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Optical Constants of Fluorite in the Extreme Ultraviolet*

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The reflecting power of a polished fluorite surface has been measured at nineteen wave-lengths from 1605A to 927A for 45°, 60°, 75° and 85° incidence, by means of a vacuum spectrograph. The method of photographic photometry followed is discussed in detail. The reciprocity law was employed and correction made for its failure in accordance with the work of Harrison and Leighton on oiled photographic films. Correction exposures were made with an inverse square law sensitometer. A vacuum chamber was arranged for this sensitometer since it was found that the reciprocity characteristics of the film were changed when it was placed in vacuum. The reflecting power data above λ1230A shows that the light dispersed by the grating was very nearly unpolarized.

The curves for index of refraction and extinction coefficient have been computed from the reflecting power data for fluorite. The extinction curve shows an absorption band of roughly 100A half-width, with maximum near λ1115A. The dispersion is anomalous in this region. The absorption increases again below λ1060A. The condition of the fluorite surface is discussed. Evidence is given indicating the presence of a surface layer having a higher absorption coefficient and reflecting power than fluorite itself.

INTRODUCTION

THE research reported in this paper is concerned primarily with the measurement of the reflecting power of fluorite for a number of wave-lengths in the extreme ultraviolet. Since these measurements have been made to obtain points lying at closer wave-length intervals than in the previous investigation by Gleason,[1] it has been possible to show in detail the variation of the reflecting power in the neighborhood of the absorption band causing fluorite to become opaque below λ1230A. In addition, several angles of incidence have been employed at each wave-length in order to permit a calculation of the optical constants from the reflecting power data. From this calculation curves have been obtained for fluorite showing the variation of the index of refraction and extinction coefficient in the spectral region near the absorption band.

It is believed that the results for the reflecting power itself are of a higher degree of accuracy than those obtained by earlier observers.[2] As the nature of the particular method of photographic photometry employed is fundamental to the accuracy of the results, the procedure followed and the improvements introduced are treated in considerable detail. It is largely upon this particular method of photometry and the care with which it has been applied that the claims of this paper must ultimately rest.

APPARATUS

A vacuum spectrograph has been adapted for measuring reflecting powers in the extreme ultraviolet. The optical system is shown schematically in Fig. 1. The light source D is a discharge tube of the type used by Powell;[3] it was supplied with tank hydrogen. The current was 0.8 ampere and the drop 700 volts. The many-line spectrum of hydrogen served as a satisfactory source from λ1610A to λ927A. Its intensity was usually constant to 5 percent during an hour. The grating (50 cm radius of curvature, 15,000 lines per inch, and of speculum), together with slits S_1 and S_2 served as a monochromator. The wave-length could be changed from outside the spectrograph by rotating the grating. The beam passing through S_2 came to a focus on the mirror surface M whose reflecting power was to be measured; after reflection it formed a somewhat out of focus image on the photographic film F. Movable black glass shutters H limited the grating aperture so that a narrow beam could be obtained. The main advantages of this arrangement were that one could use a small mirror and still make measurements fairly near grazing incidence, and that the image on the film was fairly uniform so that one could easily measure its opacity accurately with the densitometer. Slit S_1 was 1 mm high and 0.2 mm wide, and slit S_2 usually 0.1 mm

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[1] P. R. Gleason, Proc. Am. Acad. Sci. **64**, 92 (1930).

[2] H. M. O'Bryan, J. O. S. A. **22**, 739 (1932); Phys. Rev. **38**, 32 (1931). P. R. Gleason, reference 1. Earlier work is cited in Gleason's paper.

[3] W. M. Powell, Phys. Rev. **45**, 154 (1934).

wide. About 2.5 mm width of grating was generally used. Under these conditions a wave-length range of 4A or less was admitted and the beam was only 0.3° wide in angle. An exposure of 10 seconds to the direct beam produced a developed density of from 0.5 to 2.0 depending on the particular wave-length employed.

In order to set the mirror at various angles to the beam it was mounted on the bottom of a vertical shaft and was adjusted so that the axis of this shaft lay in its surface. Four angles of incidence, 45°, 60°, 75° and 85°, were generally used and these were set by means of a circle carried on the top of this shaft with four notches milled in the periphery, 10°, 15° and 15° apart, into which a pin fell. A crude control was provided to turn the mirror to approximately the correct angle from outside the spectrograph. The pin then fell into the proper notch and set the angle precisely. The mirror and circle as a whole were oriented correctly to the direct beam, and this adjustment was checked periodically, by using the central image from the grating and making visual observations through a window. In order to obtain reflecting powers, it was necessary to make exposures to the direct as well as to the reflected beam. To this end, the mirror mechanism was mounted on ways so that it could be raised as a whole out of the light path.

The photographic film *F* was bent to a cylinder with axis coincident with the axis about which the mirror turned. This ensured the same length of light path from film to grating for any angle at which the mirror was set. The film could be moved vertically by means of ways and thus room was provided for 36 exposures each 1 mm high, at each angle of incidence. An electromagnetic shutter behind S_2, together with a switch actuated by a telechron motor, allowed exposures of 10 seconds to be made to better than 1 percent accuracy.

In order to keep the specimen to be tested as clean as possible use was made of a side chamber designed for the preparation of mirror surfaces by evaporation or sputtering. The entire mirror mechanism could be raised into this chamber, shut off from the rest of the spectrograph by means of a sliding gate and placed on a separate pumping system, without altering its adjustment or destroying the vacuum. The mirror was kept in this chamber until a good vacuum was established in the spectrograph and exposures were to be started. This reduced the chance of contamination by condensation of grease vapors, a necessary precaution. The position of the mirror in the spectrograph proper was only 4.5 cm from the photographic film *F*, and during the process of evacuation the thick oil coating on this film sometimes effervesced a little.

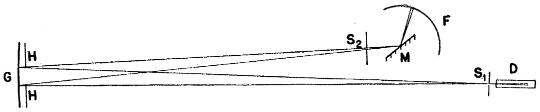

FIG. 1. The optical system.

Scattered light of spurious wave-lengths, except that which arose from the grating surface itself, was eliminated by suitable diaphragming. The intensity of the remainder was minimized by selecting for use the best portion of the grating by means of the shutters *H*. Tests made by introducing in the light path fluorite and other substances having definite spectral transmission limits showed that the intensity of the scattered light was never more than 4 percent of that of the useful light. The reflection coefficient data should not be in error by more than 1 percent, or at most 2 percent on this account, since through the visible and ultraviolet fluorite has no regions of very great reflecting power.

PHOTOGRAPHIC PHOTOMETRY

The method of photographic photometry developed by Harrison and Leighton[4] for use with oil sensitized photographic materials makes possible a considerable increase in the accuracy of photometric measurements in the extreme ultraviolet. The reciprocity law can be used for photometry in this region only provided a correction for its failure is properly applied. Harrison and Leighton showed that this correction can be made by virtue of the fact that the oil layer on the surface of the film absorbs the incident extreme ultraviolet light completely and fluoresces in the very near ultraviolet. It is this fluorescent radiation which really exposes the film, and its intensity is proportional to that of

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[4] G. R. Harrison and P. A. Leighton, J. Opt. Soc. Am. **20**, 313 (1930).

the incident radiation. Therefore correction exposures for the reciprocity law failure can be made at the wave-length band at which the oil is found to fluoresce. This general method has been followed with great care in the present work, and several important systematic errors involved in its application have been encountered and eliminated.

For making the reciprocity failure correction exposures, an inverse square law sensitometer of the type described by Jones[5] was used. It was necessary to obtain a light source for it whose spectrum should be as similar as possible to the fluorescence spectrum of the oil used as sensitizer. Cenco 11021-C pump oil was chosen to sensitize the film; its fluorescence spectrum was photographed under irradiation from the Hg λ2537A line through the kindness of Dr. F. Rieke. A 200w tungsten lamp with a pair of filters was found to imitate this fluorescence spectrum quite well. One filter was of cuprammonium 1 cm thick, the other was an equal thickness of iodine dissolved in carbon tetrachloride. These solutions were conveniently held in Pyrex culture flasks. To keep their temperatures constant a water cell and fan were necessary. Finally, two flashed opal glasses separated 1 cm served to make a diffuse light source with uniform intensity distribution over a sufficiently large solid angle. The sensitometer lamp, like the discharge tube, was run on direct current and so there was no possibility of any intermittency error.

The basic method of making exposures and corrections which the author has found most suitable for determining the reflecting power is best explained by giving an example. The direct beam in the spectrograph has intensity I. After reflection from the specimen its intensity is IR, where R is the reflection coefficient. Let us suppose that exposures are made with these two beams and it is found that a 10 second exposure to the direct beam and a 100 second exposure to the reflected beam produce the same density, say 1.0. Suppose also that exposures for these same times have been made in the sensitometer on the same film. From the latter it is found that a 10 second exposure to light of intensity I', and a 100 second exposure to light of intensity $I'/12$, produce this same density, 1.0. Then, according to the work of Harrison and Leighton, since the times and blackenings were identical respectively for spectrograph and sensitometer exposures, the intensity ratios must have been the same also. Hence we have $IR/I=(I'/12)/I'$, whence $R=1/12$, the reflection coefficient desired. In actual practice one could almost never chance upon times and intensities such that each of these four exposures would come out to be of precisely the same density. It was always necessary to make enough exposures so that the desired times and intensities could be found by interpolation. It was a convenience to make the actual computation in two stages: first, to calculate the reflecting power from the spectrograph exposures using the reciprocity law, obtaining 1/10 in this instance; second, to correct this value for the failure of the law by means of the sensitometer exposures.

This exposure procedure has several advantages. Firstly, it is as straightforward as possible. It makes no assumption concerning the form of the blackening *vs.* exposure relationship. Secondly, the correction exposures have the same density as the spectrograph exposures. This is very necessary because the reciprocity failure changes with change in density. Lastly, Webb[6] has shown that under exactly the conditions set forth in the above example the reciprocity failure is independent of wave-length. Therefore if the filter combination should not precisely reproduce the fluorescence spectrum of the oil, or if the latter should depend somewhat on the wave-length of the exciting radiation, no error is introduced. Of the latter possibility, however, Harrison and Leighton write that they have found no indication.

If Harrison and Leighton's method of photographic photometry is to yield results which are entirely free from systematic error, it has been found essential in the present work that all factors which affect the reciprocity characteristics of the film be kept the same for the sensitometer exposures as for the vacuum spectrograph exposures. Chief among these factors are vacuum conditions, temperature at the time of exposure, and extent of development.

It was found that placing the film in vacuum

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[5] L. A. Jones, J. Opt. Soc. Am. & Rev. Sci. Inst. **7**, 305 (1923).

[6] J. H. Webb, J. Opt. Soc. Am. **23**, 316 (1933).

during exposure altered the reciprocity characteristics considerably. Since the film was exposed in vacuum in the spectrograph, it was necessary to arrange a vacuum chamber in which to place it while making exposures in the sensitometer. For Eastman Commercial Safety Film (that used throughout this work), the effect of evacuation was large enough so that a reflecting power of 10 percent would have been determined as 9 percent if the correction exposures had not been made in vacuum. However, the size of this effect varied considerably between different batches of this film. If phosphorous pentoxide were placed with the film in the vacuum chamber, the change in reciprocity failure upon evacuation took place more rapidly. A few minutes exposure to wet air or to room conditions caused the reciprocity failure to return toward that for film which had not been placed in vacuum, while dry air or hydrogen, admitted after thorough evacuation, produced no further change. It seems reasonable, therefore, to ascribe this effect to a change in the water content of the photographic material.

The temperature of the film at the time of exposure has been shown by Webb[7] to affect greatly the reciprocity characteristics. For the reciprocity correction to apply properly it was therefore desirable to keep the spectrograph and the sensitometer at the same temperature, and this was done to within ½°C.

The extent to which development is carried also considerably influences the reciprocity characteristics as Jones, Hall and Briggs[8] have shown. In order that the vacuum spectrograph and sensitometer exposures be processed in precisely the same way, reciprocity failure correction exposures were made in the sensitometer on each film immediately after removal from the vacuum spectrograph, utilizing the spaces between the spectrograph exposures.

In measuring the densities of the developed images by means of a microphotometer, it was necessary to take care that the microphotometer slit was small enough so that it covered an area of the spot over which the density was approximately constant. Otherwise an average density value would have been obtained for which it would have been difficult to determine the reciprocity failure correction properly.

Under these conditions, density *vs.* log time curves exposed in the spectrograph were parallel to those exposed in the sensitometer, as would be expected from Harrison and Leighton's work, provided the intensity was such that approximately the same densities were produced for the same exposure times.

Several steps have been taken to minimize the erratic errors involved in this method of photographic photometry. The film was sensitized by dipping into the undiluted oil and draining overnight. It was necessary that its position during this process and also while in the spectrograph was such that the oil would not flow between positions on the film corresponding to different angles of reflection. A small variation in oil thickness did arise, but affected in like fashion the sets of exposures to the direct beam and to the beam reflected at the several angles, respectively. The effect of oil flow on each of these series could then be detected and corrected for by means of the exposures made to the direct beam, since the latter were given equal times. Drift in the intensity of the light source, occasionally troublesome, was also corrected for by means of this series of "direct" exposures. This could be done since one "direct" exposure was always made following four "reflected" exposures.

Considerable effort was made to secure even development. The oil coating was washed off the film in three successive baths of petroleum ether. The film was held uniformly immersed in the developer by means of a glass clamp, and the brush method was employed during rinsing and the first minute of fixing, as well as during development. To detect and to make partial correction for any remaining unevenness in development and for gradual variation in emulsion sensitivity over the film, a number of identical "control" exposures covering the parts of the film which remained unused were made with the sensitometer immediately following the reciprocity correction exposures.

The magnitudes of the erratic errors inherent in the photometric method as described have been determined. The probable actual error in

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[7] J. H. Webb, J. Opt. Soc. Am. **25**, 4 (1935).

[8] Jones, Hall and Briggs, J. Opt. Soc. Am. **14**, 223 (1927).

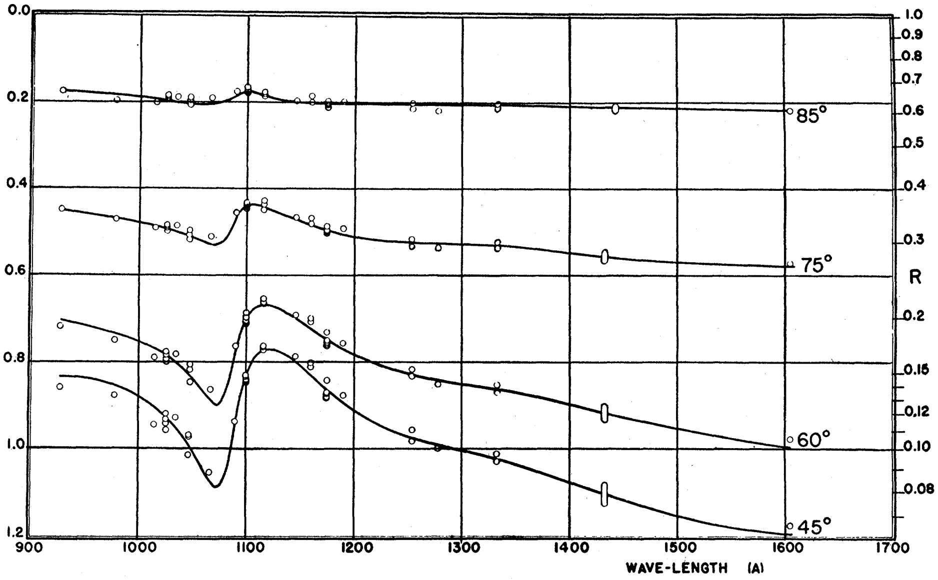

FIG. 2. Reflection coefficients for fluorite for four angles of incidence plotted on a logarithmic scale.

the density of an individual exposure in the extreme ultraviolet was found to be 0.0076 for an average density of 1.3 and contrast of 1.6. This figure was obtained by examining all the ultraviolet exposures on the runs reported in this paper, after correction had been made as described for drift in the intensity of the source and for oil flow. By considering all the control exposures, a similar figure was obtained for the exposures made in the reciprocity sensitometer. The probable actual error in mean density for these was 0.0044, the average density being 1.0 and contrast 1.5. The area of film over which these exposures were made was 30 cm^2. The probable error in a single measurement of reflection coefficient was less than 2 percent, as computed from these two separate errors and the number of exposures of each kind made on each run. This value includes the effect of all errors in the photometric method which were of an erratic nature.

REFLECTING POWER RESULTS FOR FLUORITE

Fluorite was selected as the first substance to measure because of its importance in extreme ultraviolet work. Furthermore, it was hoped that information concerning the absorption band which causes fluorite to become opaque below λ1230A could be obtained from the optical constants as calculated from the reflecting power data. Fluorite was well adapted to such a calculation because its transparency to wave-lengths longer than 1230A enabled the polarizing action of the grating to be determined. Moreover, the calculation could be checked to some extent because the index of refraction was already known down to λ1311A from transmission measurements of Handke.[9]

The fluorite specimen used in this work was a plate 4.5 cm long, 2.7 cm wide, and 2 mm thick. It was obtained from Zell in Baden and was polished by Bausch and Lomb. Its surfaces were flat to better than a wave-length and contained only a few fine scratches. The two surfaces were not parallel, however. Therefore it was possible to mount it so that the reflection from the rear surface, which appeared down to λ1230A, was well separated from that from the front. The reflecting power was found to be quite constant over its surface.

The cleaning procedure which gave the most reproducible results and the cleanest surface, was to scrub the fluorite lightly with Kleenex moistened first in water, then in carbon tetrachloride, then in petroleum ether. After this, the specimen was soaked for at least an hour in several changes of petroleum ether. Finally, a

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[9] Landölt Bornstein Tables, fifth edition, p. 911.

fine stream of Merck's petroleum ether containing only 0.0002 percent nonvolatile matter was run over the surface for five minutes. This procedure was carried through before each run.

The results here presented are from fourteen runs on this single fluorite specimen, each made under as nearly as possible the same conditions. During each run, measurements were made at four different wave-lengths, one-quarter of the available exposures being allotted to each. In order to check results from different runs against each other, one particular wave-length was repeated on each run. λ1433A was selected for these control exposures, except when the shortest wave-lengths were desired. Then λ1047A was used, since the intensity of the hydrogen spectrum at λ1433A was very great compared to that below λ1020A.

The reflecting power data obtained for four angles of incidence are shown in Fig. 2. The reflection coefficient R, has been plotted on a logarithmic scale against wave-length so that equal increments vertically represent equal fractional errors or differences in R. Each point is the result of a single run, except that at λ1433A, where the points were too numerous, their range is shown.

The best smooth curves were drawn after first correcting these points by means of the λ1433A control exposures. This correction was possible since it was found that if the reflecting power results at λ1433A for a particular run were lower than the average, the results for the three other wave-lengths used during that run were almost always also low, and to about the same extent. This indicated that a change had occurred in some factor not under perfect control, but which affected the results at each wave-length by roughly the same amount for each angle, respectively. To make at least partial correction for such a change, the results for the other three wave-lengths for that run were brought up by the same amount that the λ1433A reflecting powers were below the average. The two runs having λ1047A as control were first corrected relative to each other, and then to λ1433A by using a run containing both λ1047A and λ1433A. The value of this correction for the shortest wave-lengths is in some doubt because it was somewhat roundabout.

TABLE I. *Reflection coefficients of fluorite.*

λ(A)	45°	60°	75°	85°
1605	0.0636	0.1014	0.265	0.604
1433	.0788	.1205	.278	.612
1333	.0948	.1371	.296	.622
1276	.1019	.1442	.298	.624
1254	.1062	.1486	.300	.624
1190	.1276	.1694	.312	.622
1175	.1368	.1778	.319	.622
1162	.1483	.1888	.328	.624
1146	.1596	.2014	.339	.631
1116	.1671	.2133	.362	.652
1100	.1459	.1995	.365	.668
1090	.1390	.1629	.336	.646
1067	.0840	.1294	.296	.625
1047	.1021	.1476	.308	.625
1035	.1114	.1585	.317	.631
1026	.1178	.1648	.323	.637
1015	.1244	.1702	.327	.640
978	.1403	.1845	.342	.653
927	.1462	.1981	.357	.671

It is hoped that the smooth curves drawn through the points after they were corrected in this way are nearly those which would have been obtained had it been possible to make measurements at all wave-lengths during a single run, though it is difficult to estimate how nearly this is the case. The values for reflection coefficient taken from these curves are given in Table I.

The reproducibility of the reflecting power measurements can best be illustrated by an analysis of the separate results at λ1433A. This appears in Table II. The reflecting power at 45° was most subject to variation. During these twelve runs the greatest departure from the mean for this angle was ±5 percent; the average departure was ±2.5 percent. The scattering of the points in Fig. 2 about the smooth curves drawn as just described is of this same magnitude. Thus under the best of conditions, variations in reflection coefficient occasionally up to about 10 percent have been found to occur at 45° with the present apparatus and technique, using polished fluorite as the test substance. Such variations are roughly three times larger than those expected from purely photographic causes and it is thought

TABLE II. *Reproducibility of results for λ1433A.*

Angle of incidence	45°	60°	75°	85°
Refl. coef., mean from 12 runs	0.0788	0.1205	0.278	0.612
Greatest departure from mean (%)	5.1	3.5	2.5	3.5
Average departure from mean (%)	2.5	1.8	1.4	1.4
Probable error in mean (%)	0.7	0.5	0.5	0.5

that they are attributable to changes in the surface condition of the fluorite. Arguments substantiating this explanation will appear in a later paragraph.

The reflecting power results for 85° are less reliable than the others since an error in setting the angle has more effect the nearer the beam is to grazing incidence. The positions of the mirror could be set relative to one another very exactly, but it was difficult to make the adjustment relative to the beam to better than 0.1° or 0.2°.

State of Polarization of the Incident Light

The state of polarization of the light incident on the specimen, as well as the index of refraction, can be calculated from the reflecting power data for wave-lengths at which fluorite is transparent. This procedure is important since a knowledge of the polarization greatly simplifies a determination of the index and extinction coefficient from the measured reflecting powers in the region of the spectrum where fluorite is opaque. From λ1230A to longer wave-lengths fluorite is fairly transparent and so Fresnel's reflection equations should apply. These equations give the reflecting power for any angle of incidence for any values of N, the index, and P, the fraction of the total incident intensity polarized with the electric vector perpendicular to the plane of incidence. In order to obtain N and P for a particular wave-length, the reflecting powers measured at 45°, 60°, 75° and 85° were compared with the corresponding reflecting powers calculated from the equations, taking a series of arbitrary values for N and P. Those values of N and P were taken as the correct ones for which the computed and experimental reflecting powers agreed most closely. This process was carried out by means of curves which are to be described in a separate paper.

Table III. *Comparison of experimental and computed reflection coefficients, λ1433A.*

Index	Polarization	$100\% \times (R_{\text{comp.}} - R_{\text{exp.}})/R$				
N	P	45°	60°	75°	85°	av.
1.749	0.460	+0.025	−0.028	−0.023	+0.005	0.021
1.736	0.470	+.018	−.021	−.012	+.009	.016
1.724	0.480	+.014	−.014	−.002	+.014	.011
1.711	0.490	+.007	−.007	+.007	+.018	.009
1.699	0.500	.000	.000	+.016	+.023	.009
1.694	0.505	−.002	+.002	+.021	+.025	.011
1.688	0.510	−.005	+.005	+.025	+.028	.016
1.672	0.520	+.021	+.002	+.030	+.030	.021

Table III shows the results of this computation for λ1433A where the most accurate reflecting power data was obtained. The percentage differences between the computed and experimental reflection coefficients are given for several values of P, N being adjusted in each case to make these differences as small as possible. A perfect agreement at all four angles simultaneously within the probable experimental error in the mean reflecting power data was not possible. The most probable values of N and P were taken as those which yielded equal percentage differences in R for 45°, 60° and 75°. R for 85° was disregarded because it was the least accurate and also gave less information concerning P and the optical constants. For λ1433A the value obtained was $P=0.49$. However, P could be varied between 0.48 and 0.505 before much increase appeared in the average difference between the computed and experimental reflection coefficients for the four angles. Hence all values of P in this range are almost equally likely. The similar results for other wave-lengths from 1605A to 1254A, as given in the first part of Table IV, show values of P also lying in this range. The data, therefore, give no indication that the light in this wave-length range dispersed by the grating was other than unpolarized.

Optical Constants of Fluorite

The index of refraction, N, and the coefficient K_0 describing the absorption,[10] can be determined from the reflecting power data for wave-lengths below the transmission limit of fluorite. The process is somewhat similar to that just described for obtaining N and P at longer wave-lengths. Below λ1230A the reflection from fluorite becomes metallic in character and generalized reflection equations apply.[10] These equations can be written in the form $R=f(I, N, K_0, P)$, where I is the angle of incidence and P describes the polarization of the incident light as before. The problem was first considerably simplified

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[10] W. König, *Handbuch der Physik*, Vol. XX, p. 242. N and K_0, as used in the present paper, are the same as König's n_0 and $n_0\varkappa_0$, respectively.

by assuming that the incident light was unpolarized. This has just been shown to be true, within experimental error, from λ1254A to λ1605A and there is no reason to suspect that it was not so to shorter wave-lengths as well. N and K_0 were then determined for each wave-length by comparing the experimental reflecting powers at 45°, 60°, 75° and 85° with the corresponding quantities computed from the general equations, selecting a series of arbitrary values of N and K_0. Those values of N and K_0 were then taken as the correct ones for which the experimental and computed reflecting powers agreed most closely. This computation was actually carried through by means of curves to be described in a separate paper.[11]

Table IV shows the results of this calculation. The percentage differences between the experimental reflection coefficients, as given in Table I, and the computed quantities are shown for the most probable values of N and K_0. As was the case to longer wave-lengths, a perfect agreement at all four angles simultaneously could not be obtained. Just as in determining N and P, the most probable values of N and K_0 were always taken as those which yielded equal percentage differences between the experimental and computed reflection coefficients for 45°, 60° and 75°. N and K_0 could be varied through a considerable range, however, before an appreciable increase appeared in the average difference for the four angles. These ranges for N and K_0 have been determined and are shown plotted against wave-length by the broken curves in Fig. 3. They give some idea of the accuracy of this determination of the optical constants. The ranges set by the experimental errors in reflecting powers lay within these limits. The correct curves, then, may with almost equal probability lie anywhere between the broken curves. However, it is thought that they should not differ greatly in shape from the heavy curves, which show the most probable values, since the latter were determined in a consistent fashion for each wave-length.

The curves of Fig. 3 give more precise information than has hitherto been available concerning the absorption band which causes fluorite to become opaque below λ1230A. It appears that a narrow absorption band exists just below the transmission limit. From the K_0 curve it can be seen that the center of this band is near λ1115A and that the half-width is roughly 100A. There is further absorption of a more diffuse character to shorter wave-lengths which causes K_0 to rise again below about λ1060A. The shape of the dispersion curve is in good agreement with that of the absorption curve. The dispersion is anomalous from somewhere between λ1130A and λ1200A to about λ1090A, as would be expected

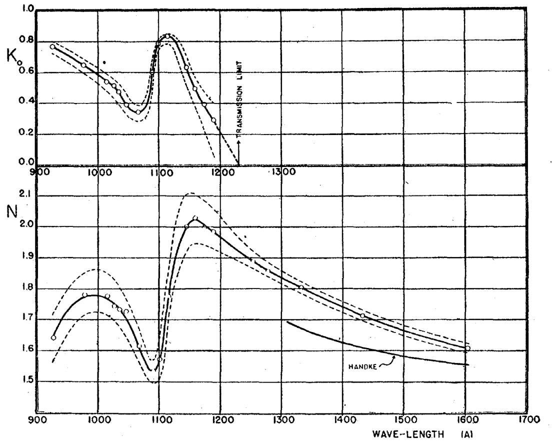

FIG. 3. The optical constants N and K_0 for fluorite. The broken curves indicate the probable error.

TABLE IV. *The optical constants of fluorite and the percentage differences between computed and experimental reflection coefficients.*

Wave-length	Optical Constants		Polarization	$100\% \times (R_{\text{comp.}} - R_{\text{exp.}})/R$				
λ(A)	N	K_0	P	45°	60°	75°	85°	av.
1605	1.607	0	0.479	−0.5	+0.5	−0.5	+1.8	0.8
1433	1.711	0	.490	+0.8	−0.8	+0.7	+1.8	1.0
1333	1.803	0	.506	0.0	0.0	0.0	+1.4	0.3
1276	1.855	0	.505	+0.4	−0.4	+0.5	+1.2	0.6
1254	1.888	0	.503	+0.7	−0.6	+0.6	+1.4	0.8
1190	1.983	0.290	0.500	+1.2	−1.2	+0.9	+2.1	1.3
1175	1.996	0.390	.500	+1.0	−0.9	+1.0	+2.3	1.3
1162	2.027	0.490	.500	+0.7	−0.8	+0.7	+2.8	1.2
1146	2.000	0.631	.500	+0.7	−0.8	+0.8	+2.8	1.3
1116	1.775	0.830	.500	+0.7	−0.7	+0.7	+3.0	1.3
1100	1.570	0.785	.500	+0.9	−0.9	+1.0	+2.3	1.3
1090	1.533	0.600	.500	+0.6	−0.6	+0.6	+3.5	1.3
1067	1.615	0.344	.500	+0.3	−0.3	+0.3	+2.5	0.9
1047	1.725	0.395	.500	+0.6	−0.5	+0.6	+2.8	1.2
1035	1.732	0.473	.500	+0.8	−0.9	+0.9	+2.8	1.4
1026	1.742	0.517	.500	+0.9	−0.8	+0.9	+2.3	1.2
1015	1.775	0.540	.500	+0.5	−0.5	+0.5	+1.8	1.1
978	1.780	0.650	.500	0.0	−0.1	0.0	+0.9	0.2
927	1.640	0.768	.500	+0.9	−0.9	+0.9	+0.9	0.9

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[11] Presented at the New York meeting, Feb. 24, 1934. Phys. Rev. **45**, 562, A25 (1934).

when crossing the center of the absorption band. It then is normal to shorter wave-lengths but appears to become anomalous again near λ1000A as the center of the next absorption band is approached. It will be of interest to follow these curves to shorter wave-lengths and to verify the trends below λ1000A, since the reflecting power data here reported is least accurate in this range.

SURFACE CONDITION

It has been seen that a perfect agreement between the experimental and computed reflecting powers could never be obtained for all four angles simultaneously. Although the remaining discrepencies were small they were of the same magnitude and sign for each angle respectively for all the wave-lengths employed. These facts appear to indicate the presence of some small systematic error in the reflecting power data. Such a systematic error has been searched for in all steps of the experimental work, but none has been found of sufficient size to account for these facts. A much more probable explanation, and one that is supported by considerable other evidence, is that a surface layer was present on the fluorite, a condition very often encountered through katoptric measurements, and that this layer caused the surface to depart from the ideal condition to which the theoretical reflection equations apply.

Furthermore, a surface layer seems required to explain the fact that the indices of refraction obtained katoptrically in the present work, are greater than those which Handke[9] has determined down to λ1311A using a dioptric method. Both dispersion curves are shown in Fig. 3 and it can be seen that the discrepancy is well outside the range of experimental error. This means that the fluorite actually reflects more light than it should according to Handke's indices and Fresnel's reflection equations; a reflecting power as low as the computed value was never observed.

A deeper insight into the character of the surface layer can be obtained from a comparison with the work of Powell.[3] From measurements of the transmission of fluorite sections of different thicknesses made in the Schumann region, Powell derived values for the loss of light on entering a single fluorite surface at normal incidence. These values included the effects of reflection, scattering, and of absorption in passing through any surface layer present. Without reflection measurements it was not possible to determine the effect of each factor separately. The percentage losses so obtained were much greater than the reflecting powers for normal incidence as calculated from either Handke's indices or the indices obtained in the present work, e.g., 14 percent, 5.5 percent and 6.9 percent for the three, respectively, at λ1433A. Both Powell's and my surfaces were well polished and treated in about the same way; hence a comparison of the respective results should be possible. Scattering can be ruled out, then, as the important factor in causing Powell's surface loss, since had it been present my reflecting powers would be lower, not higher, than those calculated from Handke's indices. Furthermore, the reflecting powers computed from my indices were much too small to account for Powell's surface losses by themselves. A layer having both a higher absorption coefficient and greater reflecting power than fluorite itself seems required by this behavior. The same conclusion was reached from simultaneous measurements of reflecting power and transmission at 45° and λ1433A made by the author, taking Powell's values of the absorption coefficients for fluorite.

That this layer consisted of some foreign substance, perhaps grease or adsorbed water vapor, which was not entirely removed by the cleaning procedure, or was picked up in the spectrograph, is suggested by the fact, mentioned previously, that on different runs results could not be repeated with as much accuracy as the photometric method allowed. Furthermore, a thin layer of oil, (Cenco 11021-C) deliberately placed on the surface was found to increase the reflecting power; a higher reflecting power was also observed when a cleaning procedure was employed which left the surface with a visible contamination.

Further evidence pointing to the presence of a layer of some foreign substance is furnished by measurements on lithium fluoride in the extreme ultraviolet. Schneider[12] found a high surface loss for lithium fluoride similar to that observed for fluorite by Powell; its magnitude depended on the cleaning procedure and could be reduced by

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[12] E. G. Schneider, Phys. Rev. **49**, 341 (1936).

heating to dull red in air. He therefore ascribed this surface loss, in part at least, to a layer of some easily volatilized substance left by the cleaning agent. In order to see whether a similar effect existed for reflection, measurements of the reflecting power of lithium fluoride at 45° and λ1433A of a preliminary nature have been made by the author using a crystal obtained from Dr. Schneider and polished by Mr. David Mann. The specimen was arranged so that it could be heated to dull red between reflecting power measurements, in vacuum all the while. Before heating it was found that the reflection coefficient was about 15 percent greater than the value computed from the index of refraction as measured dioptrically by Schneider, a discrepancy nearly the same as was observed for fluorite. After heating, however, the reflection coefficient decreased to the computed value to within experimental error. It seems probable, then, on account of this similarity between surface losses and reflecting powers, respectively, that the surface layers on fluorite and lithium fluoride were of a similar character. It is thought, therefore, that had it been possible to heat fluorite without shattering it, indices of refraction in much closer agreement with those of Handke would have been obtained.

It is possible, however, that the surface layer was not entirely one of a foreign substance, and that it included a region of fluorite in which polishing had disturbed the crystal structure and so altered the optical constants. No direct evidence bearing on an effect of this kind has been obtained in the present work. However, the work of Margenau[13] in the ultraviolet and of Hilsch and Pohl[14] down through λ1600A lends some support to this point of view. They have shown that the condition of the surface can cause a shift in the center of an absorption band amounting to as much as 44A. However, in the case of fluorite a shift of 125A, which is greater than they have reported, would be required to account for the whole discrepancy between the dispersion curves.

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[13] Margenau, Phys. Rev. **33**, 1035 (1929).

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

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A Very Accurate Test of Coulomb's Law of Force Between Charges

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The exponent 2 in Coulomb's inverse square law of force between charges in empty space has been found experimentally to be correct to within 1 part in 10^9. The well-known electrostatic experiment of Cavendish and Maxwell with concentric metal globes was replaced by a quasistatic method in which the difficulties due to spontaneous ionization and contact potentials were avoided. A "resonance electrometer" (undamped galvanometer with amplifier) was placed within the globes, the input resistor of the amplifier forming a permanent link connecting them, so as to measure any variable potential difference between them. It was shown theoretically that the presence of the resonance electrometer would have no effect on the result and that it could replace electrically a part of the inner globe. The galvanometer was observed through a "conducting window" at the top, made so by covering it with salt water. No effect was observed when a harmonically alternating high potential V (>3000 volts), from a specially designed "condenser generator" operating at the low resonance frequency of the galvanometer, was applied to the outer globe. The sensitivity was such that a voltage $v=10^{-6}$ volt was easily observable above the small fluctuations due to Brownian motion.

If the exponent in the law of force were not exactly 2 but rather $2\pm q$ then $q<v/VF(a, b)$ where $F(a, b)=0.169$, a and b being the radii of the globes. This gives $q<2\times 10^{-9}$ in space remote from matter. The formula for $F(a, b)$ was derived by Maxwell's theory in which the effect of gravity is assumed negligible. Reasons are given for believing that this assumption does not invalidate the result.