

analysis by C. J. Humphreys of the visible and near ultraviolet data, carried out simultaneously with the present investigation, made possible a rather complete identification of these odd terms. The exact description of many of the 128 lines classified in Table III was made possible by the very generous cooperation of Dr. Humphreys. All of the low terms of Xe III have been located and many intersystem combinations have been found. The consolidated term table for Xe III will be published by Humphreys elsewhere<sup>11</sup>

<sup>11</sup> C. J. Humphreys, Bur. Standards J. Research (in press).

together with his analysis of the longer wavelength portion of this spectrum. The ionization potential is 32.0 volts.

The experimental part of this work was made possible by a grant to Dr. K. T. Compton from the Carnegie Institution of Washington. Some of the technical assistance necessary in plate measurement and reduction has been provided by a grant to the writer from the Permanent Science Fund of the American Academy of Arts and Sciences. The careful work of Dr. Carol A. Rieke in this capacity is gratefully acknowledged.

### The Christiansen Filter Effect in the Infrared

R. BOWLING BARNES AND LYMAN G. BONNER,\* *Palmer Physical Laboratory, Princeton University*

(Received March 23, 1936)

A brief discussion is given of the history, construction, and applications of Christiansen light filters for use in the visible and ultraviolet regions of the spectrum. These filters, which consist of a powder of some crystalline or glassy substance suspended in a transparent medium, depend for their action upon the equality of refractive indices of powder and medium for some one wave-length of light. The theory of the effect in the infrared is briefly discussed, and methods are given for preparing and mounting the powders. The principal factors affecting the shape and size of the transmission peak, namely, the angle at which the two dispersion curves cross, the size of

particle used, the thickness of the powder layer, and the solid angle included by the light striking and leaving the filter are discussed. Experimental results include transmission curves and wave-lengths of the transmission maxima for the following crystalline powders dispersed in air: quartz, MgO, calcite, marble, CaSO<sub>4</sub>, eleven alkali halides, and three monovalent thallium halides. Curves are also given for quartz, MgO, and NaCl dispersed in organic liquids. The transmission peaks measured lie between 3 $\mu$  and 90 $\mu$ . In conclusion are discussed possible applications of the Christiansen effect in the infrared.

WITHIN the past few years, several papers have appeared in the literature in which various uses of Christiansen light filters have been discussed. One commercial company has advertised in the *Review of Scientific Instruments* that it can furnish various crystals in a powdered form suitable for use in the construction of these filters. In Germany the firm of Schott and Genossen-Jena offers for sale such filters under the name "monochromatic universal filters." Although the Christiansen filter effect has been known since 1884 it has lain dormant until the appearance of these papers except for brief descriptions which have appeared in each

edition of Wood's *Physical Optics*. Even today the effect as such is not known to the average physicist. It is the purpose of the present paper to review the subject very briefly and then to describe the construction and several uses of such filters in the near and far-infrared. It will be shown that these filters may be used (1) to produce monochromatic beams of infrared radiation, (2) to eliminate the undesired short wavelength radiation in a grating spectrometer, (3) to determine the refractive indices of various fluids in the near-infrared.

If curve *a* of Fig. 1 represents the dispersion curve of a crystal, and curve *b* that of a given transparent medium, then a suspension of small

\* National Research Fellow.

particles of this crystal in the medium should possess a maximum of transmission at the wave-length corresponding to the point of intersection of the two curves *a* and *b*. This wave-length we shall designate as  $\lambda_{\text{Chr}}$ . The reason for this transmission obviously lies in the fact that only at this wave-length is the sample optically homogeneous. Light of this wave-length passes through the cell unaffected, while light of all other wave-lengths suffers refraction at every particle-medium interface and is scattered strongly. In the case that  $\lambda_{\text{Chr}}$  lies in the visible region of the spectrum, directly transmitted light has the color corresponding to this wave-length. The direct image is surrounded by a haze having the color complimentary to  $\lambda_{\text{Chr}}$ .

C. Christiansen<sup>1</sup> first noticed this effect in 1884 while studying particle-liquid mixtures in an attempt to determine the refractive indices of various crystals. He explained the effect correctly and showed that light of practically any color could be obtained by varying the curve *b* of Fig. 1 so that it crossed *a* at the desired wave-length. He further pointed out that since the two curves *a* and *b* respond differently to changes in temperature, the point of intersection, would shift if the temperature of the cell were varied.

In 1885 Lord Rayleigh<sup>2</sup> published a paper entitled "On an Improved Apparatus for Christiansen's Experiment." From then until 1927 the filter effect was unused. At that time

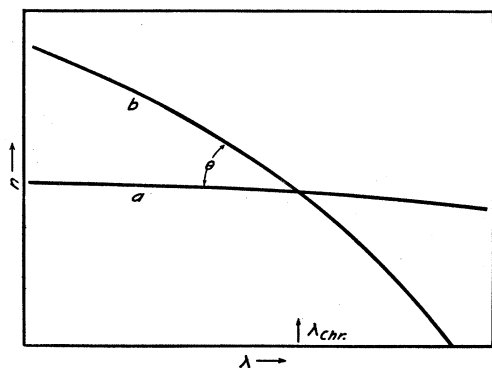


FIG. 1. Curve *a* represents the dispersion curve of a crystal, and *b* that of a transparent medium. The two intersect at an angle  $\theta$  at the point  $\lambda = \lambda_{\text{Chr}}$ .

<sup>1</sup> C. Christiansen, *Ann. d. Physik* **23**, 298 (1884); **24**, 439 (1885).

<sup>2</sup> Lord Rayleigh, *Phil. Mag.* **20**, 358 (1885).

Weigert<sup>3</sup> and his co-workers published the first of a series of papers in which attention was directed to the fact that with proper temperature control and regulation such filters could be used quantitatively for the production of monochromatic light.

By correct choice of the substances involved,  $\lambda_{\text{Chr}}$  may be shifted from the visible to the ultraviolet or infrared regions of the spectrum. Christiansen, Staude, and others had previously suggested this possibility, and in 1932 Kohn and von Fragstein<sup>4</sup> published an account of the construction of a Christiansen filter for the ultraviolet. By using particles of fused quartz and a mixture of 56 percent benzol and 44 percent ethyl alcohol they obtained suitable filters having  $\lambda_{\text{Chr}} = 3600\text{A}$  at  $20^\circ\text{C}$ . With filters of this type they were able to isolate any desired region from  $3000\text{A}$  on up into the visible. Individual lines of the mercury spectrum could be filtered successfully. These filters were also used by von Fragstein in his work on the determination of the reflection power of metals in the visible and ultraviolet regions.

In a still more recent paper, McAlister<sup>5</sup> has presented a rather thorough account of "The Christiansen Light Filter: Its Advantages and Limitations." Practical suggestions are given concerning the construction of a filter which may be used in an intense beam of light for the production of monochromatic light. The filters were made of borosilicate crown glass and a solution of carbon disulphide in benzene at  $20^\circ\text{C}$ . A series of filters covering the entire visible range, each having a half-width of about 100 to  $200\text{A}$  were prepared. Fig. 2 is taken from McAlister's paper. Since a complete description is given by McAlister of the various choices of materials, particle size, etc., which are most advantageous for filters designed for use in this part of the spectrum, no further discussion of these points will be presented in this paper.

Other recent papers on the Christiansen effect include one by Abbot<sup>6</sup> on the applications of

<sup>3</sup> F. Weigert and H. Staude, *Zeits. f. physik. Chemie* **130**, 607 (1927); F. Weigert, H. Staude and E. Elvegard, *ibid.* **B2**, 149 (1929); F. Weigert and J. Shidei, *ibid.* **B9**, 329 (1930).

<sup>4</sup> H. Kohn and K. von Fragstein, *Physik. Zeits.* **33**, 929 (1932).

<sup>5</sup> E. D. McAlister, *Smithsonian Misc. Collections*, Vol. 93, No. 7 (1935).

<sup>6</sup> C. G. Abbot, *J. Opt. Soc. Am.* **25**, 42 (1935).

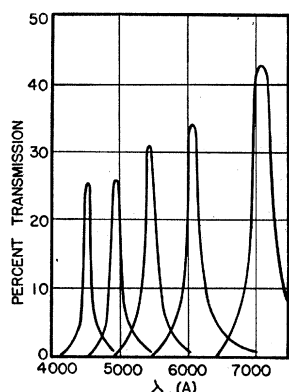


FIG. 2. Transmission curves of a series of five filters consisting of borosilicate crown glass particles immersed in mixtures of carbon disulphide and benzene (McAlister).

Christiansen filters to stellar energy spectra and one by Denmark and Cady<sup>7</sup> on the optimum grain size for these filters for use in the visible spectrum.

In order to demonstrate the principles involved in the construction of Christiansen filters the authors have found the following procedure both simple and expedient. A glass absorption cell having plane parallel windows is first filled with powdered fluorite ( $\text{CaF}_2$ ) whose refractive index  $n_D = 1.434$ . Care should be taken to insure that the particles are clean and dry. Benzene, whose refractive index  $n_D = 1.501$ , is now poured into the cell until the latter is roughly half full. Again powdered fluorite is added to refill the cell. To this ethyl-alcohol  $n_D = 1.362$  is added and the cell thoroughly shaken. This addition is continued until the light transmitted by the cell takes on a reddish hue. Each additional drop of alcohol decreases the refractive index of the liquid causing  $\lambda_{\text{Chr}}$  to shift towards shorter wave-lengths. Sufficient alcohol should be added to cause the transmitted image of a lamp filament to be clear yellow. The scattered light will be the complementary color to  $\lambda_{\text{Chr}}$ .

It is easy to see in the case of our fluorite-benzene-alcohol cell that the value of  $\lambda_{\text{Chr}}$  is a function of the temperature. If the cell be cooled in a stream of tap water,  $\lambda_{\text{Chr}}$  will shift to a deep red. Upon returning to room temperature  $\lambda_{\text{Chr}}$  will again be yellow. Placing the cell over a

steam radiator will cause  $\lambda_{\text{Chr}}$  to be blue or violet. A temperature either too high or too low will cause the color to disappear  $\lambda_{\text{Chr}}$  being either in the ultraviolet or the infrared.

#### THE CHRISTIANSEN FILTER EFFECT IN THE INFRARED

Many investigators<sup>8</sup> have studied the transmission of various powdered crystals mounted in such a way that the surrounding medium was air. These powders have invariably shown a rather high transmission peak on the short wave-length side of the characteristic frequency. No attention was paid to this abnormally high transmission although the curiosity of the investigators should have been stirred by the fact that a layer of powder shows a trend just opposite to that shown by a thin single crystal of the same material. Fig. 3 shows the general type of curve found in the literature. Pfund showed that, in case the average particle size was larger than  $\lambda_0$ , the wave-length of the characteristic absorption, this high transmission peak occurred at the wave-length at which the reflection of the crystal was a minimum, and explained the effect on this basis. The reflection power of a crystal is given, however, by the formula

$$R = \frac{[(n-1)^2 + n^2\kappa^2]}{[(n+1)^2 + n^2\kappa^2]}.$$

At a wave-length well removed from  $\lambda_0$ , since  $\kappa$  is nearly equal to zero,  $R = (n-1)^2/(n+1)^2$ . We

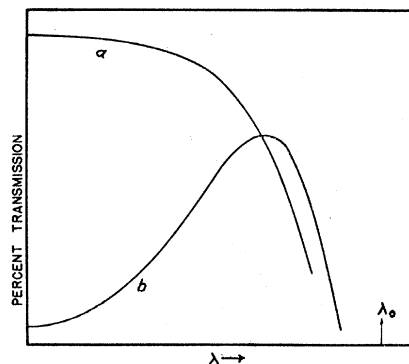


FIG. 3. Typical transmission curves of plate and powder. *a* is the transmission of a crystalline plate and *b* that of a powder of the same substance.

<sup>8</sup> A. H. Pfund, *J. Opt. Soc. Am.* **23**, 375 (1933); A. H. Pfund and S. Silverman, *Phys. Rev.* **39**, 64 (1932); S. Tolksdorf, *Ber. Diss.* 1928; O. Reinkober, *Zeits. f. Physik* **3**, 1 (1920).

<sup>7</sup> H. S. Denmark and W. M. Cady, *J. Opt. Soc. Am.* **25**, 330 (1935).

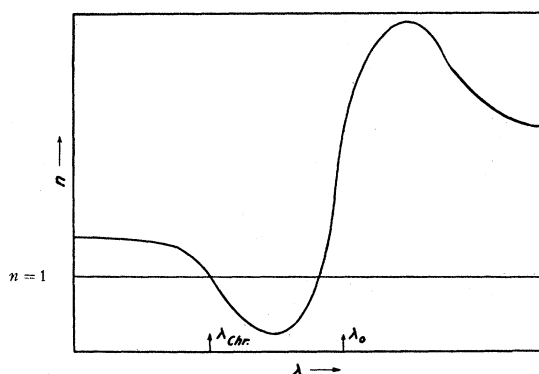


FIG. 4. Typical dispersion curve of a crystal for wave-lengths in the neighborhood of  $\lambda_0$ . At  $\lambda_{Chr}$  the index of the crystal is equal to that of air.

see then that this transmission peak also corresponds with the wave-length at which the refractive index of the crystal is unity, hence that at this point the dispersion curve of the crystal crosses that of air. It was pointed out by one of the authors<sup>9</sup> that this abnormal transmission is to be explained by a lack of refraction and not of reflection, and is in reality a true Christiansen filter effect. In Fig. 4 is shown a characteristic dispersion curve for a crystal in the neighborhood of  $\lambda_0$ . In the case of particles even a thin layer will be opaque due to refraction over most of the range. At some point, however, the indices of crystal and medium, which is air in this case, cross as is shown in the figure and a rather high transmission results.

#### PREPARATION OF FILTERS

The powder to be studied is usually dusted onto some material transparent in the desired wave-length region. Rocksalt plates may be used for the base material in the near infrared, while for wave-lengths  $>30\mu$  thin sheets of paraffin ( $\sim 0.5$  mm in thickness) have been found quite satisfactory. Nitrocellulose films may be used over the whole infrared although some difficulties arise as a result of the characteristic absorption of the nitrocellulose, and trouble is frequently experienced in making the powder stick to the

film. This last difficulty may sometimes be avoided by making a thick suspension of the powder in water, pouring this onto the film, and allowing the water to evaporate. In the near infrared a second rocksalt plate may be put over the particles if necessary, while in the case of paraffin as base material the powder may be pressed gently into the surface of the paraffin.

As will be shown later, the size and degree of separation of the powder is important in determining the characteristics of the Christiansen peak. For best results the particles should be all larger than  $\lambda_{Chr}$ , to increase the short wave opacity. On the other hand, if they are too large the true absorption of the crystal will cut down the size of the transmission peak. The particles should therefore be only slightly larger than  $\lambda_{Chr}$  in diameter, and the separation should be sharp. In the experience of the authors, this separation may be most easily performed in one of two ways.

If the particles are insoluble in water they may be separated by allowing them to fall through a known height of water. Stoke's law, assuming spherical particles, may be used to calculate the velocity of fall for the various particle sizes desired. The procedure is simple. The material is ground to as fine a powder as possible in an agate mortar and then placed in a cylinder of water high enough to give a convenient time of fall. After a thorough shaking they are allowed to settle for a time equal to that calculated for particles slightly larger than those desired to fall the full height of the vessel. At the end of this time the water and smaller particles are quickly decanted and the process repeated several times on the remaining powder. The particles that have been poured off are now taken and the time of fall increased to that for particles slightly smaller than those desired. The decantation process is continued until a sharp line of demarcation is seen between powder and clear liquid during the time of fall. A check with a microscope has shown in several cases that the diameter calculated, even with the assumption of spherical particles, was not far different from that obtained. Samples have been prepared in which the diameter ranged from  $10\mu$  to  $12\mu$ ,  $12\mu$  to  $15\mu$ , etc. For quartz particles in water the times to fall one inch for  $1\mu$  and  $100\mu$  particles are 28,200 and 2.82 seconds, respectively.

<sup>9</sup> R. B. Barnes, R. R. Brattain and R. S. Firestone, *Phys. Rev.* **47**, 792 (1935). Since in regions removed from the characteristic frequency the reflection power of the crystals studied is usually about five percent, reflection losses alone could not account for the opacity found for powder layers only two or three particles thick.

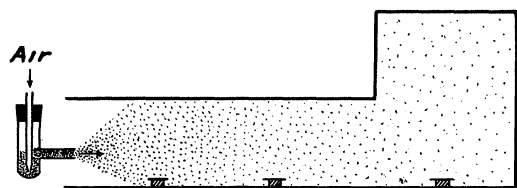


FIG. 5. An apparatus for separating powders according to particle size by an air stream method.

Particles soluble in water may be separated by the same method if a suitable liquid can be found. Otherwise the separation may be effected by allowing them to settle out of an air blast under suitable conditions. In Fig. 5 is diagrammed a method which we have found convenient in separating some of the alkali halides. A steady stream of air is blown into the tube through the nozzle. Particles are carried out of the jet by the air stream and enter the box, which serves to reduce cross currents. Receptacles placed at various points catch particles of different sizes, the smallest landing the greatest distance from the jet. The separation may, of course, be regulated also by the strength of the air blast. The separation here is not as sharp as that obtained by the other method, and the necessary conditions must be determined empirically for each size and variety of particle, but even so separations satisfactory for most purposes may be made.

#### FACTORS DETERMINING THE CHARACTERISTICS OF THE PEAKS

There are, in all probability, three principal factors regulating the sharpness and height of these Christiansen transmission peaks and these will be taken up in order.

(1) The width of the peak will obviously be some function of the angle ( $\theta$  of Fig. 1) at which the dispersion curve of the crystal crosses that of the medium. If the angle is small refraction at the surface becomes small for a wave-length appreciably removed from  $\lambda_{\text{Chr}}$  and the peak is broad, while for a large angle the peak will tend to be sharper.

(2) Particle size, as was mentioned above, and the thickness of the powder layer play quite important parts in determining the characteristics of the transmission peak. In case any large

fraction of the particles are of diameter  $\rho \ll \lambda_{\text{Chr}}$ , the layer will not be completely opaque for  $\lambda < \lambda_{\text{Chr}}$  due to a simple powder effect.<sup>10</sup> On the other hand since, for the case of particles in air,  $\lambda_{\text{Chr}}$  is always in the neighborhood of and on the short wave side of  $\lambda_0$ , the true absorption of the crystal is appreciable. If, then, any large fraction of the particles are of diameter  $\rho \gg \lambda_{\text{Chr}}$  this true absorption may reduce the percentage transmission at the center of the peak considerably. For the same reason the thickness of the powder layer is important. Microphotographs of filters which we have used have shown that a layer only 2 or 3 particles deep will be quite opaque in the region  $\lambda < \lambda_{\text{Chr}}$ .

(3) Since the action of these filters depends, not on absorption of the undesired light, but simply on scattering, the efficacy of the filter will be in part determined by the angle at which the light strikes the powder layer, and by the solid angle included in the observation method. The maximum efficiency will of course be obtained if only light emerging perpendicular to the face of the filter is used. We have found the filters to be quite satisfactory, however, even when used at the focus of an optical system of aperture  $f : 2$ . Some improvement may be obtained in such a case by using two filters spaced such a distance apart that the light scattered by the first is well removed from the light beam before it strikes the second.

#### EXPERIMENTAL RESULTS

##### Apparatus

Two types of apparatus were used in performing the experiments reported in this paper. For the region 1–15 $\mu$  a rocksalt prism spectrometer was used. In this region were investigated principally the Christiansen peaks resulting from anomalous dispersion in the neighborhood of the inner vibration frequencies of complex crystals, and also the peaks for crystals embedded in media other than air. For investigation between 30 and 130 $\mu$  a wire grating spectrometer of the type described by Barnes<sup>11</sup> was used. The spacing constant of the grating was 0.4 mm, but

<sup>10</sup> A. H. Pfund, Phys. Rev. **36**, 71 (1930).

<sup>11</sup> R. B. Barnes, Rev. Sci. Inst. **5**, 237 (1934).

since in order to facilitate measurements wide slits were used the full resolution of the spectrometer was never obtained. In this long wave region were found principally the peaks due to lattice vibrations of the alkali halide crystals. In all cases percentage transmission curves were obtained by taking readings, at each wavelength, of the energy with the sample in, and out of, the light beam. The samples were placed at the focus of a strongly converging beam.

## Results

(1) *NaCl*. Of the systems investigated in the present work, the one about which the most data from other sources have accumulated, and which gives complete confirmation of the theory of the Christiansen effect is that of NaCl powder immersed in  $\text{CS}_2$ . The peak for rocksalt in air should occur at  $32\mu$ , as is shown both by the dispersion and reflection curves, but because of experimental difficulties we were unable to verify this. The peak for the NaCl- $\text{CS}_2$  system, however, falls in a readily accessible region, and in one in which the dispersion curves of both crystal and medium are well known. The dispersion of  $\text{CS}_2$  has recently been determined by Pfund,<sup>12</sup> while the values for rocksalt have long

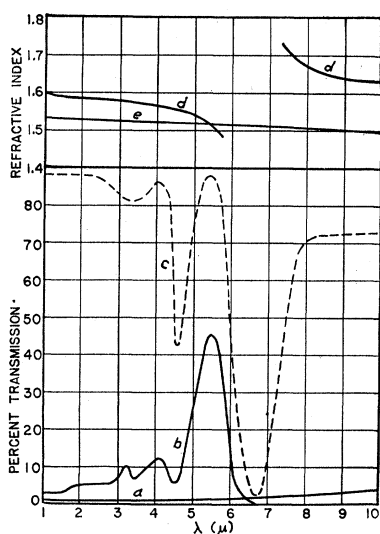


FIG. 6. NaCl powder immersed in  $\text{CS}_2$ . The transmission curves are *a*, the dry powder; *b*, the powder wet with  $\text{CS}_2$ ; *c*, pure  $\text{CS}_2$ . At the top are shown the dispersion curves of *d*,  $\text{CS}_2$ , and *e*, NaCl, showing that they intersect at  $\lambda = \lambda_{\text{Chr}}$ .

<sup>12</sup> A. H. Pfund, J. Opt. Soc. Am. 25, 351 (1935).

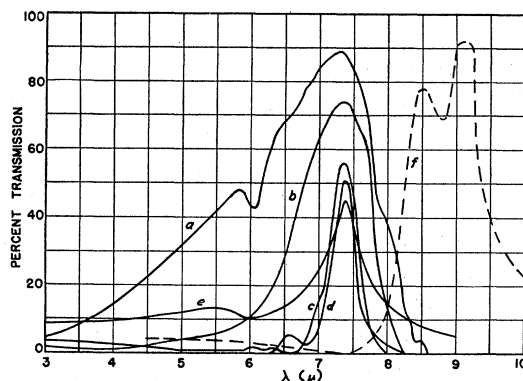


FIG. 7. Effect of particle size on the quartz Christiansen peak. The curves are for the following sizes: *a*, 5-10 $\mu$ ; *b*, 10-20 $\mu$ ; *c*, 30-40 $\mu$ ; *d*, 50-60 $\mu$ ; *e*, unseparated powder. Curve *f* shows the reflection power of a quartz plate.

been known from Paschen's work on the dispersion of a prism of the material. The cell for this investigation was made by putting a thin layer of finely powdered NaCl between rocksalt plates, sealing three of the edges with water glass, and flowing  $\text{CS}_2$  into the space between. Fig. 6 shows the curve obtained. *a* is for the dry NaCl powder, *b* for the powder wet with  $\text{CS}_2$ , and *c* is the transmission curve of pure  $\text{CS}_2$ , taken from Pfund. At the top are shown the dispersion curves for the two materials, and it may be seen that they cross exactly at the wavelength,  $5.45\mu$ , at which the Christiansen peak occurs.

(2) *Quartz*. Powdered quartz was available in great quantity, and since the material is quite insoluble in water and so could be readily separated by the rate of fall method, most of the experiments on the effect of particle size have been made on this crystal. One of the fundamental vibrations of quartz, which is probably an inner vibration of the  $\text{SiO}_4$  tetrahedron occurring in the structure, lies at about  $9\mu$ . The Christiansen peak, expected just on the short wave side of this falls experimentally, for the powder in air, at about  $7.35\mu$ . Fig. 7 shows the transmission curves for approximately equal layers of quartz particles of various thicknesses, mounted on nitrocellulose films. The small irregularities on the sides of the curves, which become particularly marked for the 5-10 $\mu$  particles, result from the true absorption of the nitrocellulose. The effect of particle size in narrowing and decreasing the height of the peak

is quite well shown by these curves. A curve is also shown for quartz particles which had undergone no separation whatsoever, and it may be seen from this that even a random selection of particles shows the Christiansen effect quite markedly. The dotted reflection curve shows that the wave-length of the Christiansen peak agrees with that of the reflection minimum. In Fig. 8 the effect of immersion in  $\text{CCl}_4$  and in a 50 percent by volume mixture of  $\text{CCl}_4$  and  $\text{CS}_2$  on the quartz peak is shown. The positions of these peaks agree well with the known dispersion curves for the substances involved.

(3) *MgO*. Fig. 9 shows the positions of the Christiansen peaks for unseparated  $\text{MgO}$  powder in air and in  $\text{CCl}_4$ . The dispersion curve of  $\text{CCl}_4$  was also obtained by Pfund,<sup>12</sup> and so the establishment of these two values,  $n=1$  at  $12.2\mu$ , 1.43 at  $9.0\mu$ , together with previously known

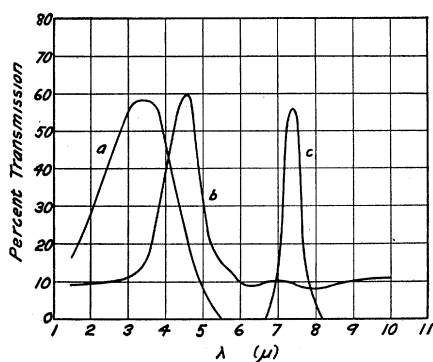


FIG. 8. Shift of the Christiansen peak for quartz powder in liquids. *a*, quartz in a 50 percent by volume mixture of  $\text{CS}_2$  and  $\text{CCl}_4$ ; *b*, quartz in pure  $\text{CCl}_4$ ; *c*, quartz in air.

TABLE I. Positions of the Christiansen peaks for various crystals.

CRYSTAL	WAVE-LENGTH (in $\mu$ )		
	CHRISTIENSEN	RESTRAHLEN	FUNDAMENTAL
LiF	11.2	26	32.6
NaCl	(32)	52.0	61.1
NaBr	37		74.7
NaI	49		85.5
KCl	37	63.4	70.7
KBr	52	81.5	88.3
KI	64	94	102.0
RbCl	45	73.8	84.8
RbBr	65		114.0
RbI	73		129.5
CsCl	50		102.0
CsBr	60		134.0
TlCl	45	91.9	117.0
TlBr	64	117	
TlI	90	151.8	

values at shorter wave-lengths, permit a rough dispersion curve to be drawn for  $\text{MgO}$ . This curve also is shown in the figure.

(4) *Carbonates*. From reflection measurements it is known that all crystalline carbonates have three fundamental frequencies, characteristic of the  $\text{CO}_3^{2-}$  radical, in the near infrared. Experiments were performed both on powdered calcite and on marble and the results, though not conclusive, indicated the presence of two peaks of  $6.2$  and  $11.1\mu$  with possibly a third at about  $9\mu$ .

(5) *Sulfates*. Only one sulfate was investigated, namely, plaster of paris ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ). A small but definite transmission peak, characteristic of the sulfate radical, was located at  $7.9\mu$ .

(6) *Alkali- and thallium-halides*. The Christiansen peaks in air were located for a total of

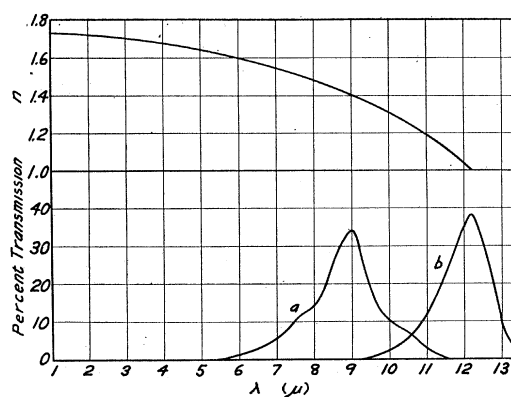


FIG. 9. *a*,  $\text{MgO}$  powder in  $\text{CCl}_4$ , *b*,  $\text{MgO}$  powder in air. At the top is shown a rough dispersion curve for  $\text{MgO}$  as determined by these two points and by measurements in the visible spectrum.

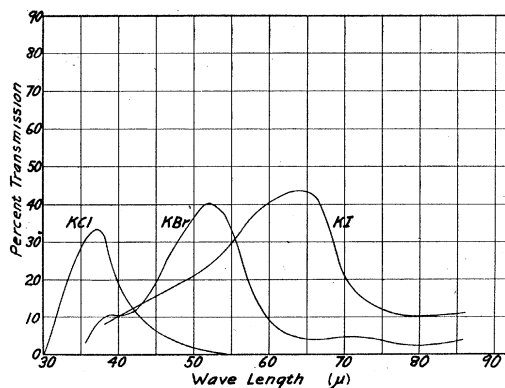


FIG. 10. Curves showing the Christiansen transmission peaks for powdered  $\text{KCl}$ ,  $\text{KBr}$ , and  $\text{KI}$ . These curves are typical of those obtained for the alkali halides.

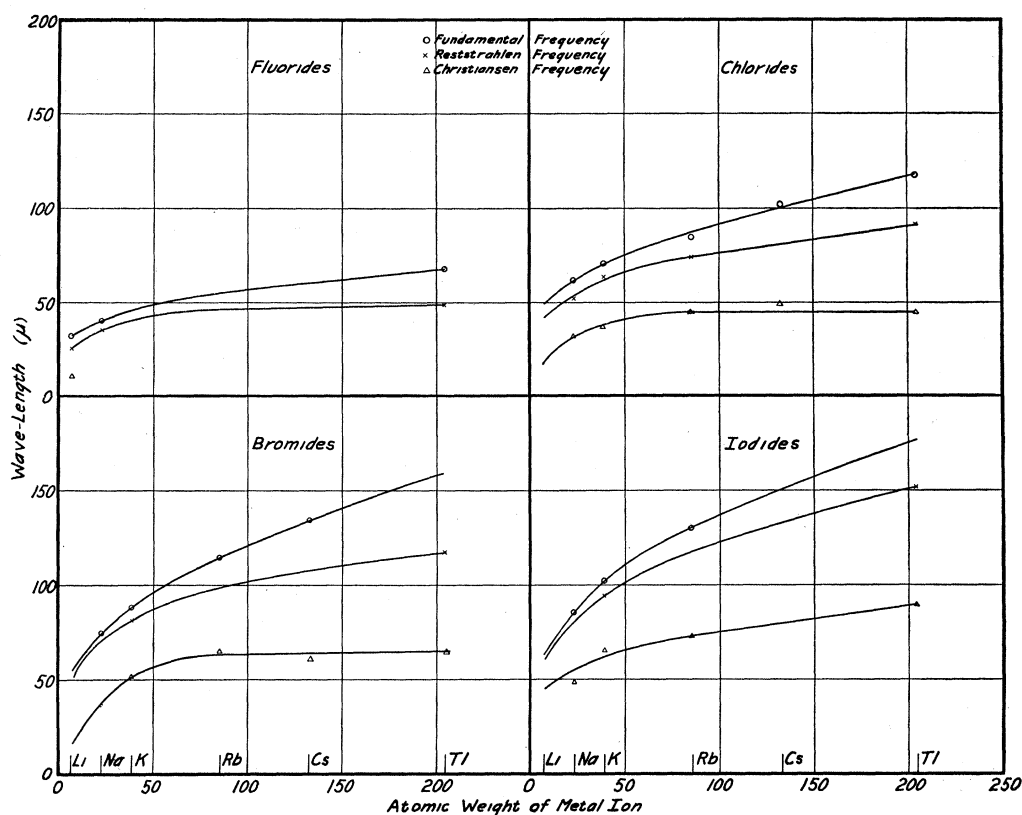


FIG. 11. Here the wave-lengths of the Christiansen, reststrahlen, and fundamental frequencies are plotted, for each halogen separately, as a function of the atomic weight of the metal ion.

eleven alkali halides, and also for three monovalent thallium halides, which also crystallize in a cubic lattice. With the exception of that for LiF these peaks all fell in the region of the grating spectrometer and so were investigated as unseparated powders mounted on 0.5 mm paraffin. Paraffin of this thickness has quite a high transmission in the infrared beyond  $30\mu$ . Crystals of this type possess only one characteristic frequency, and hence only one Christiansen peak. Table I gives the positions of the peaks for all the crystals of this type investigated. Included in the table for purposes of comparison, are the wave-lengths of the fundamental frequencies and reststrahlen frequencies for the same crystals, as given by Barnes.<sup>13</sup> Fig. 10 gives the actual measured transmissions for the powders of KCl, KBr, and KI, while in Fig. 11 the three types of frequency, Christiansen,

reststrahlen, and fundamental are plotted, for each halogen separately, as a function of the atomic weight of the metal ion.

#### USES OF THE CHRISTIANSEN EFFECT IN THE INFRARED

Below we shall discuss briefly several interesting and important applications of the Christiansen effect in connection with infrared spectroscopy.

(1) In the use of grating spectrometers one of the most difficult problems that arises is that of the elimination of overlapping orders. With most gratings, in order to make measurements at a wave-length  $\lambda$  all energy of wave-length less than  $\lambda/2$  must be removed. Many devices such as selective sources and receivers, filters, prism monochromators, etc., have been used. In a good many cases the desired effect may be attained more simply by the use of a suitable Christiansen

<sup>13</sup> R. B. Barnes, Zeits. f. Physik 75, 723 (1932).



filter. In the near infrared powders of quartz, LiF, MgO, and doubtless many other crystals have sharp and conveniently located peaks. In the far infrared the alkali halides form a series, together with the monovalent thallium halides, covering quite a range of wave-lengths. By proper choice of particle size these filters may be made quite opaque in the short wave regions but will still possess a high transmission in the neighborhood of the peak.

(2) The production of comparatively monochromatic beams of light by means of these filters immediately suggests their possible use in the construction of a survey spectrometer for the far infrared, similar to the reststrahlen method introduced by Rubens. Since only a source, two mirrors, and a receiver would be required the apparatus would be simple. Whereas the reststrahlen method requires one or more good sized crystals of each material, which are often difficult or impossible to obtain, only a small amount of the crystal powder is needed to make one of these filters. Using only the substances investigated in the present work, some fifteen or twenty different wave-lengths are available between  $6\mu$  and  $90\mu$ , and it is very likely that this list will be extended by further work in the field.

(3) Since the very existence of the Christiansen effect depends upon the equality of the refractive indices of particle and medium for some wave-length, we have here a method for determining dispersion curves in the infrared. In case the dispersion of either crystal or medium is known, the measurement of the Christiansen peak gives one point on the dispersion curve of the other. Since it is usually easier to obtain the dispersion curves of crystals in the infrared than of liquids, a series of such crystal powders could be used to establish points on the dispersion curves of liquids. In the inverse case, the dispersions of some liquids are known, and in the previous section were shown curves of the transmissions of MgO, NaCl, and quartz immersed in  $\text{CS}_2$  and  $\text{CCl}_4$ .

(4) It has recently been pointed out to us by Professor E. U. Condon, that since the measurement of the Christiansen peak in air gives one point on the dispersion curve of the crystal, namely, that at which  $n=1$ , this value may be used in the classical dispersion equation, together with values from the visible and ultraviolet regions of the spectrum to determine the intensity constant characterizing the infrared absorption band of the crystal. This problem will be discussed in a later paper.

MAY 15, 1936

PHYSICAL REVIEW

VOLUME 49

## The Band Spectrum of Boron Fluoride

HERBERT M. STRONG AND HAROLD P. KNAUSS, *Mendenhall Laboratory of Physics, Ohio State University*

(Received March 16, 1936)

The spectrum of boron fluoride as excited by the electrodeless discharge has been photographed at both high and low dispersion. Sixteen new bands were observed in the region between  $\lambda\lambda 3712$  and  $2580\text{\AA}$ . These bands degrade to the violet; have five head-forming branches, and resemble very closely the third positive bands of CO, a result to be anticipated from the fact that CO and BF both possess ten extranuclear electrons and should therefore

have similar electronic configurations. Two systems were found with a common lower electronic level: an *A* system ( $\nu^{(0,0)}=32,020.5\text{ cm}^{-1}$ ) of 12 bands and one isotope band, and a *B* system ( $\nu^{(0,0)}=37,991\text{ cm}^{-1}$ ) of three bands. The constants obtained from the vibrational analysis are:  $\omega_e'$ ,  $1631.40\text{ cm}^{-1}$ ;  $\omega_e''$ ,  $1323.64\text{ cm}^{-1}$ ;  $x_e'\omega_e'$ ,  $23.10\text{ cm}^{-1}$ ;  $x_e''\omega_e''$ ,  $9.40\text{ cm}^{-1}$ .

### INTRODUCTION

THE BF molecule is isoelectronic with  $\text{N}_2$  and CO, hence considerable interest attaches to its band spectrum. Largely because of difficulties in exciting and isolating the band

spectrum of BF, it has been inadequately investigated. The chemically stable compound of boron and fluorine,  $\text{BF}_3$ , is a gas at room temperature, and a Geissler discharge in  $\text{BF}_3$  has been used by several investigators in searching for BF