interesting of these thermoluminescence studies are the spectral studies in which an attempt was made to determine the wavelength of the thermoluminescence given off. No similar studies could be found in the literature so this may be the first time that a spectral study of this kind has been made.

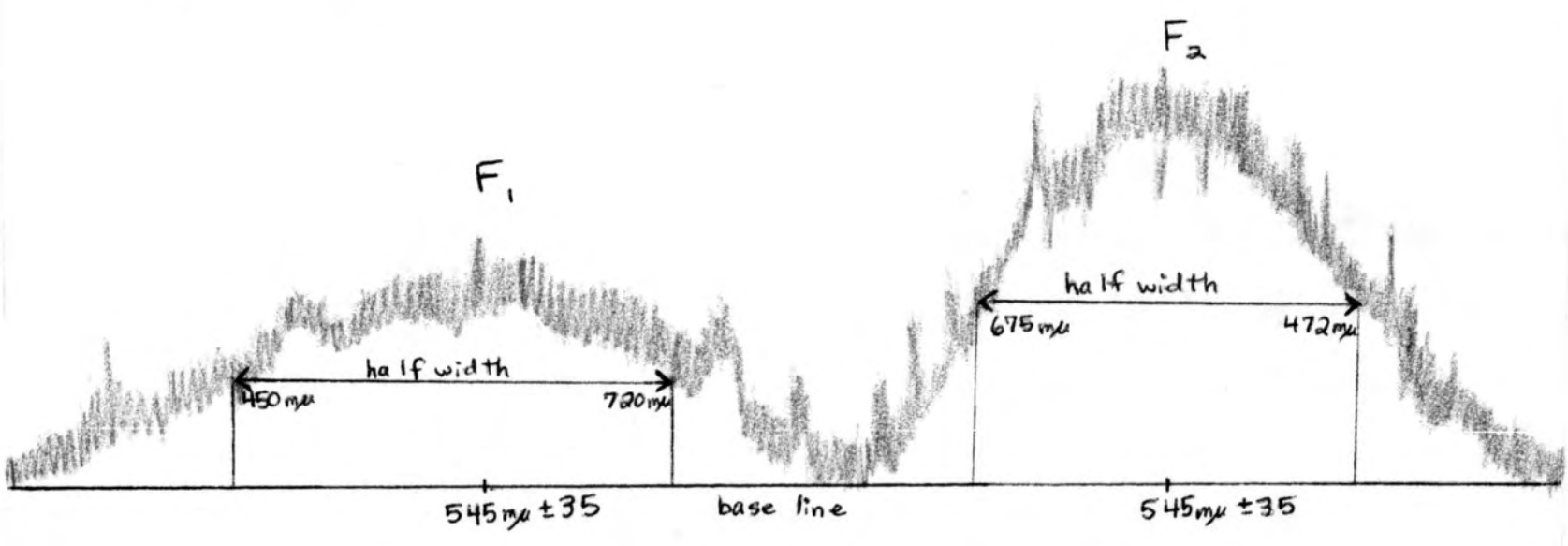
The first results were not too conclusive. The thermoluminescence effect with the monochromator in position was barely observable above the background dark current. Also for the first few spectrophotometer runs, the wrong wavelength range was swept (approximately 3900 to 5000 Å or 390 to 500 mμ). Some typical spectrophotometer charts are shown in Figures 12 through 15. The wavelength bands are seen to be very broad with half-widths around 200 mμ or more. The average value of the wavelength for the F₁ obtained directly from the curves of thermoluminescence vs. wavelength was 570 mμ within an average of ± 34 mμ. The F₁ value within the smallest range of wavelengths was 582 ± 20 mμ. The average value of the wavelength for the F₂ obtained from the curves was 550 mμ within an average of ± 29 mμ. The F₂ value within the smallest range of wavelengths was 545 ± 16 mμ.

In order to correct for the effect of intensity variation of

NEW HARSHAW 5

Figure 12

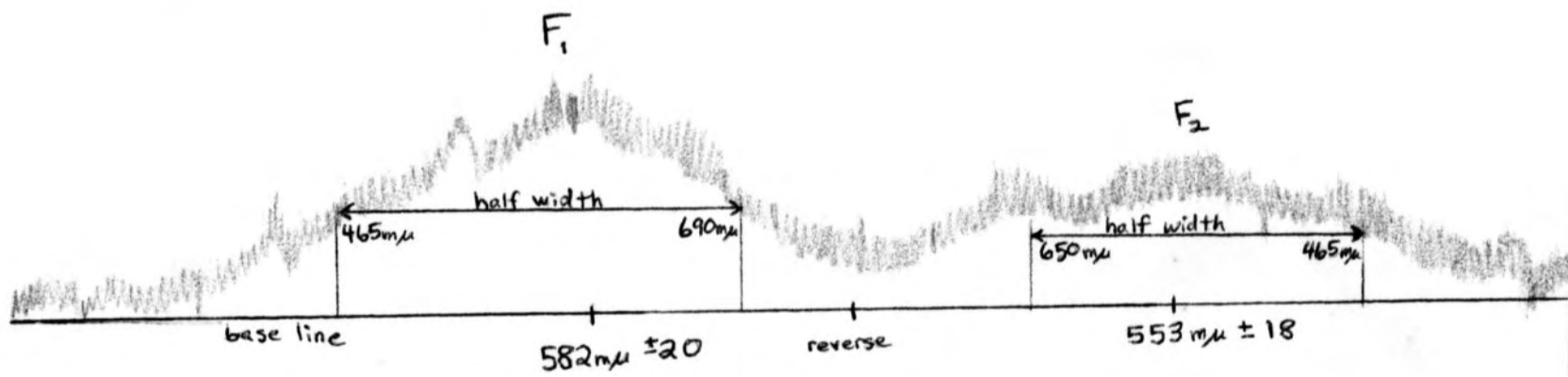
1.0 mm slit width
35 kv, 20 ma, 4 hr.
swept 6.50 → 4.00 and reversed
Chart speed - 2 inches per min.
Slow heating rate



NEW HARSHAW 5

Figure 13

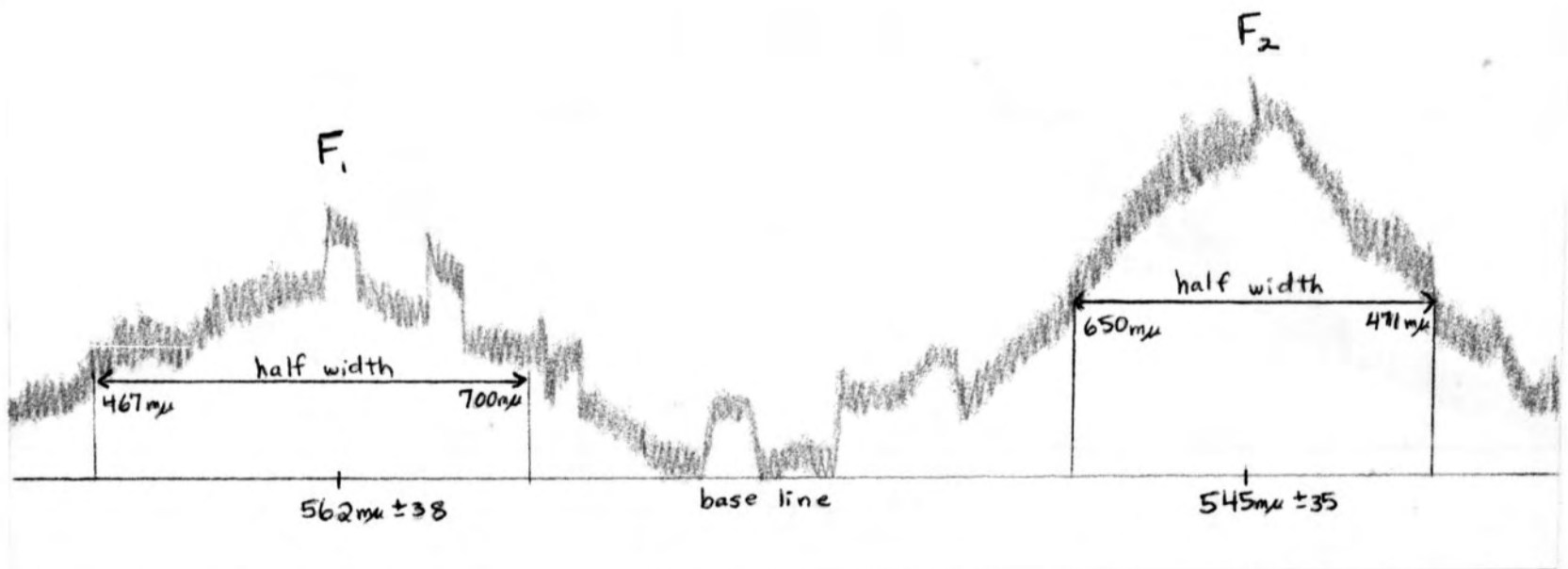
0.5 mm slit width
35 kv, 20ma, 4 hr.
swept 6.50 → 4.00 and reversed
Chart speed - 2 inches per min.
Regular heating rate



NEW HARSHAW 5

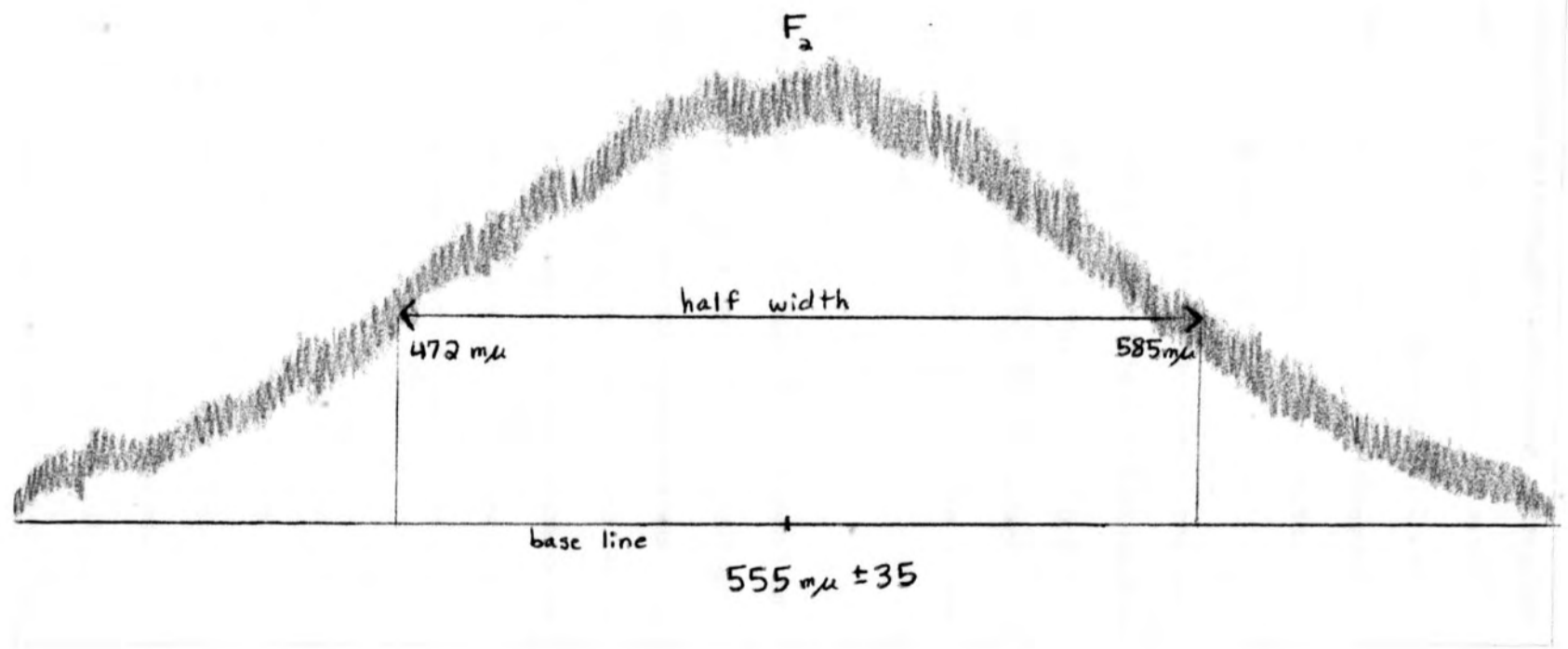
Figure 14

1.0 mm slit width
35 kv, 20 ma, 12 hr.
swept 6.50 → 4.00 and reversed
Chart speed - 2 inches per min.



OAK RIDGE QUENCHED 4 Figure 15

1.0 mm slit width
35 kv, 20 ma, 30 min.
swept 7.00 → 3.50
Chart speed - 4 inches per min.



the thermoluminescence during the spectrophotometer sweep, a regular thermoluminescence run was made on the same crystal and the ratio of the spectral run intensity to the regular intensity $I(\lambda)/I$ was formed. This ratio was then plotted as a function of wavelength. The peaks calculated in this manner corresponded to wavelengths of 580 m μ and 590 m μ for F_1 and 557 m μ and 545 m μ for F_2 .

The energy difference between the state which the electron has been excited into and the state which it falls into when luminescence occurs is related to the wavelength by the formula $E = h\nu = hc/\lambda$. Using the average values of the peak wavelength, E_1 , the energy difference of the F_1 is 2.18 eV and E_2 , the energy difference of the F_2 is 2.26 eV.

Effect of Thickness

A brief study of the effect of the thickness of the crystal on the thermoluminescence was conducted. Four crystals were given the same x-ray exposure and their subsequent thermoluminescence was measured. The results showed that the peaks were sharper and better defined for crystals having a smooth surface. Also the luminescence intensity was greater for the thicker crystals indicating the formation of more F centers in the same amount of time.

Sources of Error

Some of the major experimental difficulties were associated with the equipment used. The crystals used for these studies were a major source of error. They lacked uniformity in size, smoothness, thickness, and impurity content even when cleaved from the same larger crystal. This made it very difficult to get reproducible results without using the same crystal. The location of the crystal

when it was mounted on the soldering iron was not always exactly the same. This had a definite effect on the amount of luminescence which reached the phototube and was recorded. Although an attempt was made to place the crystal in the same position, this was not always the case. If crystals of uniform size had been used, some kind of mark on the soldering iron could have been utilized to insure that the crystals were always mounted in the same location. Another source of poor results especially in the spectral study, was the phototube used. A phototube with a spectral response up to 8500 Å would have been much better for determining the wavelength of the emission especially for the F_1 since the reduction of the sensitivity to zero at 7000 Å may have cut out some of the luminescence which was still being emitted.

Other sources of error were associated with the techniques used. The main error here was the lack of uniform coloration since the crystals were x-rayed on one side only. Another error arises from the fact that the crystal was not kept in total darkness from the time it was x-rayed until the thermoluminescence run was made. Care was taken, however, to keep the background light which the crystal was exposed to down to a minimum, since light bleaches out the F centers.

Summary and Conclusions

Thermoluminescence was seen to be a valuable technique for studying F centers since it provided a simple means of separating the two different kinds of F centers, so that their characteristics could be separately determined. The studies on the growth of F centers, in agreement with similar studies by Jain and Mehendru, clearly

indicated that the F_1 centers were formed from vacancies already present in the crystal since their growth saturated in about four hours, and the F_2 centers were formed from vacancies generated during irradiation since they continued to grow for as long as sixteen hours of exposure to radiation.

The studies with the quenched crystals were not very conclusive. Quenching did have the effect of greatly increasing the luminescence intensity especially of the low temperature impurities and it even generated a one-sided impurity in the New Harshaw crystals. This combined technique of quenching the crystals and measuring their thermoluminescence may be of value for determining the relative purity of a group of crystals on which thermoluminescence studies have been made, since "the number, height and positions of the observed thermoluminescence peaks are very sensitive to the background or deliberately introduced impurity."¹⁷

The activation energy studies were also not very conclusive because of the wide variation of energies for the same peak. A better value for the F_1 activation energy could be found if the method of peak resolution suggested by Jain and Mehendru had been employed. Perhaps a value for the F_2 activation energy also could have been obtained. They suggested that a slow heating rate ($5^\circ\text{C}/\text{min}$) would resolve the two thermoluminescence peaks. Alternately, a relatively pure first peak could be obtained by using small times of x-irradiation and a relatively pure second peak could be obtained by using large irradiation times and removing the first peak by partial thermal bleaching.¹⁸

The spectral studies have some very interesting consequences. It

was seen that the peak emission wavelength for the F_1 and F_2 centers differed. The energy difference corresponding to this wavelength difference was about 0.08 eV. This is very close to the difference in activation energies for the F_1 and F_2 of 0.10 eV obtained by Jain and Mehendru. On the basis of this information, two different energy level diagrams can be proposed. If one assumes that both F_1 and F_2 centers are formed in traps at the same energy level and that recombination occurs for both types of F centers at the same energy level, an energy level diagram like the one shown in Figure 16 would explain the difference of approximately 0.10 eV in both activation energy and emission energy for the F_1 and F_2 centers.

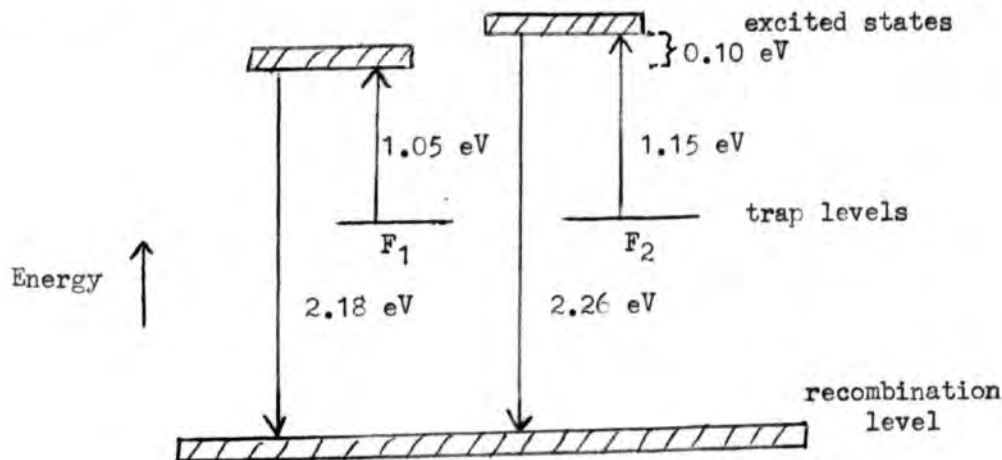


Figure 16

One can also assume that the F_1 and F_2 centers are formed in traps at different energy levels and that recombination occurs at different energy levels. In this case an energy level diagram like the one shown in Figure 17 would explain the activation and emission energy differences. A much more extensive study of these energy differences must be carried out before one can determine if either of these proposed energy level diagrams is correct.

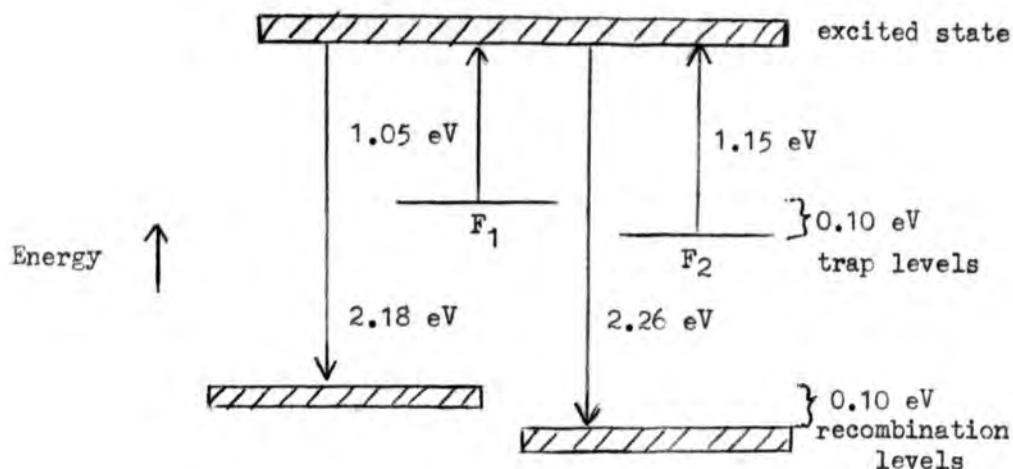


Figure 17

One can conclude from the study of the effect of crystal thickness on thermoluminescence that crystals of uniform thickness with smooth surfaces must be used to obtain reproducible results.

These thermoluminescence studies have pursued only a few of the numerous possibilities for F center study. Much more work needs to be done both in verifying some of these experimental results and performing similar experiments with other alkali halides such as potassium bromide or sodium chloride. It would be interesting to see if a variation in either the alkali ion or the halide ion would have a definite effect on the growth of the F₂ centers. A study of this kind could lead to a better understanding of the mechanism for F center formation by irradiation. Spectral studies coupled with activation energy studies for different alkali halides could indicate whether the energy difference of 0.10 eV for the different types of F centers was characteristic of potassium chloride, or characteristic of F centers in general. Thermoluminescence studies could also be performed on crystals irradiated at liquid nitrogen temperature.

The number of studies yet to be performed is vast and the only limitation is the imagination of the investigator.

Footnotes

- ¹James H. Schulman and W. Dale Compton, Color Centers in Solids (New York, 1962), p. 3-4. Figure 1 taken from p. 4.
- ²S. C. Jain and P. C. Mehendru, "Evidence of Different Types of F Centers from Thermoluminescence Studies in X-Irradiated Alkali Halides. I. Highly Pure KCl Crystals," Physical Review, CXL (November 1, 1965), p. A958.
- ³Charles Kittel, Introduction to Solid State Physics, (New York, 1967), p. 572-573. Figure 2 is taken from p. 573.
- ⁴Robert A. Levy, Principles of Solid State Physics (New York, 1968), p. 434-435.
- ⁵Schulman and Compton, Color Centers, p. 219.
- ⁶P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, "Formation of F Centers in KCl by X Rays," Physical Review, CXXII (January 15, 1961), p. 484.
- ⁷Jain and Mehendru, "Different Types of F Centers," p. A957.
- ⁸Mitchell, Wiegand, and Smoluchowski, "F Centers in KCl," p. 495.
- ⁹Schulman and Compton, Color Centers, p. 18-19.
- ¹⁰Julian A. Crawford, "Research Topic for Small Colleges: Thermoluminescence," American Journal of Physics, XXXIV (March 1966) p. 236. Figure 3 is diagram Crawford refers to as Figure 1.
- ¹¹Schulman and Compton, Color Centers, p. 44.
- ¹²Crawford, "Research Topic," p. 235.
- ¹³Schulman and Compton, Color Centers, p. 38-39.
- ¹⁴Jain and Mehendru, "Different Types of F Centers," p. A960.
- ¹⁵P. Bräunlich, "Comment on the Initial-Rise Method for Determining Trap Depths," Journal of Applied Physics, XXXVIII (May 1967) p. 2516.
- ¹⁶Jain and Mehendru, "Different Types of F Centers," p. A967.
- ¹⁷Ibid., p. A971.
- ¹⁸Ibid., p. A967.

Bibliography

- Bräunlich, P. "Comment on the Initial-Rise Method for Determining Trap Depths," Journal of Applied Physics, XXXVIII (May 1967), 2516-2519.
- Crawford, Julian A. "Research Topic for Small Colleges: Thermoluminescence," American Journal of Physics, XXXIV (March 1966), 235-239.
- Jain, S. C. and P. C. Mehendru. "Evidence of Different Types of F Centers from Thermoluminescence Studies in X-Irradiated Alkali Halides. I. Highly Pure KCl Crystals," Physical Review, CXL (November 1, 1965), A957-A971.
- Kittel, Charles. Introduction to Solid State Physics. New York, 1967.
- Levy, Robert A. Principles of Solid State Physics. New York, 1968.
- Mitchell, P. V., D. A. Wiegand, and R. Smoluchowski. "Formation of F Centers in KCl by X Rays," Physical Review, CXXI (January 15, 1961), 484-498.
- Schulman, James H. and W. Dale Compton. Color Centers in Solids. New York, 1962.