THE SOFT X-RAY ABSORPTION OF EVAPORATED
THIN FILMS OF TELLURIUM

BY

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VITA

The author, son of Mr. and Mrs. George W. Woodruff of LaGrange, Ohio, was born on May 5, 1925. He graduated in June, 1943 from LaGrange High School and matriculated at Oberlin College in February, 1943 with a full tuition scholarship. After joining the U. S. Naval Reserve V-1 in February, 1943, he was called to active duty July 1, 1943 and assigned to Oberlin College in the V-12 program for reserve officers' training. This added some Naval duties to the usual college curriculum. He completed five semesters in Oberlin, attended Midshipman's School, and was commissioned as Ensign U.S.N.R. Duty in Florida and Rhode Island, where he taught tactical radar and emergency ship handling, preceded release to inactive duty in June, 1946. Graduation from Oberlin with an A.B. in physics took place in June, 1947.

Graduate studies in optics were begun at the Institute of Optics, the University of Rochester, September, 1947 and have been under the direction of his advisory committee including Drs. Brian O'Brien, Robert E. Hopkins, M. Parker Givens, and Joseph B. Platt. 97 hours of graduate credit in optics, 39 hours in physics, and 6 hours in mathematics have been completed. Graduate assistantships in optics were held from

September, 1948 to January, 1954 and scholarships from February, 1952 to January, 1954. The assistantships involved research in solid state from September, 1952 to January, 1954 under Dr. Givens, research in thin films under Dr. Harry D. Polster from June, 1949 to September, 1952, and teaching geometrical and physical optics laboratory under the direction of Drs. Hopkins and Givens from September, 1948 to June, 1949. He also had experience during the academic year 1950-51 teaching first year physics recitations. Public Law 346, the G. I. Bill, provided financial assistance from July, 1946 to January, 1952.

Publications have been: Refractive Index Measurement of ZnS, Harry D. Polster and Robert W. Woodruff, J.O.S.A. 43, 326 (1953); Soft X-ray Absorption of Tellurium, Robert W. Woodruff and M. Parker Givens, J.O.S.A. 43, 817 (1953) and Bull. Am. Phys. Soc. 29, No. 1, Abstract B5 (1954).

The writer was married June 24, 1950 to Edythe W. Parker of Evanston, Illinois. Edythe is a graduate of the University of Rochester, 1948, with a Master's Degree in physics in 1952.

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CHAPTER I

INTRODUCTION

Tellurium, element number 52, follows sulphur and selenium in Group VI of the periodic table. Like selenium, tellurium is an intrinsic semiconductor. An item of particular interest in a description of this solid is the energy level structure. By means of soft x-ray absorption, the density of levels in the unfilled portion of the conduction band may be qualitatively described. In this thesis is an outline of the theory of this process, a detailed account of the experimental procedure used to measure the absorption coefficient, and a discussion of the results of the measurements.

CHAPTER II

THEORY

Materials in the solid state have energy level structures which differ from those of free atoms. In the latter the levels are discrete, while in solids they are broadened into bands. This broadening is caused by the proximity of neighboring atoms and the consequent interaction of overlapping wave functions.

The bands can be considered to be composed of a very large number of levels (of the order of the number of atoms in the crystal), which are so close together that they may be described by a continuous function $N(E)$, where $N(E)dE$ is the number of energy levels between energy E and $E+dE$. A schematic diagram showing this relationship is given in Figure 1.

If the highest band of some material is only partly filled, as shown in Figure 1a, there are available energy levels just above the highest filled level into which electrons may be raised by an electric field and metallic conduction can occur. Direct evidence for the distribution of energy states in metals is the result of experiments in soft x-ray spectroscopy.

If the highest level in which there are any electrons is

FIGURE I
SCHEMATIC REPRESENTATION OF
DENSITY OF LEVELS

completely filled, there can be no net flow of charge. When this condition obtains, the material is an insulator. This is indicated in Figure 1b.

The distinction holds even when there are more electron states than valence electrons. A classic example is diamond, in which there are 8 states and only 4 electrons. Kimball¹ has shown that the 8 states are separated by a large forbidden gap into two bands of 4 states each. The lowest band is completely full and the upper empty. Hence, diamond is an insulator.

Tellurium has a somewhat similar structure, but the forbidden gap is only 0.34 ev.², so it is classed as an intrinsic semiconductor.

A description of the energy levels of a solid includes both position and structure of the bands. An investigation of the filled portions may be made by the study of the emission process. As indicated in Figure 2, an electron falls from an upper filled level to a lower level, in which an opening has been made by some means. Here the emitted intensity is given by $I \propto \nu^3 f(E) N(E)$, where ν is the frequency and $f(E)$ is the

1. Kimball, G. E., Jour. Chem. Phys., **3**, 560-564 (1935).

2. Nussbaum, Allen, Electrical Properties of Pure Tellurium and Tellurium-Selenium Alloys, p. 29, Technical Report #1, Contract AF-33-(616)-78, University of Pennsylvania, 1953

EMISSION AND ABSORPTION PROCESSES

FIGURE 2

square of the dipole moment³. The value of $f(E)$ depends on exact wave equations. These have not been calculated and, hence, it is possible only to make a qualitative measure of $N(E)$.

The unfilled portions of the energy level structure may be investigated by a study of the absorption of light. Figure 2 shows this schematically. In the absorption process an electron is raised from an inner level to an unoccupied state in the valence band. At a given frequency the absorption $\propto f(E) N(E)$ ⁴. Again $N(E)$ can be only qualitatively determined because of the unknown value of $f(E)$. It is, however, reasonable to assume that the absorption band approximates the shape of the $N(E)$ function.

Also to be considered is the fact that the raising of an electron out of an inner level alters the crystal so that the energy level structure observed is really that of a slightly perturbed lattice.

In the free atom transitions are allowed or forbidden according to the l-selection rule, which states that orbital angular momentum may change by ± 1 unit. In solids this rule does not hold exactly, since the wave functions of the outer

3. Mott, N. F. and Jones, H., The Theory of the Properties of Metals and Alloys, p. 126, London; Oxford University Press, 1936.

4. Ibid., p. 128.

bands are not pure⁵. This mixing of wave functions will be invoked to account for certain observed transitions.

Tellurium has six valence electrons, which are situated as follows: two electrons are in the 5s states, the 0_1 level, and four are in 5p states, the 0_2 . Actually, there are 6 p-states available, but because of the hexagonal chain structure^{6,7} of tellurium, as sketched in Figure 3, the states with wave functions lying along the chain axis will be at a somewhat higher energy, since they are more overlapping⁸. This is represented schematically in Figure 4. Also shown in the diagram are the d-levels. These, however, will be mixed with p and f states, so transitions may occur to energies more than 0.34 ev. above the filled levels.

As pointed out by Skinner⁹ and Siegmund¹⁰, the transitions from rather shallow levels are most useful for the study of

5. Ibid., p. 74.

6. Von Hippel, A. R., Jour. Chem. Phys., 16, 372-380 (1948).

7. Grison, E., Jour. Chem. Phys., 19, 1109-1113 (1951)

8. Nussbaum, Allen, Op. cit., p. 41.

9. Skinner, H. W. B., Reports on Progress in Physics, Vol. V, p. 257-283, (1938).

10. Siegmund, W. P., An Investigation of the Absorption by Selenium in the Soft X-ray Region, p. 53-54, The University of Rochester, Doctoral Thesis, 1951.

**Schematic Representation of Tellurium Lattice
(after Grison)**

FIGURE 3

SCHEMATIC DIAGRAM OF ENERGY LEVELS
(After Nussbaum)

FIGURE 4

structure of the unfilled portions of the valence bands. The reasons for this are (1) these shallow levels are narrower in energy than deep levels¹¹ and (2) the requirement on resolving power is reduced if one wishes to resolve 0.1 volt in a 100 volt transition (N to the conduction band) rather than 0.1 volt in a 10,000 volt transition (K to the conduction band).

The transitions involved are from N levels to the unfilled portion of the O level. The energies for the transitions have been predicted by Bohr and Coster¹² and others^{13,14} from limiting frequencies of emission series. These predictions will be discussed more fully in a later section and comparison will be made with the results of this investigation.

11. Prins, J. A., *Physica*, 2, 231-238 (1935).

12. Bohr, N. and Coster, D., *Zeits. für Physik*, 12, 342-374 (1923)

13. Nishim, Y., *London, Edinburgh, and Dublin Phil. Mag. and Journal of Science*, 49, 521-537 (1925)

14. Chamberlain, Katherine and Lindsay, George A., *Phys. Rev.*, 30, 369-377 (1927)

CHAPTER III

EXPERIMENT

A. APPARATUS

1. The Spectrograph

The vacuum spectrograph, available at the Institute of Optics for use in this research, has been described in detail by Siegmund¹⁵ and certain modifications have been discussed by Carter¹⁶. In brief, the instrument is a grazing incidence mount of a Johns Hopkins 2 meter aluminum grating with 30,000 lines/inch. The grating and photographic plate holder (on the Rowland circle) are mounted on a cantilever support over which fits a metal bell jar riding on horizontal tracks, as seen in the photograph in Figure 5a.

The angle of incidence is approximately 85° . In an attempt to reduce the stray light within the spectrograph, a set of baffles was designed and mounted in the tube carrying the slit assembly. These baffles serve to eliminate the reflections from the tube walls and from the slit assembly itself. With this modification it is possible to obtain clean

15. Siegmund, Op. cit., p. 6-45.

16. Carter, D. E., A Study of the Soft X-ray Absorption of Thin Films of Iron and of Iron Oxide, p. 11-17, The University of Rochester, Doctoral Thesis, 1954.

(a)

(b)

Figure 5: Photographs of the Spectrograph

spectra at wavelengths as short as 100 Å.

The source is within the vacuum system, although the chamber is evacuated by a separate small glass oil diffusion pump. A picture of this chamber and the associated vacuum system is shown in Figure 5b. The vacuum system on the spectrograph itself is a DPI MC-500 oil diffusion pump. A single Cenco Hypervac is sufficient to back both oil pumps.

The source is a spark between copper or silver electrodes from $1/6 \mu\text{f}$ condenser charged to about 30,000 volts. The power supply, shown in Figure 6, is a slightly modified version of that used by Siegmund¹⁷. The resistances R_1 and R_2 have been increased to the values indicated. This increased the time constant of the circuit and, thereby, made the sparking rate more controllable. Installation of an adjustable air gap in series with the spark gap was made during the course of this research. This air gap, constructed of aluminum rod slightly rounded on the ends, was maintained at about $1/2''$ separation--the width determines the breakdown voltage. In parallel with the internal spark source was a resistance of 15 meg-ohms. When the air gap became conducting, the 30 KV were applied to the internal spark gap which was kept small so

17. Siegmund, Op. cit., p. 39-41.

P Powerstat, rating 2 kw
T₁, T₂ H.V. Transformer, Thordarson
 Type T42479, rating 1 kw
T₃, T₄ Filament Transformer
V₁, V₂ Vacuum Rectifier, Kenotron 8020

C₁, C₂ 0.3 μ fd
R₁, R₂ 0.5 meg (5-100 k, 50 w)
R₃ 2.5 k
R₄ 15 meg (15-1 meg, 2 w)

POWER SUPPLY FOR SOURCE

FIGURE 6

that it would not have any control over the rate of sparking.

The slit is about 1 cm. long and .003 cm. wide. The jaws are of stellite (nickel, tungsten, and cobalt alloy) and are adjustable. The plate holder is provided with clamps every 5" so the 10" plates can be positioned every half plate length. The occulting diaphragm has a 1/4" spacing and the plate holder may be moved (with some overlap) so five exposures may be made on a two inch plate.

The photographic plates used were Eastman Kodak Spectroscopic Plates, Type SWR Extra-thin, size 2" x 10".

The sample is placed just to the grating side of the slit so that it will be somewhat protected from the spark. Two films may be placed in the vacuum system at one time and changed from one to the other without disturbing the vacuum. This may be accomplished by means of the "vacuum bottle" designed and described by Carter¹⁸. This design has been slightly modified by the addition of a milled slot connecting the two openings. This allows a more free passage of air to the back of the film that is not in use and, thereby, reduces the breakage of films caused by unequal air pressure.

18. Carter, Op. cit., p. 14-16.

2. Wavelength

The wavelengths were determined basically from tables of the copper spark spectrum by Kruger and Cooper¹⁹. They list the prominent lines found in a source similar to our vacuum spark from 100 Å to 450 Å. Using this data and estimated position, a fit can be made between existing lines and the listed lines on a smooth curve of wavelength versus distance along the plate. This is shown in Figure 7. Once this curve is firmly established, the wavelength may be read off for any plate so long as any one line is recognized.

The silver spectrum was easily calibrated by making a set of exposures which gave a comparison with copper. The run consisted of superimposed copper and silver spectra flanked by two different exposures of each for identification of both light and dense lines. The wavelengths of the silver lines were determined from known copper lines and the wavelength versus distance curve. Further verification for the silver lines was found in a paper²⁰ in which certain prominent silver lines are listed.

19. Kruger, F. S. and Cooper, P. G., Phys. Rev. 44, 826-830 (1933).

20. Bloch, L., Bloch, E., and Farineau, J., J. Phys. Rad., 3, 437-457 (1932).

WAVELENGTH CALIBRATION

FIGURE 7

The distance along the plate was measured to an accuracy of about 0.1 mm., which corresponds roughly to 0.1 Å. Hence, the error in any one point on the absorption curve is 0.1 Å. The lines used were generally about 1 Å apart. Hence, it was impossible to tell the position of the peak to better than 1 Å.

B. ABSORBER

1. Film Requirements

Since absorption is a function of the ratio of energy transmitted through the film to incident flux, it is necessary to make at least two exposures; one with the sample in the beam and one without. In practice, it is better to make one exposure through a thick absorber and one through a thin, since this should eliminate the effect of reflectivity at the interfaces.

The large absorption of tellurium ($\sim 10^5 \text{ cm}^{-1}$) requires that the samples be thin in order to allow exposures of reasonably short times. Thin samples (a few hundred Angstroms thick) of tellurium were found not to be strong enough to hold together without support. Films of tellurium on celluloid broke as soon as the celluloid was dissolved in amyl acetate; films on rock salt broke when water was applied to dissolve the salt. (Note: It is possible for certain films to be made in these ways, e.g. selenium thicker than about 1000 Angstroms.) Since unsupported tellurium films were not obtainable, it was necessary to employ a substrate. Celluloid was chosen for several reasons: films of uniform thickness are easily produced, tellurium can be deposited on it in a continuous layer,

and the absorption is known. A measurement by O'Bryan²¹ of the absorption coefficient of celluloid showed a peak at 800 Å. Using an extrapolation of his results, the absorption varies from less than 10^5 cm.^{-1} below 200 Å to about $6 \times 10^5 \text{ cm.}^{-1}$ at 400 Å. The value $4 \times 10^5 \text{ cm.}^{-1}$ at 300 Å means that a 500 Å thick film would transmit about 13% of the incident flux. Actually the variation in absorption of celluloid is of little import since identical thicknesses are used for each pair of tellurium films, and, hence, are not involved.

2. Preparation of Thin Films

The celluloid substrate was produced by dropping one drop of cellulose nitrate dissolved in amyl acetate onto the surface of distilled water. The solvent evaporated in a few seconds, leaving the celluloid film floating on the water. An estimate of the thickness and uniformity was obtained by observing the reflected interference colors as evaporation of the solvent progressed. Most of the films used were dark (not black, however), hence, less than $\lambda/4$ or 800 Å (using the index 1.65 from O'Bryan²²). Siegmund²³ measured one in

21. O'Bryan, H. M., J. O. S. A. 22, 739-748 (1932).

22. Ibid.

23. Siegmund, Op. cit., p. 63

this thickness range to be 500 Å.

The celluloid film was removed from the water by placing on it a clean glass plate with a hole 1 1/2" in diameter in it; the celluloid adhered to the glass and it was possible to pick it up off the water surface. To avoid cracks and uneven stretching of the film it was necessary that the plate not be vibrated during the lifting. This plate was then placed in the evaporation chamber.

Two different evaporation systems were used for the deposition of films. During the first portion of the work, the exploratory part, a small chamber was operated. This consisted of a 12" diameter and 12" deep chamber with a glass cover. The vacuum system was a DPI MC-275 oil diffusion pump backed by a Cenco Hypervac. Measurement of pressure was accomplished with a Pirani gauge in the fore line and a DPI VG-1A ionization gauge attached to the chamber. Pressures of 5×10^{-5} mm. Hg were easily attainable, but the pumping speed was not sufficient to maintain this pressure during rapid evaporation. For this reason a faster system was used for the silver evaporation in connection with the measurement of thickness and for all evaporations thereafter.

The larger system of metal bell-jar type with a glass cover was evacuated by means of a DPI MC-500 oil diffusion

pump backed by a Kinney VSD 5-5-6. An RCA 1949 ionization gauge was used to measure the pressure, which could be maintained below 3×10^{-5} mm. Hg during evaporation.

A modified DPI-type ionization control circuit was used to control both the VG-1A and the RCA 1949 tubes.

After a pressure of 2 to 3×10^{-5} mm. Hg was reached, a boat containing tellurium was heated electrically and the tellurium evaporated. The evaporation was very rapid even at dull red temperature. After the required optical density (or amount), A_1 , was obtained on one half of the film (measured with a photocell or estimated visually), a baffle was moved and an additional amount of tellurium, A_2 , was deposited over the whole area of film. Half the area then had the amount $A_1 + A_2$ and the other half only A_2 .

In Figure 8 the two views of the evaporation chamber show the arrangement of the plate carrying film, the baffle, and a monitor plate, the position of which was known with relation to the film, and the boat some 13" below. The monitor plate was used as a measure of the thickness of the tellurium film, as described below.

The sample holder from the spectrograph was then washed, and dried, and the films laid on it, celluloid surface down to insure adherence. One of the openings in the sample holder was

ARRANGEMENT FOR THE
EVAPORATION OF FILMS

FIGURE 8

covered with a thick tellurium film and the other a thin film.

Evaporated films of tellurium have recently been shown to be not completely crystalline when deposited on substrates below 200° C.²⁴. However, the resistivity of these films is of the same order of magnitude as bulk tellurium. This indicates that there is probably a tendency for microcrystals to anneal into a near-crystalline form. That the films are continuous layers is also borne out by microscopic study of the evaporated films on celluloid. There is no evidence of grainy appearance as with deposits of metals such as zinc and aluminum, which do not wet the celluloid. Siegmund²⁵ argues that the valence band structure for amorphous selenium is similar to that of the crystalline material. This is based on work by Keck²⁶ and Hendus²⁷. Keck showed that both forms have chain structure and Hendus found the distances to nearest neighbors nearly identical in both forms. Since tellurium and selenium are isomorphous, this same argument is applicable here.

24. Sakurai, T., and Munesue, S., Phys. Rev., 85, 921 (1952).

25. Siegmund, Op. cit., p. 94.

26. Keck, P. H., J. O. S. A., 41, 53-55 (1951).

27. Hendus, H., Zeits. für Physik, 119, 265-286 (1942).

The oxide of tellurium is not very easily produced and is white. Since there is no whitening and since resistivity does not change markedly upon exposure to dry air, it is presumed that the films as used in the spectrograph were pure tellurium. A sample of the bar of tellurium used throughout this experiment was analysed spectroscopically. There were only traces of impurities.

3. Measurement of Thickness

The thickness of each tellurium film was determined indirectly from its optical density. First, the relationship between optical density and physical thickness was obtained by making an interferometric measure of the thickness of a film of known (measured) optical density. The interferometer plate and monitor had been placed in known positions with respect to the "boat" containing tellurium. Half the interferometer plate had first been covered with a baffle, which had a straight edge. After the evaporation of tellurium, the plate had been exposed to air, the baffle and monitor plate had been removed, then aluminum had been deposited over the whole area of the plate. Aluminum was used since silver reacts with tellurium. A second plate had been coated with silver to a density of about one. The interferometer arrangement is shown

in Figure 9a. The fringe pattern, which is shown in the idealized Figure 9b, was photographed. Distance A, the fringe shift, divided by distance B, the fringe spacing, is the thickness in terms of half waves. The accuracy of the measurements is approximately 5%.

Now for each of these determinations the optical density of the monitor plate was measured on an Ansee Sweet Densitometer and after taking account of its position with respect to the interferometer plate, a plot was made of the thickness versus optical density. This is reproduced in Figure 10. The estimated total error in thickness is less than 10%.

An attempt was made to check this value by weighing tellurium films evaporated onto microscope cover glass. First the weights of five pieces of glass were determined, then several layers were deposited with the density of each layer measured and the corresponding thickness read from the curve of Figure 10. The volume of tellurium on each glass was then computed by adding these thicknesses, total about 0.2 microns, and multiplying by the measured area. Using the difference in weight of glass and tellurium and the clear glass, average .4217 grams, the value of the density was calculated as

(a)

Films on Rear Flat

Fringe Pattern

(b)

ARRANGEMENT FOR THICKNESS MEASUREMENT

FIGURE 9

THICKNESS VERSUS OPTICAL DENSITY

FIGURE 10

$5.50 \pm .4$ grams/cm.³. This is 12% below the listed value²⁸, but evaporated films are often less dense than bulk material and also there was a chance of systematic error in these measurements. Overall, the interferometric measure of thickness is the more reliable.

For each pair of tellurium samples used in the absorption measurement the optical density of the corresponding monitor plate was determined using the same instrument and, after corrections for the position in the evaporation chamber, the density values obtained were entered on the above graph and the thickness of each ascertained. The difference in the thicknesses of these films was the actual absorbing thickness.

28. Handbook of Chemistry and Physics, p.304, Cleveland, Ohio, Chemical Rubber Publishing Company, 1947.

C. PROCEDURE

1. Adjustments and Evacuation

The sample holder with the films mounted was placed in the vacuum bottle and positioned in the spectrograph approximately one half inch on the grating side of the slit.

The alignment of the silver or copper electrodes in the source chamber was done primarily during assembly; however, the adjustment to set them equidistant from the slit was accomplished using the window in the side of the source chamber. This adjustment prevented the electrodes from burning off in an uneven manner and occluding the spark. It was discovered that very careful alignment allowed the gap to be used many thousands of sparks before the electrodes required dressing. Movements in the other directions adjusted the optical alignment to fill the grating. These also were carefully done and, of course, were not changed during the set of exposures.

After the photographic plates were loaded, the valve between the mechanical pump and the system was slowly opened to the point at which pumping started. After a few minutes it was opened slightly more, and so on, until fully open in about forty minutes. This slow pumping reduced any "rush" of air in the vicinity of the very fragile films.

After about eight hours of roughing, the oil diffusion

pumps were turned on. In about three or four hours the pressure was about 5×10^{-5} mm. Hg. Liquid nitrogen was then applied to the cold trap and the spark run intermittently for about two hours. This quite thoroughly outgassed the source chamber as indicated by the fact that the fore line pressure would rise only slightly when the sparking rate was doubled. Toward the end of the outgassing cycle, an attempt was made to establish the rate of sparking at some constant value, since relative line intensities can be influenced by the rate. This was unnecessary after the introduction of the external gap into the circuit. The rate was changed by varying the voltage in the primary circuit and, hence, the voltage build-up time. Changing the width of the gap could have accomplished the rate change also, but this would have influenced the energy output by changing the breakdown potential.

With the external gap in series with the spark source the rate remained constant without adjustment, but to avoid arcing, the internal gap had to be gradually decreased. However, this should not have influenced the breakdown potential, since the gap was always very small.

2. Exposure

As the exposures were started, the sample was turned to place it perpendicular to the light path--it had been turned out of the way to avoid breakage by small particles from the source during outgassing. The photographic plate was put in position 1, the shutter opened, the spark and clock started.

After a predetermined number, A, of sparks had occurred, the voltage was turned off, the plate moved to position 2, and the sample changed from thin to thick taking advantage of the vacuum bottle and the O ring seal. Then the spark was started again. After a certain larger number, B, the voltage was turned off and the plate moved to position 3. Then 2B sparks were run after which the plate was moved to position 4 and sample changed from thick to thin. Then 2A sparks were allowed to occur before the plate was moved to position 5 for A sparks. This completed the exposure so the shutter was closed, the diffusion pumps turned off and cooled, and the high voltage turned off and shorted. As soon as the pumps were cool, air could be let in, very slowly at first, and with slowly increasing rate--taking in excess of one hour to reach atmospheric pressure.

Positions 2 and 3 (B and 2B) and positions 4 and 5 (2A and A) gave the data for two independent determinations of

the characteristics of the photographic plate. Only plates on which reasonable agreement occurred were used. 2B and 2A were placed adjacent to one another in order to facilitate visual examination for gross absorption and estimation of exposure errors. The two identical exposures of A sparks, positions 1 and 5, provided an indication of the reproducibility. The arrangement is evident in the reproduction of a plate shown in Figure 11.

The time involved in the actual exposures varied from slightly more than one hour to as many as five hours. The numbers ran from about 200 to about 20,000 sparks. Very large numbers were avoided as much as possible since chance of film breakage increases as the number of sparks.

3. Development and Visual Inspection

The next step was development of the photographic plates, which were Eastman Kodak type SWR on extra thin glass (0.75 mm. thick). The size was 2" x 10", but the useful length was about 1/2" to 3/4" less than the 10" since the emulsion was non-uniform at the ends.

These plates are extremely sensitive to hypo, a contamination of a few parts per million causing noticeable change in fog level. The sensitivity to oils that are present on the

1
2
3
4
5

Position 1: Thin Tellurium Film 1 spark
Position 2: Thick Tellurium Film 2 sparks
Position 3: Thick Tellurium Film 28 sparks
Position 4: Thin Tellurium Film 24 sparks
Position 5: Thin Tellurium Film 1 spark

Figure 11: Reproduction of a Spectroscopic Plate

human hands results in dark streaks spreading in from the edge of the plate. Wearing clean rubber gloves while handling plates eliminates this effect. (Surgeon's rubber gloves, thoroughly washed, rinsed, and dried, allowed the wearer to retain some sensitivity in his fingertips.)

The pressure sensitivity of emulsions of such low gelatin content is well known and care must be exercised at every handling of the plates. For instance, it is advisable not to attempt to replace the packet in its box, but to use a wider box to avoid forcing and, hence, pressure marks in the emulsions.

The two plates were developed simultaneously in D-19 in a tray. Continuous agitation was supplied by rocking the tray while the temperature was maintained at approximately 65° F. Development was continued for three to four minutes, which is essentially the time for complete development.

The plates were then rinsed in water at 65° F. and placed in hypo at the same temperature. The fixing time was about twenty minutes. The plates were washed in cold water for about one and a half hours and, after a dip in Photoflo solution, placed in vertical position for drying overnight.

After development and before photometry a visual inspection was made to ascertain if the plate was worth the several days

involved in complete analysis of the data. Several conditions had to be met: the plate had to be unfogged; it had to be free of streaks caused by any contamination, e.g. hypo, or caused by moving one plate over another face to face either when packing or unpacking; the number of pinhole had to be small; and the developed density, and hence exposure, had to be within certain limits. The last named limits arose from the fact that the deflection of the densitometer is directly proportional to transmitted light, not density, so transmissions of less than a per cent were indicated with little accuracy. On the other hand, faint lines were not easily distinguished from the background.

The requirements listed above were in addition to having the absorbing films remain in good condition throughout the exposures. This meant that the films, as well as being unbroken, be free of an excessive number of pinholes in the area of the films actually in the beam. The effect of the pinhole type of damage is described in Chapter III.

4. Microdensitometer

The density of each line in the spectrum was measured using a Sinclair Smith Recording Microphotometer. This instrument, available to the author through the kindness of

the Department of Chemistry of the University of Rochester, is a radiometer-type device. The deflection of the radiometer vane, recorded on a 4" x 10" photographic plate, is proportional to the transmitted intensity. The plate being photometered moved at 5.6 mm./minute, which was slow enough to give accurate values for even the narrow lines.

With each microphotometer trace was placed an "opaque" line, that is, the level of zero transmission. It was obtained by closing the shutter and running the recording plate through rapidly. In Figure 12 is shown a portion of a thick-thin pair of traces. The spectrum lines are represented by the peaks pointing toward the "opaque" reference line. Regions of high absorption can be seen.

Figure 12: Superimposed Pair of Microdensitometer Traces

D. ANALYSIS OF DATA

1. Plate Characteristics

The microdensitometer traces were mounted on a Bausch and Lomb comparator (2" objective and 5X eyepieces) which could be read on the vernier to tenths of millimeters in both x and y directions. The plates were mounted in pairs, the traces resulting from the exposures through the thick tellurium films together (positions 2 and 3), and those through the thin together (positions 4 and 5), and then thin (position 1) alone.

The two plates were first matched in x and at the "opaque" reference line, then placed parallel to the x and y directions of the comparator. The x position was fixed at a given spectral line to read a given number and the y position fixed to read 90.0 mm. at the "opaque" line.

The comparator was set on each spectrum line, the distance along the plate, x, noted and the height of the deflection, y, for each read off and listed. The y's for the other three exposures were read off and listed in the same manner. The criterion for setting of y for each line was as consistent as possible over the considerable time involved. The errors caused by inadvertent change of the criterion and arising from inaccuracies of settings on the peaks are

negligible.

The procedure followed to obtain the plate characteristics contained an intermediate step. This required a plot of the deflection y_{exposure} at a fixed wave length for exposure A sparks (or B sparks) versus the deflection y_2 exposure at the same wave length for the exposure 2A (or 2B). Actually, curves based on exposures through both thick and thin films (B and A) are used and the average taken. The two curves basically constitute independent measurements of the plate characteristics and, hence, the data was used only if there was good agreement between the curves as in Figure 13. The average of these has been plotted in Figure 14a.

Data from curves of this type were then used to construct a plot of relative exposure versus deflection y . First there was arbitrarily taken some point, y_a , on the curve of Figure 14a in the region of small deflection. This was established as relative exposure 1 and plotted in Figure 14b. Now it can be seen that for twice that exposure the deflection was y_{2a} . This was relative exposure of 2. Now for deflection $y_b = y_{2a}$ there was corresponding y_{2b} for which exposure was 2×2 or 4. This process, continued to the largest values of y available, established a curve. More points were determined by taking as a starting value some point on the relative

FIGURE 14 PLATE CHARACTERISTICS

exposure curve and repeating the process. Figure 14b shows the completed smooth curve relating exposure to deflection of the microphotometer.

2 Calculation of Absorption

From this curve can be read an exposure to correspond to each measured deflection of every spectral line. The ratio of these relative exposures, thick/thin, multiplied by the inverse ratio of the actual number of sparks through each film gives transmission at that line of the spectrum of a thickness of tellurium equal to the difference in thickness of the thick and thin samples. The equation $T = e^{-\mu x}$, where μ is the absorption coefficient and x the thickness, provides, for each spectral line, a value of μx . Changing distance along the plate to wavelength units, as described in Chapter III, the absorption curve may be drawn for that particular wavelength range covered by the spectroscopic plate. One of the curves is shown in Figure 15 with the points from the two thick-thin pairs indicated by circles and crosses.

AN ABSORPTION CURVE

FIGURE 15

CHAPTER IV

RESULTS AND CONCLUSIONS

The curve showing the absorption coefficient of tellurium as a function of wavelength between 100 Å and about 400 Å is shown in Figure 16. The values at the longer wavelengths were obtained primarily from one plate which had nearly perfect internal consistency (i.e. positions 1 and 5 of identical exposure had nearly identical densities and Y_2 exposure versus Y_{exposure} curves from thick and thin samples had the same shape). The other plates in this wavelength region using both copper and silver sources only corroborated these results as to shape and approximate value of μ . At the shorter wavelengths three separate absorption measurements were used--two were averaged to obtain the absolute value of μ and the other, a plate with less perfect agreement of Y_2 exposure versus Y_{exposure} curves, only indicated the shape and position of the peak.

Fluctuations of the source are the cause of the largest errors in these measurements of absolute value of absorption coefficient. There are possible changes both in the amount of light and the distribution in various lines. Fairly large numbers of sparks and alternation from thin to thick absorbers

ABSORPTION OF TELLURIUM

FIGURE 16

smooth out the random changes, but do not affect the progressive alteration of the character of each spark.

Variation in sensitivity of the photographic plate caused by slight fogging, marks made in packing, etc., adds to the error.

The effects of these two sources of error are evident in Figure 15, where, as pointed out in Chapter III, two thick-thin pairs are plotted with the curve drawn through the average. The variations are somewhat greater in the data for shorter wavelengths.

A calculation was made to determine the effect of any variation in thickness of the film on the slope of the absorption curve. The basic equations were:

Thin: $T_{\lambda_1} = A e^{-\mu_1 x_a} + B e^{-\mu_1 x_b}$

$$T_{\lambda_2} = A e^{-\mu_2 x_a} + B e^{-\mu_2 x_b}$$

Thick: $T_{\lambda_1} = A e^{-\mu_1 x_c} + B e^{-\mu_1 x_d}$

$$T_{\lambda_2} = A e^{-\mu_2 x_c} + B e^{-\mu_2 x_d}$$

where T_{λ} is transmission at a specified λ ; A and B are fractions of the area with thicknesses x_a and x_b , or x_c and x_d ; and μ_1 and μ_2 are absorption coefficients at λ_1 and λ_2 .

Only for extreme variation in the thickness of a film does the slope change significantly. Such fluctuations could only be caused by pinholes. Applying the formula above to the

case of a 1000 Å thick-500 Å thin film combination with pinholes in only the thick film, it was found that pinholes covering .01 % of the area changed the slope by less than 1%, .05% by about 10%, and .1% by about 25%. Microscopic examination of several films showed pinholes covering less than 0.1% of the area, much less in most cases.

As a result of these calculations and observations, the maximum slopes were chosen selecting the curve for Figure 16.

The limit of accuracy in wavelength is about 1 Å on the position of the peaks, as explained in Chapter III. The overall accuracy of the thickness measurement was about 10%, as discussed in Chapter III.

In certain plates which exhibited poor agreement between Y_2 exposure versus Y_{exposure} curves there appeared some correlation between the intensity of spectral lines and their absorption by the film. Some small remainder of this effect may account for the slight fluctuation in the absorption curve away from the bands.

The salient features of the curve are the double peak at about 300 Å and the large peak at about 155 Å. The double peak indicates that the transitions from N_{IV} and N_V are separated by this experiment. The peaks occur at 292 Å and 302 Å with width at half maximum of 20 Å for the double peak.

Skinner and Johnston²⁹ define the position in wavelength of the absorption edge as the maximum plus half the edge diffusion. On this basis the edges are at 309 Å (40.0 ev.) and 297 Å (59.6 ev.). The N_{IV} edge is estimated at 299 (41.3 ev.) using the 10 Å separation of the peaks as a basis for the estimation.

Bohr and Coster³⁰ predicted these N_{IV} and N_V edges from limiting frequencies of emission bands to be at 303 Å and 314 Å. More recently Chamberlain and Lindsay³¹ proposed 289 Å and 291 Å.

As pointed out elsewhere, these peaks have been obtained with both copper and silver spectra, so there can be little doubt as to their existence and position, although the relative heights may be subject to the errors mentioned earlier in this section.

The shape of the band can be interpreted to the extent that the rather sharp rise on the long wavelength side of the

29. Skinner, H. W. B., Phil. Trans. Roy. Soc. A, 239, 95-134 (1940).

30. Bohr, N., and Coster, D., Zeits. für Physik, 12, 342-374 (1923).

31. Chamberlain, K., and Lindsay, G. A., Phys. Rev., 30, 369-377 (1927). There is no mention in their paper of their recognition of the doublet nature of one of the initial levels. Disregard of this fact could produce error in the 291 Å value of the N_V level.

band at about 300 Å indicates that p (or f) states begin rather abruptly and have a narrow band of high density. If the diagram by Russbaum (Figure 4) gives the approximate values, it is possible that the peak arises from transitions from an N level to the middle part of the d-perpendicular, which can be nearly pure p (or f) from mixing of d and p (or f) states. The broadening at the base of the absorption curve can be attributed to the p (or f) states within the d-parallel band. Of course, this argument applies to both the N_{IV} and N_V levels separately.

The broad absorption band centered around 155 Å has an estimated width at half maximum of nearly 100 Å. The "edge" falls at 207 Å (59.6 ev.). The expected transition is from $N_{II,III}$ to the conduction band and should occur at about 105 Å (117.5 ev.) according to Bohr and Coster³² or 108 Å (114.5 ev.) according to Nishim³³. The discrepancy between these values and the experimental one is so large that there is serious doubt of the identification.

The width of the band is very large--too large to be explained by the widths of the N levels or valence band with

32. Bohr and Coster, Op. cit.

33. Nishim, Op. cit.

any reasonable numbers. The value of the absorption coefficient relative to that of $N_{IV,V}$ band is also as large as any previously reported for other substances.

Notwithstanding the difficulty of interpretation, there can be little doubt of the existence of the band on the photographic plates. It is easily seen upon even casual visual inspection. That the height of the peak is at least the same magnitude as the $N_{IV,V}$ band is well established, as is the fact that it appears only when there are absorbers in the beam. There remains besides absorption only the possibility of some unexplained reflection, interference, or scattering phenomena in the sample.

In summary, a measurement has been made of the absorption of thin films of tellurium. The bands of higher values of absorption coefficient have been interpreted as indications of transitions from N levels to unfilled levels. From this followed conclusions concerning the energy level structure in the conduction band.

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