THE REFRACTIVE INDEX OF LIQUIDS FOR X-RAYS

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Abstract

The refractive index for x-rays was measured for several liquids by the method of total reflection. A monochromatic beam ($\lambda = 1.537$A) was obtained by using a copper target in the x-ray tube and by selectively reflecting the beam from a calcite crystal. This beam was, in turn, reflected at a grazing angle from a thin film of the liquid being studied, spread on a plane glass mirror. As the index of refraction for x-rays is less than unity, the beam will be totally reflected at angles smaller than the critical angle, a sudden reduction occurring in the intensity of the reflected beam at the critical angle. Photographs, taken while the mirror was being rotated, showed such an edge. A discussion is given of the effects on the microphotometer curves of the slit width of the microphotometer, the width of the crystal slit, the rotation of the mirror and the finite width of the spectral line. From measurements of the curves, the values of δ, which is equal to $1-n$, were obtained and compared with the values calculated by means of the simplified form of the Drude-Lorentz dispersion formula. The results are.—

Substance	δ (experimental)	δ (theoretical)
Water	3.69×10^{-6}	3.53×10^{-6}
Butyl phthalate	3.57×10^{-6}	3.57×10^{-6}
Ethylene glycol	4.08×10^{-6}	3.88×10^{-6}
Triethanolamine	3.86×10^{-6}	3.91×10^{-6}
Glycerine	4.41×10^{-6}	4.34×10^{-6}
Glass	8.19×10^{-6}	....

Introduction

Measurements of the refractive index for x-rays of various solid materials have been made by several investigators. Stenström noticed that the wave-length of a spectral line, calculated by means of Bragg's formula gave values, for higher orders than the first, in disagreement with each other. This was attributed to the refraction of the x-rays in the crystal from which reflection was taking place. Using this deviation, values for the refractive indices of calcite, rock salt and gypsum were determined. A more direct method for measuring the refraction of x-rays seemed desirable. Since the use of a prism at minimum deviation, as in the case of ordinary light, had previously failed, Bergen Davis[1] and his co-workers suggested the use of unsymmetrical reflections from crystal wedges. A. H. Compton[2] was led, by the fact that the index of refraction for x-rays of most substances is less than unity, to suggest that its value could be determined from the critical angle of total reflection.

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[1] B. Davis and H. M. Terrill, Proc. Nat. Acad. Sci. **8**, 357 (1922); B. Davis and R. V. Nardroff, Proc. Nat. Acad. Sci. **10**, 60 (1924); **10**, 384 (1924).

[2] H. Compton, Phys. Rev., **20**, 60 (1922); Phil. Mag. **45**, 1129 (1923).

The first two methods, the deviation from the Bragg relation and the use of the crystal wedge, are limited to solid crystals. The method of total reflection, however, is applicable to any substance which can present a smooth surface from which to reflect x-rays. It is only natural that solids should be chosen at first for the purpose of studying the refractive index by this method since they can, in general, be prepared with definite, plane, highly polished surfaces. However, it is evident that the method can be extended to the use of liquid films on solid mirror surfaces.

The Drude-Lorentz formula for dispersion may be applied to the case of x-rays in the simplified form, $n=1-\delta=1-Ne^2/2\pi m\nu^2$, provided the natural frequencies of the electrons in the atoms of the substance are sufficiently far removed from the frequency of the x-rays concerned. Here, n is the index of refraction, N is the number of electrons per unit volume, e and m refer to the charge and mass of the electron and ν is the frequency of the x-rays.

It is evident from the Drude-Lorentz formula, that the value of δ increases with an increase in the density of the material used as a reflecting surface and also with an increase in the wave-length of the x-rays. It has been pointed out, however, by Prins and others,[3] that increasing the wave-length of the x-rays or increasing the absorption coefficient of the material, greatly diminishes the sharpness with which the intensity of the reflection is reduced at the critical angle of total reflection. Since the absorption coefficient is roughly proportional to the density, the lighter substances should have a sharper critical edge.

In order to make an accurate determination of δ, it is desirable that δ be as large as possible, though it is equally important that the critical edge be sharp in order to locate accurately the critical angle of total reflection. A good compromise is obtained by using reasonably soft x-rays and a reflecting material with a small absorption coefficient. The use of organic liquids, therefore, should be especially appropriate since their absorption coefficients for x-rays are generally low. Futhermore, the use of the simplified form of the Drude-Lorentz formula is justified for the liquids and x-rays used in the work reported here. The copper $K\alpha_1$ line was used and the value of ν for this line ($\lambda=1.537$A.U.) is approximately 2×10^{18} per second. Oxygen was the heaviest constituent element in the liquids studied and the "frequency" of its K electrons is of the order of 0.1×10^{18} per second, making the ratio of the squares of these two frequencies only 1/400.

The author is aware of but one other measurement of the refractive index of liquids. Kellerman[4] reflected a beam of x-rays from a cylindrical surface on which was placed a thin film of the liquid to be studied. The photographs obtained show a direct and a reflected beam which fades out at the critical angle of total reflection. From a measurement of these photographs the critical angle was calculated. The geometry of the method is, however, somewhat

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[3] J. A. Prins, Zeits. f. Physik **47,** 479 (1928); J. E. Henderson and E. R. Laird, Proc. Nat. Acad. Sci. **14,** 773 (1928); M. Schon, Zeits. f. Physik **58,** 165 (1929); E. Dershem, Phys. Rev. **34,** 1015 (1929); M. A. Valough, Jour. d. Physique et Rad. Ser. VII, **1,** 261 (1930).

[4] K. Kellerman, Ann. d. Physik, *Series 4,* **2,** 185 (1930).

involved and the author has, accordingly, endeavored to use a simpler method.

Method and Apparatus*

The method used here is essentially the same as the one commonly used in dealing with a solid mirror. A fine beam of monochromatic x-rays was reflected on to a photographic plate from the surface of a thin film of the liquid placed on a glass mirror. The films were so thin that there was no tendency, on tilting the mirror, for the liquid to flow but instead would rotate with the mirror, which was moved through only a few minutes of arc. As the surface was rotated, the intensity of the reflected beam was suddenly reduced at the critical angle of total reflection. If θ_c is the critical, grazing angle of incidence, we have, $\cos \theta_c/1 = n$, where n, the index of refraction, is slightly less than unity. It is usually convenient to use δ, where $n = 1 - \delta$ and therefore, $\delta = 1 - \cos \theta_c = 2 \sin^2 (\theta_c/2)$. Since θ_c is of the order of ten minutes of arc, the sine may be replaced by the angle and $\delta = \theta_c^2/2$.

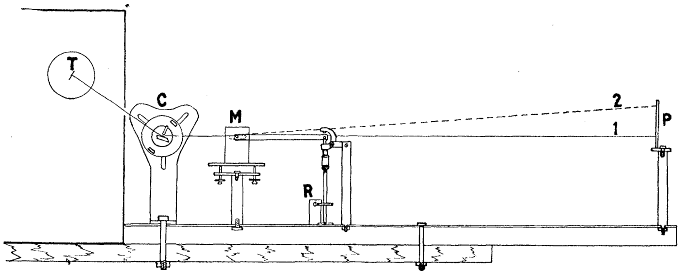

Fig. 1. *Schematic diagram of the apparatus.* T is a water-cooled, copper target, x-ray tube, operated at 36 kv and carrying a current of 25 m.a. Radiation from the target passed through a wide slit in the lead box housing the tube and fell on a calcite crystal C, which was provided with a Seemann wedge slit. The copper $K\alpha_1$ and $K\alpha_2$ lines were reflected horizontally from the crystal and passed through a thin cellophane window into a brass box housing the mirror, M. The position of M was so adjusted that the $K\alpha_2$ line always completely missed the mirror and a portion only of the $K\alpha_1$ line was reflected. The direct beam (1) and the reflected beam (2) left the box by another cellophane window and finally impinged upon a photographic plate P, which was placed 108.5 cms from the mirror. The mirror was rotated by means of a lever, one end of which was fastened to the axle of the mirror mounting and the other end rested on the micrometer caliper which was rotated very slowly by means of an electric clock motor.

In order to reduce the evaporation of the thin film of liquid on the surface of the mirror during an exposure, usually lasting for six to twelve hours, the mirror was mounted in a tight brass box measuring $6 \times 8 \times 10$ cms. A small dish containing some of the liquid was placed in the lower part of the box to assist in maintaining as nearly as possible, saturation of the vapor in the box. Some difficulty was experienced in getting the liquids to stick to the surface of the glass mirror, in a thin film. The method adopted was to clean the mirror thoroughly and then with a clean, rubber finger-stall on the finger, rub a small quantity of the liquid over the surface. The mirror was then placed in its mounting and installed in the brass box. In a short time an

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* The method of experimenting was suggested by Dr. T. H. Osgood.

inspection through one of the cellophane windows would ascertain if the film had polished over uniformly or if it were necessary to repeat the process. It is to be noted, that in the case of the more viscous liquids used, even with the greatest care, it was not possible to obtain a perfectly smooth film over the entire surface of the mirror. The effect of this will be discussed along with the results.

The mirror mounting was supported in the box on two axles whose axis of rotation coincided with the surface of the mirror at its center. One axle fitted in a bearing in a fixed wall of the box and the other projected through a removable wall. On the outer end of this axle was clamped a rod, 26 cm long, for rotating the mirror. The end of this arm was raised by the micrometer caliper, driven by a small motor, so as to give the mirror a rotation of 3.4 minutes of arc per hour. For most of the photographs it was necessary to rotate the mirror three or more times through the same angle in order to obtain a suitable record on the plate.

The x-ray tube used was a copper target, water-cooled Coolidge type tube constructed in the laboratory and pumped continuously during operation. It was found that each time after a preliminary run of about half an hour, the tube would settle down to a very steady condition with fluctuations in the current of less than five percent. This would produce a corresponding fluctuation in the intensity of the reflected beam, but since the region was usually gone over several times, irregularities due to these fluctuations would tend to be smoothed out.

Microphotometer curves were obtained by means of a microphotometer constructed by Dr. Croup in the University laboratory.

RESULTS

Before it was possible to make use of the microphotometer curves, of which Fig. 2 is a sample, it was necessary to study the effects of the width of the microphotometer slit, the wedge slit at the crystal, the rotation of the mirror, the finite width of the spectral line and the non-uniformity of the liquid film.

In order to determine the effect of the width of the microphotometer slit, a microphotogram was made of a photograph of a very sharp line drawn on a sheet of paper. A direct measurement of the width of the line on the photographic plate by means of a dividing engine and a measurement of the microphotogram of the line led to an effective slit width of 0.022 cm.

In the sample curve, Fig. 2, AC, the horizontal projection of the straight portion of the curve at the left edge of the direct beam is 0.41 mm, and DE, the horizontal projection of the straight portion in the region of the critical edge is 0.86 mm. In both cases this width is larger than 0.22 mm, the effective slit width of the microphotometer. Since such is the case, the effect of the slit here, as can be shown from simple considerations, is to round off the ends of the straight portion without displacing it or changing its slope. In the figure, a line is dotted in to show the expected microphotometer curve for a slit width of 0.22 mm, assuming the straight portion of the curve to extend all the way from the maximum to the minimum ordinate. It is seen that this dotted curve, while it does not exactly fit the microphotogram, suggests that the assumption of a sharp bend at D is at least approximately correct. A better fit is noted at A and C.

Referring to the left portion of Fig. 3, two parallel monochromatic rays are drawn from the target T, which are limited by the Seemann slit A, and by reflection from the calcite crystal. It it is assumed, for the moment, that the crystal is perfect and the width of the spectral line is infinitesimal, each ray in the beam defined by these two limiting rays, in order to be reflected by the crystal, must be parallel to those rays.

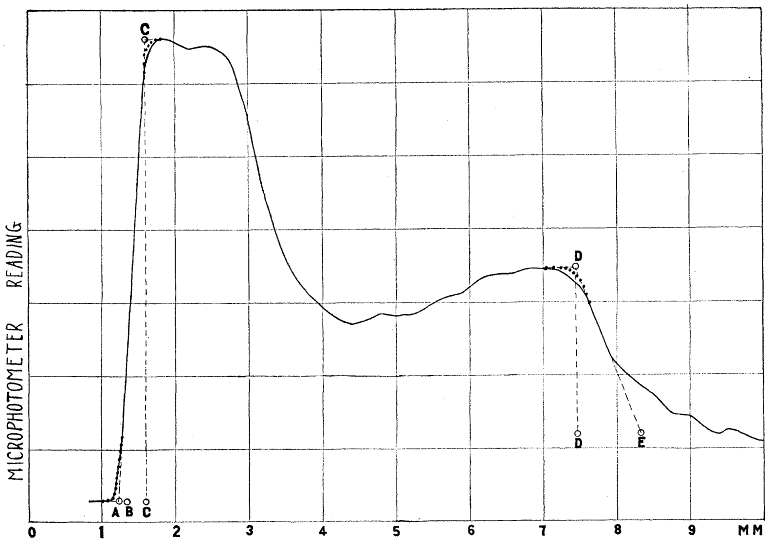

Fig. 2. *Sample microphotometer curve taken from a plate for ethylene glycol.* The broad, double hump, at the left of the figure is due to the direct beam. The right hand portion of this hump is due to the $K\alpha_2$ line which has entirely missed the mirror and the left hand portion of this hump is due to that part of the $K\alpha_1$ line which also missed the mirror. At the extreme left of the hump, however, is a region affected by that part of the $K\alpha_1$ line which was progressively cut out by the mirror as it was rotated. The part of the curve between the abscissas 6 and 8 mm, contains a hump which rises gently on the left and then falls off abruptly on the right, with a straight line as a portion of its right slope. Somewhere within the region of this hump lies the point corresponding to the critical edge. Microphotometer readings were taken every tenth of a millimeter.

From the geometry of the figure we have the relation, $CD = 2\ AB \cos\theta$. The distance AB, measured on a dividing engine, was 0.0142 cm. The value for θ for the $K\alpha_1$ line of copper is given by Siegbahn,[5] as $14° 41' 46''$. This leads to a value of 0.0137 cm for CD.

Suppose the mirror to be placed in the path of this parallel beam of width CD (as in Fig. 4) in such a way that the ray KL is reflected at the critical angle from the very edge of the mirror. In like fashion all other rays in the

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[5] Siegbahn, The Spectroscopy of X-rays. Oxford University Press (1925).

beam between the limiting rays KL and HJ will be reflected at the critical angle. The width of the beam KH will be less than that of CD, for the width of KH, calculated from the length of the mirror (4 cm) and the critical angle (for ethylene glycol, $\theta_c = 9' \, 34''$) is about 0.011 cm, which is less than the value of CD given above. Thus the mirror will always be reflecting over its entire length as long as it is not too near either edge of the $K\alpha_1$ line.

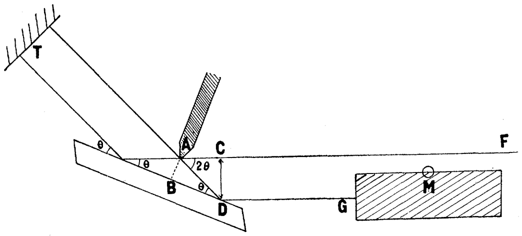

Fig. 3. *Diagram showing a beam from the anticathode T, crystal wedge slit and the mirror M.* The width of the spectral line is assumed zero and the crystal perfect.

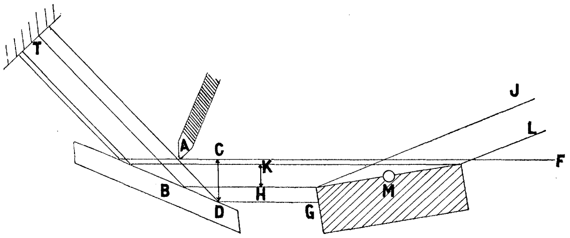

Fig. 4. *Diagram showing the beam KH limited by the mirror when at the critical angle.* The width of the spectral line is assumed zero and the crystal perfect.

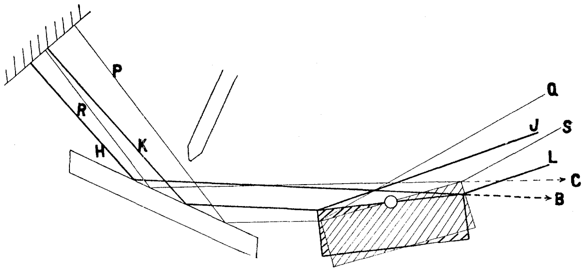

Fig. 5. *Diagram showing (1) the beam of shortest wave-length limited by the rays HL and KJ, and (2) the beam of longest wave-length limited by the rays PQ and RS, reflected from the mirror in each case when the mirror is set at the critical angle.*

When the mirror is parallel to the beam, the width of the portion of the beam passing by the mirror is $CK+(1/2)KH$, or in the case of ethylene glycol, equal to $CK+0.0056$ cm, tending to give an image in the direct beam 0.0056 cm wider than when the mirror is at the critical angle. However, as the mirror is rotated from its parallel position to that of the critical angle, a portion of the direct beam will be progressively cut out, being reflected from the mirror. The result is that the edge of the direct beam is no longer sharp but shades off over a region 0.0056 cm wide. (AC Fig. 2).

It has been assumed so far that the radiation was strictly monochromatic. It is well-known that x-ray lines reflected from crystals, have finite widths due to the real width of the line, the finite resolving power and imperfection of the crystal, nonhomogeneity of the beam, etc. A. H. Compton[6] has found an angular width for the tungsten lines of about half a minute of arc. A measurement of the width of the copper $K\alpha_1$ line from a photograph taken with the mirror out of the way, resulted in a width at its half maximum of slightly more than two minutes. This larger value is to be expected for the longer wave-length copper line.

If we now consider the beam incident on the mirror as no longer composed of a single wave-length but having a definite, though small, range of wave-lengths, we may divide this range into a large number of beams, each of a single wave-length, and reflected at a slightly different angle from the crystal. In Fig. 5, the beam HK is the one of shortest wave-length which will be reflected from the mirror when it is set at the critical angle. The beam PR is the corresponding one of longest wave-length. Before the mirror has been rotated to the position for total reflection, the ray HL will pass by the mirror and reach the photographic plate at B, Fig. 2, as a part of the direct beam. The region between A and B will be reached by the rays in the beam HK which pass by the mirror as it is rotated from its horizontal position to the critical angle. This is only strictly true if the ray KL is limited by the wedge slit, as otherwise, rays of slightly shorter wave-length can pass the edge of the mirror.

Similarly, for the beam PR (Fig. 5), the ray RS will reach the point C (Fig. 2) before the mirror has rotated to the critical angle and the other rays in the beam which are able to miss the mirror will reach points a short distance to the left of C. Thus as the mirror is rotated the region ABC will be reached by rays which are progressively cut out. The point B then corresponds to the ray HL of shortest wave-length and is reflected at the very edge of the mirror when it is set at the critical angle for this ray.

The critical point for the ray HL will lie to the left of the critical points for the other rays of longer wave-length. There are two reasons for this, first, because the angle θ at the calcite crystal is smaller, and then, because the critical angle increases with the square of the wave-length. Thus the critical angle, will correspond to the point D, in Fig. 2, at the peak of the curve at the critical edge.

The reason that the curve falls off with a constant slope for some distance beyond the critical edge for the ray CF of shortest wave-length, is that the critical points for the rays of longer wave-length and the rays in other parts of the same monochromatic beam, fall farther and farther out beyond the one we are considering, and hence carry over some reflection beyond the first critical point. In fact the horizontal projection of the straight portion at the critical edge is approximately twice the horizontal projection of the straight portion at the left edge of the direct beam. This results from the

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[6] A. H. Compton, Phys. Rev. **19**, 68 (1922).

fact that the reflected beam is rotated through twice the angle through which the mirror is rotated.

In order to save exposure time, the procedure usually was first to place the mirror parallel with the beam and then rotate it through a small angle in order to obtain the direct beam record on the plate. Next the mirror was turned to within a couple of minutes of arc of the critical angle and the slow rotation commenced. In consequence of this, there should appear on the plate, between the direct beam and the region in which the critical angle appears, a space which is unaffected. However, in Fig. 2, it can be observed that the minimum ordinate for the reflected radiation is somewhat greater than that for the left edge of the direct beam. This is due largely to the fact that the film of liquid was not strictly uniform. It is to be noted, however, that the curves obtained for the glass mirror, whose surface was very smooth, show the minimum ordinate for both the direct and reflected beam to be about the same. For the liquids in which difficulty was experienced in maintaining a uniform film, the difference in the minimum ordinate for the direct and reflected beam was greatest. This, however, does not obscure the critical edge since the bulk of the radiation is regularly reflected in the manner described earlier in this paper. The principal disadvantage lies in the reduction in intensity of the reflected beam and consequent necessity for longer exposure times.

TABLE I. *Summary of results.*

Substance	Formula	Mol. Wt.	Density gm/cm^3	Distance *BD* (cms)	θ Expt.	δ Expt. $\times 10^{-6}$	δ Calc. $\times 10^{-6}$
Water	H_2O	18.016	0.998	0.58 ± .02	9′20″	3.69 ± .20	3.53
Butyl Phthalate	$C_{16}H_{22}O_4$	278.22	1.167	0.569 ± .008	9′11″	3.57 ± .08	3.57
Ethylene Glycol	$C_2H_6O_2$	62.05	1.115	0.608 ± .009	9′49″	4.08 ± .09	3.88
Triethanolamine	$C_6H_{15}O_3N$	149.13	1.12	0.590 ± .007	9′33″	3.86 ± .09	3.91
Glycerine	$C_3H_8O_3$	92.06	1.26	0.632 ± .009	10′12″	4.41 ± .10	4.34
Glass*				0.861 ± .003	13′55″	8.19 ± .03	?

* The composition of the glass mirror was not definitely known.

Of the liquids measured by Kellerman, referred to earlier in the paper, glycerine was the only one also measured here. He also used the wave-length $\lambda=1.537$A.U. and obtained for glycerine, $\delta=3.8\times 10^{-6}$, which is somewhat lower than the value obtained here.

It seems reasonable to assume that the point *B* in Fig. 2, corresponds to the position reached by the ray which is later reflected at the critical angle to *D*. The distance *AB*, calculated from the theoretical value of the critical angle and the length of the mirror, varied from 0.0053 cm for water to 0.0059 cm for glycerine. Since the points *B* and *D* correspond to the direct and reflected ray at the edge of the mirror, the distance from the photographic plate was measured to the edge of the mirror. This measurement was made by placing a long steel rod against the plate and making a scratch on the rod at the point corresponding to the edge of the mirror. The rod was then measured on a good metal metric scale, obtaining 108.42 cm as the distance. The distance measured on the microphotograms have a probable error of about 0.08 mm for all the liquids except water, for which the plates obtained were not as satisfactory as in the case of the other less volatile liquids. The experimental values for δ were calculated from the distance *BD* measured on the plate by means of the microphotometer curves, from five to eight curves being obtained for different positions on each plate. The error is probably less than two percent. It is further seen, in the following table, that the values calculated from the Drude-Lorentz dispersion formula give values for δ in agreement within the experimental error.

CONCLUSION

The method of total reflection for measuring the refractive index for x-rays gives values for liquids comparable in accuracy with those for solids. The method is applicable to any liquid which can be kept in the form of a film on a smooth solid surface. By modifying the apparatus so as to keep the solid mirror at a lower temperature than the surrounding atmosphere, it should be possible to extend this method to more highly volatile liquids.

The author wishes to acknowledge his indebtedness to Dr. T. H. Osgood for his guidance in this problem, also to Dr. A. G. Worthing and Dr. E. Hutchisson for their interest in the preparation of this paper.