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The Absorption of Ionic Crystals in the Ultraviolet*

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In order to extend the measurements of Hilsch and Pohl on the ultraviolet absorption bands of the alkali halides below 1600A, lithium fluoride has been used as a support for thin films of the salts. Selected lithium fluoride plates of one millimeter thickness when properly cleaned were consistently transparent to 1050A. The compound to be studied was distilled onto the lithium fluoride within a Thibaud spectrograph. A silver solder Carboloy hot spark and Ilford Q plates were used to make the measurements. Comparison of spectra transmitted by the lithium fluoride plates with and without absorbing films of approximately 0.05 micron thickness show, in addition to the bands reported by Hilsch and Pohl, a number of bands below 1600A whose widths vary between 0.3 and 1.3 electron volts. Observations made on some of these compounds by A. Smith, using a less direct method, agree very poorly with these measurements. A comparison of the observed bands with the computations by A. v. Hippel shows fairly complete agreement. Results on several other halides show only a series of sharp absorption edges with continuous absorption toward shorter wave-lengths.

SINCE lithium fluoride plates which are transparent to wave-lengths as short as 1050A can be obtained, it has been possible to extend absorption measurements on thin films of the alkali halides beyond the limit of fluorite. Hilsch and Pohl,[1] using a double fluorite monochromator with photoelectric cells, have measured the absorption bands of these salts above 1600A. This limit, almost 400A above the limit of transmission of a thin plate of fluorite, was set by the high surface loss and absorption of the lenses and prisms. In order to avoid similar light losses with the lithium fluoride, the thin plates which were used as supports for the extremely thin films of the salts under observation were placed in a grating vacuum spectrograph rather than in a prism instrument.

The spectrograph was of the Thibaud[2] plane grating type, as shown in Fig. 1, with a defining slit, and a knife edge in front of the grating. The slit consisted of a small plate glass mirror separated from the edge of a razor blade by shims. This slit, consisting of a real jaw (the edge of the blade) and a virtual jaw (the image of the knife edge in the mirror), was mounted on a brass cone which could be rotated about an axis through the surface of the mirror. The light source—a spark between silver solder and tungsten carbide (Carboloy) electrodes, excited by a 40,000 volt a.c. transformer coupled with a 0.01 mf condenser—was placed slightly out of the line passing through the slit and grating. By a simple rotation of the slit mirror the image of the spark could be brought into alignment with the optical axis of the spectrograph, thus eliminating the usual tedious adjustment by motion of the electrodes. A further advantage of this slit was that the light reflected from the mirror at grazing incidence was only slightly

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* Presented at the New York meeting of the American Physical Society, October, 1936.

[1] Hilsch and Pohl, Zeits. f. Physik **59**, 812 (1930).

[2] Thibaud, Physik Zeits. **29**, 241 (1928).

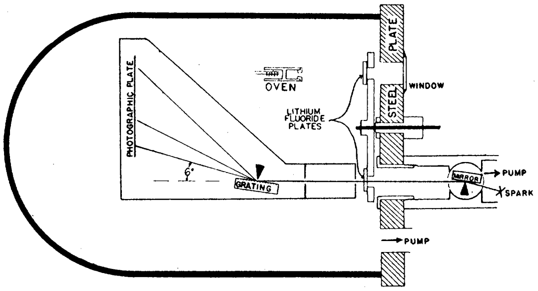

FIG. 1. Diagram of vacuum spectrograph.

diminished in intensity, while all material from the spark which might have contaminated the absorbing surface was condensed on the glass. It was necessary to clean the slit and mirror occasionally.

The grating had 15,000 lines to the inch and was used at 3° from grazing incidence. With the plate holder 7 cm from the grating, the whole spectrum from the central image to 2400A could be photographed on a plate 6 cm long. Although the dispersion was rather small, 40A/mm at 1600, it was sufficient for studies of the structure of the absorption of solids. Because of overlapping orders, the useful range of the instrument was limited to wave-lengths below 400A for studies of solids deposited on celluloid, or to the region above 1050A with lithium fluoride, which eliminated the shorter wave-lengths. With an effective width of the entrance slit of 0.2 mm and the grating slit 0.08 mm, the spectral lines were quite sharp. At longer wave-lengths the lines were considerably narrower than the central image, probably due to the greater width of the diffracted wave emerging from the grating at angles farther from grazing incidence. As the width of the spectral lines in this intermediate region is largely determined by the diffraction pattern of the slit system, it was not possible to use very narrow slits, as with x-rays.

The use of Ilford Q 3 plates was suggested by Professor K. T. Bainbridge. These plates were about ten times as fast as the ordinary plates sensitized with fluorescent oil, and were free from the spots and fog usually found on Schumann plates. Although this type of emulsion was not capable of giving great density, it had sufficient latitude for limited photometric measurement of the absorption.

Since the spectrograph was originally built to study the absorption of thin layers of alkali halides deposited on thin celluloid[3] films, all parts were designed to facilitate the preparation of films by evaporation. Since many of the salts are deliquescent, the preparation of the films and the absorption measurements had to be carried out without exposing the material to the atmosphere. For this reason the spectrograph and evaporation outfit were fastened in adjacent positions on a steel plate 12 inches square and one inch thick, mounted vertically. The plate was ground flat to accommodate an 11-inch Pyrex bell jar which was sealed in place with Apiezon Q compound. Removal of the bell jar made the entire spectrograph readily accessible. The spark chamber, turned from solid brass, was fastened to the opposite side of the plate. Electrical leads to the distilling furnace, mechanical leads for controlling the plate holder and for moving the absorption films, and pump connections, were made through the steel plate.

The distilling ovens were cylinders of molybdenum or iron heated by radiation from a tungsten spiral, as previously described.[4] The molybdenum, because of its greater thermal conductivity, was more suitable for use with high melting point salts. In order to reduce danger of contamination the salts were placed in thin platinum thimbles which were inserted into the ovens.

The lithium fluoride plates on which the salts were deposited were held near the circumference of a 4-inch disk. Rotation of the disk carried the lithium fluoride from a position in front of the oven into the path of the light. By slowly turning the plate of lithium fluoride past the edge of a diaphragm a few millimeters away it was possible to obtain a film which was wedge shaped in thickness. The thickness as judged by the visible light reflected from the film varied from zero to about a micron in a distance of four or five millimeters. The lithium fluoride plates were sufficiently large so that several such wedges could be prepared from different fractions of the distillate from the oven. Since the section of the film used was less than 0.2 mm wide it was possible to examine a number of portions of

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[3] O'Bryan, Phys. Rev. **49**, 944 (1936).

[4] O'Bryan, J. O. S. A. **26**, 122 (1936).

each film. Comparison exposures were always taken through an uncoated section of the lithium fluoride. There was no sensible impairment of definition on insertion of the lithium fluoride plates between the slit and the grating.

The lithium fluoride was cleaned by heating to a temperature near red heat after carefully wiping with cotton soaked in ethyl ether. Selected plates of 1 mm thickness when cleaned in this manner were consistently transparent to 1050A. Although this treatment does not give a perfectly clean surface,[5] the more violent cleaning methods which may be used on glass cannot be applied to lithium fluoride because they destroy the surface.

Since the light source varied in intensity during the exposures, accurate transmission measurements were impossible. However, since there was relatively little variation in the spectral distribution of the light, a fairly reliable estimate of the change in transmission with wave-length could be made. Fig. 2 shows typical microphotometer curves for the fluoride, chloride and bromide of potassium. By comparing photometer traces similar to those shown it was possible to obtain the curves given in Fig. 3. Exposures through the salts were compared with exposures of roughly the same density taken through the lithium fluoride alone. The relative heights of the absorption bands are probably correct to within 25 percent, but the actual absorption coefficients are very uncertain. Since the best thickness of salt film to show the absorption maxima was in the neighborhood of 0.05 micron for all of the salts, the absorption coefficients are all of the same order of magnitude. However, this thickness is too thin to show interference colors and can be estimated only by extrapolation from the region of the wedge shaped film where the colors may be seen. Because of this uncertainty in thickness and the variation in intensity of the source, the absorption is plotted in arbitrary units.

Films of the alkali halides estimated at 0.05 micron showed about 10 percent transmission at the point of maximum absorption. These figures give an absorption coefficient in the neighborhood of 4×10^5 per centimeter. Thus these salts which show the greatest transparency over most of the spectrum are more opaque than other materials in the region where absorption sets in.

In the region above 1600A these experiments overlap the measurements of Hilsch and Pohl.[1] The curves in this region have been drawn as dotted lines (Fig. 3) to show the values previously observed, but the wave-lengths of the maxima are the new determinations. In the cases where the measurements agree to within experimental error, only the curve for Hilsch and Pohl's results has been drawn. Certain bands in lithium bromide and lithium iodide previously reported were not found even in films ten times the normal thickness used. Several samples of these chemicals from completely different sources of supply were consistent but failed to show these bands.

Since Hilsch and Pohl used fluorite rather than lithium fluoride, films of potassium chloride were

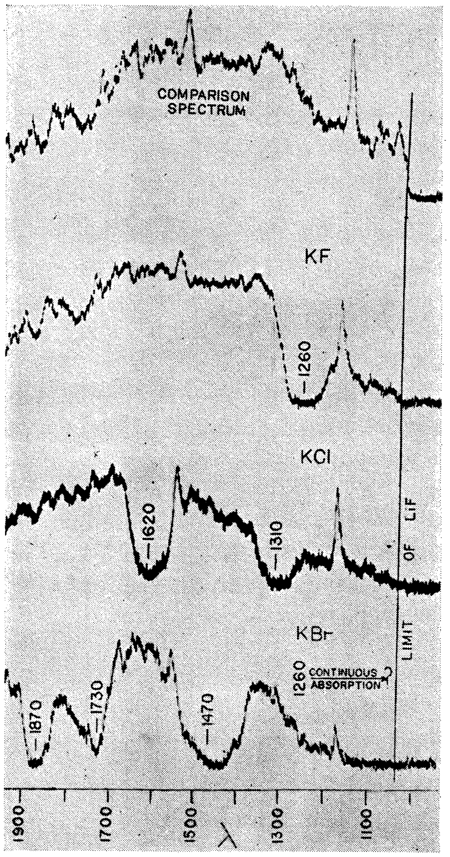

FIG. 2. Microphotometer traces for thin films of potassium salts deposited on lithium fluoride.

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[5] Schneider, Phys. Rev. 49, 341 (1936).

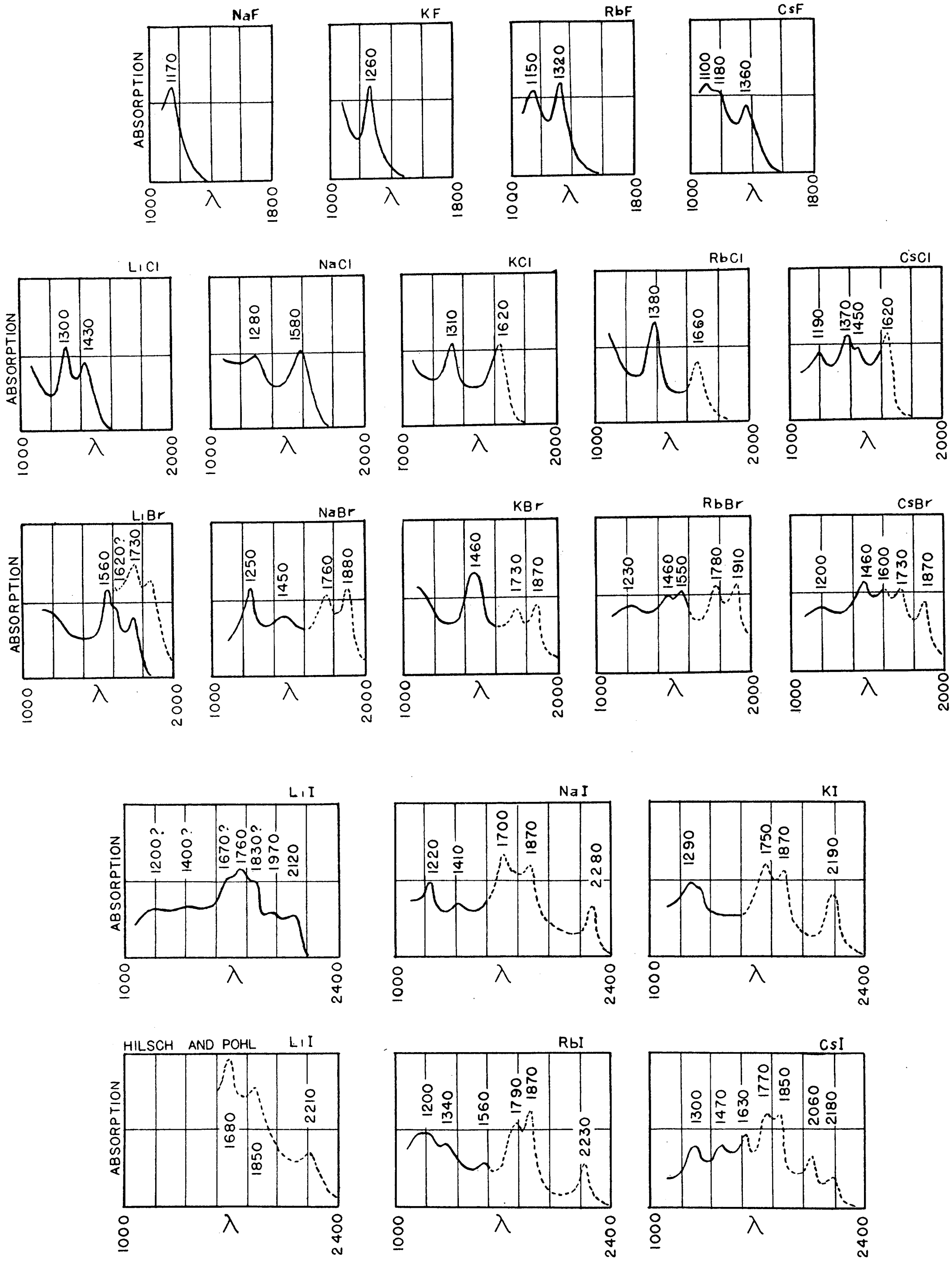

FIG. 3. Absorption of the alkali halides (arbitrary units) plotted against wave-length in angstroms. Dashed curves given by Hilsch and Pohl; solid line curves obtained in these experiments.

deposited on lithium fluoride, fluorite and quartz. There was no measurable difference in the position and width of the bands. This indicates that the evaporated deposit does not assume the structure of the underlying substance but rather retains its own crystal structure. Hilsch and Pohl[1] have compared the absorption structure of evaporated films and films prepared by freezing from the liquid in the region above 2000A, and find a slight shift toward the violet for the evaporated deposits, but no essential difference in structure. Since the films must be composed of very small imperfect crystals, the structures of the bands are probably slightly shifted from the positions expected in a large single crystal.

Since the method of distillation used in these experiments was essentially one of fractionation with only the middle portion used, the more volatile impurities should have been removed, yielding a quite pure salt. In order to determine the effect of impurities a mixture of nine parts of potassium fluoride and one part of potassium chloride was placed in the oven. Since the melting points and boiling points were not identical the film was probably not of this proportion. In the normal thickness only the band of lithium fluoride appeared, while with films about ten times as thick, the bands of both salts were observed. The position of the maxima were not greatly altered and the band widths were only slightly increased. This evidence indicates the presence of an impurity in the lithium salts measured by Hilsch and Pohl. In one case where the lithium iodide was distilled onto the lithium fluoride without sufficient preliminary heating to dry the salt and drive off the more volatile materials, a weak band was observed in the position of the long wave-length band reported by Hilsch and Pohl. Since this band appeared when a very moist sample of the salt was used, it seems probably that it was due to the presence of water. The bands observed in the carefully dried films of lithium bromide and iodide are more consistent with the calculations of von Hippel[6] than those found by Hilsch and Pohl. Most of the band positions computed by von Hippel from an atomic model of the crystal are in excellent agreement with the observed values. The bands of the lithium salts do not agree as well as those of the other alkali halides with calculations from this type of model. Because several different sources of the lithium salts have been studied exhaustively from the experimental side, it seems improbable that impurities can be the cause of this disagreement. Since the positive ion is much smaller than the halide, it may be necessary to consider excited states of the lithium. The structure of the lithium K absorption[3] in these salts points toward the existence of such excited levels.

In the short wave-length region these measurements overlap observations of A. Smith[7] on the intensity of the light reflected at normal incidence by a grating covered with a thin layer of salt. Absorption bands were assumed to give minima of reflection under these conditions. There is no agreement between the results of the two methods. Furthermore the absorption of sodium chloride deposited on celluloid is far less intense for the band at 372A than for the bands in the Schumann region, while the results of Smith indicate the opposite. Because of the extreme difficulty in separating the factors effecting reflection from films on gratings, such measurements cannot be taken as a definite proof of the existence of absorption bands. The existence of selective reflections from cleavage surfaces of

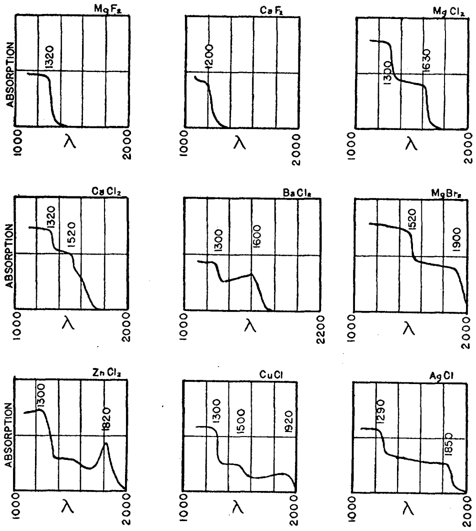

FIG. 4. Absorption of some metallic halides (arbitrary units) plotted against wave-length in angstroms.

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[6] Hippel, Zeits. f. Physik **101**, 680 (1936).

[7] Smith, Phys. Rev. **44**, 520 (1933).

single crystals indicates the presence of absorption bands. The observations of A. H. Pfund[8] on sodium and potassium chloride crystals show such reflection maxima just to the long wave-length side of the bands observed by the transmission method. This displacement is to be expected on account of the change in the index of refraction in the neighborhood of a region of high absorption. Estimates of the positions of the absorption bands from the reflection maxima by Pfund agree well with those found by the transmission method.

In Fig. 4 the absorption structures of a number of halides of the alkaline earths and other elements are shown. These substances show little selective absorption, tending rather to a continuum with a relatively sharp edge at long wave-lengths. These results are similar to the observations of H. Fesefeldt[9] on a large group of compounds in the region above 1600A. Since the crystal systems of these salts are in general more complicated than that of the alkali halides, part of the difference in the absorption structure may be due to the lattice. The difference in valence may be another contributing factor. In all of this group of compounds the absorption coefficients were much smaller than those of the alkali halides, film thicknesses of 0.1 micron or greater being necessary to give measurable absorption.

In conclusion the authors wish to express their appreciation of the kindness of Professor G. P. Baxter of the department of chemistry for preparing several salts which are extremely rare, and to thank Professor T. Lyman for his continued interest in the progress of these experiments.

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[8] Pfund, Phys. Rev. **31**, 315 (1938).

[9] Fesefeldt, Zeits. f. Physik **64**, 741 (1930).

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The Modification of Spectral Lines by Very Close Collisions[1]

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As a result of a survey of the spectra of Hg, Cd and Tl when a few centimeters pressure of a rare gas is added to a discharge through the vapor of these metals, it is concluded that bands of the type first reported by Oldenberg on the short wave-length side of the resonance line Hg 2536.7 probably occur with all metal lines, and with a total relative intensity of the same order of magnitude. The effect of collision induced emission seems in general to be negligible. The occasional appearance of diffuse maxima may be explained by a chance relationship between the potential curves which describe the interaction of the colliding atoms.

Introduction

CONSIDERABLE study has been devoted to the influence of surrounding atoms on the frequency of the radiation emitted from excited atoms of a gas, or absorbed by normal atoms.[2] A simple case of this general problem is that of a metal vapor at low pressure in the presence of a high pressure of some inert gas, under conditions of excitation such that only the former is excited. Any modification of the spectral lines of the metal must then be primarily caused by neighboring atoms in the normal state, and the effects of chemical binding forces and of resonance forces between excited atoms of the same species are eliminated. Under these conditions the metal lines show an asymmetrical broadening and shift, usually to long wave-lengths, which increase with the density of the inert gas. These pressure effects are due to perturbation of the emitting or absorbing atom by many comparatively distant foreign gas atoms, and must generally be studied at pressures of the order of atmospheres. This

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[1] Extract from a thesis submitted to the department of physics of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] For a summary see Margenau and Watson, Rev. Mod. Phys. **8**, 22 (1936).

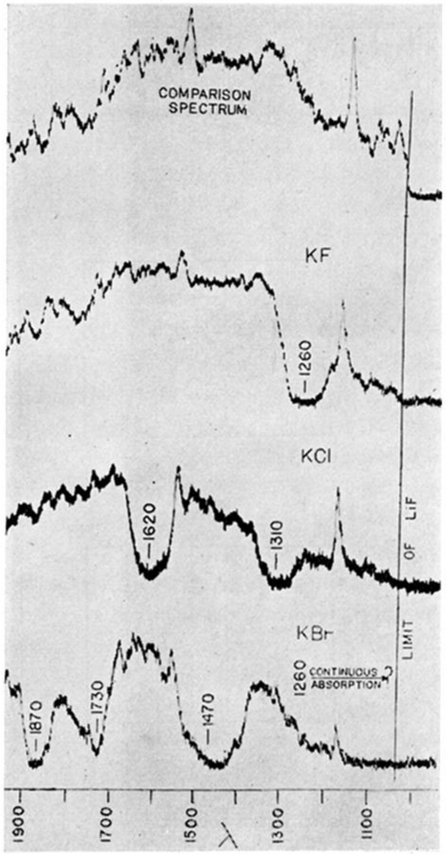

FIG. 2. Microphotometer traces for thin films of potassium salts deposited on lithium fluoride.