# INVESTIGATIONS IN THE FAR INFRARED

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ABSTRACT

An instrument is described for investigations of the reflectivity, transmissivity and emission of various materials over the spectral range 20 to 150$\mu$. The following measurements are reported: Reflectivities of rough surfaces, galena, $\beta$-magnesia, zincite, stibinite, corundum, sphalerite, molybdenite and cuprite. Transmissivities of KBr, KI a layer of KCl evaporated on a lacquer film, a thin film of amorphous quartz, liquid $CCl_4$, and powdered Al and Cu. Emission of liquid and solid NaCl near the melting temperature.

## INTRODUCTION

IN THE near infrared a prism spectrometer is useful for preliminary investigations when high resolving power is not required. It is the purpose of this paper to describe an instrument to play a similar role in the far infrared and to present the results of investigations carried out with this instrument.

This new instrument employs the reststrahlen method of obtaining monchromatic bands of radiation. The instrument is so designed that investigations on the reflectivity, transmissivity and emission of various materials may be expeditiously carried on over the spectral range 20 to 150$\mu$. In order to see that the results obtained by the reststrahlen method may be equivalent to those obtained in the near infrared with a prism spectrometer it is necessary to bear in mind that the practice of representing position in the infrared spectrum by wave-length is less natural than representation by frequency. This is because the width of absorption lines, the distance between lines and the extension of an absorption band, are, when plotted against frequency, approximately the same in all regions of the spectrum, that is to say, they do not depend on wave-length. For filters the sharpness of transition from opacity to transparency will be the same. In order to get an equally accurate picture of a spectrum in any region of the infrared the number of observations per unit spectral range, on a frequency scale, is the same. The so-called far infrared, i.e. wave-lengths greater than 20$\mu$, is not very wide when frequencies are considered. The importance of this region is due to the character of its spectra rather than their quantity. In fact the far infrared from 20–150$\mu$ corresponds, in frequency range, to approximately $\frac{1}{2}\mu$ at 3$\mu$. This means that the twelve rather uniformly distributed wave-lengths which were employed for the present investigation correspond to about 24 points per $\mu$ at 3$\mu$. This is about five times the frequency of points taken by Coblentz[1] in his classical studies with a prism spectrometer.

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[1] W. W. Coblentz, Investigations of Infrared Spectra, 1908.

### The Restrahlen

Table I, taken in part from "Das Ultrarote Spektrum" by Schaefer and Matossi, describes the twelve reststrahlen bands used in the present investigation.

Table I.

| Number of reflections | Crystal mirrors | Filter (3 mm paraffin in each case) | Wave-length in $\mu$ | Frequency in $\sim$/cm | Energy in cm of deflection (scale at 3 meters) |
|---|---|---|---|---|---|
| 4 | Quartz | 1 cm KCl | 20.7 | 483 | 44 |
| 3<br>1 | Fluorite<br>Metal | 5 mm KCl | 23 | 435 | 18 |
| 2<br>2 | Fluorite<br>Calcite | 3 mm KBr | 27.3 | 366 | 42 |
| 4 | Calcite | none | 29.4 | 340 | 95 |
| 3<br>1 | Fluorite<br>Metal | 0.4 mm quartz<br>1.2 mm KBr | 32.8 | 305 | 2.6 |
| 3<br>1 | Aragonite<br>Metal | 0.4 mm quartz | 41 | 244 | 1.6 |
| 4 | NaCl | 2 mm quartz | 52 | 192 | 5.2 |
| 4 | KCl | " | 63 | 159 | 2.0 |
| 4 | KBr | " | 83 | 120 | 1.6 |
| 4 | KI | " | 94 | 106 | 1.0 |
| 4 | TlBr | " | 117 | 85 | 1.7 |
| 4 | TlI | " | 152 | 66 | 1.0 |

The use of a paraffin window for the thermocouple (about 3 mm in thickness) has the advantage that it does not transmit the short wave-length reststrahlen of quartz at $8.7\mu$ and calcite at $6.7\mu$ to the receiver. With this filter the use of the 20.7 and $29.4\mu$ reststrahlen is exactly the same as the other reststrahlen.

The substitution of a 1 cm KCl filter for the 2.5 mm AgCl filter recommended by Rubens and Nichols[2] for the $20.7\mu$ reststrahlen is justified by transmission curves given by Rubens and Trowbridge[3] for AgCl and KCl.

Regarding the $41\mu$ reststrahlen, Rubens[4] states, "Die Reststrahlen von Arrogonit waren, wie ihre Zerlegung im Gitterspektrum erkennen liess, ziemlich inhomogen und zeigten zwei Maxima, ein schwächeres bei 35, ein stärkeres bei $41\mu$."

In the present experiments, the $27.3\mu$ rays were not polarized as specified by Liebisch and Rubens.[5]

Four calcite mirrors gave radiations which were transmitted by quartz. These were the $94\mu$ radiations observed by Rubens. The fraction of the cal-

[2] H. Rubens and E. F. Nichols, Wied. Ann. **60,** 418 (1897).
[3] H. Rubens and A. Trowbridge, Wied. Ann. **60,** 724 (1897).
[4] H. Rubens, Berliner Berichte, p. 199, (1919).
[5] H. Liebisch and H. Rubens, Berliner Berichte 1919, p. 876.

cite reststrahlen transmitted by 2 mm quartz was 0.0136. In the data which follow in this paper this lack of homogeneity in the 29.4$\mu$ reststrahlen was disregarded.

## The Apparatus

The apparatus has been described in an earlier paper.[6] However, there have been several alterations of the earlier form of the apparatus. These are shown in Fig. 1 and are described below;—The Welschbach mantle, used previously, was replaced by a Globar heater. The use of a Kahlbaum paraffin window with a Globar heater gives the advantages of the Welschbach mantle, namely a scarcity of near infrared radiations without the disadvantages of its fluctuations. The Globar heater (3/8″×8″) was mounted in a cooled brass cylinder—the radiations emerging through a circular hole in the center of the

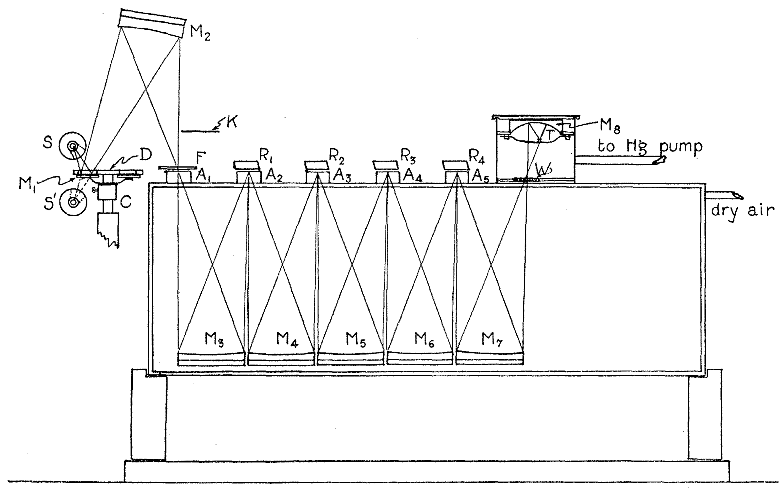


Fig. 1. Diagram of apparatus.

cylinder. For reflectivitives this source was placed in the position $S$ (see Fig. 1) the emitted radiations being reflected to $M_2$ by means of the mirror $M_1$. By revolving the disk $D$ the mirror $M_1$ may be either of the three samples being investigated or a silver mirror. These are clamped under the four symmetrical holes in the disk by the collar and spring washer $C$. For measuring transmissions the Globar heater takes the position $S'$. One of the holes in the disk is open in this case and the other three are covered with samples.

When the silver mirror reflects the energy from the heater to $M_2$ the reststrahlen energy may be determined by observing the galvanometer deflection as the metal shutter, $K$, is successively placed in and out of the radiation path. For transmission, the reststrahlen energy is determined with the radiation passing through the empty hole. The ratio of the reflected or transmitted energy to the reststrahlen energy gives respectively the reflectivity or transmissivity of the sample. In practice, the reflection or the transmission of three samples was determined each time the reststrahlen energy was determined.

[6] John Strong, Phys. Rev. **37**, 1565 (1931).

The radiations collected by $M_2$ are passed through the filter $F$ and then through the aperture $A_1$. $M_3$ collects this energy to reflect it to the first reststrahlen mirror $R_1$. After four successive reflections $R_1$ to $R_4$ the mirrors $M_7$ and $M_8$ focus the radiation onto the thermocouple receiver. The thermocouple window, $W$, is 3 mm paraffin (Kahlbaum M.P. 68–70°C). The advantage of using the auxiliary mirror, $M_8$, to give a small focus on the thermocouple receiver is represented by a factor of 4.

The air in the apparatus was dried by passing it over $CaCl_2$ and $P_2O_5$. A continuous stream of dry air made diffusion of moisture into the apparatus through the holes $A_1$ to $A_5$ impossible. These holes were each covered with a lacquer membrane. The reststrahlen crystals and filters were painted with very thin colorless lacquer to protect them from attack by atmospheric moisture.

The apparatus was protected from thermal fluctuation by a felt jacket. The restrahlen crystals $R_3$ and $R_4$ were covered with a metal housing so the thermocouple could not "see out." This practice adds to the steadiness of the galvanometer.

The galvanometer used with the thermocouple was a L. and N. type H.S. and was mounted on a vibrationless support. The scale, placed at 6 meters from the galvanometer, was read with a 24 power telescope to 1/10 mm.

The galvanometer was given 15 seconds to come to equilibrium between readings. This time was accurately measured with a metronome to facilitate the cancellation of drift. The reflectivities or transmissivities of three samples may be determined four times at each of the twelve wave-lengths in an afternoon if the apparatus is kept working constantly.

The advantages of this apparatus for making preliminary spectral investigations by the reststrahlen method may be summarized as follows; (1) The reststrahlen crystals required are small, making them more easily obtainable. (2) The change from one set of crystals to another may be made quickly without disturbing the dry air in the radiation path. (3) The use of a paraffin filter facilitates measurement at 20.7 and $29.4\mu$.

The following measurements illustrate the applicability of this instrument for preliminary investigations in the far infrared.

## Reflectivities

### Rough surfaces

Lord Rayleigh[7] showed, by qualitative experiments, that rough surfaces reflect long infrared waves almost as well as polished surfaces. The practice of using a rough mirror to isolate the near infrared from the far infrared makes the quantitative investigation of the reflectivity of rough surfaces desirable. In order to study this, three rough mirrors were prepared by grinding brass on brass with 400, 200 and 60 carborundum. The reflectivities of these mirrors in the far infrared are shown in Fig. 2. The large variations of the observed points from the curves are probably due to some interference effects rather than to experimental error.

[7] Lord Rayleigh, Proc. of the Royal Inst. XVI, p. 563, 1901.

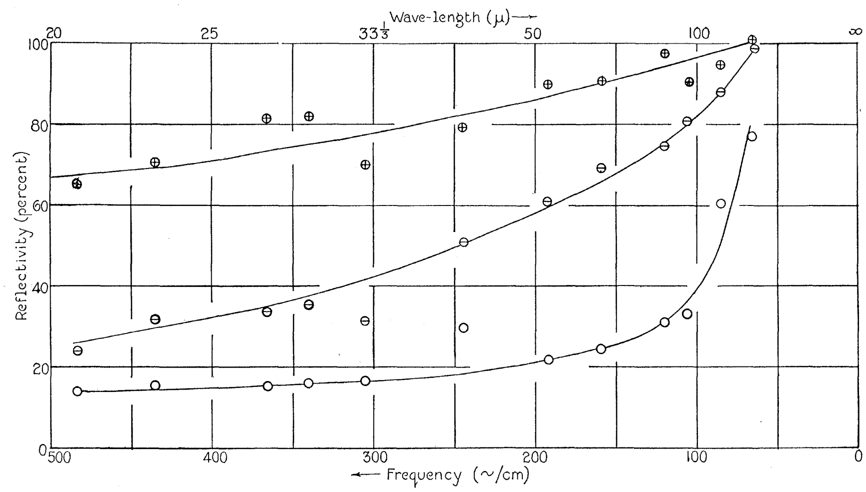


Fig. 2. Reflectivities of brass ground with 400 carborundum, crosses; 220 carborundum, thetas; and 60 carborundum, circles.

### Galena

The measurements of the reflectivity of galena are shown in Fig. 3. It will be observed there are two maxima, one near 80$\mu$ and the other near 120$\mu$. The sample was polished to a high luster except at places where small pieces of the crystal chipped out. The surface used was parallel to a cleavage plane.

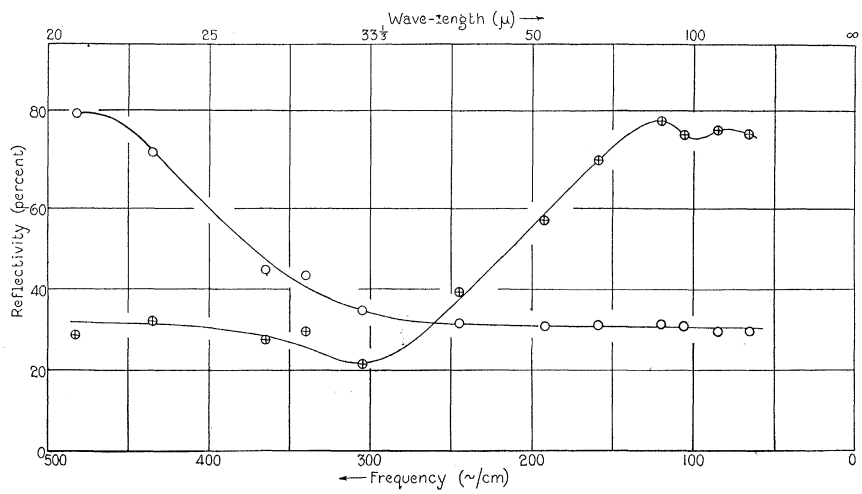


Fig. 3. Reflectivity of beta-magnesia, circles, and galena, crosses.

Four galena reflectors gave a reststrahlen whose intensity when filtered by 2 mm of quartz was 1.3 times that of the rocksalt reststrahlen. The reflection of galena for these radiations was 72 percent. The transmissivity of 0.1 mm black paper was 22 percent. For 152$\mu$ the transmissivity of the paper was 38 percent.

**Magnesia**

The reflectivities of magnesia for the far infrared are shown in Fig. 3. The sample was from a dense polycrystalline mass fused in an electric furnace. The exact position of the reflection maximum can only be determined with higher resolving power than was here obtainable.

**Zincite**

The reflection of a natural zincite crystal is shown in Fig. 4. The reflectivity is not to be considered as accurate in absolute value because the zincite was not sufficiently uniform to take a good polish. The surface was, however, much less rough than the 440 brass shown in Fig. 2. The curve is drawn with maxima at 22 and 28$\mu$ to agree with the predictions of S. Tolksdorf.[8]

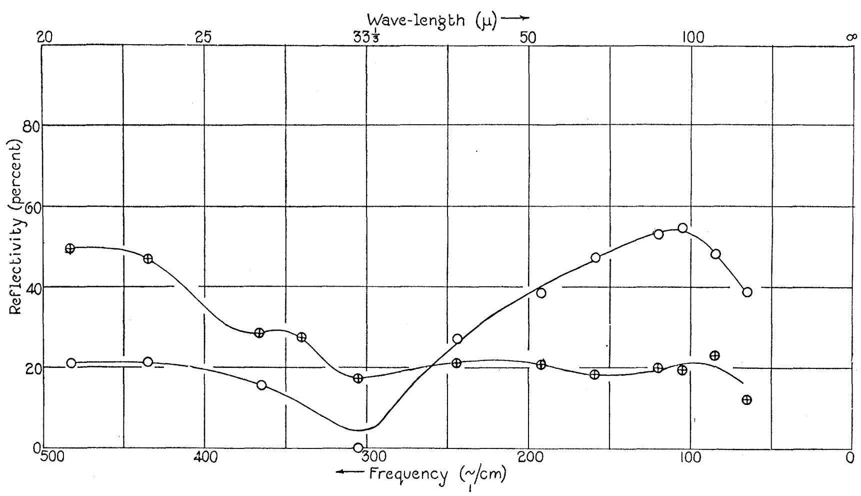


Fig. 4. Reflectivities of zincite, crosses and stibinite, circles.

**Stibinite**

The sample of stibinite was cleaved from a small crystal. It was neither flat nor large enough for the hole in the plate *D* (see Fig. 1). Nevertheless the results plotted in Fig. 4 indicate a maximum of reflectivity at 94$\mu$.

**Sphalerite**

Because of nonuniformity this crystal did not take a good polish. As a consequence of this, the reflectivities are not to be considered quantitatively correct. The results (Fig. 5) agree with those of Rubens for (ZnFe)S in having a maximum at 30.9$\mu$.

**Corundum**

The sample was not large enough to afford quantitative investigations. The results (Fig. 5) show maxima at 23$\mu$ and 27$\mu$ which may possibly be the fundamental bands whose overtones were observed by Coblentz[9] at 11.8 and

[8] S. Tolksdorf, Zeits. f. phys. Chem. **132,** 161 (1928).

[9] W. W. Coblentz, Investigations, part V, p. 18, 1908.

13.5μ. It will be observed there is a third and weaker maximum at 52μ. In Fig. 6 the reflectivities of cuprite and molybdenite are shown. Neither of these substances showed very remarkable spectra in the infrared. The samples were not perfect, so a quantitative interpretation of the results is not justified.

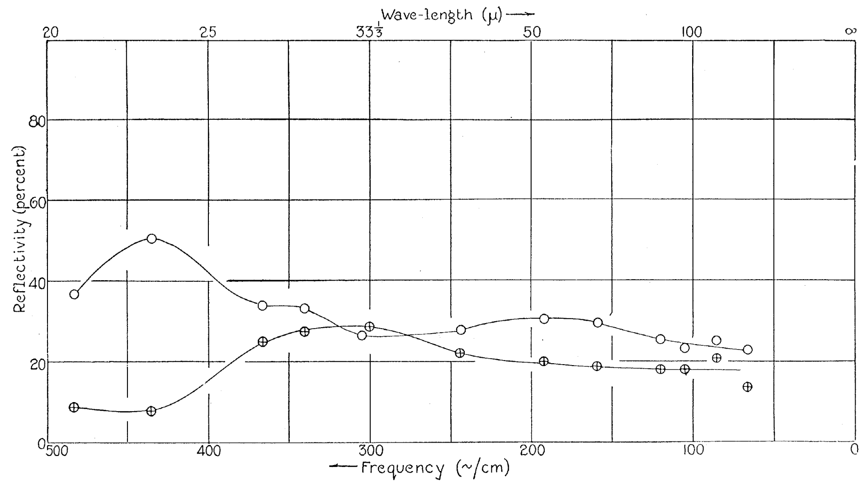


Fig. 5. Reflectivities of corundum, circles, and sphalerite, crosses.

### Transmissivities

**KBr and KI**

The transmission of 3.19 mm of KBr and 0.83 mm of KI is plotted in Fig. 7. It is well to keep in mind the result reported in an earlier paper,[6] namely that 2 cm of KI transmits 50 percent of the 32.8μ reststrahlen. These results do not distinguish between loss of light due to surface reflection and that due to body absorption.

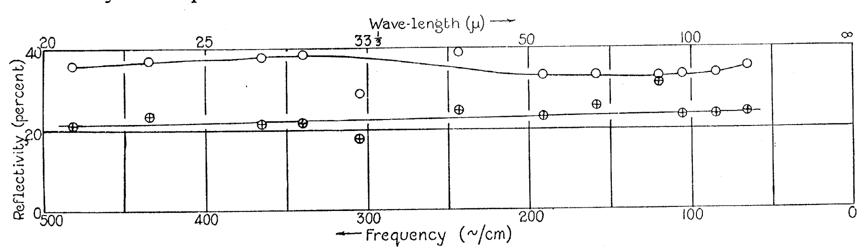


Fig. 6. Reflectivities of cuprite, circles; and molybdenite, crosses.

**KCl evaporated on a lacquer film**

This experiment was made to see if an evaporated film would not be free of the anomaly reported by Hirsekorn[10] for the lacquer films on which KCl smoke was deposited. The evaporated film gave only a single absorption at the expected position. The sample was prepared by evaporation of KCl onto a lacquer film in vacuum. Hirsekorn evaporated at atmospheric pressure and

[10] H. G. Hirsekorn, Ann. d. Physik 6, 985 (1930).

observed two maxima of absorption on either side of the region of metallic reflection for KCl.

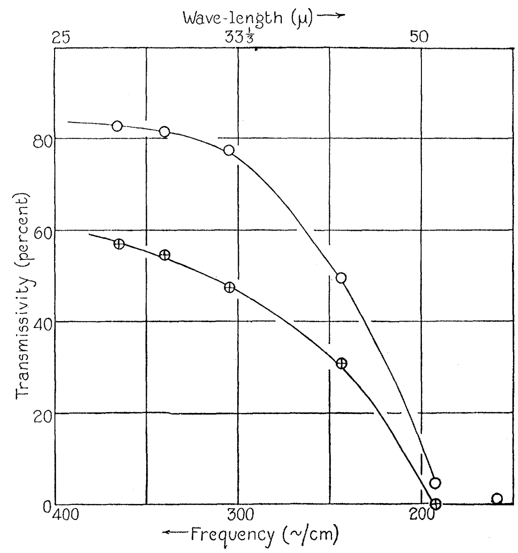


Fig. 7. Transmissivities of 3.19 mm KBr, crosses; and 0.83 mm of KI, circles.

## Quartz film

Thin films of amorphous quartz have been used as absorption cell windows in the far infrared by Czerny.[11] For such purposes it is useful to know their transmission. This is shown in Fig. 8 for a film, about $10\mu$ thickness, of

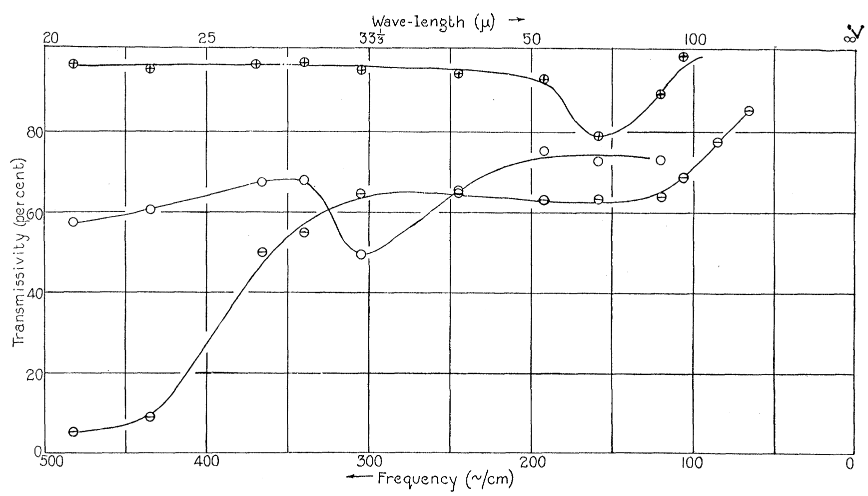


Fig. 8. Transmissivities of $10\mu$ film of amorphous quartz, thetas; liquid $CCl_4$, circles; KCl evaporated on lacquer film, crosses.

[11] M. Czerny, Zeits. f. Physik **44,** 235 (1927).

amorphous quartz. The increase in transmission beyond 83$\mu$ may be ascribed to the destructive interference between the light reflected from the front and back surfaces of the quartz film.

### $CCl_4$

$CCl_4$ has a band system analogous to $CH_4$. Trumpy[12] has predicted for $CCl_4$ an active frequency at 311$\sim$/cm. This is the only active frequency in the far infrared. In order to test for the presence of this band a solution of $CCl_4$ in paraffin was placed between two thin paraffin sheets. This was chosen in preference to the gas method because of the low vapor pressure of $CCl_4$. The transmission of this sample showed a minimum at the predicted position in the spectrum (see Fig. 8).

I believe this method of studying the transmission of liquids in the far infrared to be superior to the use of a thin cell bounded by windows because it is free from objectionable interference effects. These effects may be particularly annoying in the far infrared where (if the windows are quartz) the reflectivities are high and the Bragg reflection consequently more troublesome.

### Copper and aluminum powders

These powders were suspended in Kahlbaum paraffin and sheets as thin as 0.15 mm proved to be opaque although this was not to be expected since the particles were small as compared with the wave-length of the radiation.[13]

## Emission

### NaCl

The emission of NaCl on a platinum ribbon was investigated just below and just above the melting temperature. The results are given in Table II.

Table II. *Ratio of emission of NaCl on Pt ribbon above melting temperature to emission below melting temperature.*

| 63$\mu$ | 52$\mu$ | 41$\mu$ |
|---|---|---|
| 1.24 | 1.01 | 1.20 |

The results are unfortunately not decisive because at the lower temperature very little NaCl volitalized whereas the molten salt sent up a little curl of smoke which may have absorbed some of the radiations as it was partially in the radiation path. However, it is probable that the characteristic frequency of NaCl at 52$\mu$ disappears on melting.

[12] B. Trumpy, Zeits. f. Physik **66**, 790 (1930).

[13] In this connection the result of another experiment is of interest. The fluorite reststrahlen was not transmitted through a tube 10 feet long filled with the smoke from burning phosphorus.