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# MEASUREMENTS IN THE LONG WAVE-LENGTH INFRARED FROM $20\mu$ TO $135\mu$

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## Abstract

The technique employed in this spectral region is discussed, special emphasis being placed upon the problem of the elimination of shorter wave-lengths. New measurements from $20\mu$ to $135\mu$, which show the transmission of 11 of the substances most commonly used in the infrared, are presented and discussed. In the light of new absorptions found in crystalline quartz, the reststrahlen measurements from Rubens are discussed. The transmission of sulphur was measured, and between $20\mu$ and $135\mu$, 8 absorption bands were located. These are compared with the Raman effect measurements of Krishnamurti. The question of an ideal substance for coating receiving elements in the far infrared is also treated.

THE infrared spectrum may now be examined by means of prisms from the visible region out to about $28\mu$.[1,2] Here, at a rather sharp boundary, prism spectroscopy comes to an end, and in order to investigate regions of greater wave-length an entirely different procedure must be followed. The two regions created by this boundary line are known as the "near" infrared and the "far" infrared. It is the purpose of this paper to present some new measurments made in the far infrared, and to discuss the technique and methods employed in investigating this part of the spectrum. The experimental difficulties increase rather rapidly as one proceeds towards longer wave-lengths. Probably for this reason, work in the far infrared has been limited. The problems which have been successfully studied are so widely scattered and so varied in subject matter, that it is rather difficult for one to obtain a clear view of the spectroscopy of this region. Accordingly, it is thought that a few remarks in this regard may not be out of place.

Our first knowledge of this part of the spectrum came from the classical experiments of Rubens and his co-workers, who, using radiations monochromized by means of the reststrahlen method,[3] were able to study the optical behavior of various materials with respect to the far infrared wave-lengths. The absorption and reflection curves which were obtained by them have furnished preliminary information of untold value to all subsequent investigators of this region.

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[1] Pohl in Göttingen has grown crystals of KBr large enough to yield prisms of 4 to 6 cm tall. The dispersion of KBr is known now to $28.5\mu$. See Gundelach, Zeits. f. Physik **66**, 775 (1930).

[2] J. Strong, Phys. Rev. **36**, 1663 (1930). Strong has grown larger single crystals of KBr, which he says are transparent to $30\mu$. Crystals of KI are transparent to $33\mu$.

[3] For details of this method and these measurements see Schaefer and Matossi, "Das ultrarote Spektrum".

It was soon realized however, that, for studying the detailed absorption or reflection of various substances, the dispersion obtained using the reststrahlen method was not great enough. The radiations so obtained were too impure, and their wave-lengths, which were really only average wave-lengths, depended too much upon such outside factors as atmospheric absorption and the condition of polarization of the original radiation. Accordingly, a new method was brought into use.[4] In this a wire grating was employed as the dispersing medium, the formerly used effect of selective reflection playing only a secondary role. This method, with a few minor changes, is today the accepted means of investigating the far infrared, and accordingly will be discussed briefly below.

## Apparatus and Methods

The apparatus used in this present work is essentially that used by Czerny in most of his investigations and is shown schematically in Fig. 1. The radiation from the Welsbach mantle, $W$, passed through a transparent shutter, $H$, which consisted of a 3.0 mm fluorspar plate, and through an opaque layer of camphor soot, $J$, before entering the first slit of the spectrometer at $S_1$. By the aid of the soot filter and the fluorspar shutter the disturbing effect of the short wave-lengths was greatly weakened. The mirrors $M_1$ and $M_2$ were each of 44 cm focal length and 10 cm diameter. By means of them the radiation emerging from $S_1$ was collimated, passed through the grating, $G$, and focussed again upon $S_2$. After leaving the spectrometer the radiation then passed through one of four openings in the brass frame $B$. Three of these openings were covered with samples to be studied, and the fourth left clear. At $R_1$ and $R_2$ were either two reststrahlen plates, or one plate and one silver mirror as the case necessitated. By means of $M_3$ a final image of $S_1$ was projected upon the thermoelement of a microradiometer, $MR$. For wave-lengths under $40\mu$ the window of the latter was a 2.0 mm sheet of paraffin, and for $1 > 40\mu$, a plate of quartz 0,4 mm thick cut perpendicular to the axis. The entire apparatus, excepting the source and shutter, was enclosed in an airtight galvanized iron case, and the air dried as thoroughly as possible with $P_2O_5$. With the microradiometer mounted upon a Julius suspension, which made use of an

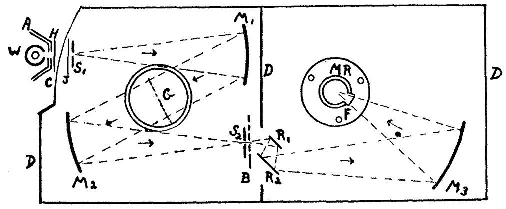

Fig. 1. Sketch of apparatus. $W$ = Welsbach mantle, $A$ = Aluminum shields, $H$ = Fluorspar shutter, $C$ = Celluloid window, $D$ = Galvanized iron case, $J$ = Opaque soot film, $S_1, S_3$ = Spectrometer slits, $M_1$, $M_2$, $M_3$ = Concave mirrors, $G$ = 0.2 mm wire grating, $B$ = Samples to be measured, $R_1$, $R_2$ = Reststrahlen plates, $F$ = Window (quartz or paraffin), $MR$ = Microradiometer.

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[4] H. Rubens, Berl. Berichte 1921, p. 8; H. Witt, Zeits. f. Physik **28,** 236, (1924); M. Czerny, Zeits. f. Physik **34,** 227 (1925); **44,** 235 (1927).

oil tank damping scheme recently described by Müller,[5] the zero, even with the scale at 5 m distance, was so steady that measurements could easily be made in the middle of the afternoon. The grating remained fixed, and the spectrometer arm carrying the source, shutter, first slit and $M_1$ was rotated about an axis in $G$ in order to pass the various wave-lengths successively through $S_2$.

Since from a radiating body having the temperature of a Welsbach mantle, approximately 1800°K, the ratio of the total energy falling in the near infrared to that in the far infrared is so extremely large, one must exercise a great deal of care in eliminating all stray or false radiation. A very small percent of the $20\mu$ energy, for example, occurring as an impurity could easily produce a deflection of the same size as that produced by 100 percent of the energy at $100\mu$. This danger is greatly increased because of the fact that gratings superpose orders. While, on account of the spacing chosen, the wire gratings in most common use automatically eliminate the even orders, for the measurements at $100\mu$ the third order of $33\mu$, the fifth order of $20\mu$, etc., are dangerous. The spacings of such a grating are always somewhat nonuniform, and therefore, in actual practice, traces of the even orders may be present along with the odd orders. Then too, Rubens showed that for $<5\mu$ the wires themselves may act as cylindrical mirrors and reflect these short wavelengths in the same direction as the diffracted $100\mu$ radiation. It follows therefore, that through some method of filtering, either by selective absorption or selective reflection, all wave-lengths shorter than half those to be used should be entirely eliminated. As yet, no ideal filter substance has been found which will meet the requirements stated above. Fig. 2 shows the extent to which

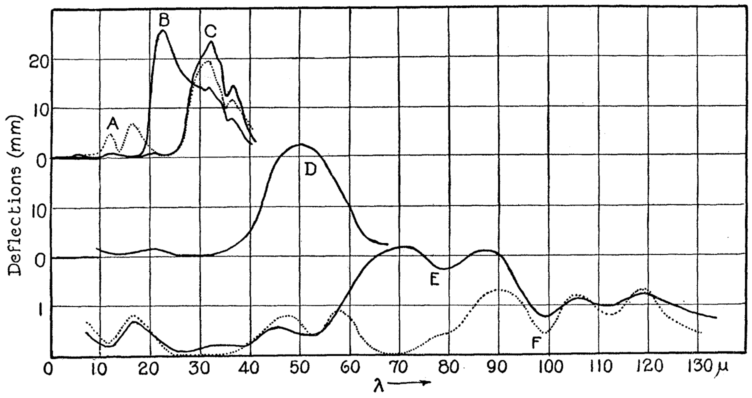

Fig. 2. Energy curves showing distribution of energy used in the various parts of the spectrum. $A=0.2$ grating, 2.5 mm slits, 2 mm paraffin, 1×Aragonite reflection. $B=0.2$ gratings, 2.5 mm slits, 2 mm paraffin, 2×$CaF_2$ reflections. $C=0.2$ gratings, 2.5 mm slits, 2 mm paraffin, 1×Aragonite×$CaF_2$ reflection. $D=0.8$ grating, 3.4 mm slits, 0.4 mm quartz ($\perp$) 1×NaCl reflection. $E=0.8$ grating, 3.4 mm slits, 0.4 mm quartz ($\perp$) 1 mm ($CaF_2$−paraffin), 1×TlCl. $F=0.8$ grating, 3.4 mm slits, 0.4 mm quartz ($\perp$) 1×TlBr. In all cases, Welsbach mantle, microradiometer, scale distance of 5 m, spectrometer $f=4.4$.

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[5] Müller, Ann. d. Physik **1**, 613 (1929).

these conditions have been fulfilled through the use of a combination of filters. The actual energies present, as are shown by the microradiometer deflections, are plotted as ordinates against the wave-lengths as abscissae. Attention is called to the increase of energy as one approaches the near infrared. This increase necessitates a change in the scale of the ordinates to 10 times that used at the longer wave-lengths. Curves $A$, $B$ and $C$ were obtained under the following conditions; Welsbach mantle, opaque camphor soot film deposited upon a $1\mu$ celluloid film, 2.0 mm paraffin window, 0.2 mm grating, 2.5 mm slits, and reflections from $1\times$Aragonite, $2\times CaF_2$, and $1\times$Aragonite$\times CaF_2$ respectively. Due to the presence of the two short wave-length maxima in the reflection power of Aragonite, curve $A$ could not be used. These disturbing wave-lengths were easily cut out by introducing the reflection on $CaF_2$, giving curve $C$. With the 0.2 mm grating the slits were used 2.5 mm wide. This was equivalent to $20'$ or $1.16\mu$. Curves $D$, $E$ and $F$ were made with Welsbach mantle, soot film as above, 0.4 mm quartz window, 0.8 mm grating, 3.4 mm slits and reflections from $1\times NaCl$, $1\times TlCl$, and $1\times TlBr$. In $E$ and $F$ it was necessary, because of the presence of too much energy between $30\mu$ and $40\mu$, to introduce a 1 mm filter of paraffin containing 1 part in 10 of powdered $CaF_2$.[6] With this grating, 0.8 mm, the slit width used was equivalent to $27'$ or $6.2\mu$. Realizing that the scale was 5 m distant from the microradiometer, the size of these deflections shows at a glance the difficulty of measuring percentage transmissions or reflections in this part of the spectrum.

Only the most sensitive receiving instruments may be used, and all outside effects such as those arising from building vibrations, sudden changes of the room temperature, etc., must be carefully controlled.[7] Because the deflections were so small, their exact endpoints were hard to determine. The following method was therefore adopted. With larger deflections, it was determined that the time necessary for the deflection to reach its maximum value was 16 seconds. A metronome was used, and regardless of the size of the deflection, the shutter was closed at the end of the first 16 seconds and the deflection noted. At the end of the second 16 seconds, the zero point was again read and due allowance made for any drift that had taken place. With the frame $B$ set so as to present the clear opening to $S_2$, 2 or 3 deflections were measured. Then, with one of the samples before $S_2$, 5 or 6 deflections were read, after which, 2 or 3 more without the sample were measured. From the average values with and without the sample in the path of the radiation, the percentage transmission was obtained. At some wave-lengths where the deflections were exceptionally small, 8 or 10 values were used in making up the averages. Even then, in some cases the results were more of a qualitative than of a quantitative nature.

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[6] M. Czerny, Zeits. f. Physik **53,** 317 (1929). Since the powdered $CaF_2$ settles to the bottom of the molten paraffin, the exact constituency of this filter is uncertain.

[7] In order to obtain constant temperature conditions, the measuring room was closed and the Welsbach mantle lighted at least three hours before beginning each series of measurements. Then, upon entering the room the observer took his place and waited still another half hour before beginning. On days when the weather changed rapidly, measurements could not be made, because the zero of the microradiometer changed rapidly also.

It should be remarked here, that since no ideal distribution of energy can be obtained, and since the slits must be rather wide, that, in regions where the absorption of the sample which is being measured changes rapidly, the slit-width effects are very noticeable. In these cases the Paschen-Runge slit-width correction[8] should be made in order to obtain the true form of the measured curve.

## Results

Most of the substances discussed below have from time to time been used in some manner in the infrared. Up to the present, however, no series of connected measurements upon them have been reported, the existing values consisting of a few measured points scattered here and there throughout the spectrum. Since from these existing measurements no complete view of the transmission of these substances could be obtained, the following measurements were undertaken, and the results there from are given in the curves which are discussed below. The percentage transmissions, irrespective of whether the loss is due to true absorption, reflection or scattering, is in every case plotted as a function of the wave-length. These measurements extend from 135$\mu$ to 20$\mu$, but wherever possible, the curves have been extended below 20$\mu$. In these cases measurements are taken from other authors, and are given here merely for the sake of better orientation and in order to present a more complete picture of the behavior of the substances in question. Since the main theme of this paper is the far infrared, the abscissae have been plotted to a scale in $\mu$ itself instead of log $\mu$ or $\nu$. This is, of course, not fair to the near infrared, and therefore I wish to express here my apologies.

### Fused quartz, Fig. 3

In the near infrared this substance absorbs very strongly. In fact one reads in the literature, that, "beyond 11.6$\mu$ fused quartz is non-transparent."

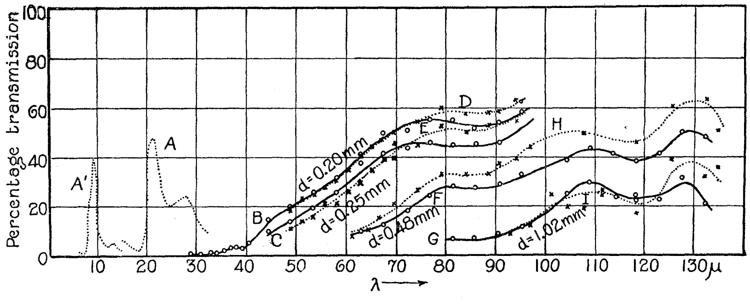

Fig. 3. Transmission of fused quartz. $A'$ and $A$ are reflection power curves. The others, percentage transmission as function of $\lambda$.

Because of this exceptionally strong absorption, the near infrared is represented in this figure by the reflection curves $A'$ and $A$ from Schaefer and Rubens respectively. Curves $B$, $C$, $F$ and $G$ show the transmission of samples having thicknesses equal to 0.20 mm, 0.25 mm, 0.48 mm and 1.02 mm. Be-

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[8] "Das ultrarote Spektrum", p. 80.

sides the general absorption for wave-lengths under 40$\mu$, absorption bands exist in neighborhoods of 86$\mu$, 118$\mu$ and $\lambda > 132\mu$. Though these bands are broad and rather weak, they indicate in all probability the presence of small groups of recrystallized quartz molecules.[9] The fact that the four samples which were measured were obtained from three separate sources where they undoubtedly underwent different annealing treatments, seems to show that the presence of these recrystallized regions is a property of fused quartz in general.[10]

Since throughout most of the above measurements the deflections were very small, of the order of 1 to 2 mm, it was thought best to remeasure the absorption of fused quartz with entirely different conditions. This was, of course, to be a test for the presence in the curves of systemmatic errors due to some fault of the apparatus, or to false radiation, etc. With entirely different filter combinations, the dotted curves *D*, *E*, *H* and *I* were measured. The agreement between these curves and the ones described above shows that the absorption bands are real, and at the same time presents an idea of the accuracy, which was obtained in these new measurements in spite of the small deflections which had to be used. In filtering out the short wave-lengths the following selective reflections were substituted for those used in obtaining the respective energy curves of Fig. 2: from 49$\mu$ to 55$\mu$ 1×NaCl, from 55$\mu$ to 70$\mu$ 1×KCl, from 70$\mu$ to 94$\mu$ 1×KBr and from 94$\mu$ to 134$\mu$ 2×TlCl.

**Crystalline quartz, Fig. 4**

Again, for similar reasons as above, a reflection power curve from Rubens is given in the near infrared. From it, curve *A*, we can read off indicated positions of rather intense absorption at 8.5$\mu$, 12.5$\mu$, 20.5$\mu$ and 26$\mu$. Curve *B* was made with a piece of quartz 0.10 mm cut perpendicular to the optic axis. After increasing in transparency, following the 26$\mu$ absorption, it shows clearly the previously known 38$\mu$[11] band. Curves *C* (1.03 mm 11), *D*(3.49 mm ⊥), and

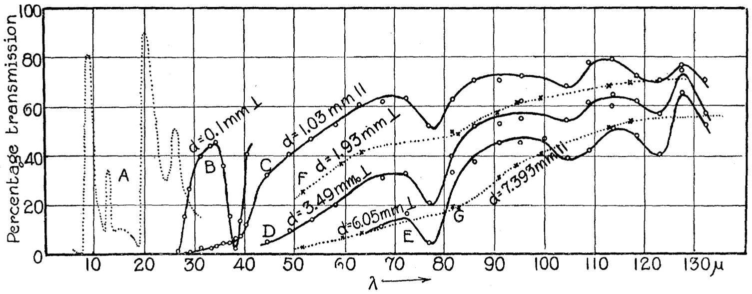

Fig. 4. Transmission of crystalline quartz. *A*, reflection curve. *B*, *C*, *D*, and *E*, transmission curves. *F* and *G*, transmission curves measured with the reststrahlen method.

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[9] The very fact that these bands lie at wave-lengths greater than say 30$\mu$, shows, according to the accepted theory of absorption in solids, that they represent frequencies characteristic of a crystal lattice.

[10] O. Reinkober, Phys. Zeits. **32,** 243 (1931). In examining the tensil strength of quartz fibers Reinkober always found centers of recrystallized quartz present.

[11] See reference 6.

$E$(6.05 mm $\perp$) show definitely bands at $77\mu$,[11] $105\mu$ and $122\mu$. The last point at $132\mu$ indicates the presence of still another band at longer wave-lengths. Towards longer wave-lengths the reflection power of quartz increases. Therefore, because of the increased losses of energy due to the reflections at the two surfaces of the samples, the transmission curves, especially $C$, after about $90\mu$ begin to run almost horizontally. No effect of interference due to these reflections however is to be seen. Attention is called to the fact that curve $C$ (1.03 mm 11) shows definitely at $38\mu$ a transparency several times higher than that of curve $B$ (0.10 mm $\perp$). This is probably an effect of dichroismus.[12]

In the case of crystalline quartz a test was also made to discover the effects, if any, arising from false radiation. With the energy curve $F$ in Fig.2 (1×TlBr) the absorption of curve $E$ from $95\mu$ to $118\mu$ was remeasured. The values agreed to within 2 percent with those of curve $E$, giving the location of the band again at $105\mu$.

The two dotted curves, $F$(1.93 mm $\perp$) and $G$(7.393 mm 11) are from Rubens[13] and show no definite evidence of absorption bands. This failure of absorption bands to show up in these curves throws a very interesting sidelight upon the method previously used in this region, namely the reststrahlen method. It seems more than a mere accident that the measured points always fell a little to one side or to the other of the quartz bands themselves. It will be noticed, that no one of the 9 measured points occurred at a wave-length which the quartz absorbed strongly. The following explanation of this fact is offered as a possibility.

Since the wave-lengths of the various reststrahlen used in the above curves $F$ and $G$ were determined by means of a quartz interferometer, they of course depended to a great extent upon the assumed absence of sharp absorption bands in quartz. In case, for example, the true maximum of the energy reflected from a given crystal fell within one of the quartz bands, it was shifted by this absorption toward longer or shorter wave-lengths as the case may be, the wave-length of the resulting maximum lying outside of the quartz band itself. Examining the curves from this point of view it seems possible, that, in the light of these new absorption bands, the center of the true reflection maximum of TlBr might lie at a wave-length slightly longer than $117\mu$. That of AgBr might in reality lie a bit below the reststrahlen value found at $112.7\mu$. The wave-length of the true reflection maximum of $Hg_2Cl_2$ might be longer than $98.8\mu$, and that of AgCl shorter than $81.5\mu$. In other words the absorption bands of the interferometer plates have caused in some cases an actual shift in the reststrahlen wave-lengths with respect to the wave-lengths of the true reflection maxima.[14] In using these reststrahlen later

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[12] H. Rubens, Berl. Berichte, p. 513, 1913. Rubens found the transmission of a plate of quartz 7.393 mm $\|$ to be a few percent higher than that of a sample 7.256 mm $\perp$. This he attributed to dichroismus.

[13] See reference 12.

[14] It must be remembered that the reststrahlen wave-length has no theoretical meaning and cannot be calculated from the constants of the crystal in question. By definition, it is simply the maximum of the energy left over after the original radiation has suffered some form

in order to determine the absorption of quartz, Rubens had approximately the same amount of quartz in his apparatus as he did when he determined their wave-lengths. Therefore, the actual energy maxima used in curves *F* and *G*, agreed with the previously measured wave-lengths, and so, no measurement was made on quartz within a region of strong absorption. If the above assumptions are true, it is then obvious that by using the same reststrahlen plates, with no quartz however in the apparatus, the bands of quartz might easily (have) appeared in curves *F* and *G*.

### Comparison of fused, and crystalline quartz

For use as a filter or window material, fused quartz seems to be better suited than crystalline quartz. Because the absorption of the former is so very much stronger than that of the latter, a thinner and less expensive piece of the fused quartz may be used to produce the desired effects. Then too, since the bands are so much broader and less intense in the fused condition, any undesirable effects of these bands, such as the shifting of the true wave-lengths of the maxima or minima of the substance which is being measured, will be greatly reduced if fused quartz is used.

Upon comparing the two sets of curves the following correlations seem possible. If the absorptions in fused quartz arise from sources similar to those in crystal quartz, that is, from groups of crystallized $SiO_2$ molecules, then the effect of the actually fused material has been to broaden the bands and to shift them towards longer wave-lengths. The broad $86\mu$ (fused) band may be the same as the sharp $77\mu$ (cryst.) band, and the $118\mu$ (fused) band the same as the $105\mu$ (cryst.) band. The band indicated at $\lambda > 132\mu$ (fused) would be the $122\mu$ (cryst.) band. Then, the supposed band at $\lambda > 132\mu$ (cryst.) would point to the presence of still a second unobserved band in fused quartz. These possibilities will be tested experimentally at a later date.

### Regarding the Raman effect of quartz

Unfortunately, no very definite comparison can be made between these new absorption bands of crystalline quartz and the Raman effect. Czerny has shown that bands occur both in the Raman effect and in the infrared at $38\mu$ and $78\mu$. At $48\mu$ however a band occurs in the Raman effect which does not occur in the infrared. A comparison has also been made previously between the two sets of values at shorter wave-lengths. Since in the Raman effect the regions where $\lambda > 80\mu$ lie so close to the exciting line, the long wave-length values which have been obtained are extremely uncertain. Krishnan[15] mentions Raman lines at $94\mu$ and $118\mu$, while Gross and Romanova[16] give $\lambda = 99\mu$, $120\mu$ and $140\mu$. It is at once seen that none of these agree with the new infrared bands, possibly due simply to the inaccuracy in the R. E. values.

Gross and Romanova also investigated the Raman effect of fused quartz, and found that out to $47\mu$ the indicated absorptions were practically the same

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of selective reflection. It depends entirely upon the distribution of the energy in the source, the selective reflection and any selective absorption which may take place.

[15] K. S. Krishnan, Nature **122,** 477 (1928).

[16] E. Gross and M. Romanova, Zeits. f. Physik **55,** 744 (1929).

as in crystalline quartz. The chief difference in the two cases, was that the bands, which were sharp in crystalline quartz were broad and diffuse in fused quartz. Surprised at the occurrence of the same bands in the two cases they raised the question regarding the possible presence of crystalline structure in the fused condition. Since in x-ray photographs no crystal structure is found in fused quartz, they concluded that there could be no recrystallized centers in their samples.[17] This conclusion, which is rather doubtful, together with the fact that the same Raman lines were present in both forms of quartz, led them to conclude further regarding crystalline quartz, ". . . , that, in this region ($8\mu$ to $70\mu$) no frequency characteristic of the crystal lattice (outer vibration) is present". This second conclusion is surely wrong. They were unable to determine the exact locations, due to the weak dispersion of their apparatus, of any bands beyond $47\mu$ in fused quartz. They state that the $78\mu$ band probably does not occur, and since this, according to infrared theory, is characteristic of the quartz lattice, they hold its failing as evidence for their above mentioned conclusions. From the absorption curves however one sees clearly that the $78\mu$ band should not occur in fused quartz at $78\mu$, but rather at $86\mu$. Too, the other long wave-length bands would not be expected to occur at the same wave-lengths as the corresponding ones in crystalline quartz.

It must be remarked however, that also in the infrared the absorption curves of fused and crystalline quartz are very similar below about $45\mu$, especially, of course, in regions where "inner vibrations" are present.

## Sulphur, Fig. 5

The dotted curve *A*, which is taken from the work of Taylor and Rideal, shows, in a plate of rhombic sulphur 6.0 mm thick, bands at $7.76\mu$, $10.73\mu$,

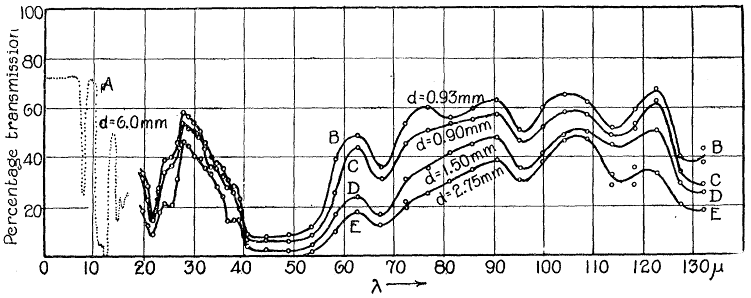

Fig. 5. Transmission of sulphur. Curve *A* is taken from Taylor and Rideal. All the curves shown here are for rhombic sulphur.

$11.9\mu$ and $14.6\mu$. Since in the present apparatus plates of sulphur 23 mm by 8 mm were required, considerable trouble was experienced in obtaining suitable samples. Thanks to the kindness of Professor Johnsen of the Mineralog-

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[17] These recrystallized groups in order to be detected by the Debye method, would have to be relatively large, i.e., of the same size as finely powdered quartz crystals. Recrystallization centers, however, many times smaller than such powder grains could easily produce the infrared absorption bands characteristic of a large crystal, and still escape detection by x-ray analyses.

ical Institute, and of Dr. von Deines of the Physical Chemistry Institute, of the University of Berlin, crystals were obtained which were large enough to yield plates of the required size. Curves *B* (0.93 mm), *C*(0.90 mm), *D*(1.50 mm) and *E*(2.75 mm) show the transmission of four samples cut from rhombic sulphur. Of these, only sample *B* was cut parallel to the base of the crystal. The other three were each perpendicular to the base, the more exact crystallographic orientation being uncertain. It must be remarked here that sulphur is extremely brittle, and when only slightly heated often shatters completely. In the grinding and polishing of the plates, this was the chief difficulty encountered. The 2.75 mm plate *E* was cut from a natural crystal, the others coming from artificially grown samples.

Upon seeing that sulphur has such sharp and intense absorption bands throughout the infrared, one immediately asks two questions. Why does sulphur, an element, absorb in the infrared? Where does it get its electric moment? From x-ray analyses it has been shown that sulphur exists in the crystal form as $S_{16}$. Taylor and Rideal believe from their work that this is in reality $(S_2)_8$, and that each of the $S_2$'s has an induced electric moment equivalent to about 0.7 times the moment it would have if one electron had actually been transferred from one $S$ to the other. The binding between the two $S$'s is assumed to be of a pseudoheteropolar nature. The question however of exactly how and why a non-metallic element such as sulphur should have such strong infrared absorptions is still a puzzling one.

From the curves given here, one sees bands at $21.5\mu$, $25.0\mu$, $37.5\mu$, $40\mu$ to $50\mu$, $67\mu$, $96\mu$, $114.5\mu$ and $\lambda > 130\mu$. The region from $40\mu$ to $50\mu$, when investigated with a finer grating, will undoubtedly show a complex structure. It is interesting to note that by the Raman effect[18] bands are found at $21.28\mu$, $23.06\mu$, $41.3\mu$, $46.25\mu$, $65.7\mu$, and $118.2\mu$. The agreement between the two sets of values is incomplete, the Raman effect failing to show the presence of the band beyond $130\mu$, and the ones at $96\mu$ and $37.5\mu$. Since the infrared absorption was the same in natural and synthetic crystals, it seems improbable that these extra bands are due to impurities. This is however not impossible. Choosing as fundamentals his Raman effect bands at $21.3\mu$, $41.3\mu$ and $65.6\mu$ Krishnamurti has published an energy scheme which explains the bands found by Taylor and Rideal as overtones. It seems improbable, however, that the final and correct scheme should so entirely overlook these equally strong infrared absorptions which lie at longer wave-lengths.

It will be noticed that curve *B*, which is the only curve measured on a plate cut parallel to the base, differs from the other three in two places. At $81\mu$ a weak band is present and the $37.5\mu$ band occurs in this sample at $33\mu$. These differences were carefully checked and are real. It will also be noticed that although sample *B* was actually thicker than sample *C*, its percentage transmission throughout was always a few percent higher than that of *C*. This is analogous to the cases cited above for crystalline quartz and is probably here also an effect of dichroismus. Assumed differences in the degree of polish of the two crystals could also cause irregulaties in the percentages of trans-

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[18] P. Krishnamurti, Indian J. of Phys. **5**, 105 (1930).

mission. This was here, however, very probably not the source of the effect, and in the case of quartz, certainly not.

### Paraffin and mica, Fig. 6

The dotted curve *A′* shows the transmission of a sheet of 68°–72°C melting point paraffin[19] 0.6 mm thick. It shows that in thicknesses of approximately 1 mm paraffin would absorb rather thoroughly the radiations shorter than 18$\mu$. Curves *A* and *B* were measured upon plates of paraffin 2.05 mm and 3.7 mm thick. From 20$\mu$ to 75$\mu$ the transparency increases uniformly, after which, absorption bands occur at 82.5$\mu$, 106$\mu$ and 127.4$\mu$.

Since paraffin may be had in so many various forms chemically, i.e., in forms varying widely in their melting points and the lengths of the chains of atoms, a test was made to see what effect these variations have on the transmission. From Kahlbaum samples were obtained having melting points at 68°–72°C and 42°–44°C, and from these two plates having exactly the same thicknesses, 2.2 mm, were cut. The results are shown in the curves marked H.M.P. and L.M.P., the two forms varying approximately 100 percent in their transmissions. It is evident that curves *A* and *B* were made from L.M.P. paraffin. It will be interesting to see if the absorption bands which occur at long wave-lengths in L.M.P. paraffin are the same in H.M.P. paraffin. Frau Kellner measured a 2 mm thickness of H.M.P. paraffin from 20$\mu$ to 38$\mu$, the results falling exactly with my (H.M.P.) curve.

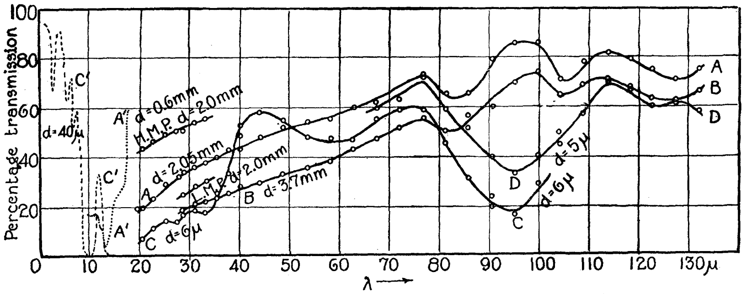

Fig. 6. Transmission of paraffin and mica. *A′*, *A*, *B*, *H.M.P.*, and *L.M.P.* are transmission curves of paraffin, *C′*, *C* and *D*, mica.

Mica is chemically also a very poorly defined substance. Previous investigations in the near infrared have shown that the various micas differ somewhat in their absorption. Curve *C′* gives the transmission of a 40$\mu$ sheet of Muscovite mica as measured by Coblentz, and shows absorptions at 2.8$\mu$, 5.5$\mu$, 6.8$\mu$, 10$\mu$ and $\lambda > 13\mu$. The samples used in the present work were of unknown origin and composition. It can only be said in this regard, that, in relatively thick sheets the mica had somewhat of a yellowish brown color while the thin samples used here were perfectly clear and colorless. The results are shown in curve *C* (6$\mu$ thick) and curve *D* (5$\mu$ thick). The samples used were split from thicker sheets, and their thicknesses measured roughly with a pocket spectroscope. It will be noted that the absorption is of a differ-

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[19] L. Kellner, geb. Sperling, Zeits. f. Physik **56**, 215 (1929).

ent order of magnitude from that met with in the compounds discussed above. The absorption of the 5μ and 6μ films is more nearly of the same order of magnitude as that of NaCl or KCl. Even in such thicknesses the near infrared is almost completely absorbed, and bands occur at 27μ, 33μ, broad regions around 59μ and 95μ, and at 123μ. The values usually found in the literature are for thicker samples and often show irregularities due to the effects of interference between radiation reflected at the front and back surfaces. Here, owing to the thinness of the films, such effects are impossible.

Mica is particularly unsuited for use in the infrared. Paraffin, on the other hand, is very suitable for removing the near infrared. Below 80μ it is exceptionally good as a window material.

## Miscellaneous, Fig. 7

Curve *A* shows the transmission of a film of celluloid of approximately 1μ thickness, formed by allowing one drop of a solution consisting of nitrocellulose and camphor dissolved in amylacetate and acetone to spread itself out upon a water surface. This curve simply corroborates what had already been stated.[20] Since these films can play such a large role in the infrared it is important to have an actual measured transmission curve covering the entire range of wave-lengths. The transmission is nowhere 100 percent, the losses being probably due chiefly to reflection and not to absorption. Curve *A* ′ taken from the work of Fräulein Tolksdorf shows the unsuitability of such a film for use in the near infrared.

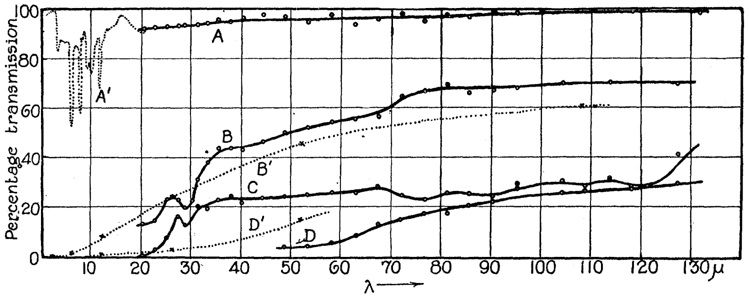

Fig. 7. Transmission of miscellaneous substances. *A* ′ and *A*, thin films of celluloid. *B* ′, *B*, *D* ′ and *D*, black paper. *C*, a 40μ thickness of cellophane.

Curve *B* is from a piece of black tissue paper which was slightly translucent for light from a 100 watt lamp. Beyond 35μ the transparency increases uniformly until 80μ is reached, and from there on to 135μ is practically horizontal. Below 35μ however, the entire style of the curve is different, showing at 28.7μ a rather sharp band. This band is probably due to the cellulose molecules themselves as it is exactly the same band as the cellophane band shown below it.

Curve *C* shows the measurements on a piece of cellophane, 0.04 mm thick, such as that used for wrapping candy boxes. From 20μ to 35μ the curve is qualitatively the same as curve *B*, the same band at 28.7μ occurring in both.

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[20] M. Czerny, Zeits. f. Physik **34**, 227 (1925).

It is possible that the rest of the curve should simply be a straight line, but I rather believe that weak absorptions are present as shown at 75μ, 90μ and 121μ.

Curve *D*, which is for a piece of black paper, 0.10 mm thick, used for wrapping photographic plates, is almost identical qualitatively with the corresponding part of curve *B*.

The dotted curves *B′* and *D′* are from Rubens and Wood and represent measurements upon approximately similar samples of paper. The agreement with curves *B* and *D* is good.

**Blackening substances, Fig. 8**

Curve *A*, is from a film of camphor soot which was deposited upon a 1μ film of celluloid. Through this thickness of soot, the filament of a 100 watt lamp showed faintly with a deep red color. Beyond 30μ the transmission is uniform and high. Such a film is therefore very suitable for removing the visible and the extremely short infrared radiations. As a coating for receiving elements however, it is out of the question. Curve *A′*, from Rubens and Wood, shows the transmission of a similar film made from candle soot. The extension of *A* would probably follow *A′* very closely.

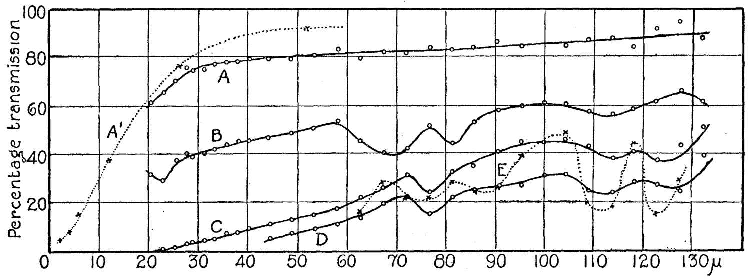

Fig. 8. Transmission of blackening substances. *A′* and *A*, soot films. *B*, Pfund's bismuth black. *C*, *D* and *E*, Rubens and Hoffman's soot-waterglass preparation.

Pfund[21] showed that if bismuth be evaporated in a vacuum of about 0.25 mm of mercury, a film is deposited upon the walls of the container which closely resembles black velvet in its blackness. Films of this bismuth-black, thick enough to be opaque to visible light, were found by Pfund to have transmissions under 1 percent, as far out as 13μ, and were therefore recommended by him for coating receivers for use in the near infrared. Curve *B* shows the transmission of such a film in the far infrared. It was deposited upon a 1μ film of celluloid, which during the depositing process had to be in contact with a plate of brass. (When this was not the case, no deposit was obtained.) Absorption bands exist at 22.5μ, 69μ, 81μ, 113μ and $\lambda > 130\mu$.

Curves *C* and *D* give the results for two films of a mixture of lampblack and waterglass approximately 0.07 mm and 0.08 mm thick. This mixture was prepared according to a method given by Rubens and Hoffmann,[22] and then painted upon thin celluloid films. These authors found that such a film

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[21] A. H. Pfund, Rev. Scient. Instr. **1**, 397 (1930).

[22] H. Rubens and K. Hoffmann, Berl. Berichte p. 424, 1922.

became transparent first around 120μ. In fact they stated, that, "... a 50μ absorbing layer of lampblack and water glass out to wave-lengths of 120μ showed no real decrease (from 100 percent) of the absorption power, ... ". However, the conditions under which they measured were quite different in one respect from those used in this present work. As a carrier for their mixture they used a film of mica 36μ thick, which according to them showed definitely interference effects. To obtain the effect due to the mica alone, the transmission for the various wave-lengths was measured before and after the mixture was painted upon it. In view of these interference effects which were present, it is questionable as to whether the values found "before" can simply be subtracted from those found "after" in order to obtain the transmission of the mixture itself. With one surface blackened the interference effects most probably disappeared, and the transmission of 36μ of mica was surely throughout most of this region, nearly zero. My samples of their mixture, approximately 70μ and 80μ in thicknesses, showed around 30 percent transmission beyond 70μ. Absorption bands were found at 76.8μ, 112μ and 125.0μ.

A rather interesting effect is shown by the dotted curve *E*. The sample shown by curve *D* was prepared, and after drying for 24 hours gave the curve *E*. Three days later an attempt to check this curve failed badly. On the next day still a third curve was obtained from the same sample. A new film, the one shown in curve *C*, was prepared and compared with the old one. The curves disagreed. After the second film was approximately a week old, the curves *C* and *D* were simultaneously measured. The agreement between these two showed that during the drying and hardening process, certain chemical changes had taken place, a final state having been reached after 4 or 5 days. It is well known that upon drying $Na_2SiO_3$ changes its condition considerably.

From the curves of this figure, one must conclude that up to the present we know of no ideal substance for coating receivers for the far infrared. Such a substance should show no sharp absorption bands, should absorb the far infrared entirely, and if possible should have a high percentage transmission for the near infrared. Czerny suggests a mixture of powdered silicates such as mica, glass, quartz and sodium silicate. Where one of the substances failed to absorb, some of the others probably would.

## CONCLUSION

In conclusion I wish to state that in this paper no attempt has been made to present a complete and final investigation of the absorption of such substances as quartz and sulphur. To do this, special attention would have to be paid to such questions as polarization, the exact crystallographic orientation of the crystal, impurities, temperature effects and losses by reflection. The purpose of this paper is to present a general view of the transmission of the substances most commonly used in the spectroscopy of the far infrared.

I wish to take this opportunity to express my thanks to Dr. M. Czerny of the University of Berlin for the use of his apparatus and for his kindly interest in this work.