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Optical Properties of Lithium Fluoride in the Extreme Ultraviolet[1]

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The absorption coefficient of lithium fluoride in the extreme ultraviolet was measured for 50 crystals produced in the laboratory. The variation in the absorption coefficients for the different crystals was almost as great as that found in natural fluorite although the individual specimens seemed more homogeneous than natural crystals. Numerical values of the absorption coefficient are given for the best specimen. The light lost from the transmitted beam on passing through a surface was studied for cleavage and polished surfaces. At short wave-lengths the loss of light was much greater than that expected for specular reflection. Tests with various cleaning agents indicated that at least a part of this loss of light was due to a layer of foreign material adhering to the surface. Considerable gain in transmission especially at short wave-lengths was obtained by careful cleaning of the polished surfaces with a highly volatile solvent followed by heating to a temperature just below red heat. The index of refraction curve for lithium fluoride was extended into the Schumann region by a modified minimum deviation method.

LARGE lithium fluoride crystals, more transparent in the extreme ultraviolet than fluorite, can be produced in the laboratory. These crystals can be cut and polished with about the same ease as fluorite and may be used as a substitute for fluorite in many optical instruments for use in the Schumann region.

PREPARATION OF THE CRYSTALS

The crystals were made by the method of Bridgman[2] which consists of mechanically lowering a crucible containing the molten salt through the core of an electric furnace. Although a vacuum furnace is not necessary, it is desirable because some constituent of the air, probably water vapor, slightly attacks the melted salt. The furnace was built with a sufficiently large region of uniform high temperature to melt all of the salt at one time. Below this region there was a high temperature gradient down to room temperature. This gradient prevents the formation of a polycrystalline mass at the top of the crucible. The time required for the formation and annealing of a crystal about three centimeters across was approximately thirty-six hours.

The crucibles made from platinum foil were cleaned by boiling in nitric acid, washing with distilled water and heating in a gas-air flame until no color was imparted to the flame by salts remaining on the surface.

Commercial lithium fluoride is unsuitable for the production of crystals transparent to the extreme ultraviolet since it contains a considerable amount of impurity. The material which gave the best result was prepared by mixing hydrofluoric acid, purified by distillation, with lithium nitrate which had been recrystallized several times. Platinum vessels were used for all steps of the purification.

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[1] A preliminary report of these experiments was presented at the Washington Meeting, April 25, 1935.

[2] Bridgman, Proc. Am. Acad. **60**, 305 (1925).

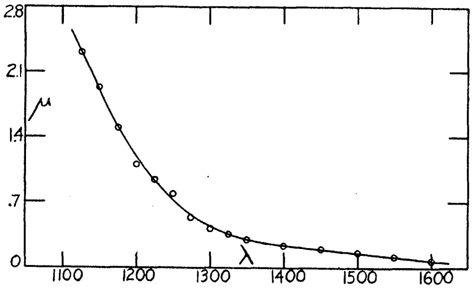

FIG. 1. Absorption coefficient per centimeter.

TRANSMISSION

The transmission of the lithium fluoride was measured photographically by the apparatus and methods described in a previous paper.[3] It is customary to represent the transmission, T, of a transparent plate of material by the expression

$$T=(1-r)^2e^{-\mu d},$$

where r is the reflection coefficient at normal incidence, μ the absorption coefficient, and d the thickness. It is immediately obvious that the reflection and absorption coefficients may be determined from the transmissions of two thicknesses of the material providing r and μ are the same for the two pieces.

ABSORPTION COEFFICIENT

In order to obtain a representative value for the absorption coefficient, it is necessary to take a number of sections from different portions of the crystal. A series of measurements on five plates cut from the same crystal and having a range of thickness from 25.0 mm to 0.5 mm showed that the absorption coefficient did not vary by more than ten percent throughout the crystal. The results for three pieces of another crystal showed about the same variation although the absolute value of the absorption coefficient was different. These measurements indicate that the lithium fluoride crystals were slightly more homogeneous than the fluorite crystals examined by W. M. Powell.[4]

Although the absorption coefficient was reasonably constant throughout a single crystal, there was an extreme variation between crystals. For example, crystals grown from commercial lithium fluoride were completely opaque below 1600A, while specimens of the same thickness (1 to 3 mm) made from the purified salt transmitted between 80 and 90 percent of the light in this region. Crystals grown from the same batch of salt under conditions as nearly identical as possible may have quite different absorption coefficients. This variation is probably due to a trace of impurity although spectroscopic analysis failed to show any definite differences in chemical constitution between the most transparent and the most opaque specimens.

Fig. 1 gives the absorption coefficient as a function of wave-length for the best of fifty lithium fluoride crystals tested. In most cases a qualitative test of the transmission near 1100A was sufficient to show that the absorption coefficient of a crystal was much higher than that of the best specimen.

LOSS OF LIGHT AT THE SURFACE

For an ideal surface the reflection coefficient, r, in the above formula is the fraction of light specularly reflected by a single surface. However, r will usually include other factors since any surface mechanism which removes light from the transmitted beam will be included in this term of the equation. Hence it is desirable to define r as the total fractional loss of light at a surface rather than as the reflection coefficient. Factors which reduce the intensity of a beam of light passing through the surface are, in addition to regular reflection, diffusion due to roughness, and absorption in a surface layer.

When the surface loss of light is computed from the transmissions of two or more thicknesses of a substance, it is necessary to have all of the surfaces polished in the same manner. A test of the reproducibility of the surfaces was made by repolishing one piece of lithium fluoride five times. Care was taken to repeat the conditions of polishing with as little variation as possible. These measurements showed that the transmission for the piece did not change by more than three percent. If repolishing changes the transmission of a plate of material, it must change the surface loss because a decrease in thickness by a few thousandths of a millimeter

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[3] Schneider, Phys. Rev. **45**, 152 (1934).

[4] Powell, Phys. Rev. **45**, 154 (1934).

should not alter the absorption in the body of the crystal. Hence the loss of light at the two surfaces did not vary by more than three percent of the total transmission on repolishing. Furthermore, since the limit of accuracy of the photographic method of measuring intensity of light is of the order of magnitude of three percent, the surfaces may be considered reproducible to within experimental error. Curves *C*, *D*, *E*, and *F* in Fig. 2 represent different surface conditions due to differences in the method of polishing for the same pieces of lithium fluoride. Since the same pieces of lithium fluoride were used in obtaining these four curves, the relative positions of the curves are accurate to about ±0.015 in the fractional loss of light at the surface. It should be noted, however, that an error in the absorption coefficient due to the inhomogeneities in the crystals might cause a consistent error in the absolute values of the surface loss of as much as 20 to 30 percent. Such an error would displace the curves relative to the axis but would shift all of them by about the same amount.

Curve *A* represents the fraction of light specularly reflected by a perfect surface of lithium fluoride. The values for this curve were calculated by Fresnel's equation from the index of refraction alone, the extinction coefficient being too small in this region to alter the result. The divergence between the theoretical reflecting power curve and the experimental curves shows that a perfect surface was never obtained.

The surfaces used in measuring curve *B* were prepared by cleaving the crystals. All of these surfaces were somewhat irregular and it is quite possible that the waviness accounts for the entire discrepancy between this and the theoretical curve. That portion of a wavy surface which is not normal to the incident beam should reflect a greater fraction of the light since the reflection increases with the angle of incidence. Furthermore, such a surface should refract an appreciable part of the light in directions other than that of the transmitted beam. Since both of these factors become more important as the index of refraction becomes higher, the increasing divergence between the theoretical and the experimental curves is reasonable.

The other curves in Fig. 2 give the fractional loss of light for a polished surface. In all cases the polishing was done with rouge on silk lubricated with water, but the cleaning following the polishing was varied. Felt and lead were tried as polishing laps, but both scratched the surface badly. Although a beeswax lap with rouge gave as good a polish as the silk, it proved unsatisfactory because the layer of wax remaining on the surface could not be removed completely. Commercial xylene was used to clean the surface shown in curve *F*. Although this liquid was almost certain to leave a layer of practically nonvolatile material on the surface, it was tried because it is frequently used alone or with oil as a polishing lubricant. Curves *D* and *E* are for surfaces cleaned with medical ethyl ether and with petroleum ether. These agents were chosen as substances which were not apt to leave a residue on the surface. Acids and bases cannot be used for cleaning because they etch the surface.

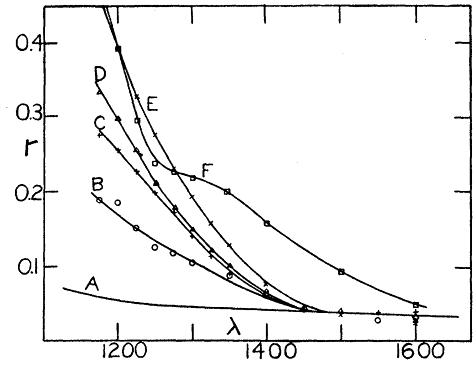

FIG. 2. Fractional loss of light at a single surface. Curve *A*, theoretical reflecting power; *B*, cleavage surface; *C*, *D*, *E*, and *F* polished surfaces cleaned, *C* by heating, *D* with ethyl ether, *E* with petroleum ether, *F* with xylene.

The differences between the curves for the polished surfaces may be explained by the assumption that a layer of material other than lithium fluoride is present on the surface. The flat portion of the xylene curve near 1300A is particularly hard to explain on any other hypothesis. This departure from the trend of the curve is about twice as great as the experimental error. The gradually increasing separation with decreasing wave-length between the other curves might be expected if the solvents etched the surfaces by different amounts, but a break in the curvature is not apt to occur from this cause. Further evidence for the hypothesis of an adsorbed layer lies in the fact that, without repolishing, a transition can be made from one curve to the other by cleaning with the different liquids.

Curve *C* is of particular interest. It was obtained by cleaning the crystals with either ethyl ether or petroleum ether then heating in air to a temperature just below red heat. The decrease in the loss of light at the surfaces is readily explained by the assumption that some volatile material was driven from the surfaces. It is hard to believe that heating to a temperature several hundred degrees below the melting point of the salt would alter the polish of the surface. Furthermore wetting the surfaces with the liquids used for cleaning brought the surface back to the state observed before heating. The discrepancy between the curve obtained for the heated specimens and the theoretical reflecting power may be partly due to an adsorbed layer which was not completely removed. In addition to this possible layer of material there must have been some diffuse scattering of light since a high powered microscope with dark field illumination showed that the surface was not completely free from scratches. There is also the possibility that the process of polishing disturbs the crystal structure near the surface sufficiently to alter the optical properties thereby increasing the loss of light at the surface. Since a small scratch on the surface may open a cleavage plane to a depth of several millimeters, it is conceivable that the cuts made by the polishing material might cause minute fractures near the surface. A broken layer of this type would scatter a considerable amount of light particularly at short wave-lengths, and, if the fissures were filled with air or some liquid, there might be an appreciable adsorption of light in the Schumann region.

Without direct measurements on the amount of light reflected by the lithium fluoride it is impossible to determine whether the change in the transmission of the surfaces with different methods of cleaning was due to an increase in the regular reflection or an increase in the absorption at the surface.

Glow discharge has been suggested as a method of cleaning surfaces. This method cannot be used on lithium fluoride because the discharge turns a surface layer of the crystal a deep red. Tests with a direct current discharge showed that both positive and negative ions were effective in producing this discoloration. The action of the ions is sufficiently weak that lithium fluoride may be used for windows on discharge tubes if there is sufficient separation between the crystal and the region of heavy ionization to prevent most of the ions from reaching the window.

INDEX OF REFRACTION

The index of refraction was measured by crossing a 26° prism of lithium fluoride with a 25 cm concave grating in a vacuum spectrograph. It was found necessary to reduce the angular aperture of the grating to slightly less than two degrees to eliminate astigmatism and to increase the depth of focus. Furthermore this reduction in the aperture made the light passing through the prism sufficiently parallel to allow the grating to form the final image without the use of a second mirror. Thus the grating served the double purpose of monochromator and focusing device. Since the slit of the spectrograph was replaced by a 0.1-mm pinhole, the spectrum appeared as a row of dots on the photographic plate which was mounted perpendicular to the beam of light from the grating.

The prism placed between the grating and the photographic plate was arranged so that it could

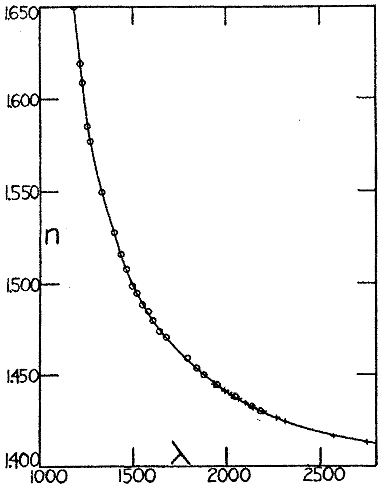

FIG. 3. Index of refraction.

be rotated about an axis passing through its center and parallel to the refracting edge. The prism could also be removed from the path of light without disturbing the vacuum. The introduction of the prism displaced the monochromatic images of the pinhole from their positions when formed by the grating alone. The tangent of the angle of deviation was then given by the ratio of this displacement to the perpendicular distance (20 cm) from the photographic plate to the prism.

When the prism was rotated about its center, each of the monochromatic images formed through the prism moved toward its corresponding undeviated image until the position of minimum deviation was reached. Rotating beyond this point caused the images to reverse their direction of motion. Thus rocking the prism through the positions of minimum deviation during the exposure gave a series of lines on the photographic plate. The ends nearest the spectrum formed by the grating alone represented the positions of the refracted monochromatic beams at minimum deviation. The index of refraction could then be expressed directly in terms of the angular displacement of the ends of these lines and the angle of the prism. Fig. 3 gives the index of refraction of lithium fluoride plotted against wave-length. The accuracy of the data is of the order of magnitude of three-tenths of one percent. As a check on the apparatus the values obtained for the index of refraction in the near ultraviolet were compared with those of Z. Gyulai.[5] His values are indicated by the crosses in Fig. 3.

CONCLUSIONS

Lithium fluoride in moderately thin pieces may be expected to transmit several percent of the light down to wave-lengths as short as 1100A, but this transmission cannot be assumed for a piece chosen at random. Impurities in the crystal, poor polish, and layers of foreign material on the surface may reduce the transmission in the Schumann region to a negligible quantity.

In conclusion the author wishes to express his gratitude to Professor T. Lyman for his continued interest in the progress of these experiments.

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[5] Gyulai, Zeits. f. Physik **46**, 80 (1927).

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Intensity Distribution of the Continuous Spectrum of Hydrogen in Mixtures with Helium and with Neon*

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Shift of intensity in the continuous spectrum of hydrogen by admixture of rare gases. The continuous spectrum of hydrogen emitted in mixtures with helium and with neon was studied. The effect of these gases was to shift the maximum of intensity to longer wave-lengths. The ratio of intensity of the spectrum emitted in pure hydrogen to that emitted in the presence of helium as a function of the wave-length was determined by photographic photometry. In order to establish the reasons for this change in distribution of energy with wave-length in the continuous spectrum, a study of the intensity distribution of the many-line spectrum in the presence of helium was made. 20 cm of helium were sufficient to *reduce the vibration* in the excited states to practically zero. Hence the continuous spectrum emitted in the presence of helium must come from transitions from the *lowest vibrational level* of its upper state.

Measurement of intensity distribution of the continuous spectrum of hydrogen in the presence of helium. The wave-length distribution of energy in the continuous spectrum for 0.6 mm of hydrogen and 21 cm of helium was determined by comparison with the radiation emitted from the positive crater of the carbon arc, taken as the best available approximation of the ultraviolet black-body radiation. Under these conditions the maximum intensity of the continuous spectrum was in the neighborhood of 3200A in contrast with about 2500A for the spectrum under ordinary conditions. The position of this maximum is in agreement with the results of Finkelnburg and Weizel. The broadness of the maximum, however, does not agree with their results nor with the theoretical curves of James, Coolidge and Present. Another possible maximum noted at 4500A suggests that more than one electronic state contributes to the observed continuum.

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* An extract from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Harvard University.