THE EXTREME VACUUM ULTRAVIOLET ABSORPTION
SPECTRA OF SILVER CHLORIDE AND SILVER BROMIDE FILMS

By

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MILITARY FALLS
MINING MONITOR
COTTON CONTENT

VITA

The author, son of Mr. and Mrs. Carl J. Koester of Fostoria, Ohio, was born on January 26, 1929, in Niagara Falls, New York. After graduating from Fostoria High School in May, 1946, he entered Carnegie Institute of Technology in September of that year with a George Westinghouse Scholarship. His undergraduate program was in physics. While at Carnegie Tech he was elected to Tau Beta Pi and Omicron Delta Kappa, and upon graduation in 1950 with a B. S. in Physics he was named an honor graduate.

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TABLE OF CONTENTS

I	Introduction	1
II	Sample Films	7
	A. Type of sample and support	
	B. Vacuum evaporation procedure	12
	C. Thickness control and measurement	13
	D. State of the sample films: photolysis and structure	21
III	Requirements of Spectrograph	26
	A. Source and overlapping of orders	26
	B. Elimination of absorbing gases	32
	C. Thin film breakage	33
	D. Detector: spectrographic plate	36
	E. Wavelength calibration	37
IV	Analysis of Data	39
	A. Construction of plate characteristic curve	39
	B. Calculation of absorption coef- ficient	43
	C. Mechanics of analysis	44
V	Theory	47
	A. General considerations	47
	B. Selection rules	57
	C. Possible transitions in the region 500 - 1500 Å	59

VI Results	66
A. Interpretation	69
B. Accuracy	71
Bibliography	76
Appendix 1	81
Interferometric thickness measurement considering phase shift on reflection from silver surfaces	
Appendix 2	86
Discharge tube characteristics and operation	
Appendix 3	93
Corrections to plate calibration	

LIST OF FIGURES

1a	Vacuum spectrograph: photograph	5
1b	Vacuum spectrograph: schematic diagram	6
2	Preparation of unsupported silver chloride film	10
3	Arrangement in vacuum evaporator	16
4	Interferometer for fringes of equal chromatic order	18
5	Fringes of equal chromatic order	20
6	Electron micrographs of silver chloride films	23
7	Discharge spectra showing helium and argon absorption	28
8	Lyman discharge tube: drawing	30
9	Lyman discharge tube: photographs	31
10	Spectra for wavelength calibration	38
11	Plate calibration data	41
12a	Construction of plate calibration curve	42
12b	Plate calibration curve	42
13	Use of drawing board and T-square in analysis of data	45
14a	Absorption of silver chloride	68
14b	Absorption of silver chloride	68a
15a	Absorption of silver bromide	68b
15b	Absorption of silver bromide	68c
16	Phase shift on reflection from silver	85

17	Voltage supply: wiring diagram	88
18	Voltage supply: photograph	88a
19	Recalibration data	98
20	Recalibration curve	99

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LIST OF TABLES

1. Reflected Interference Colors	15
2. Electronegativity Differences for Various Crystals	54
3. Some Physical Properties of Several Crystalline Materials	55
4. Peaks in Silver Halide Absorption Curves Compared to Silver Ion Levels	69

INTRODUCTION

Spectroscopy in the vacuum ultraviolet region has yielded important information about the energy and distribution of electron states in atoms and in solids. The history of the field has been reviewed by Siegmund,¹ and he has given a description of the vacuum spectrograph at the Institute of Optics.

In the 1930's interest developed in using vacuum spectroscopy to investigate energy levels in the solid state. Since then both emission and absorption studies have been made on elements and compounds. Emission of radiation results when an electron makes a transition from a higher energy state, which in the solid may be one of a band of energy levels, to a lower energy state. If the band of energies of the final state is much narrower than the band corresponding to the initial state, then the emission studies reveal information about the width and structure of the band containing the initial states.

1. W. P. Siegmund, Thesis, University of Rochester (1951) pp 1-45

Absorption of radiation results when an electron makes a transition from a lower energy state to a higher (permitted) state. If the band of energies corresponding to the lower state is narrow compared to that of the upper state, the absorption spectrum yields information on the width and structure of the band of upper (final) states.

For absorption measurements in the vacuum ultraviolet or soft X-ray region the samples have usually been thin films vacuum evaporated onto a support which was relatively transparent in the spectral region of interest. Several materials have been used as supports, the most popular being celluloid for the region below 600 A and thin lithium fluoride crystals for the region above 1050 A. Between these wavelengths both celluloid and lithium fluoride absorb very heavily, as do most materials. It is undoubtedly partly for this reason that in this spectral region no previous absorption studies on supported thin films have been reported. To be sure, there has been work on the absorption of gases and on the absorption of self-supported thin films

between 600 and 1050 A.^{1,2} But for solids which cannot be put in the form of unsupported thin films the absorption measurements contained in this work are, to the author's knowledge, the first to be reported in the spectral region, 600 - 1050 A.³

The physical properties of the silver halides have been of widespread interest for many years, and especially since 1938 when a large advance in explaining the photographic process in terms of physical properties of the single crystals was made by the Gurney-Mott theory.⁴

The absorption of blue and near ultraviolet light, which is responsible for the basic sensitivity of the crystals, generally increases with decreasing wavelength.

1. H. M. O'Bryan (J. Opt. Soc. Am., 22, 739-748 (1932) measured the absorption of thin celluloid films from 300 A to 1000 A. In another paper (Phys. Rev. 57, 995-997, 1940) he found that the plastic formvar has a maximum absorption at about 900 A.
2. N. Astoin and M. B. Vodar (J. phys. et radium, 14, 424-425, 1953) show the transmission of selfsupporting aluminum and silicon monoxide films in the regions 100 - 750 A and 100 - 1350 A respectively.
3. Among the solids which probably have their fundamental absorption in or near this region are zinc oxide (P. Seitz, The Modern Theory of Solids, McGraw-Hill, New York, 1940, p 450) and lithium fluoride. See also N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals, Oxford, Clarendon Press, second edition (1948) p 78
4. R. W. Gurney and N. F. Mott, Proc. Roy. Soc. (London) A164, 151-167 (1930); Electronic Processes in Ionic Crystals, pp 227-232

Early studies¹ indicated that a long wavelength tail of absorption extended well into the visible region. More recent measurements² with carefully prepared and annealed silver chloride crystals show that the absorption of pure single crystals is lower than previously thought at wavelengths longer than 2600 Å, and is very low above the edge which occurs about 4000 Å.

Fesefeldt's curves¹ show the absorption coefficient of silver chloride still increasing with decreasing wavelength at about 1850 Å. In silver bromide there is some indication of a peak at 2000 Å. Schneider and O'Bryan³ measured the absorption from 2000 Å down to 1050 Å of silver chloride films evaporated onto lithium fluoride. The absorption was observed to rise as wavelength decreased, but no maximum was observed.

The purpose of the work reported here was to extend the absorption measurements on silver chloride and silver

1. H. Fesefeldt, Z. Physik, 64, 741-748 (1930); H. Fesefeldt and Z. Gyulai, Gott. Nachr., 226 (1929); R. E. Slade and F. C. Toy, Proc. Roy. Soc. (London) A97, 181-196 (1920)
2. P. D. Milliman, Thesis, Cornell University, 1953 (Unpublished); M. A. Gilleo, Phys. Rev., 91, 534-542 (1953); F. C. Brown, Phys. Rev., 97, 355-362 (1955)
3. E. G. Schneider and H. M. O'Bryan, Phys. Rev., 51, p 297 (1937)

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ONTON EKIV

bromide to shorter wavelengths, to locate the absorption maxima in each material along with any associated structure, and to find the magnitude of the absorption coefficients in the regions of strong absorption.

Figure 1a shows an over-all view of the grazing incidence spectrograph at the Institute of Optics. Figure 1b, page 6, is a schematic diagram of the instrument with the discharge tube in place. The components which are new or altered for this research are fully described in the text.

Figure 1a. General view of vacuum spectrograph

VACUUM SPECTROGRAPH

A To pump

D Light source: discharge tube

F F₁, F₂ Alternate positions for sample films

G 2m grating, 30,000 lines per in., 85° angle of incidence

H Helium or argon supply

P Plates

Q Quartz capillary

S Slit

V 15 KV on .3 μ fd discharged once per second

W Pirani Gauge.

X ~~Differential~~
manometer

FIGURE 1b 1

II SAMPLE FILMS

A. Type of sample and support

For absorption measurements in the extreme vacuum ultraviolet where the absorption coefficients of most solid materials are 10^5 or 10^6 per cm., the samples must be in the form of very thin films, 50 to 2000 Å in thickness. These films are readily prepared by vacuum evaporation onto a suitable support. If the sample film plus backing is to be used in the spectrograph then the backing must be relatively transparent in the spectral region of interest. Thin crystals of calcium fluoride and lithium fluoride can be used in the regions above about 1400 and 1050 Å respectively. Celluloid can be made in such thin sheets that it will transmit well in the soft X-ray region below about 500 Å. With care the films can be made thin enough to transmit fairly well over the entire extreme ultraviolet region with a broad absorption maximum of about $1.1 \cdot 10^6$ per cm. at 800 Å.¹ O'Bryan made films of formvar 200 Å thick which transmitted 50 per cent of the radiation at 300 Å and had a maximum absorption at 900 Å.² Recently, vacuum evaporated films of aluminum and silicon monoxide have been found

1. H. M. O'Bryan, J. Opt. Soc. Am., 22, pp 739-748 (1932)
2. H. M. O'Bryan, Phys. Rev., 57, pp 995-997 (1940)

to be relatively transparent in the vacuum ultraviolet region.¹ These may find use as backing materials for absorption measurements.

An alternative approach is to remove the support material from the sample and insert only the sample in the spectrograph. One difficulty in this procedure is to prevent breakage of the sample film during the removal of the support. A method which proved useful in the case of aluminum films is described by Carpenter and Curcio.²

For silver chloride and silver bromide it was desired to survey the absorption spectra over the region 200 to 1550 Å, then to study in detail the sections which showed absorption maxima. Celluloid is a satisfactory support material for wavelengths below 400 Å. But for longer wavelengths the celluloid films have to be less than about 200 Å thick in order to transmit sufficient light.

Films of celluloid are prepared by letting a drop of collodion solution fall on a distilled water surface.

1. N. Astoin and M. B. Vodar, *J. phys. et radium*, 14, pp 424-425 (1953)
2. F. E. Carpenter and J. A. Curcio, *Rev. Sci. Instr.*, 21, 675 (1950)

After the collodion spreads over the surface and the solvent (usually amyl acetate) evaporates, the resulting thin film of celluloid will adhere to a metal frame lowered from above and can be lifted from the water. The thickness of the film depends on the concentration of the collodion solution, thinner films resulting from more dilute solution. When a film as thin as 150 Å is lifted from the water by a metal frame which has an opening of reasonable size, say $1/8'' \times 1/2''$, the film invariably breaks.

An attempt was made to prepare unsupported films of silver chloride. One possibility was to dissolve it in a solvent, placing a drop of the solution on water or other liquid, allowing the solvent to evaporate, and picking up the remaining film. This was found to be impractical because the common solvents do not dissolve silver chloride, and liquids such as sodium thiosulfate solution (hypo) and ammonia which dissolve it do so by forming complex radicals with the silver ion.¹ This did not seem desirable from the point of view of producing uniform films of predictable crystal structure. One

1. T. H. James and G. C. Higgins, Fundamentals of Photographic Theory, New York, Wiley (1948) pp 131-133

attempt was made to form a film by dissolving silver chloride in ammonia solution, and allowing a drop of solution to dry. Only small crystals resulted.

Another effort to produce unsupported silver chloride films was somewhat more successful. Rock salt crystals were cleaved to the approximate dimensions 10 mm x 10 mm x 2 mm and one face was polished, using a salt saturated solution with rouge on pitch. Silver chloride was vacuum evaporated onto the polished surface, using the techniques described in section II B. Then the crystal was placed polished face up in a dish, as shown in figure 2.

Figure 2. Preparation of unsupported silver chloride films

The water level was raised to the silver chloride films. After the salt dissolved, the film floated on the surface and could be picked up on a suitable holder. Plexiglass with one millimeter holes was found to be effective, provided the surface was roughened by sanding. No films thinner than about 1500 Å were successfully picked up. These were too thick for absorption measurements in the wavelength region around 1000 Å. Films which survived the lifting operation presented an irregular appearance, probably due to the flexing of the film on the water surface when pieces of salt fell away.

An incidental observation during this work was that exposure to room lights considerably weakened the silver chloride films. The formation of photolytic silver was presumed to be the cause. A darkroom safelight with a yellow-green filter proved to be a satisfactory source of illumination.

Following the unsuccessful attempts to prepare very thin self-supporting films of silver chloride it was found possible to make thin celluloid supports. Instead of using a frame to lift the celluloid from the water, a

fine metal mesh was used. Using a mesh¹ with .7 mm square holes, 10 holes per cm., 100 Å films could be picked up. After the film dried the mesh could be cut to desired size with scissors without breaking the celluloid except along the cut.

B. Vacuum Evaporation Procedure

The general techniques of vacuum evaporation used in this laboratory have been described by Siegmund,² Carter,³ and Woodruff.⁴ The apparatus consisted of an upright brass cylinder 12" in diameter with a Herculite glass cover plate. A Kinney VSD 5-5-6 forepump and a DPI MC-275 diffusion pump obtained a vacuum of approximately 7×10^{-5} mm of mercury. The pressure increased to about twice this value during the evaporation. The vacuum chamber was fitted with electrical connections and a rotatable baffle holder.

The silver halides were not evaporated from a molybdenum boat or from tungsten wires because of the

1. The mesh used was copper base, nickel plated, Lektromesh manufactured by the C. O. Jelliff Mfg. Corp., Southport, Conn.
2. W. P. Siegmund, op. cit., 62-66
3. D. E. Carter, Thesis, University of Rochester, 1954, pp 19, 20
4. R. W. Woodruff, Thesis, University of Rochester, 1954, pp 14, 15

probability that a reaction would occur, forming molybdenum or tungsten halides. Any metal coming into contact with the silver halide should be a weaker reducing agent than silver, the only such metals being platinum and gold. A platinum crucible¹ was used to hold the silver halide, as shown in the diagram below.

C. Thickness Control and Measurement

Common methods for controlling thickness of films during evaporation are to observe the interference colors by reflected light, to measure the reflected or transmitted intensity at a certain wavelength, to measure the state of polarization of reflected light, and to observe the transmitted intensity (of an absorbing

1. This precaution may not have been entirely necessary. Silver bromide films were obtained by slow evaporation from a molybdenum boat by Mr. J. F. Hamilton at the Eastman Kodak Research Laboratories (Private communication). Spectroscopic analysis showed a detectable but very small amount of molybdenum in the films.

film).¹ Since the silver halide films are quite transparent and only the order of 100 Å thick, the methods utilizing reflected colors, reflected intensity, and transmitted intensity are not applicable. Instead of using the polarization method a simpler, though less accurate, technique was employed.

Beside the celluloid films, which were shielded from the boat by the rotatable baffle, was a glass monitor plate (see Figure 3). The heater current was adjusted to a convenient value. As the thickness of the silver halide deposit on the monitor increased, the reflection colors on the monitor were noted and a plot made of thickness vs time. The conversion from color to thickness was made by means of table 1, assuming indices of 2.07 and 2.25 for silver chloride and silver bromide respectively. When a constant rate of evaporation had been established, the baffle was moved aside for an appropriate time, allowing the silver halide to deposit on the celluloid. First the baffle exposed both "thin" and "thick" films; then it covered the thin film and allowed the additional deposit on the thick.

1. These methods are reviewed by K. M. Greenland, *Vacuum*, II, 216-230 (July 1952)

Table 1. Reflected Interference Colors

For unsupported thin films or films of higher index than that of the support. Compiled from: H. Kubota, J. Opt. Soc. Am., 40, 146-149 (1950); G. C. Monch, Optik, 9, 75-83 (1952) (Summary of work by G. Quinke, A. Rollett, and G. C. Monch)

Optical Thickness nt (A)	Color	Approximate Optical thickness at which color changes (A)
0	Indefinite Gray Lavender Whitish	
1000		1300
	Pale yellow	1560
	Definite yellow	
2000	Brown yellow	2050
	Orange	2300
	Red	2410
	Purple	2500
	Violet	2700
3000	Indigo	2920
	Blue	3000
	Green-blue	3480
		3720
4000	Green	4120
	Yellow-green	4310
	Yellow	4640
	Orange	4790
5000	Red (or orange brown)	4970
	Magenta	5430
	Violet	5740
6000	Blue	6000
	Blue-green	6390
	Green	6850
7000		

For the purpose of accurately measuring the thicknesses of the halide films, a quartz optical flat was placed in the evaporator at the same distance from the boat as the centers of the celluloid films. The arrangement is shown schematically in figure 3. The quartz

Figure 3. Arrangement in vacuum evaporator of celluloid support films, glass monitor, quartz flat, and rotatable baffle (As seen from the boat)

plate was later silvered by vacuum evaporation and used in an interferometer utilizing fringes of equal chromatic order as described by Tolansky.¹

1. S. Tolansky, Multiple-beam Interferometry of Surfaces and Films, Oxford, Clarendon Press, 1948. The techniques for producing the best fringes are further discussed by Tolansky in Vacuum, 1, 75-91 (1951)

Schematic diagrams of the quartz flat and the interferometer¹ are shown in figure 4. The silvered surface on the reference flat and the silvered surface on the flat with films have a small air gap between them; hence, they form essentially an interference filter. With white light incident on the interferometer only certain wavelengths are transmitted, those for which the expression $n\lambda = 2t$ is satisfied. All other wavelengths are reflected. Here n = order number, λ = wavelength, t = true separation plus an equivalent distance introduced by the phase shift. When t is several microns, solutions of the equation exist for several wavelengths, $\lambda_1, \lambda_2, \dots, \lambda_n, \dots$, in the visible region of the spectrum. When viewed in a spectrometer, the reflected light shows a continuous spectrum with several dark lines, the so-called fringes of equal chromatic order.

The quantity t changes discontinuously across the edge AB. There is a shift, then, in the wavelengths for which the equation is satisfied. This shift is a measure of the thickness of the film. The expression²

1. The interferometer used was designed by Mr. Frederick Card and built at the Institute of Optics.
2. S. Tolansky, Multiple-beam Interferometry of Surfaces and Films, Oxford, Clarendon Press, 1948, p 111

INTERFEROMETER FOR FRINGES OF EQUAL CHROMATIC ORDER

FIGURE 4

is $dt = \frac{n}{2} d\lambda$. A more exact expression, which does not ignore the phase shift on reflection, is derived in appendix 1. It shows that the value of t does not depend on the phase shift but only on the change in phase shift with wavelength. The resulting correction is negligible.^{1, 2}

The reflected spectra were photographed using a Bausch & Lomb "large wavelength spectrometer" with camera attachment. Figure 5 shows five typical spectra, two from the thick film, two from the thin film, and one from the region where no film was deposited. Measuring the fringe shift is conveniently done by projecting the spectra onto a screen or by using a comparator with a wide field of view.

A thickness determination was made at each fringe and the average taken. The average error of the mean was about 5 Å for each film; hence the thickness difference was known to about 7 Å.

1. G. D. Scott, T. A. McLauchlan, and R. S. Sennett, *J. Appl. Phys.*, 21, 843-846 (1950) also found that the phase shift causes a negligible correction to the simple thickness formula. This article contains a discussion of other possible errors in measurement of thickness.
2. W. P. Koehler, *J. Opt. Soc. Am.*, 43, 738-743 (1953) calculates the effect of phase shift by a different approach than that used in appendix 1. He also finds that the effect is negligible.

Figure 5. Fringes of equal chromatic order in reflection

At the top and bottom of photograph are the green and yellow lines from a mercury spectrum, for calibration.

D. The State of the Sample Films: Photolysis and Structure

The amount of actinic light reaching the films was kept to a minimum. For practical purposes the sensitivity of silver chloride extends from the violet to shorter wavelengths. Silver bromide is sensitive to wavelengths shorter than about 5000 Å. The films were handled either in complete darkness or in the light of a darkroom safelight, the filter on which transmitted essentially only wavelengths above 5400 Å.

However, at two times during each experiment the films were exposed to some actinic light. The first was during the formation of the films in the vacuum evaporator. Because the heater was red hot, there was undoubtedly some small amount of blue and violet light reaching the films. The second occasion was in the spectrograph. It was fundamental to the measurement that enough radiation had to pass through the film to expose the SWR plate, which itself owes its sensitivity to silver halides.

An attempt was made to study the structure of the thin films of silver halides on celluloid using an

electron microscope.¹ Most of the films used were silver chloride evaporated rapidly (300 to 400 Å per minute) onto celluloid of nominal thickness, 125 Å.

The most striking observation of this work was that the electron beam produced rapid sublimation and/or agglomeration of the film. As one watched the image of a particular portion of the film he could see portions of the film with mean dimensions of perhaps 1000 Å disappear. After this process continued for a few seconds it left a film with large open spaces. A sequence of electron micrographs of an 1100 Å film of silver chloride taken with low beam intensity on Kodak Contrast Lantern Plates appears in figure 6. Even at the end of the first exposure, seven seconds after this portion of the film was exposed to the beam, some holes (light areas) have formed.

The sublimation of thin films of metals in the beam of an electron microscope was studied by Levenstein.² For zinc and tellurium, the melting points of which are near that of silver chloride, he observed sublimation.

1. Mr. L. Peachey, of the Section of Electron Microscopy, University of Rochester Atomic Energy Project, kindly took the electron micrographs.
2. H. Levenstein, J. Appl. Phys., 20, 306-315 (1949)

Time in seconds
at start and
end of exposure

1 - 7

15 - 21

30 - 36

54 - 60

Figure 6.
Sequential electron micrographs of an 1100 A film of
silver chloride evaporated on celluloid

Films were exposed continuously to low intensity elec-
tron beam starting at time zero.

In our studies, films of silver chloride of about 100 Å thickness showed agglomerated structure even in the micrograph which was taken during the first four seconds that the area was exposed to the beam. There are two possible explanations

1. The film had this agglomerated structure initially.
2. The agglomeration was caused entirely or in part by the electron beam. This is reasonable; for, if the beam can cause a definite change in an 1100 Å film in seven seconds, it can probably cause large changes in a 100 Å film in a small fraction of that time.

With the present data it does not seem to be possible to decide between these explanations.

Electron micrographs were taken at the Kodak Research Laboratories¹ of silver bromide films prepared by very slow (overnight) evaporation onto celluloid or glass. The transmission micrographs show film structure similar to that in figure 6, the percentage of open area decreasing with increasing thickness. One transmission

1. The electron micrographs were supplied to the author through the kindness of Mr. J. Hamilton and Dr. F. A. Hamm of the Kodak Research Laboratories.

micrograph of a film of approximate thickness, 200 A, showed a fairly continuous structure, (open area was four to eight per cent of total area) as did a replica of the deposit on glass.

An important difference between the films prepared by Mr. Hamilton at the Kodak Research Laboratories and the films used in the present work was the rate of deposit. The former were evaporated overnight, the latter in ten to twenty seconds. Rate of deposit is known to have a large effect on the continuity of thin films. Sennett and Scott¹ found that silver films deposited in two seconds were continuous at smaller thickness than were films formed in twenty minutes.

The preceding considerations leave open the question of whether or not the films used in this work were continuous and if not, what was the percentage of open area. This must be kept in mind in the interpretation of the results.

1. R. S. Sennett and G. D. Scott, J. Opt. Soc. Am., 40, 203-211 (1950)

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STANDARD FILMS

III REQUIREMENTS OF SPECTROGRAPH

In order to measure absorption coefficients in the extreme vacuum ultraviolet there are several requirements of the spectrograph which are fairly obvious and important. First the source must produce radiation of the desired wavelength, a continuous spectrum being most desirable, but closely spaced lines being acceptable. Second, overlapping of orders must be avoided by eliminating wavelengths shorter than those of interest. This can be done in some cases by proper selection of the source, in other cases by using a gaseous or solid filter. Third, gases such as oxygen and nitrogen which absorb strongly in the spectral region below 2000 Å must be eliminated from the radiation path. Fourth, the sample has to be in the form of a thin film, as described in the preceding section, and remain intact during an exposure. Fifth, the detector must be sensitive to the radiation and must be capable of calibration.

A. Source and overlapping of orders

Previous investigators using the vacuum spectrograph at the Institute of Optics employed a high voltage spark

between metal electrodes.^{1,2,3} This source gives satisfactory line spectra between 100 and 400 Å. Above 400 Å, the intensity falls off and second order lines are troublesome. Discharge tubes are useful sources in the near and vacuum ultraviolet, and Lyman type discharge tubes have yielded continuum down to 270 Å⁴ and lines at still shorter wavelengths. A schematic diagram of the latter type source is shown in figure 1b along with the spectrograph. A capacitor charged to high voltage is discharged through a quartz capillary in which there is a low pressure of gas. The end of the capillary is open to the spectrograph slit so that the radiation need not pass through any quartz.

The radiation is due partly to excitation of the helium or argon. Most of the continuum at long wavelengths is thought to result from blackbody radiation of particles torn from the capillary walls.^{5,6} In the

1. W. P. Siegmund, op. cit., pp 37-41; M. P. Givens and W. P. Siegmund, *Phys. Rev.*, 85, 313-314 (1952)
2. D. E. Carter, op. cit., pp 12, 13
3. R. W. Woodruff, op. cit., pp 8, 9
4. G. Rathenau, *Z. Physik*, 87, 32-56 (1933); J. A. Anderson (*Astrophys. J.*, 75, 394-406, 1932) also described experiments with discharge tubes.
5. Rathenau, op. cit., pp 37, 38; Also J. C. Boyce, *Rev. Mod. Phys.*, 13, 20 (1941)
6. R. E. Worley, *Rev. Sci. Instr.*, 13, 67-71 (1942)

spectrum are strong lines due to multiply ionized silicon and oxygen. These elements no doubt come from the quartz capillary.

Worley¹ pointed out that if helium is used as the gas, radiation below its ionization limit at 504.5 Å is strongly absorbed. Thus interference from second order is eliminated in the region 504.5 - 1009 Å. This idea has been extended by using argon, for which the cutoff is at 786 Å. Figure 7 shows spectra of helium

Figure 7. Spectra of radiation from discharge tube wavelength at left edge: 444 Å, at right edge 894 Å

(with low - .3 μ fd - and high - 1.1 μ fd - capacitance), hydrogen and argon. It is interesting to note that the principal series for helium and argon are seen in absorption in these spectra. The helium and argon cut-offs are quite effective under normal operating conditions,

1. R. E. Worley, Rev. Sci. Instr., 13, 67-71 (1942)

that is .5 to 1.5 mm of pressure measured at the exhaust tube of the source. The spark current comes from a capacitor of $.3 \mu\text{fd}$ charged to 15 KV. The effect of gas pressure is discussed further in appendix 2. A few weak lines can be seen in figure 7 in the argon spectrum below the cutoff. They can be eliminated by using higher pressure of argon in the source. Thus the region 505 to 1572 Å can be covered in two steps, using first helium in the discharge tube and then argon.

Several designs of Lyman discharge tubes have been built.¹⁻⁶ For the present purpose a modification of the source described by Rathenau was selected. A detailed diagram appears in figure 8 and photographs in figure 9. Features of this design include:

1. A window in the rear of the cathode for aligning the capillary with the slit and grating
2. Adjusting screws for centering the capillary

1. T. Lyman, *Astrophys. J.*, 60, 1-4 (1924); The Spectroscopy of the Extreme Ultraviolet, Longmans, Green, and Co., New York, 1928, pp 41-49
2. G. R. Harrison and P. A. Leighton, *J. Opt. Soc. Am.*, 20, 313-333 (1930)
3. G. Rathenau, *Z. Physik*, 87, 32-56 (1933)
4. G. Collins and W. C. Price, *Rev. Sci. Instr.*, 5, 423-425 (1934)
5. R. E. Worley, *Rev. Sci. Instr.*, 13, 67-71 (1942)
6. P. Lee and G. L. Weissler, *J. Opt. Soc. Am.*, 42, 80-84 (1952); Wainfan, Walker, Weissler, *J. Appl. Phys.*, 24, 1318 (1953)

LYMAN TYPE DISCHARGE TUBE

FIGURE 8

MILBERRY, RAYMOND
ONION SKIN
COTTON CONTENT

31

Figure 9. Lyman discharge tube

3. Variable cathode length to keep the end snugly against the quartz tube
4. Baffles in the anode which can be removed for cleaning and replacing.

As a capillary tube is used, the hole enlarges until after 50,000 to 70,000 sparks the tube is no longer usable. The amount of continuum decreases as the hole enlarges. During one run, perhaps 5000 to 8000 sparks, the average amount of radiation per spark stays fairly constant, varying no more than fifteen per cent. Relative intensities of spectral lines stay constant within about five per cent. Assuming that during a run these variations occur gradually, their effect can be reduced by a considerable factor by proper design of experiment and analysis of data. For example, exposures through the thin film were made before and after the exposures through the thick film and the former were averaged.

B. Elimination of absorbing gases

Boyce¹ has pointed out that the partial pressure of oxygen in a spectrograph having a path length of four

J. C. Boyce, Rev. Mod. Phys., 13, 1-57 (1941) (See pp 4,5)

meters must be no more than a micron of mercury in order to transmit 50 per cent of the radiation at 1450 A. He concludes that the air pressure in the spectrograph should therefore be .01 to .1 microns. When the metal spark was used as a source, two oil diffusion pumps backed by a single mechanical pump served to keep the pressure at about .05 micron.¹ For the discharge tube the flow of gas from the source through the slit kept the helium or argon pressure rather high in the spectrograph. Pumping out the spectrograph to about 8 microns before admitting any gas, using pure (99.9%) gas supply, and pumping continuously with mechanical pumps during a run served to keep the partial pressure of oxygen and nitrogen low enough that absorption due to these gases was negligible. It was also important to flush well the gas supply system and to warm up the source for about 1000 sparks before beginning a run.

C. Thin Film Breakage

The techniques for making the thin films of silver halide on celluloid are described in sections II A and II B. In the initial stages of the work the samples

1. D. E. Carter, op. cit. p 17

were inserted in the spectrograph by means of the vacuum bottle described by Carter.¹ This provided a convenient support and allowed two films to be exposed successively without disturbing the vacuum. Because the film being exposed was directly behind the slit, any particles from the source which came through the slit could puncture the film. Even with the precautions described in appendix 2, only about one-third of the film sets survived a run.

In order to reduce the breakage of films, a new holder was made which positioned them between the grating and the plates (P_2 in figure 1b). The increased distance from the slit proved effective in reducing the number of particles getting to the films and hence reduced the breakage. In the design of the new holder consideration had to be given to the effective size of the beam diffracted from the grating, so that the films would fill this beam.

Width: Direct measurements from the geometry showed that if all the wavelengths from all parts of the grating were to reach the Rowland circle the films had to be three inches wide.

1. Carter, op. cit., pp 14, 15

Height: Astigmatism caused by a grating used at near grazing incidence is so great that the image of a point source is a line several times the length of the grating rulings.¹ Therefore, the radiation is diverging in the vertical direction after it leaves the grating, and

Schematic diagram showing effect of astigmatism (not to scale)

converging only in the horizontal direction. The effective beam height, h , at the film, then is less than the height of opening in the mask, m , which is about 6mm. If a slit source is considered instead of

1. A table published first by H. G. Beutler (J. Opt. Soc. Am., 35, 327, 1945) shows that for a point source at 85° angle of incidence, a two-meter grating with 30,000 lines per inch gives an image at 1000 A/ which is about eight times as long as the grating rulings.

a point source, the height of the slit ($s = 6$ mm) must be added in order to obtain the true effective beam height, H . $H = h + s < m + s$. Therefore, H is less than $m + s = 6 + 6 = 12$ mm. The films were made about 14 mm in height in order to cover this effective beam width.

Detector

Kodak SWR plates, a type with special low-gelatine emulsion, were used. The handling precautions and development procedure recommended by the manufacturer were followed.¹ Precautions which are especially important are to avoid abrasion of the sensitized surface, not to use plates which have been at room temperature for more than about two weeks, and to inspect the plates for irregularities before using them by viewing a red safelight through the plates.²

1. Kodak Materials for Spectrum Analysis (Data book), Eastman Kodak Co., Rochester, N. Y., Second edition (1954) pp 19, 22, 23. Plates were developed for four minutes in D-19 diluted 1:1 at 68°F.
2. The inspection of SWR plates was suggested by Mr. W. L. Goffe who noted that any plates having irregularities in emulsion thickness could thus be eliminated.

E. Wavelength Calibration

One important aspect of the project was to calibrate the Rowland circle, i.e., to determine wavelength as a function of distance along the plate. This was done for the region 100 - 400 Å by Carter (pp 32,33) and Woodruff (p 10). Starting from their data and using the following procedure it was relatively easy to extend the calibration to longer wavelengths. Three exposures were made on a set of plates, the first being from a copper spark, the second a superposition of the copper spark spectrum and a discharge spectrum with no movement of the plateholder between exposures, and the third a discharge spectrum alone. Below 450 Å the copper spark and discharge tube wavelengths were found from the calibration curve mentioned above. The copper lines were checked against those given by Kruger and Cooper¹ and the discharge lines were checked against those given by Boyce and Robinson.² At longer wavelengths, the Boyce and Robinson data proved to be most valuable. Not only the first order emission lines were useful in constructing

1. D. G. Kruger and F. S. Cooper, Phys. Rev., 44, 826-830, (1933)
2. J. C. Boyce and H. A. Robinson, J. Opt. Soc. Am., 26, 133-143 (1936)

the calibration curve, but also second order lines and absorption lines of He I and O I, and (on other spectra) absorption lines of A I and H I.

Figure 10 is a set of spectra used in the wavelength calibration work. Certain fiducial lines are marked.

Figure 10. Spectra for wavelength calibration
 Line 1 (Plate #2 along Rowland circle) Cu spark plus He discharge, He discharge
 Line 2 (Plate #3) Cu spark plus He discharge, He discharge
 Line 3 (Plate #4) Cu spark plus He discharge, He discharge
 Line 4 (Plate #4 $\frac{1}{2}$) He discharge (.3 μ fd), He discharge (1.1 μ fd), H₂ discharge (.3 μ fd)

IV ANALYSIS OF DATA

A. Construction of plate characteristic curve

On each set of plates are several spectra. The minimum number of spectra is three: an exposure of N sparks through the thin film, $2N$ sparks also through the thin film, and RN sparks through the thick film. R is chosen so that the densities of most lines on the "thick" spectrum will be between the densities of corresponding lines on the two "thin" spectra. In order to check on the internal consistency, other spectra are also included. They consist of $2RN$ sparks through the "thick" film to check the characteristic curve, as described in appendix 3, and N sparks through the "thin" film, to check the constancy of the spark. Typical values for N and R are $N = 600$ and $R = 3$.

The developed spectrographic plates were measured on a Sinclair Smith recording microdensitometer made available to the author through the courtesy of the Chemistry Department. This instrument is described by Leighton, et. al.,¹ and the radiometer used as detector

1. P. A. Leighton, Sinclair Smith, and F. C. Henson, Rev. Sci. Instr., 5, 431-434 (1934)

is described in detail by Smith and Wilson.¹ Briefly, the operation is as follows. A light source provides illumination from below the plate. The spectra are enlarged using a 16 mm microscope objective onto a screen containing the slit. Light passing through the slit is focused on one vane of the radiometer. A second beam of light, the recording beam, reflects from a mirror on the radiometer suspension and is received on a 4" x 10" plate. The deflection is proportional to the intensity passing through the spectroscopic plate. The spectroscopic plate can be moved at a number of speeds by the motor and fine screw. A speed of 5.6 mm per minute is slow enough to prevent overshoot on most dark lines. The ratio of recording plate speed to spectroscopic plate speed can be varied. A convenient ratio is 2:1.

The microphotometer traces of the spectra from N and 2N sparks contain the information from which the characteristic curve is constructed. The method for constructing the characteristic curve, which is described in the following paragraphs, is essentially that given

1. S. Smith and O. C. Wilson, Jr., *Astrophys. J.*, 76, 117-123 (1932)

by Woodruff and Givens.¹ At a certain wavelength the deflection (d_g) for the exposure of N sparks and the deflection (d_{2g}) for twice that exposure are measured. Repeating this for several lines one can plot a curve as shown in figure 11. Each point (d_{2g} , d_g) on the

Figure 11.

curve contains the information that a deflection d_{2g} represents twice the exposure of a deflection d_g .

To convert these data to a characteristic curve the first step is to select an arbitrary d_g and an

1. R. W. Woodruff and M. P. Givens, Phys. Rev., 97, 52-54 (1955)

arbitrary value of E , say 1. These are plotted in figure 12a. From the d_E vs d_{2E} curve the value of

Figure 12a.

Figure 12b.

d corresponding to twice this exposure can be found, and it is plotted at $E = 2$. Again referring to the d_E vs d_{2E} curve, the value of d corresponding to $E = 4$ is found. In this way the curve in figure 12b is constructed. It is plotted as d vs E rather than as E vs d for a reason which will appear in section IV C.

Intermediate points can be found as follows. For an arbitrary value of E , say 1.5, find the corresponding

d_H . Then from figure 11 find d_{2E} and plot vs $2E$. Continue for d_{4E} and $4E$, etc. If the points lie on the curve already drawn, the curve can be assumed to be correctly drawn. If not, some adjustment of the curve is necessary.

B. Calculation of absorption coefficient

Relative exposures, E_{thin} and E_{thick} , can then be found from the characteristic curve. The value of the absorption coefficient is given by

$$\alpha = \frac{1}{T} \ln R \frac{E_{thin}}{E_{thick}} \quad (1)$$

T = thickness of additional layer of silver halide
i.e., "thick" minus "thin"

R = ratio of number of sparks = $\frac{N_{thick}}{N_{thin}}$

Several remarks and modifications must be made in connection with the procedure just outlined. They deal with reciprocity law failure in the emulsion, change of calibration with wavelength, and scattered light. They are discussed in appendix 3.

The several calculations described in the appendix are designed to correct for these effects, and they result in the corrected exposures e_{thin} and e_{thick} .

The absorption coefficient is then

$$\mu = \frac{1}{t} \ln R \frac{e_{\text{thin}}}{e_{\text{thick}}} \quad (2)$$

For all data reported here both the quantities α and μ have been computed and plotted. Corresponding α and μ curves show about the same average absolute magnitude, which indicates that the latter is not critically dependent on the correction procedure. In each case peaks in the curve μ are much more pronounced than those in the curve α . This is to be expected since the effect of background is to reduce the contrast in the plate and therefore in the absorption computed from the plate.

C. Mechanics of analysis

A few words are in order concerning the mechanics of the analysis procedure. Each absorption curve was based on at least one hundred points, and each point was computed from three or more readings from the microdensitometer traces. With this large number of measurements to take, a rapid method was desired for finding the exposure E corresponding to a given densitometer deflection.¹

1. One device for this purpose was recently (cont.)

After a characteristic curve (d vs E) was constructed, it was mounted on a small drawing board along with the densitometer trace, as shown in figure 13. When the T-square was brought to a certain point on the trace, the corresponding E was read directly from the

Figure 13. Use of drawing board and T-square in analysis of data

curve. Traces corresponding to several exposures of the same spectral region could be superimposed on the

1. (cont.) proposed by J. D. Purcell (J. Opt. Soc. Am. 44, 679-684, (1954)). It employs a cam cut to the characteristic curve of the emulsion. The cam moves the densitometer trace with respect to a recording plate. The trace on the recording plate is proportional to exposure. If used for our purpose this device would have required the making of a large number of cams corresponding to characteristic curves for different parts of the spectrum, different lots of plates, and different exposure conditions.

board, and the values of E determined for a particular wavelength.

The T-square and drawing board were also used along with a pair of dividers to construct the d_E vs d_{2E} curve, from which the d vs E curve was derived. Traces of N sparks through the thin film and $2N$ sparks through the thin film were superimposed. At a certain wavelength the d_{2E} was measured with the dividers on the $2N$ spark exposure. Then the T-square was moved up to the corresponding point on the N spark exposure. At the right-hand end of the T-square on a piece of graph paper, the distance d_{2E} was measured in the x direction starting from $x = 0$. This located a point (d_E, d_{2E}) . The procedure was repeated for other wavelengths until a curve could be drawn through the points.

The accuracy of the method can be judged from the variability in a group of readings on the same point. When reading values of E the average error was about one per cent. The accuracy in constructing the d_E vs d_{2E} curve was about the same. Most of this error was due to difficulty in judging the exact maximum of the trace of a line, and this difficulty is independent of the method used to convert d to E .

V THEORY

A. General considerations

In explaining many of the electrical and optical properties of solids the band theory has been quite successful. The nearly free electron approximation considers electrons moving in a periodic potential. The electron wavefunctions are plane waves modified by a periodic function. They are called Bloch functions.¹ Only certain energy bands are permitted. Other energy bands are forbidden. It is interesting that if an electron had the energy corresponding to the center of a forbidden band, then its wavelength would be such that it would be reflected from the lattice planes of the crystal.

Another approach which predicts bands of permitted energy in the crystal is the approximation of tight binding, or Heitler-London scheme. In this method it is assumed that the electrons can be assigned to particular atoms but that the wavefunctions of the outer electrons overlap with those of neighboring atoms to a certain

1. See for example, C. Kittel, Introduction to Solid State Physics, Wiley, New York (1953) p 249 or F. Seitz, The Modern Theory of Solids, McGraw-Hill, New York (1940) Chapter 8

extent. Because of this overlap, states which correspond to discrete levels in the atom are broadened into bands.

Thus the band picture of the solid is arrived at in two different ways. The relative merits of one or the other method in a particular problem depend on the physical situation.¹

Because of the Pauli exclusion principle the electrons do not all fall to the lowest energy state of a band, but distribute themselves so that each has a different wavefunction, characterized by the propagation vector, k . When the crystal is in its lowest energy state, for each electron moving in one direction with a certain speed there is one moving in the opposite direction with the same speed. A band may be filled with electrons if the number of available electrons equals the number of states in the band. If an electron is removed from an otherwise filled band, the absence of the electron is called a "hole," and it can move through the crystal by motion of the remaining electrons.

1. F. Seitz, *ibid.*, pp 301-303, 408, 412

In ionic crystals, such as the alkali halides, the so-called valence band consists of electron states corresponding to the outer (valence) shell in the negative ion. This band is full in the alkali halides. The conduction band (or bands) on the other hand is the group of states which exist for an extra electron introduced into the crystal. The wavefunction for one of these states spreads throughout the crystal. Near an ion the electron wavefunction has the symmetry of a wavefunction or a mixture of wavefunctions characteristic of the ion. An electron in one of these states is free to move under the influence of an electric field, and thus produce a current.

An electron can be excited from the valence band to one of a group of conducting states. Strictly speaking, these conducting states are not exactly the same as the conduction band states mentioned in the preceding paragraph, for the system is now perturbed by the hole in the valence band. Only with this reservation can we call the conducting states formed in this manner by the name, conduction band. An important result of the perturbation caused by the hole is the formation of discrete states for the electron in the neighborhood of the hole. These are discussed in the following paragraphs.

When a photon of sufficient energy is absorbed, it can cause an electron to jump from the filled band to the conduction band of an insulator. Absorption measurements in the ultraviolet have yielded information about the energy gap between these two bands. They have also shown evidence for another mechanism of absorption, the formation of the exciton.

The exciton is an excited state of the solid. One way of visualizing the exciton is to think of it as an electron bound to a hole by a coulomb force, much as an electron is bound to a hydrogen nucleus. The combination hole plus electron can move through the crystal.¹ Peaks in the absorption curve of alkali halide crystals attributed to excitons have been observed by Hilsch and Pohl² and Schneider and O'Bryan.³

1. For a further discussion of the exciton, see Kittel, *op. cit.*, p 320; Mott and Gurney, *op. cit.*, pp 90-93, 230; F. Seitz, The Modern Theory of Solids, pp 408-419. More recent discussions of excitons are given in D. L. Dexter, *Phys. Rev.*, 83, 435-438 (1951); W. R. Heller and A. Marcus, *Phys. Rev.*, 84, 809-813 (1951); and D. L. Dexter and W. R. Heller, *Phys. Rev.*, 91, 273-278 (1953)
2. R. Hilsch and R. W. Pohl, *Z. Physik*, 59, 812-819 (1930)
3. E. G. Schneider and H. M. O'Bryan, *Phys. Rev.*, 51, 293-298 (1937)

The ions in crystals such as the alkali halides are held together primarily by electrostatic forces, also called polar or ionic forces. The Madelung potential¹ is the energy a negative (or positive) ion gains from the Coulomb potential in going from a point at ∞ to its lattice site in the crystal, assuming all other

1. The Madelung energy is the principal part of the binding energy of an ionic crystal. Other terms which enter into the binding energy (in the Born-Mayer approximation) are:

Repulsive energy: It arises from the force which keeps ions apart.

Dipole-dipole: Atoms or ions induce dipoles on each other and these mutually attract (F. Seitz, The Modern Theory of Solids, p 84; Kittel, *op. cit.*, p 7).

Dipole-quadrupole: This very small energy results from attraction between dipole moments and quadrupole moments on ions in the crystal.

Zero-point: When ions or atoms are in a crystal they are required by quantum mechanical considerations to have vibrational energy, even at absolute zero of temperature. Isolated atoms, of course, do not have this vibrational energy. The zero point energy reduces the binding energy of the crystal (Seitz, The Modern Theory of Solids, p 86).

For the purpose of computing energy levels of electrons in the crystal the Madelung energy is important because it represents the electrostatic potential at a lattice site. The other terms represent interactions between ions, and so are relatively less important to electronic levels.

ions remain in their undisturbed lattice positions. This potential depends on the lattice spacing, and also on the arrangement of ions in the lattice. That is, the Madelung energy is different for the body centered cubic lattice than for a face-centered cubic lattice with the same lattice spacing.

In most crystals, including the silver halides, the polar, or ionic, bond is not the only bond which determines the properties of the solid. The covalent bond must also be considered. The latter type of bond is formed when two (or more) electrons are shared by a pair of atoms.

The bond between atoms in a molecule or in a crystal needs not be exclusively ionic or exclusively covalent. The bond may resonate between the two types and as a result it is more stable than either bond alone.¹

The electronegativity, x_a , of an atom, "a", is defined as the power of the atom in a molecule to

1. L. Pauling, The Nature of the Chemical Bond and the Structure of Molecules and Crystals, Cornell University Press, Ithaca, N. Y., 2nd ed. (1948) pp 8-12

attract an electron to itself. It has been found¹ that electronegativity is roughly proportional to the sum of the ionization energy, I_a , and the electron affinity, A_a , of the atom. That is,

$$x_a = k(I_a + A_a)$$

where the constant of proportionality, k , is $\frac{1}{5.64}$ when I , A , and x are in electron volts. In a bond between two atoms, a and b , the difference in electronegativities of the atoms, $|x_a - x_b|$, is a measure of the degree to which the bond is ionic. That this is reasonable can be seen as follows. The greater the ionization potential of the negative ion, a , and its electron affinity, and the lower the ionization energy and the electron affinity of the positive ion, b , the greater will be the probability that the negative ion will have the electron at any given time.

Table 2 shows how the quantity $|x_a - x_b|$ is computed for several crystals. The values of $|x_a - x_b|$ show that the bonds in silver chloride and silver bromide can be expected to have more covalent character than in the alkali halides. Pauling¹ has put this on a quantitative

1. L. Pauling, op. cit., p 66

	<u>Negative Ion</u>			<u>Positive Ion</u>			$(\chi_a - \chi_b)$
	I_a (ev)	A_a (ev)	χ_a (approx.) $= (I_a - A_a)$ 5.64	I_b	A_b	χ_b (approx.)	
LiI	10.44	3.14	2.41	5.39	0	.96	1.43
NaCl	12.96	3.83	2.98	5.14	0	.91	2.07
CsF	17.42		4.06	3.89	0	.69	3.37
AgCl	12.96	3.83	2.98	7.57	?	1.8	1.18
AgBr	11.84	3.65	2.75	7.57	?	1.8	.97
Dia- mond			----			----	0

Table 2. Electronegativity
Differences for Various Crystals¹

basis and shows that for lithium iodide each bond has about 10 per cent covalent character, and in sodium chloride each bond is about 5 per cent covalent. In the silver halides, on the other hand, Pauling² estimates

1. Sources of data: Ionisation potentials: G. Herzberg, Atomic Spectra and Atomic Structure, Dover, New York, second edition, 1944, pp 200, 201
Halogen electron affinities: P. Seitz, The Modern Theory of Solids, p 49
Electronegativity values: silver, Pauling, op. cit., p 73; fluorine; Pauling, op. cit., p 64; others computed.

that each bond is about 24 per cent covalent in silver chloride and about 26 per cent covalent in silver bromide.

Table 3 gives some physical properties of alkali halides, silver halides, and covalent crystals. This

	Index of Refraction n (Ref. 1)	High Frequency Dielectric Constant n^2	Location of First Fundamental Absorption (Ref. 2)	Resistivity at 300° C ohm-cm (Ref. 3)
NaCl	1.54	2.38	1580 Å	10^9
KBr	1.56	2.43	1875 Å	10^9
AgCl	2.07	4.29	≈ 4000 Å	10^3
AgBr	2.25	5.08	violet	10^2
Silicon	3.46	11.96	$\approx 1\mu$	15
Germanium	4.12	16.41	$\approx 2\mu$	5 (room temp.)
Diamond	2.42	5.84	< 2300 Å	10^{14}

Table 3. Some Physical Properties of Several Crystalline Materials

1. All except Si and Ge taken from Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland (1953) 35th edition ($\lambda = 5893$ Å) For Si and Ge the values of n at 2.0μ are given. They were measured by H. B. Briggs, Phys. Rev., **77**, 287 (1950)
2. NaCl: E. G. Schneider and R. N. O'Bryan, Phys. Rev., **51**, 293-298 (1937)
KBr: R. Hilsch and R. W. Pohl, Z. Physik, **52**, 812-819 (1930)

(cont.)

table illustrates that all the properties of the silver halides cannot be classified as either close to those of the alkali halides or close to those of the covalent crystals.

The question arises as to how the binding energies of the crystals are affected by the partial covalent nature of the bond. Pauling¹ states that the resonance between two competing bonds, e.g., the ionic and the covalent, is at lower energy than either bond alone, other factors (such as lattice spacing) being constant. It appears that in the silver halides this additional bond energy is not large, for lattice energies calculated

2. (cont.) AgCl: M. A. Gilleo, Phys. Rev., 91, 538, 540 (1953) and F. C. Brown, Phys. Rev., 97, 357, (1955)
 Silicon: H. B. Briggs, Phys. Rev., 77, 727-728 (1950)
 Germanium: H. B. Briggs, J. Opt. Soc. Am., 42, 686-687 (1952)
 Diamond: T. S. Moss, Photoconductivity in the Elements, Butterworths, London (1952) p 103
3. F. Seitz, Modern Theory of Solids, p 55; W. Lehfeldt, Z. Physik, 85, 717-726 (1933)
 Silicon: G. L. Pearson and J. Bardeen, Phys. Rev., 75, 865-883 (1949)
 Germanium: K. Lark-Horowitz, Elect. Engng., N. Y. 68, 1047 (1949) Quoted by T. S. Moss, op. cit., p 126
1. L. Pauling, op. cit., pp 10, 35, 36

by Born and Göppert-Mayer¹ on the basis of a purely ionic bond agree with the experimental values within .2 ev, i.e., within 2.5 per cent.

		AgCl (ev)	AgBr (ev)
Lattice Energy	Calculated	8.80	8.55
Per Ion Pair	Observed	8.91	8.75

B. Selection rules

The validity of the atomic selection rule, $\Delta l = \pm 1$, in the case of soft X-ray spectroscopy has been discussed by Skinner.² Briefly, the argument is that the transition probability is determined by an integral taken over the volume in which the wavefunctions of the initial and final state overlap. In this region, relatively close to the nucleus, the l values of both the initial and final wavefunctions are quite well defined.

For the transitions considered in this work, both the initial states ($\text{Cl}^- 3p$, $\text{Br}^- 4p$, or $\text{Ag}^+ 4d$) and the final states have wavefunctions which have lost some of

1. M. Born and M. Göppert-Mayer, Handbuch der Physik 24/2, Springer, Berlin (1933) p 727
2. H. W. B. Skinner, Reports on Progress in Physics V, The Physical Society, London (1938) p 274

their atomic character. However, it is likely that transitions corresponding to $\Delta \ell = \pm 1$ are more probable than those which violate the rule.

Another selection rule to be considered is that which results from conservation of momentum. The momentum $\underline{p}$ of the incident photon plus the momentum $\underline{k}$ of the electron in its initial state must equal the momentum $\underline{k}'$ of the electron in its final state. Since the momentum of the photon can be neglected,¹ the selection rule is $\underline{k} - \underline{k}' = 0$. This means that a photon could not cause an electron to jump from the top of the filled band ($k = \frac{\pi}{a}$) to the bottom of a conduction band where $k = 0$. In a perfect crystal this selection rule is valid. But most crystals (and especially evaporated thin films) contain enough imperfections that the rule is relaxed.²

1. By the de Broglie relation the momentum of a photon is given by $p_\lambda = \frac{h}{\lambda}$. The momentum of an electron with $k = \frac{\pi}{a}$, where a = lattice spacing of the crystal, is $p_e = \frac{hk}{2\pi} = \frac{h}{2a}$. Because λ for visible and ultraviolet light is so much greater than a , p_λ is negligible with respect to p_e .
2. P. Seitz, Rev. Mod. Phys., 23, 332, 333 (1951); Also R. M. Blakney and D. L. Dexter, Phys. Rev., 96, 227, 228 (1954)

C. Possible transitions in the region 500 - 1500 Å
Excitation of silver ion

It has been suggested¹ that the peaks at 2600 Å and 3200 Å in silver chloride and silver bromide respectively, observed by Fesefeldt and Gyulai,² may be due to excitons. That is, they may correspond to excitation of a p electron from the halide ion. It is possible that excitations of the silver ion 4d electrons is responsible for some absorption in the region 500 - 1500 Å.

In the isolated silver ion, Ag^+ , one of the 4d electrons can be excited to a 5p level. There are twelve different levels, the energy depending on the configuration of the remaining 4d electrons.³ A transition from the ground state ($4d^{10}$, 1S_0)⁴ to any

1. F. Seitz, *ibid*, p.330; Mott and Gurney, *op. cit.*, pp 93, 94, 100, 101, 137-140; Also D. L. Dexter, *Phys. Rev.*, **83**, 435-438 (1951)
2. H. Fesefeldt, *Z. Physik*, **64**, 741-748 (1930); H. Fesefeldt and Z. Gyulai, *Gott. Nachr.*, 226 (1929)
3. See for example R. F. Bacher and S. Goudsmit, Atomic Energy States, McGraw-Hill, New York (1932)
4. The meaning of the spectroscopic level notation used here is as follows: Small letters, s, p, d, indicate the angular momentum quantum number of a single electron. s means $\ell = 0$, p means $\ell = 1$, etc. The notation $4d^{10}$ indicates 10 electrons whose quantum numbers are $n = 4$ and $\ell = 2$.

(cont.)

MILERS FALLS

ONION SKIN

BOTTOM CONTENT

of the twelve levels satisfies the selection rule, ($\Delta l = \pm 1$). Only three satisfy the rule, ($\Delta J = \pm 1, 0$, but not $J = 0 \rightarrow J = 0$). They are:

$3p_1$	10.32	ev	above	ground	state	(1199 A)
$1p_1$	11.10	"	"	"	"	(1116 A)
$3d_1$	11.14	"	"	"	"	(1111 A)

Of these, only the $1p_1$ state also satisfies the rules ($\Delta S = 0$ and ($\Delta L = \pm 1, 0$).

In the solid there are undoubtedly available to a silver ion 4d electron, states whose wavefunctions, ψ_i , near the silver ion are made up in part of 5p wavefunctions of an isolated ion. A more detailed discussion of the nature of the wavefunctions in the

4. (cont.) The capital letters, S, P, D,... indicate the total orbital angular momentum quantum number, L, of the atom. S means $L = 0$, P means $L = 1$, etc. Superscripts to the left of these letters are the multiplicities of the levels and are determined by the formula $M = 2S + 1$, where S in this case is the total spin quantum number of the atom. The vector sum of L and S is the total angular momentum, J. This number is written as a subscript to the right of the letters S, P, D, etc. Symbolic representation of the state of the atom is then $M_{L,J}$.

The symbolism and selection rules are summarized in G. R. Harrison, R. C. Lord, J. R. Loebourow, Practical Spectroscopy, Prentice-Hall, New York (1948) Chapter 10.

solid would be beyond the scope of this thesis. However, in general we can say that transitions from the $\text{Ag}^+ 4d$ levels to states ψ are expected, that the width of the observed absorption will be much greater than that of $4d \rightarrow 5p$ in the isolated ion, and that the energy associated with these transitions may be less than that for the $4d \rightarrow 5p$ in the isolated ion.¹

Photoelectric absorption by a negative ion p electron

The ultraviolet absorption of silver bromide has been studied theoretically by Allen.² He used a model consisting of a bromide ion in a hole in a uniform dielectric. When an electron is ejected the field of the hole is screened by the polarization of the medium. It is argued that this reduces the absorption at the spectral edge and causes the maximum to occur at higher energy. The predicted absorption coefficient shows a gradual increase with energy from the edge (estimated at 6.25 eV) to the maximum value of $1.4 \cdot 10^6$ per cm. at about 14.6 eV (850 Å), with a gradual decrease at higher energy.

1. F. Seitz (Rev. Mod. Phys., 23, 330 1951) points out that an excited electron can take advantage of the lattice fields to reduce its energy.
2. J. R. Allen, Can. J. Phys., 31, 218-224 (1953)

Presumably, the principal results would be similar for silver chloride, that is, a rather diffuse absorption with the maximum value the order of 10^6 per cm. occurring at an energy well above that at the edge.

Excitation of negative ion s states

Transitions from the Cl^- 3s and Br^- 4s states to conduction states with some p symmetry are possible sources of absorption.

The energies of these s levels are not certain.¹ But at least for the chloride ion the 3s level can be estimated as follows. Consider two different excitations of an isolated chloride ion, in which an electron is just freed from the ion.

The difference in energy is obviously the energy of the atomic transition $3s^2 3p^6 \rightarrow 3s^1 3p^6$. This can

1. They are not listed in the standard energy level references: Bacher and Goudsmit, op. cit., U. S. Bureau of Standards Circular #467 (1949) International Critical Tables, 6, pp 35, 36

be estimated from data on singly ionized argon.

Argon II (once ionized argon) has the same electronic configuration as chlorine I (un-ionized), only the nuclear charge and mass are different. The $3s\ 3p^6$ level in A II is $108,730\text{ cm}^{-1}$ above the ground state, $3s^2\ 3p^5$. To establish a ratio between energy levels in A II and Cl I, compare the levels $3p^4\ 4s$:

A II	Cl I	Ratio: $(E_{Cl\ I})/E_{A\ II}$
$134,208\text{ cm}^{-1}$	71,954	.536
135,052	72,484	.536
135,568	72,823	.537

Thus in Cl I the energy of the $3s\ 3p^6$ level above the ground state, $3s^2\ 3p^5$, can be estimated at

$$.536 \cdot 108,730 = 58,300\text{ cm}^{-1} = 7.19\text{ ev}$$

Therefore it takes about 7.2 ev more energy to excite a 3s electron to a certain level than to excite a 3p electron to that same level. On an energy level diagram for the isolated ion the 3s state would be drawn 7.2 ev below the 3p state.

In the solid there are some states beginning about 3 ev above the Cl^- 3p band. An absorption edge in silver

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chloride appears to be at 4100 or 4200 Å (3ev).¹ Photoconductivity is also observed in the near ultraviolet region.² These states could therefore be expected to start about 10 ev above the 3s levels. The exact energy would depend on the relative perturbations produced in the solid of the 3p and 3s levels. In this work we will not attempt to discuss the nature of the excited states but merely state that if transitions from the Cl^- 3s level to the states are permitted, then absorption starting at about 10 ev and increasing at higher energies can be expected.

For silver bromide the $4s^2 4p^5 \rightarrow 4s^1 4p^6$ energy cannot be calculated as has been done for the corresponding case in chlorine, because the appropriate data on Kr II are not available. However, it is probably a little less than the energy for the corresponding chlorine transition.

Doublet structure

The ground state of a halogen atom is a doublet, the separation for chlorine and bromine being .11 and

1. See M. A. Gilleo, Phys. Rev., 91, 538, 540 (1953)
F. C. Brown, Phys. Rev., 97, 357 (1955)
2. Seitz, Rev. Mod. Phys., 23, 338-342 (1951) and
M. A. Gilleo, op. cit., p 538

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.45 ev respectively. In the alkali bromides the bromine doublet structure shows in absorption,^{1,2} with the possible exception of lithium bromide. However the chlorine structure is not resolved. O'Bryan and Skinner³ have shown by soft X-ray emission studies that in silver bromide the bromide 4p band is wider than the corresponding bands in all the alkali bromides except lithium bromide. Therefore the wide 4p band may hide the doublet structure in silver bromide.

In summary, the considerations on the preceding few pages have shown that absorption structure is to be expected in silver chloride and silver bromide in the region of 1000 - 2000 Å. The shape of the structure may help to identify the origin of the absorption.

1. R. Hilsch and R. W. Pohl, Z. Physik, 59, 812-819 (1930)
2. E. G. Schneider and H. M. O'Bryan, Phys. Rev., 51, 293-298 (1937)
3. H. M. O'Bryan and H. W. B. Skinner, Proc. Roy. Soc. (London) A176, 229-262 (1940)

VI RESULTS

Curves of absorption coefficient vs wavelength for two sets of silver chloride films and two sets of silver bromide films are given in figures 14 and 15. The absorption coefficient is computed from equation 2, page 44. The value of T in each case is the difference in average thickness of the two sample films. It must be recalled from section II D that the films are probably not uniform in thickness and that they may not be entirely continuous. Only with this reservation, then, can the absolute magnitude of the absorption be considered representative of the bulk material.

The correction for background which was discussed in appendix 3 was used on the runs: silver chloride B, silver bromide B, and silver bromide A below 900 Å. It was not considered necessary on the rest of the data because the background was negligible.

Reciprocity effects were removed in the silver chloride curve A by the second of the two methods described in appendix 3. The other runs were analyzed using the first method, in which separate characteristic curves were constructed for the "thin" and "thick" exposures.

Each silver chloride curve was drawn so that it would follow the experimental points as closely as possible while at the same time it would be consistent with the other data on silver chloride. The same criterion was used in drawing the silver bromide curves. Dashed portions of the curve represent regions where the data left the exact shape somewhat in doubt. However, the qualitative features in the dashed regions (such as the high absorption of silver chloride compared to silver bromide at short wavelengths) have been confirmed by examination of other runs.

The general features of the silver chloride absorption are the gradual rise with decreasing wavelength at long wavelength, punctuated by relatively narrow absorption peaks at 1230 and 1165 Å. There are broader maxima at about 1120 and 950 Å. The absorption at wavelengths shorter than 800 Å remains high.

For silver bromide the absorption has a broad maximum centered at about 1470 Å with two narrower bands at 1260 and 1170 Å. The absorption coefficient remains high to about 950 Å; at shorter wavelengths it falls rapidly. There was some evidence for narrow

Figure 14a.
(Average thicknesses of evaporated films
 "Thick" 186 $\text{\AA}$
 "Thin" 149 $\text{\AA}$
 Difference 37 $\text{\AA}$)

Figure 14b.
(Average thicknesses of evaporated films
"Thick" 63 Å
"Thin" 7 Å
Difference 56 Å)

Figure 15a.
(Average thicknesses of evaporated films
"Thick" 128 $\text{\AA}$
"Thin" 43 $\text{\AA}$
Difference 85 $\text{\AA}$)

Figure 15b
 (Average thicknesses of evaporated films
 "Thick" 207 Å
 "Thin" 130 Å
 Difference - 77 Å)

peaks at 1035 and 975 Å, but the scatter of experimental points was too great to permit confidence in their reality.

A. Interpretation

It seems likely that the two peaks between 1150 and 1300 Å, which appear in both the silver chloride and silver bromide absorption, result from excitation of the silver ion. Table 4 gives a summary of the pertinent data.

	<u>Å</u>	<u>ev</u>	<u>Å</u>	<u>ev</u>
AgCl	1165	10.62	1230	10.07
AgBr	1170	10.59	1260	9.83
Average		10.60		9.95
Isolated Ag ⁺ (3d, 1p)		11.12		(3p)10.32
Difference		.5		.4

Table 4. Peaks in Silver Halide Absorption Curves Compared to Silver Ion Levels

It is reasonable that the excited states in the crystal should be at lower energy than the corresponding ones in the ion, for an excited electron can take advantage of the lattice fields to reduce its energy.¹

1. P. Seitz, Rev. Mod. Phys., 23, 330 (1951)

The broad absorption maxima centered at about 1120 Å in silver chloride and at about 1470 Å in silver bromide appear to be the type of absorption predicted by Allen¹ for silver bromide. That is, the absorption spreads over many electron volts, having a broad maximum of about 10^6 per cm. at an energy well above the edge (estimated by Allen to be at 6.25 eV for silver bromide). The agreement is not complete, however, for Allen's calculations show a maximum absorption at 850 Å for silver bromide, whereas the present work shows it to be about 1470 Å.

We propose that the strong absorption in silver chloride centered about 950 Å, and the relatively high absorption of silver bromide in the region 950 - 1150 Å may be due in part to excitation of the chloride 3s and bromide 4s electrons, respectively. In the theory section a rough calculation is made which shows that absorption due to excitation of Cl^- 3s electrons might be expected for energies greater than 10 eV (1200 Å). Excitation of the bromide 4s electrons is expected at somewhat lower energy.

1. J. R. Allen, Can. J. Phys., 31, 218-224 (1953)

The measurements on silver chloride agree with Schneider and O'Bryan's curve¹ to the extent that the absorption generally rises with decreasing wavelength down to their limit of 1100 Å. However, the sharp rise at 1290 Å which they report is not observed in the present data.

B. Accuracy of the Results

Systematic errors could cause the absorption curve determined from one run to be different from that determined in a different run. The factors involved are: uniformity of celluloid thickness, uniformity of sample films, measurement of the sample film thickness, avoiding pinholes in films, constancy of average intensity of the discharge tube, stability of zero and sensitivity of the radiometer in the microphotometer, precision in construction of characteristic curve, and accuracy in correction for background and reciprocity effects.

Random errors which could cause scatter of experimental points are: variation of relative intensities

1. E. G. Schneider and H. M. O'Bryan, Phys. Rev., 51, 297 (1937)

of spectral lines, irregularities on the spectroscopic plates, uneven development, granularity of plates, error in reading exposure values from the characteristic curve, and (to a limited extent) poor estimation of the background level. It is worthwhile to examine each of these sources of error.

Celluloid thickness: While the collodion solution was drying on the surface of the water the reflected interference colors were watched and a region of uniform thickness was selected. The celluloid supports for thin and thick silver halide samples were from adjacent portions of such a uniform area.

Sample film thickness: Because of the increased distance of one end of the film from the crucible and the angle at which the molecules strike, there is a variation in average film thickness of about six per cent over the length of the film. The difference in thickness, T , was determined to within about 7 Å, which represents from 8 per cent to 19 per cent error in the values of T used in this work.

Sample film uniformity: This problem is discussed in section II D. The uncertainty in the film structure is probably the largest source of error in the magnitude of the absorption.

Pinholes in films: If, after a spectrograph run, it was found that the films had more than a permissible area of pinholes, the films and the spectrographic plates were discarded. The permissible area of pinholes was calculated on the basis that the ratio of light passing through pinholes to light passing through the rest of the film should be no more than 1/100.

Variation in average intensity from source: This is discussed in section III A.

Radiometer zero drift or change in sensitivity of microphotometer: No zero drift was detectable, and the sensitivity change was found to be negligible over a period of several hours.

Construction of characteristic curve: The prime source of error here was the scatter of experimental points on the d_g vs d_{2g} plot. The characteristic curve was probably accurate to a few per cent.

Corrections for background and reciprocity effect: These corrections were done as carefully as possible. Although it would have been desirable to have some independent method to check the accuracy of the background correction, it was reassuring to find that the magnitude of the absorption was not critically dependent

on the correction. The same remark applies to the reciprocity corrections.

Relative intensities of spectral lines: This is discussed in section III A.

Irregularities on the spectrographic plates, development, and granularity: These include abrasion marks, pinholes in the emulsion, and emulsion coating marks - especially near the ends of plates. The Schumann type of plate is particularly subject to errors such as these. Development was made as uniform as possible by constant rocking of the developing trays. Granularity was not a serious problem. Since the spectrograph slit was maintained fairly wide ($60 - 100\mu$) the image of a spectral line was much wider than any irregularities caused by grain.

Errors in reading values from characteristic curve:

As was discussed in section IV C, the average error was about one per cent. This was not serious in view of other errors.

Estimation of background level: The background correction involves subtracting the nearly constant background, B, from the exposures, E_1 , E_2 , etc., which can vary widely from one line to the next. If too high a

background value, B' , is selected, then the ratio

$\frac{E_1 - B'}{E_2 - B'}$ may be quite different from the true ratio

$\frac{E_1 - B}{E_2 - B}$. Thus the apparent relative intensities of spectral lines could be altered.

Since there was no independent check on the background level, this effect was undoubtedly responsible for some of the scatter of experimental points.

In summary, the major sources of error are considered to be: film structure, change in average or relative intensity of spectral lines, plate irregularities, and background correction. All in all, the experimental procedure yields results which are largely reproducible and show a definite difference between the absorption of silver chloride and that of silver bromide.

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Appendix 1

Interferometric thickness measurement considering phase shift on reflection from silver surfaces

Channeled spectra are obtained, in the method of Tolansky, by multiple reflections of white light between highly reflecting surfaces. See section II C for the details of the procedure. Tolansky derived a simple equation relating the thickness of the film being measured (Δt), the order number of interference (n), and the wavelength shift of a fringe ($\Delta \lambda$).¹ The equation is

$$\Delta t = \frac{n}{2} \Delta \lambda$$

It is worthwhile to derive the relation between these quantities in a more general manner, considering the effect of an arbitrary phase shift on reflection

1. Tolansky, op. cit., p 111. The quantities Δt and $\Delta \lambda$ are used here instead of dt and $d\lambda$ since as Tolansky points out, dt and $d\lambda$ do not have to be small.

from the highly reflecting (silvered) surface. Let ϵ = phase shift at each surface in radians. ϵ can be a function of wavelength.

If the light is incident normally on the interfaces, i.e., $\theta = 0$, then the phase difference between two successive transmitted rays is

$$\delta = 2\pi \frac{2t}{\lambda} + 2\epsilon \quad (3)$$

Constructive interference will occur when

$$\delta = n2\pi \quad (4)$$

Substituting (4) in (3) we have

$$n\pi = \pi \frac{2t}{\lambda} + \epsilon$$

or

$$2t = \lambda \left(n - \frac{\epsilon}{\pi} \right) \quad (5)$$

This is the condition for a maximum of transmission. By the reversibility principle it is also the condition for a minimum of reflection.

Consider two successive fringes (minima of reflection) at λ_0 and λ_1 . The order number, n , of the fringe at the longer wavelength, λ_0 , is one less than the order number, $n + 1$, of the adjacent fringe at shorter wavelength, λ_1 . For each of these fringes equation (5) is satisfied, so we have

$$2t = \lambda_0 \left(n - \frac{\epsilon_0}{\pi} \right)$$

$$2t = \lambda_1 \left(n + 1 - \frac{\epsilon_1}{\pi} \right)$$

where ϵ_0 and ϵ_1 are the phase shifts at λ_0 and λ_1 respectively. Eliminating t from the two equations and solving for n we have

$$n = \frac{\lambda_0 \frac{\epsilon_0}{\pi} + \lambda_1 - \lambda_1 \frac{\epsilon_1}{\pi}}{\lambda_0 - \lambda_1} \quad (6)$$

Now if there is an infinitesimal shift, $d\lambda$, in a fringe, which corresponds to a change in thickness dt of the space between silvered surfaces, we have by differentiation of equation (5)

$$dt = \frac{d\lambda}{2} \left(n - \frac{\epsilon}{\pi} \right) - \frac{\lambda}{\pi} \frac{d\epsilon}{d\lambda} d\lambda$$

Assuming that the relation will hold for finite changes, Δt and $\Delta\lambda$, we have for the fringe at λ_0 :

$$\Delta t = \frac{\Delta\lambda}{2} \left(n - \frac{\epsilon_0}{\pi} \right) - \frac{\lambda_0}{\pi} \left(\frac{d\epsilon}{d\lambda} \right)_{\lambda_0} \Delta\lambda$$

After substituting the value of n from equation (6) this expression reduces to

$$\Delta t = \frac{\Delta\lambda}{2} \left\{ \frac{\lambda_1}{\lambda_0 - \lambda_1} \left(1 - \frac{\epsilon_1 - \epsilon_0}{\pi} \right) - \frac{\lambda_0}{\pi} \left(\frac{d\epsilon}{d\lambda} \right)_{\lambda_0} \right\} \quad (7)$$

Note that the theory ignoring phase shifts gave the result

$$\Delta t = n \frac{\Delta\lambda}{2} = \frac{\Delta\lambda}{2} \left(\frac{\lambda_1}{\lambda_0 - \lambda_1} \right)$$

Equation (7) reduces to this if

$$\epsilon_1 = \epsilon_0 = \frac{d\epsilon}{d\lambda} = 0$$

(i.e., no phase shift) or if

$$\epsilon_1 - \epsilon_0 = \frac{d\epsilon}{d\lambda} = 0$$

(i.e., constant phase shift). Neither of these conditions is fulfilled in the case of silver. The fractional correction, c , to the simple theory is given by

$$c = \frac{\frac{\Delta\lambda}{2\pi} \left\{ \frac{\lambda_1}{\lambda_0 - \lambda_1} (\epsilon_0 - \epsilon_1) - \lambda_0 \left(\frac{d\epsilon}{d\lambda} \right)_{\lambda_0} \right\}}{\frac{\Delta\lambda}{2} \left(\frac{\lambda_1}{\lambda_0 - \lambda_1} \right)}$$

$$= \frac{1}{\pi} \left\{ \epsilon_0 - \epsilon_1 - \frac{\lambda_0}{\lambda_1} (\lambda_0 - \lambda_1) \left(\frac{d\epsilon}{d\lambda} \right)_{\lambda_0} \right\} \quad (8)$$

The following table gives values of the correction computed for two typical fringes. The values of ϵ and $\frac{d\epsilon}{d\lambda}$ were taken from the curves reproduced in figure 16.

λ	ϵ	$\frac{d\epsilon}{d\lambda}$	$\epsilon_0 - \epsilon_1$	$\frac{\lambda_0}{\lambda_1} (\lambda_0 - \lambda_1) \left(\frac{d\epsilon}{d\lambda} \right)_{\lambda_0}$	c
$\text{\AA}$	rad	rad/ $\text{\AA}$	rad		
6000	.519	$-.116 \cdot 10^{-3}$	-.065	-.0632	.0005
5500	.584	$-.157 \cdot 10^{-3}$	-.087	-.0865	.0002
5000	.671				

The corrections, .05 and .02 per cent, are negligible.

Since the corrections calculated by the preceding method are negligible it is interesting to re-examine the assumption on page 83 that the differential relation will also hold for finite changes.

Denote by λ'_0 the wavelength of the fringe from the coated portion which has the same order number as the fringe at λ_0 from the uncoated portion. t'_0 is the physical separation of the plates in the coated region.

Without approximation, then, equation (5) is satisfied for λ_0 and λ'_0 as follows:

$$2t_0 = \lambda_0 \left(n - \frac{\epsilon_0}{\pi} \right) \qquad 2t'_0 = \lambda'_0 \left(n - \frac{\epsilon'_0}{\pi} \right)$$

Subtracting the latter equation from the former, substituting the value of n from equation (6), and using the definitions $\Delta t_0 = t_0 - t'_0$ and $\Delta \lambda_0 = \lambda_0 - \lambda'_0$ we have

$$\Delta t_0 = \Delta \lambda_0 \frac{\lambda_1}{2(\lambda_0 - \lambda_1)} + \frac{\Delta \lambda_0}{2\pi(\lambda_0 - \lambda_1)} (\lambda_0 \epsilon_0 - \lambda_1 \epsilon_1) - \frac{1}{2\pi} (\lambda_0 \epsilon_0 - \lambda'_0 \epsilon'_0) \quad (9)$$

Taking as a typical example a case where $\lambda_0 = 5500 \text{ \AA}$, $\lambda_1 = 5000 \text{ \AA}$, and $\lambda'_0 = 5460 \text{ \AA}$, we have

$$\begin{aligned} \Delta t_0 &= 40 \frac{5000}{2(500)} + \frac{40}{2\pi(500)} (3225 - 3360) - \frac{1}{2\pi} (3225 - 3235) \\ &= 200 - 1.72 + 1.59 = 200 - .13 \quad (\text{\AA}) \end{aligned}$$

Thus the correction to the elementary equation (page 81) is $.13/200 \approx .07\%$. This correction is negligible with respect to the error introduced by the fringe width.

Figure 16.

The phase shift, ϵ , on normal reflection is calculated from the equation

$$\tan \epsilon = \frac{2k n_0}{k^2 + n^2 - n_0^2}$$

where n and k are the index and absorption coefficient, respectively, of silver and n_0 is the index of the surrounding medium, taken to be 1.0 in this case. Values of n and k for silver are from L. G. Schulz and F. R. Tangherlini, J. Opt. Soc. Am., 44, 357-368 (1954). The first derivative curve is found by drawing tangents to the phase shift curve.

Appendix 2

Source characteristics and operationDescription

A detailed drawing of the source is shown in figure 8. In addition there are the following auxiliary components. The pump is a Cenco Hypervac 20. Leading off the exhaust tube, close to the source chamber, are two vacuum gauges: a G. E. thermocouple gauge and an inclined mercury manometer. The former is useful in the range 1 - 500 μ , the latter in the range .5mm - 10 mm.

Soldered into the cathode are a Will high vacuum needle valve and a Hoke valve (V1) in series. The

former can be used to regulate the flow of gas, but for the very small flow needed in this application,

the needle valve is not accurate or constant enough. Attached to the Hoke valve by means of vacuum rubber tubing is a glass capillary which very effectively limits the gas flow. In parallel with the capillary is a stopcock (V2), normally closed, which can be used for more rapid flushing of the supply system. A copper tube leads to the gas supply tank, at which point there is a Hoke valve (V3) in addition to the regulator.

For the high voltage supply a standard circuit is used. A diagram is shown in figure 17 and a photograph of the housing appears in figure 18. With minor changes the circuit can be used for either 30 KV or 15 KV supply. The 15 megohm leakage resistors reduce the voltage on the capacitor to a safe level within a few seconds after the transformer is turned off. The meter in series with the resistance is calibrated to read the voltage on the capacitor directly in kilovolts. The air gap is set at about $1/8$ inch. This gap controls the breakdown voltage.

Alignment

For most effective operation of the discharge tube it is necessary to have the center of the capillary, the baffles, and the slit on the same straight line,

Figure 17. High voltage supply circuit

P1, P2, P3	Pilot lights	T3	High voltage transformer, Thordarson type T42479 Rating: 1KW
F1, F2	Fuses, 1 ampere	A	Ammeter, 0-10 amps
T1, T2	Filament transformers	PS	Powerstat, 2KW rating
V1, V2	Vacuum rectifiers Kenotron 8020		
C1, C2	.3 μ fd		
R1, R2	500 K Ω (5 100 K Ω , 50 W resistors in each)		
R3, R4, R5	15 meg Ω (15 1 meg Ω , 2 W resistors in each) These resistors are for safety		
R6	2500 Ω This resistance discourages the spark from jumping from either electrode to the ground		
MA	Milliammeter 1 ma corresponds to 15 KV on one condenser

Figure 18. High voltage supply housing

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and this line must intersect the grating. Once the grating, slit, and baffle positions have been fixed more or less permanently, the only adjustment necessary is of the capillary tube. This must be done whenever a new capillary is inserted or the glass wool is repacked.

A simple method for alignment is to allow white light to fall on the grating at such an angle that visible light is diffracted back through the slit. Looking through the window in the end of the electrode one can see the light coming through the slit and can use the adjusting screws to center the capillary on the light path.

Operation

As mentioned in section III B, it is important that residual air be removed from all parts of the spectrograph before an exposure is made. After pumping out the main chamber, the source chamber, and the supply system (to the valve V3) to about 10μ , one lets some gas into the supply system by opening V3 while V2 is closed. Closing V3 and opening V2 allows the gas to be pumped out of the supply system. This is repeated three or four times. Then the steady flow of gas through the glass capillary is begun and continued for 10 to

30 minutes before turning on the high voltage. After a warm-up period of about 1000 sparks, the exposure may be begun. While the spark is operating, a stream of air should be used to keep the cathode cool.

Characteristics

The source is usually operated at 14 to 15 KV and $.3 \mu$ fd, 50 to 80 sparks per minute. Using SWR plates, a slit width of about 60 microns, and with the dispersion of about 2A/mm at 1000 A, a good exposure is obtained in about 40 sparks.

The rate of gas flow into the source is important for several reasons. If the gas pressure is too low the 15 KV will not be sufficient to initiate the discharge. If the pressure is too high, any impurity gases such as oxygen will absorb the radiation strongly. A study on argon indicates that when the pressure (measured at the thermocouple gauge, which was corrected for argon) exceeds .5 mm the cutoff at 736 A is very pronounced. If, however, the pressure is below .2mm the absorption is much reduced and very strong lines appear in the region 200 - 300 A. A similar effect has been noticed for helium.

A fine silica dust is formed in the discharge tube and thrown toward the slit. Some of the particles, at least, are known to be charged.¹ A set of baffles is put in the anode to make the field irregular in an attempt to deflect the particles. It is only partly effective. Perhaps a more efficient baffle could be designed. Some dust reaches the slit and tends to clog it if the opening is less than 10 or 15 μ . The production of dust seems to be more severe when argon is used than when helium is used. Dust which gets through the slit may do permanent damage to the grating, so every effort should be made to prevent it from reaching the grating.

The data obtained with the discharge tube do not appear to be as consistent as those obtained with the vacuum spark between metal electrodes. This observation is based on comparison of the scatter of points in the present data with that shown by Siegmund, Carter, and Woodruff.

During a spark the momentary current in the circuit is quite high. The high voltage leads to the discharge

1. R. E. Worley, Rev. Sci. Instr., 13, 67-71 (1942)

tube form a loop from which some radio frequency radiation can be broadcast.

The radiation at first was strong enough to be picked up in the circuit of a sensitive detector used in connection with the Physics Department's small cyclotron, three floors below. About eight cycles of ten megacycle radiation were being received during each spark. This situation was remedied by reducing the area of the loop, i.e., by moving the high voltage supply quite close to the discharge tube.

Maintenance

About every 20,000 sparks (two runs) the air gap electrodes should be cleaned and respaced, and the glass wool around the capillary should be repacked. If the latter is not done, the spark will find a path through the glass wool and will then bypass the capillary.

After each run the slit should be inspected to see that it is not being clogged by dust, and if necessary the slit should be cleaned. The baffles should be removed and cleaned.

When the capillary tube has enlarged to about 3.5 mm diameter the continuous radiation will be weak. It should be replaced.¹

1. The quartz tube and capillary assemblies were obtained from the Amersil Co., Chestnut Ave., Hillside, N. J.

Appendix 3

Correction to plate calibration

The characteristic curve is constructed using the assumption that the reciprocity law is valid. In the work of Kebler, McCormick, and Sawyer¹ it is reported that for SWR plates used in the region 230 - 330 Å small differences in calibration curves were found which could be attributed to reciprocity failure. Data from the Kodak Research Laboratories² indicate that for visible light and exposure times greater than one second there is some reciprocity law failure for SWR film, the emulsion having slightly more sensitivity and a little higher contrast at higher intensities.

In the present work small effects attributed to reciprocity failure³ were occasionally detected. When two d_E vs d_{2E} curves were constructed, one from a pair

1. R. W. Kebler, W. W. McCormick, and R. A. Sawyer, J. Op. Soc. Am., 44, 270-275 (1954)
2. Private communication
3. It is to be understood that the intermittency effect also enters here. But we use the single phrase, reciprocity effect, since as Mees points out (C. E. K. Mees, The Theory of the Photographic Process, Macmillan, New York, revised edition 1954, pp 213, 215) the intermittency effect is a result of reciprocity failure.

of "thin" exposures and one from a pair of "thick" exposures, they were sometimes significantly different. This was true even when the first and last exposures on the plate showed that the spark had remained essentially constant during the run. When this occurred, two characteristic curves were plotted, one for the "thin" (high intensity, short exposure) and one for the "thick" (low intensity, long exposure), and the two curves were made to cross each other at the average value of E_{thick} . The "thin" (high intensity) curves showed more contrast than the "thick" (low intensity).

Occasionally it was found that the absorption coefficient, μ , as determined by equation 2 at a certain wavelength, had a definite correlation with the intensity of the source at that wavelength. That is, a plot of μ vs λ had some peaks in the same places as a plot of E vs λ .¹ This unfortunate situation was attributed to reciprocity failure and it was noticed early in the research before separate characteristic curves were plotted for "thin" and "thick" exposures. The effect was corrected as follows. Let $\bar{\mu}$ = average

1. This effect was also noticed by Woodruff, op. cit.
p 32

value of absorption coefficient, μ , over a certain spectral region. Let E = the exposure value of a line on the spectrum obtained through the thin film. The assumption was made that the distribution of values of E was random. A plot was made of $(\mu - \bar{\mu})$ vs E , determining the best straight line $(\mu_0 - \bar{\mu}) = a + bE$ through the points (also through the center of mass of the points). Then, for a particular value of E the quantity $(\mu_0 - \mu)$ was determined from the graph and subtracted from the corresponding μ . As is evident, this procedure was aimed at correcting the symptom rather than the disease. But it was a small correction and so did not change the main features of the absorption structure. The correction described on the preceding page was considered more reliable.

The construction of the characteristic curve also assumes that the curve is not wavelength dependent over a finite spectral range. And it was found that within experimental error the d_E vs d_{2E} curve (and hence the characteristic curve) stayed constant over a reasonable range, from $1/6$ to $1/2$ of a plate. During the construction of the d_E vs d_{2E} curve care was taken to notice when points began to fall significantly far from the already established curve. A new d_E vs d_{2E} curve was

then constructed. For a run in which one and a half 10-inch plates were analyzed there were at least three separate E vs d curves.

Scattered light poses a difficult problem when working with: 1. a source which produces a large amount of radiation outside the region of interest; 2. a sample which transmits a very small fraction of the radiation of interest but a large fraction of other wavelengths.

In our case the source produces a great deal of visible and near ultraviolet light as well as the extreme ultraviolet radiation which is of interest. And the silver halide plus celluloid films transmit only 2 to 10 per cent of the extreme ultraviolet, but about 90 per cent of the visible radiation.

When the sample is in position F_2 (figure 1b), the mesh can scatter some long wavelength radiation onto the plates. The main source of scattered light, however, appears to be the grating surface itself.

It was desirable to correct for the background in the analysis of data. The first step was to determine the background level as a function of position along the plate for each spectrum.

Just below the argon cutoff the background was simply the observed exposure, because there was essentially no radiation of wavelengths 750-780 Å. At longer wavelengths the background could be determined in regions where there was high absorption due either to argon (lines) or to oxygen (bands). It was observed that the background decreased with increasing wavelength. A plot was made of background vs wavelength.

It was possible, using this plot, to subtract the background (B) from the observed exposure (E) to obtain e' , an approximation to the true exposure at the desired wavelength. The plate characteristic curve (figure 12b) assumed that the exposure was caused by a single wavelength. The actual exposure, however, was produced by far ultraviolet radiation superimposed on background radiation of unknown wavelength. Since the characteristic curves for the two in general should be different it was desirable to recalibrate the far ultraviolet exposures.

Let us designate by e the true exposure, which corresponds to e' . The symbol $e'(e)$ means the approximation, e' , which corresponds to the true exposure, e .

The information necessary for a recalibration was contained in a plot of $e'(2e)$ vs $e'(e)$ for a set of nearby wavelengths.

Figure 19. recalibration data

If the points fell along the straight line $e'(2e) = 2e'(e)$, then it was evident that no correction was necessary. Usually the points fell off this line; then the best line, OD, was drawn through them.

From the $e'(2e)$ vs $e'(e)$ plot, analogous to the $d(2E)$ vs $d(E)$ plot of section IV A, was constructed the curve e vs e' . The method was the same as used to obtain the d vs E curve in section IV A. That is, a

value e' was plotted vs an arbitrary value of e , say 1.

From figure 19 the value of e' corresponding to $e = 2$

Figure 20. Recalibration curve

was found. $e'(2)$ was then plotted at $e = 2$. This procedure was continued until the end of the line OD was reached.

From the recalibration curve the quantities e_{thin} and e_{thick} were found. The values of e were usually close to the corresponding values of e' indicating the correction was small.

With the background correction completed, the values of absorption coefficient were computed by the relation

$$\mu = \frac{1}{T} \ln R \frac{E_{\text{thin}}}{E_{\text{thick}}}$$

For all data reported here both the quantities

$$\alpha = \frac{1}{T} \ln R \frac{E_{\text{thin}}}{E_{\text{thick}}} \quad \text{and} \quad \mu = \frac{1}{T} \ln R \frac{E_{\text{thin}}}{E_{\text{thick}}} \quad \text{were calculated}$$

for each point and curves were drawn for each. The similarities and differences between the two curves are discussed in section IV B, and curves of μ vs λ are given in section VI.