CERTAIN OPTICAL AND ELECTRO-MAGNETIC PROPERTIES OF HEAT WAVES OF GREAT WAVE-LENGTH, I.

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IN a recent paper¹ the present writers described a method by which it is possible to obtain fairly homogeneous heat rays of great wave length without the aid of the usual spectrum apparatus. The method was based upon the principle that if the total radiation from a source emitting waves comprising a great range of different wave-lengths be reflected from a surface, the reflected rays will, in general, have a composition different from the incident rays. Waves which correspond to regions of heavy absorption in the substance of the reflecting body, and which it in consequence reflects as a metal, will have greatly the advantage over all other rays in the reflection spectrum, and in the remainder, after several successive reflections on surfaces of the same material, these rays only will be found in measurable quantity.

The matter contained in the present paper may, for convenience of treatment, be divided into four parts. The first part gives in detail the changes in the arrangement of apparatus by which a great improvement in both the sensitiveness and the accuracy of measurement was obtained. The second part contains the account of results obtained by the application of the improved method to a wider range of substances. The third part deals with the absorption reflection and refraction of long heat waves in a variety of media. The fourth part describes a number of experiments which reveal the electro-magnetic character of heat waves of great wave-length.

I.

Improvements in Apparatus.

The changes introduced in the order of apparatus described in the earlier paper were: First, the substitution of a Linnemann zircon-

¹ PHYSICAL REVIEW, IV., p. 513, 1897, and Naturw. Rundsch., 11 Jahr'g., No. 43, 1896.

ium burner instead of the incandescent platinum foil coated with powder. By this change long waves in somewhat greater intensity were obtained, doubtless, because the zircon could be heated to a much higher temperature than the powders of such substances as fluorite for example. Second, in the interest of greater purity and homogeneity of the rays obtained, four or even five reflecting surfaces were used instead of three. Third, in place of the bolometer of the earlier study a torsion radiometer was substituted. The last two of these substitutions led to the much more complicated arrangement of apparatus shown in Fig 1.

a is the zircon plate of the Linnemann burner, b a concave silver mirror of great focal length, $p_1 p_2 p_3 p_4$ plane surfaces of the substance studied. The reflecting spectrometer $s_1 e_1 e_2 s_2$, upon the table g of which a coarse wire grating could be placed for wave-length measurements, was so arranged that either a bolometer or radiometer could be used and Fig. 1 shows the arrangement of apparatus chosen for the radiometer. In this arrangement the slit s_2 , in place of the eye piece or bolometer wire, remained fixed and the arm of the spectrometer carrying the mirror e_2 could be turned through any given angle and its position accurately read from the graduated spectrometer circle. An image of the slit s_2 was projected upon one wing of the radiometer at R by the aid of a concave silver mirror c of short focal length.

In this arrangement of the spectrometer the relation between the angle α , through which the mirror e_2 moves as read from the spectrometer circle, and the diffraction angle φ is not a simple one, yet a proportionality between the two for small values of α is easily proved. The course of the middle ray in the spectrometer $s_1 e_1 e_2 s_2$ is shown in Fig. 2 for the zero position, and for a neighboring position of the moveable arm e_2 . Let the angle between the two positions of the mirror arm be α and the corresponding defraction angle φ . Further

Fig. 1.

Fig. 2.

let w' represent the angle between n' the optic axis of the mirror e_2' and the ray $s_2 e_2'$, and w represent the corresponding angle between n the optic axis of the mirror e_1 and the ray $s_2 e_2$ then

$$w' = w + \alpha - \beta$$

where β represents the angle between $s_2 e_2'$ and $s_2 e_2$. The reflected ray $s_2 e_2$ corresponds to the incident ray $e_1 e_2$, the reflected ray $e_2' s_2$ corresponds to $A e_2'$; whence the angle ϕ is the difference in direction between $e_1 e_2$ and $A e_2'$, and consequently

$$\phi = \alpha + w' - w = 2\alpha - \beta$$

From this relation it appears that the assumed proportionality between ϕ and α holds at best only as a close approximation for small values of α . In the present case the greatest and least values of α were comprised between $+3^\circ$ and -3° . The best evidence of the trustworthiness of this assumption in the present application, lies in the observation that the diffraction images occur at equal angles on either side of the central image about which they occupy symmetrical positions. The effect of a lack of proportionality between α and β would be such that for negative values of α the differential coefficient $\partial\beta/\partial\alpha$ would be greater, and for positive values less than for $\alpha=0$. As it was impossible from the dimensions of the apparatus to establish the relation of α to β with sufficient accuracy by direct linear measurements, the spectrometer was empirically calibrated by a series of measurements in the diffraction spectra to be given later in detail.

For quite another reason the present arrangement was applicable only to small deviations. The angle of diffraction $\phi = 2\alpha - \beta$ which in the present case equalled approximately 1.7α was such that for large values of α a noticeable displacement of the diffracted bundle of rays between the movable mirror e_2 and the slit s_2 occurred. As here used the maximum displacement amounted to ± 7 mm. which could not have caused any displacement of the observed energy maxima because the concave mirrors e_1 and e_2 were considerably

larger than the diffraction grating so that in both extreme positions the whole diffracted bundle was caught by the mirror e_2 .

This arrangement of the spectrometer is without doubt less rigorous than that proposed by Wadsworth¹ which likewise permits both slits to remain fixed, yet the simplicity of the arrangement here used is in its favor.

Apparatus.

The spectrometer has been described in an earlier paper by one of the present writers² and the grating was the same one used in the earlier study. Suffice it here then to say that the circle of the spectrometer could be read to seconds, and the grating constant, as optically determined and as directly measured on the dividing engine, was $0.3716 \pm \text{mm}$. The grating from its peculiar construction gave only spectra of the odd orders.

By the aid of an eye-piece mounted directly behind the fixed slit s_2 , with the grating on the spectrometer table at g , the empirical calibration of the spectrometer was made by reading the settings for the images of the sodium line on both sides of the central image. The results are shown in Table I.

TABLE I.

Order of Spectrum.	Deviation observed		$\frac{r+l}{2}$ observed.	Computed.	Difference δ''
	left l	right r			
5	16' 17"	16' 23"	16' 20"	16' 20"	0
9	29 45	29 45	29 45	29 42	-3
13	43 0	42 45	42 57	42 54	-3
17	56 20	56 0	56 10	56 6	-4
21	69 25	69 10	69 17	69 18	+1
25	82 35	82 20	82 28	82 30	+2
29	95 55	95 30	95 42	95 42	0
33	109 5	108 35	108 50	108 54	+4

The numbers in the table show that beyond the image of the 13th order a systematic asymmetry appears between the position of the images on the right and the corresponding images on the left, which

¹Wadsworth, Phil. Mag., 49, p. 337, 1894.

²H. Rubens, Wied. Ann. 54, p. 270, 1894.

in the case of the image of the 33d order reaches 30'' of angle, but the mean values of the images right and left still agree perfectly with the computed values. The computed values correspond to the diffraction of a grating with a constant of 0.6139 mm. The ratio of this apparent constant to the real constant 0.3716 is 1.6522—a factor with which the observed angles of deviation α are to be multiplied to obtain the true diffraction angle φ . The magnitude of this factor depends on the position of the fixed slit s_2 , it was, therefore, necessary to determine the position of this slit from time to time. The uncertainties produced by the slight changes in position thus observed affected the values obtained by quantities less than 0.2 per cent.

Instead of the grating described above, a similar grating of higher dispersion, made of gold wires, was often introduced, the constant of which was 0.0662+ mm.; but the inferior quality of this grating, when compared with the former one, rendered the results obtained by its aid even less trustworthy.

The torsion radiometer resembled closely the instrument previously described by one of the present writers.¹ In the new radiometer no fluorite window was used, but instead a plate of chloride of silver $2\frac{1}{2}$ mm. thick in place of the mica plate. The chloride of silver was found to transmit rays of 24μ wave-length partially.² The new radiometer vanes were very much smaller than in the old suspension—measuring only 6 mm. long by 1.5 mm. wide and 5 mm. across from the outer edge of the one vane to the outer edge of the other. The vanes were coated with finely powdered black oxide of iron. The disturbance of a very troublesome tremor of the radiometer suspension encountered at first, due to a tremor of the building, was completely excluded by suspending the instrument as a whole from a wall-bracket according to the method of W. H. Julius.³ It was further possible to so completely screen the radiometer from outside thermic disturbances that the single throws,

¹E. F. Nichols, PHYSICAL REVIEW, IV., p. 297, 1897; also Berl. Ber. 5, Nov., 1896 and Wied. Ann., 60, p. 401, 1897.

²The diathermancy of chloride of silver for waves of great wave-length was first discovered by C. Schulze-Sellack, Pogg. Ann., 139, p. 192, 1870. The plates used here were selected from among those made and used by Schulze-Sellack.

³W. H. Julius, Wied. Ann., 56, p. 151, 1895.

measured on a scale 3,000 scale divisions from the instrument, were trustworthy to 0.2 scale division. In spite of the heavy absorption of the chloride of silver radiometer window for the long waves the radiometer proved to be approximately three times as sensitive as the platinum bolometer, earlier described. If the differences shown by the two instruments in freedom from extraneous disturbances be taken into account the effective sensitiveness of the radiometer was more than five times that of the bolometer. In spite, however, of this great gain in sensitiveness of the radiometer over the bolometer, the radiometer could only be used after some material for a window had been discovered by the aid of the bolometer which transmitted partially, at least, the radiations in question.

II.

The Application of the Method.

Preliminary studies of the substances fluorite and quartz have been communicated in an earlier paper.¹ In quartz another region of metallic reflection has been found which was overlooked in the earlier study, owing to the presence of a rocksalt lens (which completely absorbed the rays of the second maximum) used to concentrate the rays from the lamp on the reflecting surfaces. The study of the short spectrum resulting from multiple reflection on fluorite surfaces has been more fully carried out with the improved apparatus which has led to more accurate results.

Substances Studied.

The method has so far been extended to the study of eleven substances including quartz, mica, fluorite, rocksalt, sylvine, crown glass, flint-glass, sulphur, potassium alum, shellac, and both rays in Iceland spar. In the first three substances regions of metallic reflection were found and the distribution of energy in the reflection maxima determined. Rays were obtained after five reflections from rocksalt, which were all but totally absorbed by the interposition of a very thin plate of the same substance. Owing to the very low intensity of these rays we have not yet succeeded in finding the position of the energy maximum in the diffraction spectrum.

¹ Rubens & Nichols, l. c.

Quartz.

The first region of metallic absorption in quartz is not so far removed from the energy maximum in the spectrum of the zirconium lamp as to make measurements of the distribution of energy in the first spectrum of rays after four-fold reflection on quartz surfaces, difficult. With the radiometer and slit widths varying from 1 to 1.5 mm. it was even possible to trace the energy curve of these rays in the higher dispersion of the spectrum of the third order.

The results of such a series of observations are shown graphically in Fig. 3, in which abscissas represent angle readings of the movable mirror arm and ordinates the corresponding throws of the radiometer. In this series the slits s_1 and s_2 were 1.5 mm. wide. The greatest throw obtained in the energy maximum of the central image was 325 mm.

Fig. 3.

Fig. 3 shows, in all, nine maxima. Of these A is the central image, B_1 , B_2 the images of the first order of the absorption band previously observed; the corresponding images in the spectrum of the third order are seen in C_1 , C_1' and C_2 , C_2' as dotted curves on the extreme ends. Of these the outermost C_1 and C_2 are the more intense.

In addition, the figure shows two sharply defined maxima D_1 and D_2 . When a plate of rocksalt 2.6 cms. thick was interposed, the energy corresponding to these bands vanished completely while the ordinates of B_1 and B_2 , C_1 C_1' and C_2 C_2' were reduced by about 10 per cent. This explains the reason why D_1 and D_2 did not appear in the results of the earlier study where, as already mentioned, a rock-salt lens was used for concentration. The distances of the maxima on either side of the central image and the wave-lengths corresponding to the settings of the spectrometer are given for two complete series of measurements in Table II. The second series does not elsewhere appear in detail.

TABLE II.

Maximum.	Angle of deviation α .		α Mean.	Wave-length λ
	Series I.	Series II.		
B_1	49'	50'	} 49' 30"	8.85 μ
B_2	50	49		
C_1	2° 31 $\frac{1}{2}$ '	2° 32'	} 2° 31' 38"	9.02
C_2	2 31	2 32		
C_1'	2 24 $\frac{1}{2}$	2 23	} 2 23	8.50
C_2'	2 22 $\frac{1}{2}$	2 22		
D_1	1 56 $\frac{1}{2}$	1 57	} 1 56 30	20.75
D_2	1 56 $\frac{1}{2}$	1 56		

In accordance with these results quartz is seen to possess narrow regions of metallic reflection in the infra-red spectrum the maxima of which correspond to $\lambda=8.50\mu$, 9.02μ and 20.75μ respectively.

The first two bands which lie close together were earlier discovered by one of the present writers.¹ The values of λ obtained at that time were 8.42μ and 8.80μ respectively of which the one is less by 1 per cent., and the other by 2.7 per cent. than the corresponding values just given. This difference is doubtless due to the increasing impurity with increasing wave-length in this region of the spectrum of the fluorite prisms in which the earlier study was made. The reason for this exists in the heavy and increasing absorption of fluorite which begins in the region under discussion. The effect of

¹ E. F. Nichols, l. c.

this sort of impurity would be to displace both maxima toward shorter wave-lengths, and for the same reason the second would suffer greater displacement than the first. This view is further confirmed by the fact that the second maximum $C_1 C_2$ in the present study is seen to be higher than the first, while the reverse was found in the earlier measurements. The possibility of such an error was foreseen, and attention called to it in the earlier paper.¹

The Ketteler-Helmholtz dispersion formula, when applied to early measurements of dispersion in quartz, placed the middle of the infra-red absorption band, assumed single, at $\lambda_2 = 10\mu$.² In this computation the form

$$n^2 = b^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2} \quad (1)$$

was used.³ It is quite possible that the new absorption band at $\lambda = 20.75\mu$ is not wholly without influence upon the dispersion in the early infra-red, or even in the visible spectrum. At any rate it is impossible to make equation (1) fit the early observations even approximately by substituting any value for λ_2 between 8.5 and 9μ where observation has placed it. On the other hand an attempt to introduce a third term of the same form as the previous two on the right side of equation (1) was more successful. With this addition the formula stands

$$n^2 = b^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2} - \frac{M_3}{\lambda_3^2 - \lambda^2} \quad (2)$$

In which $\lambda_2 = 8.85\mu$ — the wave-length of the approximate center of absorption as shown by the mean value of B_1 and B_2 in Table II. λ_3 was put equal to 20.75μ — the wave-length of the middle of the absorption band D_1 . Equation (2), while it contains the same number of arbitrary constants earlier used,⁴ is in harmony with the new measurements as well as with the old.

Table III contains the observed values of the refractive index for

¹ E. F. Nichols, l. c. *PHYS. REV.*, p. 308.

² H. Rubens, *Wied. Ann.* 54, p. 476, 1895.

³ Wherein n is the index of refraction, λ the wave-length and b^2 , M_1 , M_2 , λ_1^2 , and λ_2^2 are arbitrary constants.

⁴ In this form the arbitrary constants are M_1 , M_2 , M_3 , b^2 and λ_1 .

a number of wave-lengths in the ultra-violet, visible, and infra-red spectrum which are compared with corresponding values computed by equation (2), in which the constants M_1 and λ_1 are those computed by Ketteler,¹ and b^2 was obtained by the aid of the equation,

$$b^2 = a^2 + \frac{M_2}{\lambda_2^2} + \frac{M_3}{\lambda_3^2}$$

and the value a^2 given by Ketteler.² The two remaining constants M_2 and M_3 were computed from the observed indices for wave-lengths 2.84μ and 4.20μ .

TABLE III.³

Wave-length λ	n obs.	n comp.	Diff. δ . 10^4	Wave-length λ	n obs.	n comp.	Diff. δ . 10^4
0.19881	1.65070	1.65077	+0.7	1.969	1.5216	1.5216	0
0.27467	1.58750	1.58757	+0.7	2.84	1.5039	1.5039	0
0.35818	1.56400	1.56395	-0.5	3.63	1.4799	1.4801	+2
0.4341	1.55387	1.5539	0	4.20	1.4569	1.4569	0
0.5350	1.54663	1.5466	0	5.0	1.417	1.412	-50
0.6563	1.54181	1.5419	+1	5.8	1.368	1.339	-290
0.7682	1.53893	1.5390	+1	6.45	1.274	1.241	-330
1.160	1.5329	1.5329	0	7.0	1.167	1.096	-710

$$b^2 = 4.57877$$

$$M_1 = 0.010654 \quad M_2 = 44.224 \quad M_3 = 713.55$$

$$\lambda_1^2 = 0.010627 \quad \lambda_2^2 = 78.22 \quad \lambda_3^2 = 430.56$$

The agreement between values of n computed from (2) and those obtained indirectly—from observation of reflection—is not close, yet the divergence would be fully explained by the assumption of the presence of from 1 to 2 per cent. of the energy belonging to $\lambda = 1.4\mu$ in this part of the spectrum, or of 0.3 per cent. of stray rays from $\lambda = 8.5\mu$. The former wave-length corresponds approximately to the energy maximum in the spectrum of the zirconium burner, the second to the middle of the neighboring absorption band in quartz.

¹ E. Ketteler, Wied. Ann. 30, p. 312, 1887.

² Compare H. Rubens, Wied. Ann. 53, p. 268, 1894.

³ The dispersion measurements between wave-lengths $\lambda = 0.19881$ and 0.35818μ are taken from Sarasin, between $\lambda = 0.4341$ and 4.20μ from Rubens and from $\lambda = 5\mu$ to 7μ from Nichols.

A second and more probable reason is doubtless to be found in the particular form of equation (2) which makes it inapplicable in the immediate neighborhood of a band of metallic absorption. As early as $\lambda=8.\mu$ the formula gives negative values for n^2 so that the limitations of the formula would appear to be the more reasonable explanation of the disagreement.

Mica.

Doubtless on account of the large percentage of silica¹ which enters into the composition of mica, rays after four reflections or surfaces of this substance yield a spectrum which resembles strikingly that of quartz just described. Fig. 4 contains the results of a series of observations of rays sent out from the zirconium lamp which, after four reflections on plane surfaces of mica, were analysed by the grating and radiometer. In this series the slits $s_1 s_2$ were opened $2\frac{1}{2}$ mm. wide.

Fig. 5.

In addition to the central image A the curve shows three maxima on either side, where regions of metallic reflection exist. That the images all belong to the spectrum of the first order, and that $D_1 D_1'$ and $D_2 D_2'$ are not repetitions of B_1 and B_2 in the spectrum of the

¹ According to the observations of Rammelsberg mica contains from 45 to 47 per cent. of silica (Neumann, Mineralogie).

third order, is that the former vanished when a rocksalt plate 2.6 cm. thick was introduced into the path of the rays. Table IV gives the exact positions and the corresponding wave-lengths for the several maxima.

TABLE IV.

Maximum.	Angle of deviation α	α Mean.	Wave-length. λ
B_1	51'	} 51½'	9.20 μ
B_2	52'		
D_1	2° 0'	} 1° 59'	21.25
D_2	1 58		
D_1'	1 43	} 1 43'	18.40
D_2'	1 43		

With the exception of the maximum at $\lambda = 18.40\mu$, the absorption bands correspond very closely to those observed in quartz. Because of the wide slits, and the low dispersion of the grating it was impossible to draw any conclusion concerning the distribution of energy in the maxima B_1 and B_2 .¹ In consequence, these two bands were compared with the corresponding quartz bands by the aid of the grating of gold wires already mentioned which gave a higher dispersion. The results thus obtained are shown in Fig. 5.

The lower curve gives the distribution of energy in the mica band, and the dotted line the same for quartz under the same circumstances. The setting for the central image in both cases was $199^\circ 55' 0''$. From Fig. 5 it appears that the reflective power of quartz in this region is much greater than that of mica. It is further seen that the elevations B_1 and B_2 consist of two separate maxima, the corre-

¹ The images in the spectrum of the third order could not be studied because too weak in energy.

sponding wave-lengths of which do not agree with the similar maxima in quartz. The wave-lengths of the maxima in mica are $8.32\ \mu$ and $9.38\ \mu$, and those for quartz $8.52\ \mu$ and $9.03\ \mu$ respectively. The last two values are in close agreement with the results of the quartz series given in Table II.

The natural conclusion from these results is, that the metallic reflection of mica, with perhaps the exception of the maximum at $18.40\ \mu$, is due to the silica which it contains. The small differences in the position of the reflection maxima are doubtless wholly due to an effect, already well known through optical studies—the influence of the solvent upon the absorption spectrum of the substance dissolved.

Fluorite.

The apparatus and method used in the earlier determination of the metallic reflection of fluorite have been fully described elsewhere.¹ In the present repetition of that study the following essential changes have been introduced, which require attention: First, the source of energy has been changed from an incandescent sheet of platinum coated with powdered fluorite to a zirconium lamp. Second, the number of reflecting surfaces was increased from three to four. Third, the arrangement of the spectrometer was changed. Fourth, the radiometer with vanes coated with black oxide of iron was substituted for the bolometer coated with platinum black. Fifth, a plate of vitreous chloride of silver, in the form of a radiometer window, was introduced into the path of the rays.

The results obtained with the present arrangement are shown in Table VI, while those obtained earlier appear in Table V.

TABLE V.

Series.	Deviation from central image.		Wave-length λ
	Right.	Left.	
I	$3^\circ 45'$	$3^\circ 41'$	$24.2\ \mu$
II	3 48	3 47	24.7
III	3 44	3 46	24.4
Mean			$24.4\ \mu$

¹ Rubens and Nichols, l. c.

TABLE VI.

Series.	Deviation from central image.		Wave-length λ
	Right.	Left.	
I	2° 13'	2° 13'	23.8
II	2 12	2 13	23.7
III	2 12	2 13	23.7
Mean			23.73

A difference appears between the earlier values and the later ones which lies altogether beyond the range of error in either case. The ground of this discrepancy was found to be a strongly selective absorption of chloride of silver. This absorption changes markedly even within the narrow limits of the short spectrum lying between 22 and 28μ . At three different points within this range, the transmission of a second silver chloride plate was studied and found to be

Fig. 6.

40 per cent. at $\alpha = 2^\circ 10'$, 37 per cent. at $\alpha = 2^\circ 15'$, and 33 per cent. at $\alpha = 2^\circ 20'$. The combination of this transmission curve with the curve representing the true distribution of energy in the reflection maximum would be such as to displace the latter toward shorter

wave-lengths by approximately $0.^\circ 3' 30''$ of angle which corresponds to a wave-length difference of 0.62μ . This, when added to the observed maximum 23.73μ , gives 24.35μ as the true position of the maximum which agrees very well with 24.4μ , the value reached in the earlier study.

The first series of observations in Table VI. is shown graphically in Fig. 6. The slit widths were 3.5 mm. The radiometer throw for the middle of the central image was 56 mm., and in the maximum of the image of the first order 12 mm. was obtained. The distribution of energy is better shown by another series of observations made with slits 2 mm. wide, the results of which appear in the dotted curve in Fig. 6, which, from its form, suggests the possibility that the observed maximum consists, in reality, of two maxima belonging to a double band as in the case of quartz and mica. An attempt to effect the further separation of the two maxima was unsuccessful on account of the small quantity of energy present in these rays.

(*To be concluded.*)