THE EXTREME ULTRA-VIOLET ABSORPTION
BY LITHIUM FLUORIDE

by

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Submitted in Partial Fulfillment
of the
Requirements for the Degree

DOCTOR OF PHILOSOPHY

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1961

Vita

The author was born in Brooklyn, New York on September 5, 1934. After graduating from Midwood High School, he entered Brooklyn College in January, 1952. He received the degree B.S. Cum Laude with a major in physics in June, 1955.

In the fall of 1955 the author undertook graduate studies in the Physics Department at the University of Rochester leading to the Ph.D. degree. Graduate assistantships and tuition scholarships were held during his tenure, 1955 to 1960 at the University of Rochester. In June of 1960 he was awarded the Master of Arts degree.

During the author's residence at the University of Rochester, his advisory committee has included Dr. R. E. Marshak, Dr. W. P. Alford, Dr. A. Roberts, and Dr. J. A. F. Randolph. His faculty advisor for the Ph.D. thesis was Dr. M. Parker Givens.

In 1954, the author married Miss Fran Krongard of Brooklyn, New York and in May, 1958 a daughter, Sara Lee, was born.

Acknowledgments

The author was privileged to have had the advice of Dr. M. Parker Givens in the preparation of this thesis report. His ready willingness to discuss the problems encountered during the course of this research proved beneficial toward the completion of this project.

The author's wife, Fran Milgram, gave great assistance in the analysis of data and in the typing of the first draft of this thesis. Without her encouragement this research report would never have been written.

The sagacious advice of Dr. H. I. Krongard is greatly appreciated. His role in the undertaking of this thesis has been of major importance.

The meticulous draftsmanship of Roman Kucil in the preparation of the various figures and curves included in this report is acknowledged.

Précis

The discrete electronic energy levels which exist in an atom widen into bands of allowed energy when similar atoms are periodically arrayed into a solid. The energy band structure which exists in the solid state can be explored using the techniques of extreme ultra-violet and x-ray spectroscopy.

A study was made to determine the absolute value of the absorption coefficient for Lithium Fluoride (LiF) between 10 and 100 e.v. The fundamental optical absorption was measured and the absorption features in this region were compared with the fundamental absorption features of the other alkali halides. The first exciton level was found to be at 12.9 e.v. Absorption structure attributed to the fluorine 2s electrons and lithium 1s electrons was observed. The absorption by the K electrons of Li^+ in LiF produced absorption peaks at the same energies that one would expect for K absorption by free Li^+ .

The absorption structure associated with the Li 1s electrons was found to be duplicated at a higher energy (13 e.v.). This suggested the possibility that a multiple process was involved in the photon absorption. That is, photon absorption produced an electron band to band transition and some other discrete loss. The excitation of a fluorine 2p electron to produce an exciton would be an energetically possible mechanism for this discrete loss.

Using the value of the F 2s absorption maximum obtained from this experiment and the value of the width of the valence band obtained from another work using emission spectroscopy, the energy band gap was estimated to be less than 14.5 e.v.

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I. EXPERIMENTAL PROCEDURE

A. Introduction

The instrument used in this research was a grazing incidence vacuum spectrograph. A detailed description of this spectrograph has been given by Siegmund¹. Essentially, the spectrograph consisted of a concave grating with 30,000 lines per inch mounted at 85° angle of incidence (i.e., 5° off grazing incidence) on a Rowland circle of one meter radius. A Lyman discharge tube was used to produce the desired radiation. Light entered the spectrograph through the entrance slit which was also on the Rowland circle. The diffracted light was then focused onto 2 in. x 10 in. photographic plates constrained to follow the Rowland circle. A diagram indicating the placement of the relevant parts is included as Fig. 1.

For light of intensity I_0 incident normally on a sample of thickness, x , the following equation is applicable:

$$I = I_0 (1-r)^2 e^{-\mu x}$$

where I_0 is the intensity of the beam incident on the sample, I is the intensity of the beam exiting from the sample, μ is the absorption coefficient of the material, and r is the reflection coefficient of the material.

The absorption coefficients of materials studied in the extreme ultraviolet portion of the spectrum have values between 10^5 cm.⁻¹ and 10^6 cm.⁻¹. This means that the samples must be in the form

VACUUM SPECTROGRAPH

FIG 1.

- A To pump
- D Light source: discharge tube
- F Alternate positions for sample films
- G 2m grating, 30,000 lines per in., 85° angle of incidence
- H Gas Supply
- P Plates
- Q Quartz capillary
- S Slit
- V 15 KV on .3ufd discharged once per second
- W Pirani guage
- X Manometer

of thin films approximately 10^{-6} to 10^{-5} cm. thick in order to detect the transmitted light. The samples were prepared in the form of thin films by vacuum evaporation.

A thick and thin sample of LiF were introduced separately into the light beam, and exposures were taken on photographic plates. A plate calibration procedure gave a relative intensity value for each value of the photographic density. The ratio of the intensity through the thick film to that through the thin film could then be found. After the difference in thickness between the thick and thin sample was obtained by using the technique of multiple-beam interferometry, the absolute value of the absorption coefficient was calculated.

An enhanced discussion of the preceding experimental procedure will be given in the following sections.

B. Preparation of the LiF Films

The most direct procedure of finding the absorption coefficient of LiF in the extreme ultraviolet region would be to measure the transmission with and without a self-supporting sample. However, films which are less than 10^{-5} cm. thick are extremely fragile and hence difficult to prepare unsupported. Some achievements in self-supporting film preparation have been reported for certain materials^{2,3,4,5}.

There are additional requirements on a thin film prepared for absorption studies in this spectral region. The absorber must be:

1. continuous
2. uniformly thick
3. mechanically strong to survive handling, exposure to ultraviolet light and exposure to possible fragments from a source of ultraviolet light.
4. of sufficient thickness to attenuate the incident beam of light to approximately one-third to one-tenth of its initial value.

An attempt to make self-supporting LiF films which would satisfy the afore-mentioned requirements proceeded as follows. A $\frac{1}{2}$ in. diameter hole was drilled through a $\frac{1}{16}$ in. thick Aluminum plate. A concentric hole $\frac{5}{8}$ in. diameter was drilled to a depth of $\frac{1}{32}$ in. The resulting Aluminum plate had one side, labeled "A", with a $\frac{1}{2}$ in. diameter hole at the surface, and the other side, labeled "B" with a $\frac{5}{8}$ in. diameter hole at the surface. A thin celluloid film was picked up on side "B", and the Aluminum plate was then placed in a vacuum evaporator with side "A" facing the evaporator heater. A LiF film was evaporated onto the surface of the celluloid, except for a shielded $\frac{1}{16}$ in. wide peripheral region. The next step was to eliminate the celluloid backing without harming the film. This was attempted by gently placing side "B" of the Aluminum plate on the surface of alcohol in a dish. The peripheral uncoated celluloid dissolved without straining the LiF film, and the celluloid under the LiF dissolved while the celluloid was floating on the alcohol. For very thin LiF films there was no success, but for films greater than approximately 800A thick it was

possible to obtain a LiF film floating upon alcohol. However, the film had cracks in it which were apparent visually due to the inevitable strains produced by the dissolving celluloid. Also, this minimum thickness attenuated the photon beam by more than one-eighth. Thus, this method was considered unsuitable for preparing LiF films for absorption studies in this spectral region.

The next approach was to use a support or substrate for the LiF film. The requirements that a substrate must meet are the same as for an absorber, except for condition number four as stated previously. Substrates are undesirable because:

1. They might introduce additional absorption bands due to the interface between the sample and substrate⁶.
2. They generally have large absorption coefficients for light in this spectral region but not for white light and near ultra-violet light. This means that the background on the photographic plate due to scattered light on the grating will be higher due to the increased exposures necessary with a substrate.

Certain metal foils could be used as substrates over restricted spectral ranges⁵. However, it is possible that the structure of the deposited LiF might be influenced by the crystal structure of the metal. It was decided to use an amorphous material, celluloid, as a substrate. Celluloid, which is one of the most transparent materials known in this region of the spectrum has an absorption coefficient of 10^5 cm.^{-1} at 100A, increasing to $6 \times 10^5 \text{ cm.}^{-1}$ at 400A and to a maximum of $1.1 \times 10^6 \text{ cm.}^{-1}$ at 800A⁷. The

region between 600A and 1000A shows the highest absorption for celluloid and is consequently the most difficult spectral region in which to examine the transmission of supported materials.

Celluloid films for use as substrates were prepared by placing one drop of a collodion in amyl acetate solution in a dish of distilled water. The solution spread over the surface and the solvent evaporated leaving a film of celluloid. It was possible to estimate the thickness of the celluloid films by noting the interference colors produced by white light reflected at normal incidence. Using the nominal value of 1.5 for the index of refraction of celluloid⁸ it was possible to use calculations of the interference colors from thin films⁹ to estimate the film thickness. It was stated that when $nt = 1500\text{A}$

where n is the index of refraction of the celluloid film
and t is the film thickness

the celluloid film will have a sandy yellow interference color. This corresponds to a thickness of about 1000A.

A solution of collodion in amyl acetate was prepared such that ten drops of solution placed on distilled water produced a sandy yellow colored film of celluloid covering an area, "A". Because amyl acetate is not soluble in water, it was believed that one drop of solution will produce a film $1/10$ as thick as the above film, or 100A thick covering the area, "A". Using this method of estimating thickness, celluloid films 60A to 250A thick were prepared. Knowledge of the thickness of the celluloid absorbers was not critical in measuring the absorption coefficient, because transmissions were

compared through two identical celluloid substrates. However, it was necessary to know the approximate thickness of the celluloid in order to estimate the fraction of light attenuated by the celluloid.

In order to keep the background level low in the spectral region above 600A, a thin layer of celluloid was required. A thin layer of celluloid slightly larger in area than the photon beam that illuminated the sample could not be produced self-supporting. However, it was possible to make a 60A thick celluloid film supported on a fine mesh screen (a number two hundred mesh electrolytic screen obtained from the C. O. Jelliff Corporation of Southport, Connecticut). This combination of screen and celluloid was capable of supporting LiF films that were up to 250A thick. The celluloid films invariably broke when attempts were made to vacuum evaporate more than 250A of LiF on them.

In the spectral region below 500A, it was necessary to produce LiF films of thickness greater than 200A to get an attenuation of one-third in the incident beam intensity. It was feasible to use a 250A thick celluloid film as a substrate. It was found that even a 250A thick celluloid layer would break during evaporation due to the forces set up by the deposited LiF. To overcome this detrimental effect, LiF absorbers were prepared with a peripheral uncoated layer in the same manner described previously for self-supporting LiF films, although no attempt was made to remove the celluloid substrate. By this means, LiF films 700A thick could be easily prepared.

1. Vacuum Evaporation Procedure

It has been known for some time that thin films of materials can be prepared by vacuum evaporation¹⁰. The sample, LiF in this experiment was heated in a high vacuum system until a molecular beam issued forth from the furnace containing the sample material. A surface in the path of this molecular beam stopped the molecules and a solid film was formed. The mechanics of thin film formation has been treated theoretically by Heavens¹⁰, and has been studied experimentally for the case of LiF^{11,12}.

The vacuum evaporation system used in this experiment was a combination of vacuum pumps enabling a pressure of 4×10^{-5} mm. Hg. to be obtained within a certain region. Specifically, the region evacuated was a 14 in. diameter by 24 in. high glass bell jar which could be raised off or onto a base plate. The base plate was equipped with a number of electrical feed-through leads. Two of the electrical leads were connected in series with a .001 in. thick platinum foil folded in half and formed in the shape of a trough or boat. The platinum foil was supported by a copper heater assembly. High current was supplied for heating the boat by means of a transformer.

Two Aluminum posts were screwed into the base plate to support auxiliary equipment. A magnetic shutter shielding the LiF molecular beam from the celluloid substrates was attached to one of the posts and operated from outside the vacuum system by another magnet. The celluloid samples and a glass interferometer plate were placed on a platform that was secured to the Aluminum posts. A

rotary shutter was placed close to the celluloid sample between the boat and the celluloid samples.

The vacuum evaporation was performed as follows. A roughing pump lowered the pressure to about 10 microns Hg. and then the pump was valved closed. A diffusion pump, a DPI MC-250, backed by a forepump was opened to the system. After one-half hour, a CEC VGIA ionization gauge in the evacuated region was degassed by heating, and the pressure was observed to be in the neighborhood of 8×10^{-5} mm. Hg. After another one-half hour of pumping, the pressure reduced to about 5 or 6×10^{-5} mm. Hg. The platinum boat containing the LiF sample¹³ was then slowly heated with the lower magnetic shutter between the boat and the celluloid films. If the platinum boat were heated too quickly, small particles of the sample would be propelled out of the boat by the violent degassing. The boat temperature was increased slowly over a one hour period to just under 700°C, and then raised quickly to a temperature near 900°C. At this temperature, the LiF melted and made good thermal contact with the boat. Evaporation was allowed to commence to clean the surface layers of any impurities which will evaporate at that temperature. The boat temperature was then raised to 1000°C for a few seconds, and then the heater current was decreased to zero. The last procedures were helpful in both evaporating contaminants in the sample, and in degassing the sample. The boat support was observed to heat during this whole degassing procedure, and it was feared that if the lower shutter were opened, the celluloid film might receive evaporated impurities from the heater. For this reason, the apparatus was allowed

to cool for one-half hour. After the heater assembly cooled, the boat temperature was raised to about 900°C. The pressure in the system was at about 4×10^{-5} mm Hg. and actually lowered to 3×10^{-5} mm Hg. during the evaporation. After letting the boat reach an equilibrium temperature near 900°C, the lower magnetic shutter was swung away, exposing one of the celluloid films and part of the glass interferometer plate. The LiF deposit built up to a thickness t , at which time the upper shutter was rotated exposing the other celluloid film and another part of the glass interferometer plate. When the LiF deposit on the latter celluloid film was of thickness t_1 , the evaporation was terminated. At this point samples of respective thickness $t + t_1$, and t_1 had been prepared. In order to eliminate the effect of the sample substrate interface, t_1 was always made greater than 30A thick.

The thick film was prepared to a thickness which would cause the light to be attenuated to one-third to one-eighth of its original intensity. If a smaller thickness were used, the finer features of the absorption curve would disappear; if a larger thickness were used, it would be found impossible to measure both the higher and lower portions of the absorption curve in the same experimental run. In fact, the highest portions of the curve were not measurable because of the low signal to background ratio.

C. Source of Radiation

An ideal source of radiation for absorption spectroscopy would have a continuous spectra of constant intensity. It is

possible to obtain a continuum over parts of the spectral region of interest¹⁴, but problems due to scattered white light and second order continuum eliminate the use of this method for absorption measurements. Instead, a source was used which gave rich line spectra over most of the spectral region of interest. The source, a Lyman type discharge tube¹⁵ was designed and built by Koester¹⁶. A description of the auxiliary high voltage system is given in the Appendix. A brief description of the source will now be given.

A high voltage electrode is placed at either end of an open quartz capillary tube. One high voltage electrode is a brass cylinder which transports a rare gas at low pressure into the capillary region. The other high voltage electrode is the entrance slit of the spectrograph. A high voltage is applied between the electrodes forming ions which initiate the discharge. The gas in the capillary ionizes and carries the discharge current. Also, studies^{17,18} indicate that a portion of the discharge occurs across the surface of the glass capillary. It is known that this latter effect permits discharges to occur over greater distances than one would expect from gas pressure vs. voltage breakdown curves¹⁷. A change in the state of the glass capillary surface will change the voltage characteristics of the discharge. The capillary surface did undergo a change due to the intense temperature associated with the gaseous plasma, and to the disruptive action of the "sliding spark". Upon examination, the inner surface of a used quartz capillary was observed to have transformed into a brown colored brittle material. A change in the nature of the discharge was clearly observable after

a new capillary tube was installed in the source. For example, during the first ten thousand sparks the visible light output changed from a bright white light to a less intense bluish light using argon. It is likely that the extreme u.v. light also varied during this period.

After 10,000 spark discharges, there was no apparent change in the visual light output from the source. It was decided not to use a new source capillary for measurements until 15,000 spark discharges had occurred in it. After this initiation period, the capillary was used for about 30,000 more spark discharges before being replaced. During the latter 30,000 sparks there was no apparent change in the visible light output of the source. It was apparent from density traces of the source line spectra that if there were any fluctuations in the source they did not affect the relative intensities of the spectral lines. Any fluctuations in the intensity of the source were too small to be detected when comparisons of an average exposure, I , with the average of twice the exposure, or $2I$ were made.

Argon and helium gas were taken from a high pressure tank. The gas pressure was reduced to 20 pounds absolute by means of a pressure reducing valve. The gas flow was then restricted by means of a narrow diameter glass capillary tube followed by a brass needle valve. An indication of the gas pressure in the source was obtained from an oil filled differential manometer.

Argon and helium were used to serve the dual purposes of source gas and filter. Argon has a rich line spectra between 800

and 1000A due to radiation from the multiply ionized gas. For wavelengths greater than 780A, argon gas is transparent; however, for shorter wavelengths the absorption coefficient of the gas is high^{19,20}. A trial run determined the source pressure to be 2.0 mm. Hg. at which filtering would begin. The gas pressure in the main spectrograph chamber was 300 microns Hg. At this source gas pressure, no second-order lines were seen between 780A and 1050A.

For wavelengths greater than 507A, helium is transparent; however, the absorption coefficient of helium is high for wavelengths less than 507A^{19,20}. Helium at 2.5 mm. Hg. source pressure and 400 microns Hg. main tank pressure filtered out wavelengths below 507A. Helium gas was expected to show line spectra between 500 and 600A, however, no helium spectra were observed. This was probably because the expected line spectra came from the normal helium atom and there was a sufficient supply of neutral helium to absorb these lines.

A spectrum common to both excited gases was observed between 100 and 1000A. This spectrum was due to oxygen in multiple stages of ionization, and also to some silicon and nitrogen lines. The relative intensities of the lines of this spectrum were found to remain constant during an exposure so that this spectrum provided good data for absorption measurements.

D. Operation of the Spectrograph

The samples were placed on a rotating arm which was between the entrance slit and the grating. When the samples were placed near the entrance slit, they broke due to fragments sputtered out of

the source by the disruptive action of the high voltage discharge. For this reason, the samples were placed nearer to the grating.

In this spectral region, nitrogen and oxygen, the main constituents of the air are highly absorbing^{20,21}. Thus, it was necessary to evacuate the spectrograph to avoid attenuation of the transmitted light. Helium and argon gas are transparent throughout portions of the region 100Å to 1000Å. These gases can be used to flush out residual gases and thus lower the partial pressure of nitrogen and oxygen.

The spectrograph source and gas lines were evacuated to a pressure of about 100 microns Hg. The system was then flushed with helium for 10 minutes with the vacuum pumps continuously evacuating the spectrograph. This action was taken to flush the spectrograph and also to increase the pumping speed. Virtual leaks within the spectrograph required a total time of at least three hours to bring the air pressure to about 10 microns Hg.

A flow of gas was begun through the source capillary. The gas flow was restricted by a small diameter glass capillary tube and then controlled by a needle valve. The high voltage was adjusted to 13 K.V. with a sparking rate of one per second. The fluctuation in the breakdown high voltage was less than the minimum observable deflection, or $1/8$ K.V., at 13 K.V.; whereas, the fluctuations were noticeably greater at voltages of 15 and 16 K.V. The breakdown high voltage came to an equilibrium value after 15 minutes.

Small amounts of impurity gases in the source can have a large effect on the relative intensity of the spectral lines due to

the production of metastable states, and possible selective absorption. Thus, it was necessary to at least keep the degassing rate constant during the exposure. The high voltage discharge was continued for one-half hour to allow the degassing rate to become constant.

The source was operated in a different way according to the spectral region of interest. For the spectral region above 780A, argon at 2.5 mm Hg. pressure in the source, and 400 microns Hg. in the main tank provided the necessary filtering action. Helium at the same pressures gave filtering action above 507A.

It was found desirable to use argon as a source gas for wavelengths below 780A. Argon has a high absorption coefficient in this region¹⁹, so it was necessary to keep both the partial pressure of argon and the beam path length in argon to a low value. This was done by using a 2.5 mm Hg. pressure of helium in the source as a carrier gas, with about 200 microns of argon. Helium at a pressure of about 2 mm. Hg. was supplied to the rear of the spectrograph. This procedure kept the diffusion of argon into the main tank to a minimum.

Helium and neon were used as source gases for wavelengths below 500A. In both cases, a source pressure of 400 microns Hg. was used, which was 100-200 microns Hg. greater than the minimum necessary to maintain the discharge.

The shutter was opened to allow a section of the photographic plate to be exposed to the spark discharge. The exposure, or total amount of light energy per unit area, was assumed to be

proportional to the number of spark discharges. By moving the plate holder to expose other portions of the photographic plate, a total of five positions could be covered. The exposed portions of the plate were called position 1, position 2, . . . , position 5. Positions 1, 2, and 5 were used to record spectra transmitted through the thick film. The spark ratio of $2:1:\frac{1}{2}$ was used for the aforementioned positions associated with the thick film. Positions 3 and 4 were used to record spectra transmitted through the thin film. A spark ratio of $2:1$ was used for these positions associated with the thin film.

The transmitted energy per unit area through the thick film was made the same order of magnitude as that through the thin film by appropriately adjusting the number of spark discharges. Or, the number of sparks used with the thick film was made larger than the number of sparks used with the thin film by a factor, R . The factor, R , was taken to be between two and three.

Because position 1 and position 2 overlapped, a position $1+2$ was created. Similarly, position 3 and position 4 created a position $3+4$. The data thus consisted of four positions (associated with the thick film) exposed in the spark ratio of $3R:2R:R:\frac{1}{2}R$, and three positions (associated with the thin film) exposed in the spark ratio $3:2:1$.

The photographic plate was developed for four minutes in Kodak D-19 developer at 20°C , rinsed, fixed, washed, and allowed to dry overnight.

A plate was considered unsatisfactory if it had any of the

following defects:

1. fog
2. splotches
3. an excessive number of scratches
4. either under-exposure or over-exposure
5. no apparent absorption spectra.

E. Data Analysis

1. Photographic Photometry

In photographic photometry the factors of speed, contrast, and latitude must be considered.

In general, a higher speed is associated with a smaller minimum exposure. A high speed would be helpful in eliminating possible slow drifts in the average light energy of each spark. A high latitude plate responds to a wide range of exposure values. A high contrast plate produces a large change in photographic density for a small change in incident light exposure. An ideal photographic plate for photometric purposes would have high contrast, high speed and infinite latitude. In practice, the above factors are dependent upon one another in such a way that increasing the merit of one factor decreases the merit of another. One of the better photographic plates used for this region, the Kodak SWR plate, has a contrast of about one and can be used over a light exposure range of 3 to 4. The Ilford Q₂ and Q₃ plates used were somewhat faster, and had lower contrast and greater latitude than the Kodak SWR plate.

For a uniform emulsion coating, the photographic density on a plate will be found to obey a one to one relationship with the incident light energy. Or, there is a characteristic curve describing the exposure versus density relationship. A characteristic curve was constructed for each 2 in. x 10 in. plate used in this experiment and used to reduce the data from that plate.

2. Density and Transmission Records

Both Ilford Q plates and Kodak SWR plates were used in this experiment. It was desirable to make density measurements on the Kodak plates and transmission measurements on the Ilford plates. The densitometer used was a Kodak Model III microdensitometer made available by the Optics Department. A Sinclair Smith microphotometer²² was made available by the Chemistry Department for the transmission measurements.

The densitometer is essentially a photoelectric cell with an associated electronic circuit giving a voltage output proportional to the photographic density of the spectral line under consideration. Light is focused onto the spectral line through a narrow scanning slit. The transmitted light is then detected by the photoelectric cell. A voltage signal proportional to the density is indicated on a Brown chart recorder. The resulting chart is a density record for all the spectral lines. A slow scanning speed is used to insure that the variations in density are followed accurately.

The microphotometer is a device using a radiometer as its main element²³. Light which passes through the photographic plate

falls on one of the vanes of the radiometer. The suspended vane experiences an angular deflection proportional to the incident intensity on the vane. A mirror, attached to the fiber from which the vane is suspended is illuminated with a separate light source. This light is brought to a graduated scale from which data can be taken. A recording attachment is included with the instrument to enable data to be photographically recorded. However, a visual method was preferred because:

1. Ilford plates have a low maximum density and thus produce small deflections. It was more accurate to read a small deflection visually than photographically.
2. Random large exposed grains, open area defects, or scratches in the region of the center of the spectral line could be detected, and another portion of the vertical spectral line could be scanned.

3. Plate Calibration Procedure

Because the calibration technique was so similar for both the transmission and density measurements, only the density measurements will be described.

The object of this calibration procedure was to assign a relative exposure value to each density reading associated with a spectral line. A method of analysis developed by Tombouljian²⁴ was used to find the relative exposure value for each spectral line.

A common zero level was chosen arbitrarily from which all density measurements were taken. After density values were assigned

to each spectral line, use was made of the fact that corresponding lines from positions 1 and 2 were in the exposure ratio of 1:2. A plot was made of the density associated with an exposure $2E$, d_{2E} , versus the density associated with an exposure E , d_E , using all of the spectral lines from both position 1 and position 2. The density values of the spectral lines from position 3 and position 4 were then used to plot more points on the d_{2E} vs. d_E curve. The resultant graph was a smooth curve as in Fig. 2a with a random scatter of experimental points. This showed that:

1. Any wavelength dependent effect on the calibration curve was so small as to be within the experimental scatter of points. Or, there were no systematic deviations from the curve dependent on wavelength.
2. The plate characteristic was maintained over different portions of the plate for the same wavelength due to the agreement between pairs of deflections from positions 1 and 2 and from positions 3 and 4.

Together, properties number one and two meant that the plate characteristic was constant over the entire physical area of the photographic plate.

An arbitrary point of low density on the d_{2E} vs. d_E curve was selected such that the abscissa of that point was associated with a relative exposure of one. The deflection associated with a relative exposure of two was simply the ordinate associated with the chosen point. For example, if A were the chosen point on the curve in Fig. 2a, then a density of a would correspond to a relative

PLATE CHARACTERISTIC CURVES

FIG 2

exposure of one. A density of $\underline{b}$ would correspond to a relative exposure of two. Now, the density corresponding to a relative exposure of four could be found by locating the d_{2E} for a d_E of $\underline{b}$. This process was repeated until a number of points of Relative Exposure (R.E.) versus density were plotted. Another point on the d_{2E} versus d_E curve was taken as having a Relative exposure equal to one, and the above procedure was repeated yielding new values of the Relative Exposure versus density (or deflection). The results of different trials were normalized into one smooth curve of Relative Exposure versus deflection as indicated in Fig. 2b. Every measured density value was assigned a relative exposure value using this curve.

Unavoidable background light due to scattered white light and continuous radiation was recorded on the plate. The background exposure had to be subtracted from the total measured exposure. The assumption was made that the background exposure obeyed the same characteristic curve as did the line spectra. An argument will be presented later to justify this assumption. The background was then the difference between the arbitrary zero value and the exposure value corresponding to the density of the base line for each plate position number. The first total signal intensity measurement was located after point B in Fig. 2b, where B refers to the background. It was noted from the curve that the range of measurable exposure values had been decreased (less latitude).

Using the density readings from positions 1, 2, 1+2, and 5, an average relative exposure was found for each spectral line of

position 1. A similar procedure involving positions 3, 3⁴, and 4 yielded an average relative exposure for each of the spectral lines of position 3. If the average deviation of a relative exposure value was greater than 15%, that reading was discarded.

It is known that:

$$E_2 = E_0 e^{-\mu x_2}$$

where E_0 is the energy per unit area incident on the thin film, μ is the absorption coefficient of the sample, x_2 is the thickness of the thin film, and E_2 is the energy per unit area exiting from the thin film.

For the thick film,

$$E_1 = RE_0 e^{-\mu x_1}$$

where R is equal to the ratio of the number of sparks used with the thick film to the number of sparks used with the thin film, x_1 is the thickness of the thick film, and E_1 is the energy per unit area exiting from the thick film.

It follows that:

$$e^{\mu(x_1-x_2)} = R \frac{E_2}{E_1}$$

R was a known constant, and E_2/E_1 was found by using the Relative Exposure versus density curve, so that $e^{\mu(x_1-x_2)}$ could be obtained as a function of wavelength, λ .

The difference x_1-x_2 will be labeled Δx . It is to be recalled that x_1-x_2 is the difference in film thickness between the

thick and thin films.

3a. Remarks on the Calibration Procedure

There were a number of reliability checks that could be applied to the experimentally determined $\mu\Delta x$ vs. λ curve.

Any systematic error due to improper subtraction of the background could be found in the following way. A series of points separated by about one Angstrom unit was selected from a slowly varying part of the $\mu\Delta x$ vs. λ curve. The densities of the corresponding spectral lines in position 1 were examined to find those lines differing widely in their respective densities. If the calculated value of $\mu\Delta x$ for each of these lines were found to be dependent upon the density, then it was likely that the estimated background exposure was incorrect. This was found to be the case in some of the experimental trials. It was found that this source of error would vanish by making a small adjustment in the measured value of the background, which was within the relative exposure uncertainty of the originally estimated background.

The 140A to 400A region was explored in first order on one 2 in. x 10 in. Ilford Q plate. Second order lines of lower intensity than the corresponding first order lines were noted in the 280A to 400A region. The resultant value of $\mu\Delta x$ determined from these second order lines agreed with the computed values from the first order lines within the experimental scatter points. This observation increased the confidence in the Relative exposure vs. density calibration.

The source used produced spectral lines covering a range of intensities greater than the latitude of the detector. This meant that not all of the spectral lines could be assigned a relative exposure number. To make use of most of the spectral lines, two experimental runs were made with similar LiF absorbers. The general exposure level of one run was made greater than for the previous run. It was observed that:

1. The spectral lines which could be used for measurements in both runs produced the same value of $\mu \Delta x$.
2. The other spectral lines yielded values of $\mu \Delta x$ which agreed with the previously established points of the $\mu \Delta x$ vs. λ curve.

F. Wavelength Determination

The fundamental grating equation states that:

$$n \lambda = d (\sin \alpha + \sin \beta)$$

$$\text{and } \beta = \frac{x}{R}$$

where n is the order of interference, d is the grating space, α is the angle the incident ray makes with the line joining the center of curvature to the grating, and β is the angle the diffracted ray makes with the line joining the center of curvature to the grating, x is the distance from the center of curvature of the grating to the spectral line, and R is the radius of curvature of the grating.

For this instrument, $d = 1/30,000$ in., $R = 2$ meters, and $\beta = 85^\circ$. It is thus possible to find the wavelength as a function

of x . A set of tables were constructed using the above relationships to give the wavelength for any value of the distance along the Rowland circle.

A recent report containing published atomic emission lines below 2000Å²⁵ was used to compare the experimentally determined spectra with the tabulated values. The procedure was as follows. From the published tables it was seen that a wavelength λ_0 , should be present in an argon discharge. The approximate location of λ_0 , was found on the photographic plate. The lines near λ_0 , on the photographic plate were compared with the other tabulated values. By a process of trial of error, each experimentally determined spectral line was assigned a wavelength number which was consistent with both the value obtained from the wavelength vs. distance tables, and the tabulated value. A direct check on the procedure was obtained by taking an exposure containing second order lines. The second-order lines were assigned wavelengths on the basis of the wavelength vs. distance curve. These second-order wavelengths were found to be within 1Å unit of twice the corresponding first order wavelengths.

The second-order wavelengths were determined in the following ways. First, two consecutive exposures were taken under the condition of filtering action and no filtering action, respectively. Any lines which were not common to both exposures were likely to be higher-order lines. Secondly, a photographic plate covering the spectral region λ_1 to λ_2 was put into a photographic enlarger. The projected image was enlarged until the second order λ_1 and λ_2

fell at $2\lambda_1$ and $2\lambda_2$, respectively. A very striking match between first and second order lines was obtained by this method. Some third order lines were found by a similar matching procedure.

G. Measurement of the Sample Film Thickness

A method described by Tolansky²⁶ was used to measure the sample film thickness. A glass interferometer flat was placed in the vacuum system near the celluloid films. One half of the flat was covered with aluminum foil. The flat was coated with the same thickness of LiF as one of the celluloid films. The rotary shutter was then rotated to expose the other celluloid film. Simultaneously, a different portion of the glass flat was exposed to the LiF molecular beam.

It was shown by Tolansky²⁶ that evaporated silver will conform to the contour of the surface on which it is being deposited. Thus, it was possible to evaporate an opaque layer of silver onto the transparent LiF film. This produced a highly reflecting surface which had the same step thicknesses as the LiF film on the glass interferometer plate.

Another interferometer flat was silvered to an optical density of 1 (10% transmission). An interference filter was then made by positioning the silvered surfaces of both flats as in Fig. 3.

The interference fringes appeared as dark lines in a continuous spectrum. The dark lines occurred for those values of the wavelength where,

$$m\lambda = 2nt_2$$

INTERFEROMETER FOR FRINGES OF EQUAL CHROMATIC ORDER

FIG 3

where m is the order number; λ is the wavelength; n is the index of refraction of the space between the interferometer plates. This has the value of one for air; t_2 is the distance between the silvered flats.

Across a step, the difference in thickness was small so that the following approximation is valid:

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

where Δt is the step-height.

The resultant fringe pattern including a step discontinuity is shown schematically in Fig. 4. Referring to Fig. 4, it is seen

FRINGE PATTERN

FIG 4

that Δt is equal to the fringe shift, A, divided by the fringe spacing, B, multiplied by $1/2$ the wavelength. Or,

$$\Delta t = \frac{A}{B} \frac{\lambda}{2}$$

All measurements of A and B were made with a traveling microscope. Δt is equal to the difference in thickness between the thick LiF film, $t + t_1$, and the thin film, t_1 . Or,

$$\Delta t = t = \Delta x$$

This was the quantity that was needed to get the absolute value for the absorption coefficient of LiF. Actually, the interferometer plate was not placed in the exact same geometry with respect to the evaporant boat as the celluloid films, so that a geometry correction of about 5% had to be made for the value of t .

1. The Structure of the LiF Films

The structure of LiF films formed by vacuum evaporation onto celluloid has been analyzed by electron diffraction studies. Shulz's¹¹ experimental results have indicated that for a film thickness of less than 100Å there was no preferred orientation. However, for a thickness greater than 100Å, there was a strongly preferred orientation in the $[111]$ crystal direction perpendicular to the substrate. The evaporated film had many internal voids (up to 30% of the total volume) in addition to an irregular surface.

Halliday et al.¹² have found that evaporated LiF films consist of crystallites in the form of long cylinders with diameters of about 100Å. These cylinders have their axes perpendicular to the

substrate. It was stated that there was a tendency for a $[100]$ crystal axis to lie along the axis of a cylinder.

Thus, two conflicting reports have appeared concerning the structure of a LiF film prepared by vacuum evaporation onto a celluloid substrate. However, both studies cited did indicate the presence of internal voids and surface irregularities. These structural defects caused an error of definition to be assigned to the thickness measurement. That is, while the measured thickness may give consistent values for the absorption coefficient, it must be realized that this measured thickness is not the physical thickness associated with a thin slice of the bulk LiF.

H. The Absorption Curve

Eight different experimental runs were used in this experiment but the value of Δx was measured for only four of the runs. The results indicated that all of the $\mu\Delta x$ curves which covered the same energy region showed similar structure, but the relative magnitudes of the structures varied from one run to another. The values of μ were calculated for each of the four runs where Δx was known. A plot of the average value of μ versus energy showed that the features in the more rapidly varying parts of the μ versus energy curve became obliterated.

Another method was found to be a better way of presenting the absorption curve. For each energy value, the average value of $\mu\Delta x$ obtained from a single experimental run was computed and plotted. This was done for all of the runs. One of the $\mu\Delta x$ curves obtained from a single trial where Δx was known was chosen at random. The experimental points of a second $\mu\Delta x$ curve were adjusted to agree in

the region of overlap with the experimental points of the first curve by multiplying the $\mu\Delta x$ readings of this second curve by an appropriate number. A process of trial and error determined the multiplicative number which preserved the reproducible features of both $\mu\Delta x$ curves. All of the other $\mu\Delta x$ curves were similarly normalized to the randomly chosen curve. An average value of $\mu\Delta x$ was then computed for each energy.

The above process yielded a curve of $\mu\Delta x$ versus energy which preserved the reproducible features found in independent trials. The spread in experimental points for one energy indicated the uncertainty in $\mu\Delta x$ obtained by this procedure. In general, the relative error in $\mu\Delta x$ for each energy value was of the order of 10 to 15%. However, the relative error in the $\mu\Delta x$ values between 11 e.v. and 15 e.v. was less than 10%, and the relative error was 20% for the peaks at 15.8 e.v., 22.5 e.v. and 62.5 e.v. in the $\mu\Delta x$ curve.

The problem remained of assigning some average thickness to the $\mu\Delta x$ curve as found above. Four measurements of different Δx had been made, and the normalization factor, N , was known corresponding to each Δx . If there were no systematic or experimental errors in any of the physical quantities of interest, then the product, $N\Delta x$, for each run would be the same. The values of $N\Delta x$ for this experiment are given in the following table.

Table 1

<u>Trial Number</u>	<u>Measured Δx (in A)</u>	<u>N</u>	<u>N Δx</u>
1	205	1	205
2	115	2.12	239
3	180	1.34	241
4	105	2.00	210

The product $N \Delta x$ for each trial is recognized as the hypothetical film thickness, $\Delta x'$, which if used in that trial will produce a $\mu \Delta x'$ curve like the randomly chosen curve. The average of all the $\Delta x'$ was equal to the nominal average thickness to be assigned to the randomly chosen curve. This average thickness was 224 A as computed from Table 1.

The average $\mu \Delta x$ curve (obtained by normalizing to a randomly chosen $\mu \Delta x$ curve) was divided by the average thickness, 224 A, to obtain a curve of μ vs. energy, E, shown in Fig. 5.

→ In two separate sheets

Figure 5 will be found in an envelope secured to the inside rear cover of this thesis report.

II. THEORY

A. Introduction

In attempting to solve the many-body problem in a solid, the approximation has been made that the starting set of wave-functions can be chosen as a combination of functions that involve the co-ordinates of only one particle^{27,28}. In the Bloch approach to the problem, it is assumed that the wave-function of each electron has the form of a plane wave modulated by the periodic field of the lattice. This formalism predicts that there will be allowed and forbidden regions of energy for electrons in the solid. The allowed regions of energy lie between a set of concentric polyhedra which are centered about the origin of the electron wave-number space. The energy discontinuities occur at the surface of the polyhedra. The form of the polyhedra is discussed by Seitz²⁷ under the topic of Brillouin zones.

In the Heitler-London scheme, it is assumed that the wave-functions are large only about single atoms or ions. This type of solution is applicable when the atoms in the lattice are far from one another, and the atomic or ionic properties of the constituent atoms are pronounced. It was shown by Mott and Jones²⁸ that for every state of an electron in the free atom, there exists a band of energies in the crystal. The energy width of the band will be greater the more the atomic wave-functions overlap. The breadths of the energy bands for the inner electrons of the atoms in a crystal

should then be small.

LiF is an ionic crystal and thus can be considered as being composed of Li^+ and F^- ions. The F^- ion has ten electrons: 2 electrons in a filled 1s orbital, 2 electrons in a filled 2s orbital and 6 electrons in a filled 2p orbital. The valence energy band in the crystal consists of states corresponding to the 2p electrons of the F^- ion.

B. Fluorine s and p Bands

The form of the density of states curve for the valence band has been measured experimentally by emission spectroscopy²⁹. An electron was removed from an inner ionic orbital by electron bombardment and an electron from the F^- ion 2p orbital made a radiative transition to the inner orbital. Because the energy band corresponding to the inner ionic state is narrow, the emission curve gave an indication of the density of states in the valence band. O'Bryan and Skinner²⁹ found that the base width of the emission curve for LiF was 4 to 5 electron-volts.

The electronic structure of the valence band was investigated theoretically by Grimley³⁰ using the assumption that the wavefunctions for the valence band can be expressed as linear combinations of the outer orbitals on the F^- ion, and the first vacant orbitals on the metal ions. The inclusion of the latter group of orbitals supposedly took into account the small homopolar binding in LiF . The full width of the F^- ion 2p valence band was computed to be 5.4 e.v., of which about 5% was due to homopolar binding.

Ewing and Seitz³¹ calculated the energy versus wave-number curves for the energy bands corresponding to the F^- ion 2s and 2p electrons and the first empty band corresponding to a Li^+ ion 2s electron. They used the method of Wigner and Seitz³² which has been applied to metals.

Basically, the method consisted of considering each ion in the lattice to be enclosed in a sphere on the surface of which the boundary conditions satisfied by the wave-function were known. The Li^+ ion core field and F^- ion core were known from previous theoretical investigations. The smallest energy separation between the valence and conduction band was predicted to be 7.5 e.v. This is obviously too small because LiF is known to be transparent up to 11.8 e.v.³³ Ewing and Seitz³¹ blamed this discrepancy upon the neglect of energy exchange terms in their approximation. They predicted a base width of about 5 e.v. for the valence band, about .5 e.v. for the base width of the next lower energy band, S, which corresponded to the F^- ion 2s electrons, and about 2 e.v. for the base width of the first empty band. The minimum separation between the valence band and the energy band, S, was predicted to be 8.1 e.v.

The energy separation between the valence and S band must be known approximately in order to interpret the absorption curve. It was possible to find the energy separation of the energy levels corresponding to the s and p electrons in the F^- ion by the following method. An electron in a configuration, "A", of the ion was completely removed from the ion. If the configuration, "A", were complex, there were different electrons available for this

transition. For the F^- ion, the configuration, "A", was $2s^2 2p^6$. It took an ionization energy H_1 to take a p electron to infinity. The resultant configuration was $2s^2 2p^5$ for atomic fluorine. In a similar manner, if the F^- ion lost a 2s electron with an ionization energy H_2 , then the resultant configuration was $2s^1 2p^6$ for atomic fluorine. By inspection, it was seen that the energy difference $H_2 - H_1$ was equal to the energy separation of the s and p ionic F^- levels. But $H_2 - H_1$ also equalled the energy separation of the $2s^1 2p^6$ atomic level and the $2s^2 2p^6$ F^- level, minus the energy separation of the $2s^2 2p^5$ atomic F level and the $2s^2 2p^6$ ionic F^- level. Thus, the 2s minus 2p energy level difference for F^- was equal to the energy difference corresponding to the atomic fluorine configurations $2s^2 2p^5$ and $2s^1 2p^6$. This separation was not obtainable from tables of atomic energy levels, but the separation could be estimated by using the tabulated energy levels for singly ionized Neon.

From a table of atomic energy levels³⁴, the value of the energy separation corresponding to the $2s^2 2p^5$ and $2s^1 2p^6$ configurations for Neon was found to be 26.9 e.v. A comparison of the energy values of corresponding states in F^0 and Ne^+ showed that the F^0 energy levels could be obtained from the Ne^+ energy levels by multiplying the Ne^+ energies by the number .47. The energy separation corresponding to the F^- ion 2s and 2p energy levels was then $.47 \times 26.9$ e.v., or 12.6 e.v.

Emission studies by O'Bryan and Skinner²⁹ have shown the existence of the 2p band but not the 2s band in LiF. They offer no explanation for the absence of the 2s band. However, they did

observe emission in BeO which was due to the Oxygen 2s and 2p bands. For BeO, which resembles LiF electronically, the 2s band to 2p band energy separation (peak to peak) has nearly the same value for the solid state as for the free oxygen ion³⁵. On this basis the 2s to 2p band separation in LiF is predicted to be about 12 e.v. This estimate agrees with the calculated value of 10.8 e.v. derived by Ewing and Seitz³¹.

C. Exciton Levels

As free positive and negative ions approach one another, they interact electrically and produce a potential of the form Ae^2/r , where A, the Madelung constant has the numerical value 1.748 for ionic crystals with the NaCl type lattice, and e^2/r is the usual Coulomb potential. At the normal interionic distance, there must exist a repulsive force between ions in order to have equilibrium. The Madelung and repulsive potential constitute the lattice energy per ion pair of the crystal.

Mott and Gurney³⁶ calculated the energy, W, necessary to remove an electron from the valence band to the vacuum level by considering a very simple charge transfer cycle. The work necessary to remove a negative ion from the crystal was assumed to be almost equal to the lattice energy per ion pair. An electron was taken from the isolated negative ion to form a neutral atom and then the halogen atom was replaced in the crystal. The value, W, for LiF was found to be about 13.5 e.v., implying that the energy band gap was less than 13.5 e.v.

Other allowed energy levels are permitted in the charge transfer model corresponding to a valence electron transition from a Fluorine ion to a nearby Lithium ion³⁷. These non-conducting levels have been called exciton levels. The position of the first exciton level in the alkali halides has been calculated^{38,39} assuming the validity of the charge transfer model. The energies obtained using this method were consistently larger than the experimentally determined values. On the basis of the charge transfer model, Overhauser⁴⁰ has predicted that there should be five lines in the low energy exciton structure for a NaCl type crystal.

Another model has been constructed to explain the exciton levels. In this model⁴¹, the exciton was considered as an excited state of the halogen ion. This model predicts an energy for the first exciton level which is in better agreement with the experimental observations than the charge transfer model.

Experimental work on the fundamental absorption in the alkali halides (except for LiF) at room temperature has been done by Hilsch and Pohl³⁸ and Schneider and O'Bryan⁴² using photographic recording. Eby et al.⁴³ have recently examined the fundamental absorption in the alkali halides (except for LiF) at 80° K and 320° K using photoelectric recording. These experiments did show absorption peaks which were associated with exciton levels. However, the absorption curves were so complex that it was not possible to determine the series limit of the exciton levels, or the energy band gap.

D. Inner Level Absorption

The study of photon absorption by an electron associated with a narrow energy band has been reviewed by Skinner⁴⁴ and more recently by Parratt⁴⁵ and by Tomboulis⁴⁶. The experimental absorption curves for different elements and compounds are given by many sources⁴⁴⁻⁴⁸.

The inner levels which are of interest are those energy levels below the valence band that have a narrow energy band width. If an inner electron absorbs an incident photon of the proper energy, the electron will make a transition to a higher empty state. In the free atom, only transitions satisfying the atomic selection rules will be allowed. In the solid, the initial state is associated with an inner level and thus the wave-function describing this state is predominantly of one type of symmetry. The wave-function of the final state is a linear combination of atomic wave-functions which have s,p,d,.... character in the vicinity of the nucleus. It is then believed that the atomic selection rules will have some validity for the case of a solid.

In LiF, the possible initial inner levels are those due to the fluorine ion 2s electrons and the lithium ion 1s electrons. The fluorine 2s band was considered previously, so that only the absorption by the lithium 1s electrons will be discussed.

The position of the Li^+ ion levels in the solid was estimated by referring to a table of energy levels for free ionic Li^{+34} . The ground state of the free Li^+ ion has the $1s^2$ electron configuration and gives rise only to a 1S_0 state. For a one-electron jump, the possible configurations are $1s2s$, $1s2p$, $1s3s$, $1s3p$, etc.

According to the atomic selection rules, when only one electron jumps, it changes its orbital angular momentum by +1 or -1. This selection rule limits the possible final configurations to $lsnp$ types where $n = 2, 3, 4, \dots$. The other selection rules state that the resultant spin remains unchanged, the total angular momentum changes by +1, 0, or -1, and the total orbital angular momentum changes by +1, 0, or -1. Also, if the total angular momentum is zero it must change by +1 or -1. These restrictions on the possible transitions allow only the following energy states shown in Table 2.

Table 2

<u>Configuration</u>	<u>Energy State</u>	<u>Energy (e.v.)</u>
$1s^2$ (ground state)	$1s_0$	75.3
$1s2p$	$1p_1$	13.4
$1s3p$	$1p_1$	5.96
$1s4p$	$1p_1$	3.36
$1s5p$	$1p_1$	2.15

O'Bryan⁴⁹ has studied the L absorption by Na in the Na halides. He observed a close correspondence between the energies of the observed absorption peaks and the energy levels of singly ionized sodium. Analogously, using the energy values given in table 2, absorption peaks might be noted for LiF near 62 e.v. and 69 e.v.

O'Bryan⁵⁰ reported that he observed absorption peaks for LiF at 60.8 e.v. and 64.6 e.v., using a photographic method of

recording absorption spectra. However, he only observed the wavelength positions at which the absorption appeared to be at a maximum. Because he did not calibrate his photographic plate, his reported values of the peaks must be considered as being incorrect. ?

E. Other Characteristic Energy Losses

An electron traversing a thin solid foil has been found to lose discrete amounts of energy^{51,52}. Pines⁵³ has interpreted these losses in terms of a collective electron model. That is, an incident electron interacts with the loosely bound valence electrons in such a way that the electrons oscillate collectively absorbing the incident electron energy in discrete units. The characteristic energy loss, E , is predicted to be given by:

$$E = \hbar \left(\frac{4\pi n e^2}{m} \right)^{\frac{1}{2}}$$

where n is the valence electron density, m is the free electron mass, e is the electronic charge, and $\hbar$ is Planck's constant divided by 2π .

The experimental results using electron-loss measurements show that insulators and ionic crystals obey the predicted formula as well as or better than the metals when a consistent assumption is made concerning the average number of valence electrons per atom⁵³. The assumption for the alkali halides is that the average number of valence electrons per atom is four. No electron-loss measurements have been made for LiF.

Optical measurements have shown that metals change from a reflecting to a transmitting region at the plasma frequency⁵⁴ in

agreement with the collective free-electron model. No optical measurements have been made for the ionic crystals in the region of the predicted plasma frequency. The calculated energy loss for LiF is about 26 e.v. assuming four free electrons per atom.

Leder, Mendlowitz, and Marton⁵⁵ have suggested that a correlation exists between the x-ray absorption structure and the discrete loss of energy of electrons passing through thin solid films. Tomboulis⁵⁶ has compared the fine structure on the high energy side of the optical absorption curve for many metals and has shown that there is almost a constant energy difference between absorption maxima for each metal.

Hayasi⁵⁷ has attempted an interpretation of the near structure from the absorption edge. He considered that an electron ejected from the K shell could be Bragg reflected in the lattice. If the Bragg reflection occurs at a Bragg angle near 90° , he stated that the ejected electron remains in the vicinity of the inner vacancy as in a type of standing wave pattern.

An increase in transition probability supposedly results because of the greater overlap of the wave functions of the initial and final states. Secondary structure was predicted at energies proportional to the reciprocal of the lattice constant squared.

The production of multiple inner vacancies should be considered as a possible source of absorption structure although the transition probability is probably smaller than for a one electron jump. For LiF it is not energetically possible to excite both Li^+ ion 1s electrons because there is not sufficient incident photon

energy. However, it is energetically possible for a Li^+ ion 1s electron and either a F^- ion 2s or 2p electron to be excited. In this case of a multiple vacancy, the ordinary absorption spectrum would be shifted by the amount of energy needed to excite a 2s or 2p F^- ion electron.

EXPERIMENTAL RESULTS AND DISCUSSION

A. Low Energy Structure

The curve of absorption coefficient, μ , versus energy, E , is given in Fig. 5 for a film with a nominal Δx of 224 Å. A dashed line was used to indicate the suggested absorption curve.

It was seen that μ rose sharply with energy at 11.6 e.v., in accordance with the observations on bulk LiF crystals³³. A narrow absorption peak of .8 e.v. full width at half-maximum had its energy maximum at 12.9 e.v. Similar narrow absorption peaks have been observed in the other alkali halides and have been attributed to an electron transition from the valence band to the first exciton level^{38,42}.

Proceeding toward higher energies it was to be noted that there was a definite shoulder in the absorption curve at 14.2 to 14.3 e.v. Similar shoulders have been observed in other alkali halides⁴³. Apker and Taft^{58,59} argued that the valence to conduction band transitions began at this value, or that this was the value of the energy band gap.

Measurements of the threshold for photoconductivity should provide supplementary information concerning the energy band gap. Taylor and Hartmann⁶⁰ did not observe any photoconductivity for a number of alkali halides including KI and LiF. They did observe that the photo-emissive threshold for LiF was near 12 e.v., which, referring to Fig. 5, is in the low energy foot of the first exciton

peak. They also observed a small peak in the photo-electric yield at 13.0 e.v. which, referring to Fig. 5, corresponds to the first optically observed exciton peak. It appeared that the optical absorption curve was similar to the photo-electric emission yield curve for LiF in the low energy region. Apker and Taft⁵⁸ have observed a similar behavior with RbI. They attributed this effect to an exciton transferring energy to an F-center, with a subsequent ionization of the F-center causing photo-electric emission.

Taylor and Hartmann⁶⁰ tentatively placed the valence band in LiF at about 13 e.v. below the vacuum level, on the assumption that the photo-electric threshold is almost the energy of the band gap. However, because the photo-electric threshold that they measured was not due to direct electron transitions from the valence band to the conduction band, their conclusion was probably incorrect.

If the exciton energy levels obeyed a hydrogen like formula⁶¹, the energy, E , of an exciton level would have been given by

$$E = \frac{13.54}{2E_0^2 n^2} \text{ (e.v.)},$$

measured from the series limit.

where E_0 is the high frequency dielectric constant and n is 1,2,3,-----.

For LiF, $E_1 = 1.8$ e.v., $E_2 = .45$ e.v., $E_3 = .2$ e.v. and $E_\infty = 0$ e.v. The first observed exciton level was at 12.9 e.v. with respect to the valence band, so that it was predicted that one would observe the exciton series limit at 14.7 e.v. using this model. Other exciton peaks would be observed at 14.25, 14.5, and 14.6 e.v. Experimentally,

it was not possible to resolve the exciton peaks near the alleged series limit because of the intense overlapping. However, peaks were observed at 12.9 e.v., and 14.65 e.v., and there was a shoulder at 14.3 e.v. which might have been due to an overlapping absorption peak.

There was so much structure in the absorption curve between 14.5 and 20 e.v. that it is not possible to assign with certainty a value to the series limit or to the energy band gap. The structure in this region was due to electron transitions from the valence band to the conducting levels in the solid, with perhaps overlapping absorption due to exciton structure.

A complex absorption structure was found between 22 and 26 e.v. There was a narrow peak of .5 to 1 e.v. full width at half-maximum centered at about 22.5 e.v. A wide band, possibly containing some unresolved structure had a maximum near 24.3 e.v. This latter wide band was associated with electron transitions from the F^- ion 2s band to the conducting levels. The narrow peak at 22.5 e.v. was probably an excitation level associated with the F^- ion 2s band.

The F^- 2s band absorption appeared to extend beyond 26 e.v. If there were any optical effect associated with the so called plasma effect, it would have been lost in the interband absorption.

B. Energy Band Gap

According to the selection rules, the final states for an absorption process were not the same for the F^- ion 2s and 2p bands. The first allowed final state for a F^- 2p band was the Li^+ 2s band.

Because the $\text{Li}^+ 2s$ band was the lowest allowed empty band, the first allowed transitions from the $\text{F}^- 2s$ band must have been to energy states that were above the $\text{Li}^+ 2s$ energy levels. Utilizing the known electron energy structure it could be stated that:

$$E_g + y + x + Z = V$$

where E_g is the energy band gap, y is the separation between the bottom of the conduction band and the first allowed state for a $2s$ band electron transition, x is the peak to peak separation of the $\text{F}^- 2s$ to $2p$ bands, Z is the half-width of the valence $2p$ band, and V is the energy separation between the $\text{F}^- 2s$ band and the first allowed energy level for a $\text{F}^- 2s$ electron transition.

In the theory section it was mentioned that $Z = 2$ e.v. Also, an argument was given in the theory section that x was of the order of 10 to 12 e.v. To get an upper limit for E_g , take $x > 9$ e.v. Experimentally, it was seen from Fig. 5 that $V \leq 25.5$ e.v. Then,

$$E_g < E_g + y < 25.5 - 2 - 9 = 14.5$$

$$\text{or,} \quad E_g < 14.5 \text{ e.v.}$$

C. High Energy Structure

Between 27 e.v. and 44 e.v., the absorption curve showed no structure and appeared to have a small slope. At about 45 e.v., there was a definite drop in the absorption coefficient.

Between 60 e.v. and 100 e.v., structure was found which was ascribed to absorption by the Li^+ ion $1s$ electrons. Absorption peaks were found at 62.5 ± 0.5 e.v. and 69.0 ± 0.5 e.v. These values agreed with the respective energies of the free ionic levels as discussed in the theory section. Other peaks were found at 75.0 ± 0.5 e.v.,

and 82.0 ± 1.5 e.v., and there was an indication of a peak near 87.5 e.v. The absorption structure between 61 and 73 e.v. appeared to be duplicated between 74 and 86 e.v., suggesting a multiple absorption process. A multiple absorption process involving the transition of a Li^+ 1s electron to a higher level and the production of an exciton due to excitation of the F^- ion 2p electron would involve a shift of the absorption curve by 12.9 e.v., the first exciton level energy.

Townsend⁶² has investigated the Mg L absorption in the ionic crystal MgO. He observed an absorption structure between 54 and 76 e.v. consisting of two peaks separated by 5 e.v. which appeared to be duplicated at 17 e.v. higher energy. He believed that this absorption structure was due to Mg $L_{2,3}$ transitions to the conducting states. It was difficult to accept this explanation because it required the existence of a forbidden range of energies 12 e.v. above the lowest empty band. However, if one were to attempt to explain this absorption structure as being due to a multiple absorption process, then it would be possible to explain the cause of the 17 e.v. absorption. By using Neiling and Hensley's² experimentally determined value of the energy of the first exciton peak for MgO (7.8 e.v.), and O'Bryan and Skinner's²⁹ emission measurements on MgO, it was seen that the excitation of an Oxygen ion 2s electron would require about 20 e.v.

D. Suggestions for Further Work

1. An emission measurement for LiF involving the F^- ion 2s electron would be desirable. This measurement would give the 2s to

2p energy difference and would complement the Li K absorption in LiF measurement.

2. A study of the K absorption in the other Li halides might clarify the origin of the K fine structure.

3. A systematic absorption study of the ionic crystals in which characteristic electron energy losses have been observed would be helpful in interpreting electron-loss measurements.

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APPENDIX I

High Voltage Circuit

The high voltage circuit for the discharge tube was similar to others used for this purpose^{1,15}. A complete description of the circuit used in this experiment was given elsewhere¹⁶. The operation of the circuit can be understood by referring to Fig. 6. A d.c.

H.V. CIRCUIT

FIG 6

high voltage was allowed to charge a .3 microfarad capacitor, C. A pair of electrodes in air, A, was placed in series with a 15 megohm resistor, R. This series combination was placed in parallel with

the capacitor, C. The Lyman discharge electrodes, L, were placed in parallel with R. The voltage across C increased until the breakdown potential across A was reached. The current surged across A, and the high voltage appeared across the Lyman tube and the resistor R. The Lyman gap was set to discharge at much lower potentials than the spark gap in air, so a discharge took place readily across the Lyman gap. This discharge made the resistance of the Lyman gap vanish, so the total current passed through this gap. There was then sufficient energy to completely ionize many Argon atoms.

The function of the air gap electrodes was to control the breakdown voltage. The separation of the air gap electrodes could be adjusted to obtain breakdown potentials of 5 K.V. to 17 K.V. A potential difference of about 13 K.V. was found to give a sufficient intensity and to give only small fluctuations in breakdown potential.

The aluminum electrodes used in the air gap became rapidly oxidized after the action of the high voltage discharge. The discolored surface of the electrodes had many apparent irregularities caused by the discharge. One attempt was made to resurface each electrode into a smooth, gleaming aluminum surface. After machining and sanding the ends of the electrodes into hemispheres the high voltage was turned on. It was found that the air gap breakdown voltage actually fluctuated more than when the electrodes were worn from use. Because of this fact, no attempt was made again to resurface the electrodes.