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The Influence of Temperature on the Intensity of Reflexion of X-Rays from Rocksalt.

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CONTENTS.

1. A THEORETICAL expression for the influence of temperature on the intensity of the interference maxima produced when X-rays are diffracted by a crystal was first obtained by Debye[†] in 1913. Suppose a beam of X-rays of wave-length λ passes through a crystal in a direction making a glancing-angle θ with a series of atomic planes whose spacing is d. Then the spectrum of the nth order may be considered as produced by reflexion at these planes, if

$$2d\sin\theta = n\lambda.$$

If the atoms lie exactly in the plane, the contributions from all of them to this spectrum will be exactly in phase ; but if, by reason of their heat-motion, they are displaced by varying small amounts from these planes, the contributions

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[*] Communicated by Prof. W. L. Bragg, M.A., F.R.S.

[†] P. Debye, *Verh. der deutsch. Phys. Ges.* xv. pp. 678, 738, and 867 (1913).

will no longer all be in phase, and the intensity of the spectrum will be correspondingly reduced. Debye in his earliest papers supposed each atom to be bound by a quasi-elastic force to a position of equilibrium lying in the atomic plane, or rather at one of the lattice points of the crystal. Owing to the heat motion, each atom is displaced at any instant by a certain distance from its equilibrium position. If we knew all the displacements at any time, we could calculate the effect on the intensity of the X-ray beam diffracted in any direction. Debye carried out the calculation for a given configuration, multiplying the intensity factor so obtained by the probability of the occurrence of the configuration, and summing up over all possible configurations obtained a value for the mean intensity of the diffracted beam in any direction. The probability of a given set of displacements was calculated according to Maxwell's distribution law. Debye obtained an expression for the intensity of the X-ray beam in any direction which consisted of two parts—the first corresponding to the scattered radiation, the second to the interference maxima. The effect of increasing temperature is to increase the scattered radiation and to diminish the intensity of the interference maxima. Debye's early calculation showed that to account for the effect of the temperature movement, the intensity of the scattered radiation had to be multiplied by a factor

$$\left(1-e^{-\frac{16\pi^2 kT}{f\lambda^2}\sin^2\frac{\phi}{2}}\right),$$

while that of the interference maxima had to be multiplied by a factor

$$e^{-\frac{16\pi^2 kT}{f\lambda^2}\sin^2\frac{\phi}{2}},$$

where T is the absolute temperature, k the gas constant, f the quasi-elastic force per unit displacement of the atom, and ϕ the angle which the diffracted beam makes with the incident beam, so that if the spectrum is supposed to be formed by reflexion from a set of planes at a glancing angle θ, $\theta=\phi/2$.

The use of the Maxwell-Boltzmann distribution law in the above calculation is equivalent to assuming that the displacements of the atoms are all independent. It is evident, however, that this assumption is not justified. The atoms are not held to fixed points of equilibrium, but to one another, and the displacements of any atom must influence those of its neighbours. The heat-motion of such a medium may be considered as a series of "elastic waves," and had been discussed by Born and Karman[*]. Debye[†] recalculated the effect of heat-motion on the interference maxima, using these ideas and taking the quantum theory into account. He found that the intensity of the interference maxima had to be multiplied by a factor e^{-M}, where

$$M = \frac{6h^2}{\mu k \lambda^2 \Theta} \cdot \sin^2 \frac{\phi}{2} \cdot \frac{\phi(x)}{x} \quad . \quad . \quad . \quad . \quad (1)$$

Here μ is the mass of one of the atoms, h is Planck's constant, Θ a temperature characteristic of the crystal, $x = \frac{\Theta}{T}$, and $\phi(x)$ is a certain function of $\frac{\Theta}{T}$ which can be evaluated. If the existence of Nullpunktsenergie is assumed, $\frac{\phi(x)}{x}$ is replaced by $\left\{\frac{1}{4} + \frac{\phi(x)}{x}\right\}$. For values of T small compared with the characteristic temperature Θ, M should be proportional to T^2, while for high values of T it should be proportional to T, as the more elementary treatment showed.

More recently the question of the effect of temperature on the scattered radiation has been considered by Faxen[‡] and by Waller[§].

2. The first experiments on the influence of temperature on the intensity of reflexion of X-rays by crystals were carried out in 1914 by Sir William Bragg[‖], who used rocksalt and sylvine. With rocksalt, experiments were made at temperatures of 15° and 370° C., and the conclusion was reached that the effect was of the same order as that calculated by Debye. More recently experiments on similar lines have been made by Backhurst[¶], who used aluminium, corundum, carborundum, diamond, and graphite. Only very general agreement was found with the theory of Debye, but it must be noticed that Debye's theory applies to a simple cubic lattice only. Quite recently Collins[**] has studied the Debye effect for aluminium, and again finds results at variance with the theory of Debye. The

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[*] Born and Karman, *Phys. Zeitschr.* xiv. p. 65 (1913).

[†] *Ann. der Phys.* xliii. p. 49 (1914).

[‡] H. Faxen, *Zeitsch. für Physik.* xvii. p. 266 (1923).

[§] L. Waller, *ibid.* p. 398 (1923).

[‖] W. H. Bragg, Phil. Mag. May 1914.

[¶] Proc. Roy. Soc. A, cii. p. 340 (1922).

[**] E. H. Collins, Phys. Rev. xxiv. p. 152 (1924).

effect of temperature on the scattered radiation has been studied experimentally by G. E. M. Jauncey[*].

3. The experiments to be described in the present paper had their origin in some work by Professor W. L. Bragg[†], C. H. Bosanquet, and the writer on the intensity of reflexion of X-rays from rocksalt, in which an attempt was made to get some idea of the distribution of the electrons in the atoms of sodium and chlorine. In the course of this work it was necessary to make allowance for the Debye factor. The only figures available for rocksalt were those of Sir W. H. Bragg obtained in 1914, and it was considered desirable to repeat them with the better apparatus at our disposal, and if possible to extend the temperature range in both directions. The intensities of reflexion were measured by the method first used by W. H. Bragg[‡], and described in detail by W. L. Bragg, James, and Bosanquet in the papers quoted. The crystal was mounted on the table of an ionization spectrometer. The ionization chamber was set at the angle appropriate to the spectrum under investigation, with a slit wide enough to receive the whole reflected beam, including both the α and α' peaks, and the crystal was rotated at a uniform angular velocity through the range of angles over which it reflected. The total quantity of electricity passing across the ionization chamber during the sweep of the crystal was measured. Let this be proportional to E. Then if ω is the angular velocity with which the crystal is swept, and I the quantity of electricity passing in unit time when the beam is allowed to enter the chamber directly, the quantity $\frac{E\omega}{I}$ is a constant for a given crystal face, and can be taken as a measure of the reflecting power of that face. The quantity $\frac{E\omega}{I}$ is called by Darwin the "integrated reflexion"—a convenient term which will be employed here.

The source of radiation was a Coolidge bulb with either a rhodium or a molybdenum anticathode. To supply the current, a transformer operated by a rotary converter of about 2·25 kilowatts capacity worked from the Corporation mains and producing alternating current at about 140 volts was used. The potential employed was usually about

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[*] Jauncey, Phys. Rev. xx. p. 421 (1922).

[†] Phil. Mag. xli. p. 309 (1921); xlii. p. 1 (1921); xliv. p. 433 (1922).

[‡] *Loc. cit.*

50,000 volts. With this arrangement it was found possible to keep the intensity of the X-ray beam far steadier than in the earlier experiments[*], when a coil and mercury break were used. A null method was used in the observations. The string of the electrometer, which was of the Lutz-Edelmann type, was connected to the inner plate of a condenser, whose outer coating could be raised to any desired potential by means of a potential divider. The sign of the potential applied to the outer coating was such as to neutralize by induction the charge received by the electrometer due to the ionization current. The potential necessary to bring the string back to its zero is then proportional to the total charge received by the electrometer during the observation. The actual readings taken were thus the readings on the potential divider, which had one hundred divisions. A maximum potential of 6 volts could be applied, and to increase the range of reading, any desired fraction of the potential could be tapped off by means of a post-office box and applied to the potential divider. The range of the instrument could be increased still further by having several inner plates of different sizes for the condenser. In this way spectra differing greatly in their absolute intensity could be compared.

The crystal was held between two jaws lined inside with asbestos, on an iron stand to which the necessary adjustments for tilt and centring could be given. The stand was mounted on an asbestos sheet supported on brass and insulated from the spectrometer table by a fused silica ring 3 cm. in height packed with kieselguhr. Over the crystal fitted a cylindrical electric furnace wound with "nichrome" wire and provided with mica windows to allow the ingress and egress of the X-rays. The furnace was surrounded by a cylinder of sheet asbestos pierced with suitable openings, and radiation downwards to the spectrometer table was further checked by surrounding the silica tube, on which the furnace was mounted, by a broad collar of asbestos sheeting. The arrangement for heat insulation proved very satisfactory, and it was possible to work for hours with the crystal at red heat with the spectrometer table only slightly warm. The whole furnace, including the silica pedestal, could be lifted off the spectrometer table and replaced while hot, so that alternate readings with the heated crystal and with the standard could be made. It was found that no appreciable change in temperature was produced by

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[*] Bragg, James, and Bosanquet, *loc. cit.*

removing the furnace from the spectrometer and placing it on another stand close beside it.

The temperature was measured by a thermocouple of iron-constantan placed in contact with the crystal face in such a position that the X-rays did not strike it. The e.m.f. generated by the couple was measured directly with a very convenient potentiometer, kindly lent for these experiments by the Cambridge and Paul Scientific Instrument Company, to whom my best thanks are due. The thermocouple and potentiometer were calibrated, using the boiling-point of water and the melting-points of tin, lead, zinc, antimony and aluminium, and from the readings so obtained a temperature-e.m.f. curve was drawn. Very closely similar curves were obtained with the different couples used, and the error in temperature should not be more than a few degrees. To ensure steadiness and uniformity of temperature, the crystal was heated for from one to two hours before readings were taken.

To determine the proper setting of the ionization chamber, which varies with the temperature on account of the expansion of the crystal and the consequent alteration in the spacing d, a series of readings were made in the region of the peak, the setting of the chamber being altered half a degree at a time, with a corresponding change in the crystal sweep. To determine the intensity of the peak, readings were taken with the chamber two degrees above and two degrees below the setting of the peak, where only the general continuous radiation from the bulb could enter it. The mean of these readings was subtracted from that corresponding to the peak, and the difference was taken as the intensity of the peak. The allowance for the general radiation is of considerable importance, since at high temperatures it may in some cases account for as much as 70 per cent. of the radiation entering the chamber at the setting of the peak. It should be noticed that any creep of the electroscope due to natural leak, or to scattered radiation, is included in the allowance for general. These factors remain practically constant as the intensity of the peak diminishes, and the increasing fraction of general radiation is no doubt largely due to this fact, although, in the case of high-order spectra, the general radiation will include reflexions of longer wavelength at lower orders, for which the decrease of intensity with temperature will be less than for the peak, and this also will cause an increase in the percentage of general as the temperature rises.

The intensity of reflexion from the crystal under investigation was compared in each case with the reflexion from the same face and the same order from a standard rocksalt crystal.

A typical comparison began with a determination of the percentage of general radiation for the heated crystal Q, and ended with a similar determination for the standard S. After the determination for Q, a series of alternate sets of readings at the peak-settings of Q and S were taken in rapid succession, Q being removed from the spectrometer and replaced by S, and so on. The mean values for Q and S obtained from these alternate readings are corrected by subtracting from each the appropriate percentage of general, and the ratio of the corrected values is taken as the ratio of the intensities of the two spectra.

4. Some difficulty was experienced in finding a crystal of rocksalt suitable for these experiments. It was found that all crystals which had a turbid appearance were destroyed on heating, owing to the swelling and bursting of the small liquid or gaseous inclusions which they contained. If care was taken to choose a perfectly clear crystal containing no inclusions, this difficulty could be overcome completely. Even with such crystals it was found that the intensity of reflexion became smaller after continued heating. A similar effect was noticed by Backhurst[*], who ascribed it to the breaking down of one complete crystal into smaller ones differently oriented. It does not seem certain, however, that this is the true explanation, at any rate in the case of rocksalt; indeed, there is some reason to believe that the reverse may be true, and that the size of the homogeneous crystal elements may be increased by heating. The effect in question is much more marked with the first-order reflexion from the (100) face than with the second, and with the second it is more marked than with the third; and this appears to be the case whether the reflexion takes place from a face, or through a slip of crystal in the manner employed in determining the absorption coefficient at the reflecting angle[†]. For example, in some preliminary experiments with a slip of crystal about 1 mm. thick, the intensity (100) before heating was found to be 0·71 of the standard. After heating to 590° C., the intensity had fallen to 0·50 of the standard, but after the

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[*] Backhurst, Proc. Roy. Soc. A, cii. p. 340 (1922).

[†] Bragg, James, and Bosanquet, Phil. Mag. July 1921, p. 1.

crystal had cooled, the intensity had only risen to 0·53. The intensity (200) before heating was 0·92; on heating to 590° it fell to 0·43 and rose on cooling to 0·83, and the permanent fall for (300) was still smaller. This behaviour suggests strongly that the effect of heating is to increase the special absorption or "extinction coefficient" of the crystal. This would have a far greater influence on the intensity of the strong (100) than on the weaker (200) and (300), and might be accounted for by a more perfect crystallization of the material of the slip. The effect is not confined entirely to the surface layers, since reflexion at a slip occurs throughout the whole thickness. The phenomenon requires investigation in much greater detail, and this work is being undertaken. Experiments showed that for (200) and spectra of higher orders, a steady state appears to be reached after several heatings to 500° or 600°. The values of the intensities are less by a few per cent. than those before heating, but are permanent in the sense that the intensities before heating and after heating, when the crystal has been allowed to cool again, are the same. No consistent values for (100) could be obtained, and consequently this spectrum was not used in the present set of experiments.

5. All the observations to be described were made by reflexion at a face. The first set of observations were made with the (300) spectrum, rhodium radiation being used. The rhodium anticathode contained ruthenium as an impurity, and the ruthenium lines caused a certain amount of trouble in determining the general radiation; so, later, the rhodium bulb was replaced by one having a molybdenum target, and with this a series of observations were made between 15° and 650° C., using the (200), (300), and (400) spectra. The results of the measurements are given in Table I.

In this table, column (1) gives the absolute temperature; column (2), R the intensity actually observed, expressed in terms of the reflexion from the corresponding face of the standard crystal at 19° C. as unity. Column (3) gives the ratio of R_T, the observed intensity, corrected in the manner described below, to R_1 the mean corrected intensity at room temperature.

TABLE I.

Rh Kα radiation. $\lambda = 0{\cdot}615$ Å.

	(1) T.	(2) R.	(3) $\frac{R_T}{R_1}$.	(4) $T^2\left(\frac{\sin\theta}{\sin\theta_1}\right)^2$.	(5) $\log_{10}\frac{R_T}{R_1}$.	(6) $\left(\frac{\lambda}{\sin\theta_1}\right)^2 \log_{10}\frac{R_T}{R_1}$.
(300)	293	0·926	1·015	$8{\cdot}58\times10^4$	+0·0064	+0·022
$\theta_1 = 19^\circ\ 10'$	292	0·911	0·998	8·53 ,,	−0·0007	−0·002
$\sin\theta_1 = 0{\cdot}3283$	291	0·908	0·995	8·47 ,,	−0·0020	−0·007
	292	0·906	0·991	8·53 ,,	−0·0031	−0·011
	413	0·701	0·765	16·89 ,,	−0·1163	−0·438
	472	0·621	0·677	21·95 ,,	−0·1696	−0·597
	513	0·535	0·582	25·83 ,,	−0·2347	−0·826
	615	0·357	0·388	36·83 ,,	−0·4114	−1·447
	630	0·351	0·381	38·58 ,,	−0·4190	−1·474
	670	0·304	0·330	43·51 ,,	−0·4818	−1·695
	778	0·169	0·183	58·21 ,,	−0·7379	−2·596
	862	0·115	0·124	70·98 ,,	−0·9060	−3·188

Mo Kα radiation. $\lambda = 0{\cdot}710$ Å.

	(1) T.	(2) R.	(3) $\frac{R_T}{R_1}$.	(4) $T^2\left(\frac{\sin\theta}{\sin\theta_1}\right)^2$.	(5) $\log_{10}\frac{R_T}{R_1}$.	(6) $\left(\frac{\lambda}{\sin\theta_1}\right)^2 \log_{10}\frac{R_T}{R_1}$.
(200)	292	0·831	0·987	$8{\cdot}53\times10^4$	−0·0057	−0·045
$\theta_1 = 14^\circ\ 37'$	292	0·845	1·003	8·53 ,,	+0·0016	+0·013
$\sin\theta_1 = 0{\cdot}2524$	292	0·850	1·009	8·53 ,,	+0·0041	+0·032
	426	0·710	0·833	18·04 ,,	−0·0793	−0·628
	575	0·595	0·692	32·69 ,,	−0·1598	−1·265
	703	0·500	0·577	46·81 ,,	−0·2390	−1·892
	843	0·362	0·413	67·94 ,,	−0·3841	−3·040
	913	0·312	0·355	79·20 ,,	−0·4500	−3·562
(300)	291	0·917	1·000	$8{\cdot}47\times10^4$	0·000	0·000
$\theta_1 = 22^\circ\ 15'$	393	0·722	0·785	15·47 ,,	−0·1051	−0·370
$\sin\theta_1 = 0{\cdot}3786$	511	0·510	0·552	25·65 ,,	−0·2582	−0·908
	625	0·339	0·366	38·04 ,,	−0·4361	−1·535
	756	0·191	0·205	55·04 ,,	−0·6882	−2·422
	898	0·102	0·109	76·70 ,,	−0·9524	−3·387
(400)	292	0·943	0·989	$8{\cdot}53\times10^4$	−0·0046	−0·009
$\theta_1 = 30^\circ\ 18'$	290	0·964	1·012	8·41 ,,	+0·0050	+0·010
$\sin\theta_1 = 0{\cdot}5045$	382	0·682	0·714	14·47 ,,	−0·1466	−0·290
	437	0·504	0·527	18·87 ,,	−0·2784	−0·551
	503	0·362	0·378	24·86 ,,	−0·4228	−0·837
	593	0·219	0·228	34·30 ,,	−0·6426	−1·272
	697	0·110	0·114	46·97 ,,	−0·9436	−1·867

6. The measured intensity R is proportional to the integrated reflexion $\frac{E\omega}{I}$, where E is the total energy reflected when the crystal is rotated with angular velocity ω, and I is the energy received by the ionization chamber when the incident beam enters it for one second. Now it can be shown that [*] [†]

$$\frac{E\omega}{I}=\frac{N^2\lambda^3}{2\mu\sin 2\theta}\cdot\frac{e^4}{m^2c^4}\cdot F^2\cdot\frac{1+\cos^2 2\theta}{2}\cdot e^{-bf(T)\frac{\sin^2\theta}{\lambda^2}}. \qquad (2)$$

In this formula N is the number of molecules per unit volume of the crystal, μ the linear absorption coefficient of the crystal, θ the glancing angle of reflexion, and λ the wave-length of the X-rays. e and m are the charge and the mass of an electron, and c is the velocity of light. The factor $\frac{1+\cos^2 2\theta}{2}$ allows for the fact that the incident rays are unpolarized, and the factor F^2 for the finite size of the atom—which, since the electrons producing the scattering of the X-rays are distributed throughout a region whose dimensions are comparable with the spacings of the atomic planes, adds to the spectra a contribution which depends on the angle of diffraction, becomes smaller as that angle increases, and is proportional to the number of electrons in the atom for very small angles of scattering [‡]. As the formula is written, the factor F^2 also includes the "structure factor" which depends on the arrangement of the atom in each repeat of the crystal pattern.

The term $e^{-bf(T)\frac{\sin^2\theta}{\lambda^2}}$ is the Debye factor which is under investigation in this paper.

We may write

$$e^{-bf(T)\frac{\sin^2\theta}{\lambda^2}}=\frac{E\omega}{I}\cdot\frac{4m^2c^4}{e^4\lambda^3}\cdot\frac{\mu}{N^2}\cdot\frac{\sin 2\theta}{1+\cos^2 2\theta}\cdot\frac{1}{F^2}\propto R_T. \quad . \qquad (3)$$

The measured intensity R, column (2), Table II., is proportional to $\frac{E\omega}{I}$. We require R_T, the corrected intensity, column (3), which is proportional to the value of the Debye factor at different temperatures. To obtain this it is

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[*] C. G. Darwin, Phil. Mag. xxvii. pp. 315 and 675 (1914).

[†] A. H. Compton, Phys. Rev. ix. p. 1 (Jan. 1917).

[‡] W. L. Bragg, James, and Bosanquet, Phil. Mag. xli. p. 309 (1921); xlii. p. 1 (1921); xliv. p. 433 (1922).

necessary to allow for the fact that μ, N, θ, and F all depend on the temperature; μ and N are proportional to the density of the crystal, which decreases as the temperature rises owing to the thermal expansion, and for the same reason θ, the glancing angle for a given spectrum, decreases as T increases. The factor F^2 depends on $\frac{\sin\theta}{\lambda}$, and thus on the temperature. The change of θ with temperature was determined by direct measurement, and from this the value for α the coefficient of expansion of the crystal was calculated. To a sufficient approximation for the purpose under consideration, the coefficient of expansion was found to be linear over the range from 0° to 500°. The value of α obtained as a mean of several experiments was 0·0000383, which is in fair agreement with that obtained by Fizeau, 0·0000402, over a much smaller range from interference measurements. From this figure, the ratios of the values of the factors $\frac{\mu}{N^2}$ and $\frac{\sin 2\theta}{1+\cos^2 2\theta}$ at any temperature to those at room temperature were calculated directly.

The allowance for the change in F^2 presents more difficulties. The values of F^2 determined by W. L. Bragg, James, and Bosanquet * for rhodium rays were used. In order to apply these determinations to the observations made with molybdenum radiation, use was made of the fact that F is a function of $\frac{\sin\theta}{\lambda}$. If the values of F^2 obtained for rhodium radiation are plotted against $\frac{\sin\theta}{\lambda_{\mathrm{Rh}}}$, the curve obtained should be independent of the wavelength, and the value of F^2 for any angle θ for molybdenum can be read off at once over the corresponding value of $\frac{\sin\theta}{\lambda_{\mathrm{Mo}}}$. The uncertainty in this correction lies in the uncertainty of the actual values of F^2, which change rapidly with θ. The corrections for $\frac{\mu}{N^2}$ and for $\frac{1}{F^2}$ go in opposite directions, so that the total correction is not large and was not over 2 per cent. in any case, which is really within the errors of experiment.

There is one other correction to be taken into account—that for the change in the "extinction coefficient." For intense spectra the value of the linear absorption coefficient

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* Phil. Mag. xlii. p. 1 (1921).

depends on the intensity of the spectrum*; hence, as the intensity diminishes with rising temperature, the effective value of μ decreases. It has been shown that, to a fair degree of approximation,

$$\mu = \mu_0 + \epsilon = \mu_0 + k\mathrm{R}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where μ is the effective absorption coefficient at the reflecting angle, μ_0 is the ordinary absorption coefficient of the crystal, and ϵ is the extinction coefficient, which is porportional to the observed intensity of reflexion. The values of ϵ for different spectra for rhodium radiation were determined in the paper quoted. More recently, Wasastjerna† has carried out a determination by a different method for molybdenum radiation, and this has been employed in the present paper. Wasastjerna finds that $\mu_0 = 16{\cdot}2$ and $\epsilon = 4{\cdot}4$ for (100). Assuming as a sufficient approximation that $\mathrm{R}_{100} : \mathrm{R}_{200} : \mathrm{R}_{300} = 100 : 20 : 5$, we can, using (4), obtain a curve giving the value of ϵ for different values of R, and so apply the necessary correction.

The extinction correction is inappreciable for the 3rd- and 4th-order spectra, and has only been applied in the case of (200). The allowance for extinction made above is very uncertain. It is known that the extinction coefficient depends considerably on the particular crystal used, and, as we have seen, it is possible that the extinction coefficient for a rocksalt crystal which has been heated is abnormally large. All that can really be claimed is that the results corrected in the manner described are probably closer to the truth than they would have been had no correction been applied at all. In any case, the correction for the (200) spectrum is not very large.

7. The values of the corrected reflexion $\frac{\mathrm{R}_\mathrm{T}}{\mathrm{R}_1}$, plotted against the absolute temperature, are shown in fig. 1.

The theory of Debye leads to the conclusion that if R_T is the corrected reflexion at temperature T; R_1 that at any standard temperature T_1 (here the room temperature); and R_0 the value of the reflexion at absolute zero, then

$$\left.\begin{aligned} \mathrm{R}_\mathrm{T} &= \mathrm{R}_0 \exp\left\{-bf(\mathrm{T})\frac{\sin^2\theta}{\lambda^2}\right\}, \\ \mathrm{R}_1 &= \mathrm{R}_0 \exp\left\{-bf(\mathrm{T}_1)\frac{\sin^2\theta_1}{\lambda^2}\right\}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (5)$$

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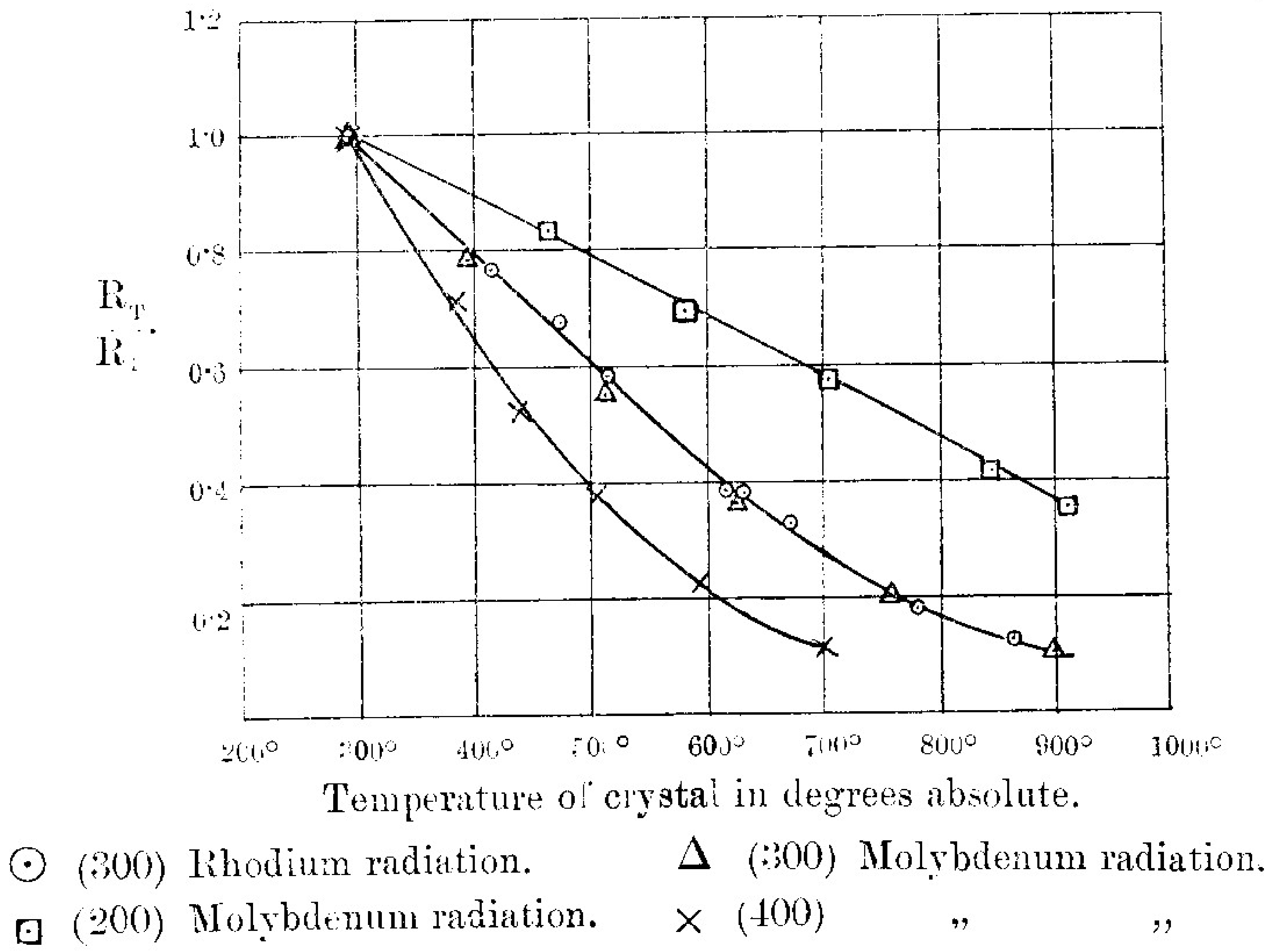
* Bragg, James, and Bosanquet, Phil. Mag. xlii. p. 1 (1921). C. G. Darwin, Phil. Mag. xliii. p. 800 (1922).

† W. A. Wasastjerna, *Soc. Sci. Fenn.* ii. p. 15.

where b is a constant, $f(\mathrm{T})$ some function of the absolute temperature, and θ and θ_1 the glancing angles at T and T_1 respectively.

Fig. 1.



Hence

$$\frac{\mathrm{R}_\mathrm{T}}{\mathrm{R}_1}=\exp\left\{-\frac{b}{\lambda^2}\left(f(\mathrm{T})\sin^2\theta-f(\mathrm{T}_1)\sin^2\theta_1\right)\right\}$$

$$=\exp\left[-\frac{b\sin^2\theta_1}{\lambda^2}\left\{f(\mathrm{T})\left(\frac{\sin\theta}{\sin\theta_1}\right)^2-f(\mathrm{T}_1)\right\}\right]; \quad . \quad . \quad (6)$$

$$=\text{const.}\times\exp\left\{-\frac{bn^2}{4d_1{}^2}f(\mathrm{T})\left(\frac{\sin\theta}{\sin\theta_1}\right)^2\right\}; \quad . \quad . \quad . \quad . \quad (7)$$

where n is the order of the spectrum and d_1 the spacing of the atomic planes at the standard temperature T_1. Thus the curve showing the relationship between $\frac{\mathrm{R}_\mathrm{T}}{\mathrm{R}_1}$ and T should be independent of the wave-length for a given order, apart from the effect introduced by the small change in the value of $\left(\frac{\sin\theta}{\sin\theta_1}\right)^2$ as the temperature changes.

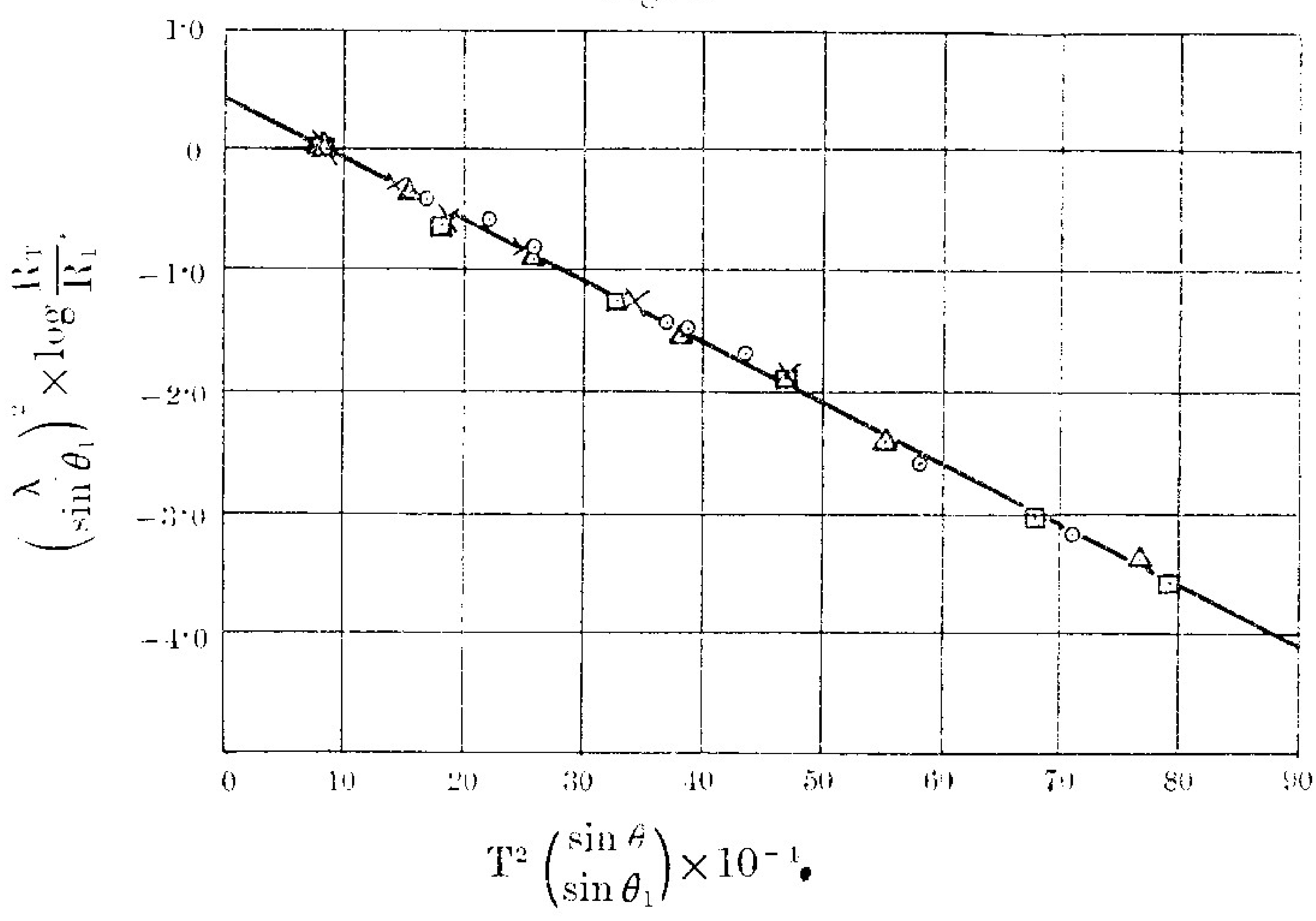
This portion of the theory is confirmed by the experiments. The curve in fig. 1 for the (300) spectrum was obtained with both rhodium and molybdenum radiation. The circles indicate the points obtained with rhodium radiation, the triangles those with molybdenum, and it will be seen that both sets of points lie on the same curve, almost within the limits of experimental error.

To find the form of $f(T)$ which agrees most closely with the observations, we write equation (6) in the form

$$\left(\frac{\lambda}{\sin\theta_1}\right)^2 \log_e \frac{R_T}{R_1} = -bf(T)\left(\frac{\sin\theta}{\sin\theta_1}\right)^2 + \text{const.} \quad . \quad (8)$$

Thus, if $\left(\frac{\lambda}{\sin\theta_1}\right)^2 \log \frac{R_T}{R_1}$ is plotted against $f(T)\left(\frac{\sin\theta}{\sin\theta_1}\right)^2$, all the points should lie on the same straight line, whatever the order of the spectrum observed, and whatever the wave-length. Debye's theory indicates that $f(T)$ should be proportional to T, but if $\log \frac{R_T}{R_1}$ is plotted against T, not even an approximately straight line is obtained. If, however, we plot $\left(\frac{\lambda}{\sin\theta_1}\right)^2 \log \frac{R_T}{R_1}$ against $T^2\left(\frac{\sin\theta}{\sin\theta_1}\right)^2$, all the 33 experimental points lie very nearly indeed on a straight line. This curve is shown in fig. 2, where the circles, triangles, squares, and crosses correspond to those in fig. 1.

Fig. 2.



⊙ (300) Rhodium radiation. Δ (300) Molybdenum radiation.
⊡ (300) Molybdenum radiation. × (400) „ „

The fact that all the points lie on the same line means that the exponent of the Debye factor is proportional to $\frac{\sin^2\theta}{\lambda^2}$

for all the spectra investigated; while the fact that a straight line is obtained when $f(\mathrm{T})=\mathrm{T}^2$ means that we can write the factor

$$e^{-b\mathrm{T}^2\frac{\sin^2\theta}{\lambda^2}}.$$

Calculating, by the method of least squares, the most probable straight line in fig. 2, we obtain

$$\mathrm{R}_\mathrm{T} = \mathrm{R}_0 e^{-1\cdot162\times10^{-5}\frac{\sin^2\theta}{\lambda^2}.\mathrm{T}^2},$$

where λ is expressed in Ångström units, as the empirical expression which fits the experimental results most closely.

8. We have seen that, according to the theoretical work of Debye, the exponent M in the temperature factor should be given by

$$-\mathrm{M} = \frac{6h^2}{\mu k\Theta}\sin^2\theta\,\frac{\phi(x)}{x},$$

where $x=\frac{\Theta}{\mathrm{T}}$, and Θ is the "characteristic temperature" which for rocksalt is 280° absolute. For values of T small compared with Θ this reduces, according to Debye, to

$$-\mathrm{M} = \frac{\pi^2h^2}{\mu k\Theta^3};\frac{\sin^2\theta}{\lambda^2}\mathrm{T}^2; \quad \ldots\ldots \quad (9)$$

while for high temperatures

$$-\mathrm{M} = \frac{6h^2}{\mu k\Theta^2}\frac{\sin^2\theta}{\lambda^2}.\mathrm{T}. \quad \ldots\ldots \quad (10)$$

The experimental results show that M is actually proportional to $\frac{\sin^2\theta}{\lambda^2}$, and this would appear to indicate that the observations are reasonably accurate, and also that the allowance for general radiation has been made correctly, for the proportion of general to characteristic radiation is very different for the different spectra examined, and different also for the same spectra in the case of rhodium and molybdenum radiations.

But the results do not agree in the least with theory as to the form of the function of the temperature contained in M. Over the range of temperature considered, M should be proportional to T, whereas the results showed that with a fair degree of accuracy it is proportional to T², which according to the theory should only be the case for temperatures up to about 50° absolute.

For high temperatures the form of M is the same as that obtained in the elementary treatment, from which

$$-M = \frac{16\pi^2 k}{f} \cdot \frac{\sin^2\theta}{\lambda^2} T,$$

where f is the force called into play when the atom is displaced by unit distance from its equilibrium position. Comparison shows then that

$$\frac{f}{\mu} = \frac{8\pi}{3} \frac{k^2}{h^2} \Theta^2,$$

or that the restoring force f is proportional to the square of the characteristic temperature.

If we take

$\Theta = 280°$,
$h = 6{\cdot}55 \times 10^{-27}$ erg. sec.,
$k = 1{\cdot}39 \times 10^{-16}$,
μ = average mass of an atom in the structure
$= 4{\cdot}85 \times 10^{-23}$ gm.,

we obtain for the case applicable to high temperatures

$$-M = 4{\cdot}89 \times 10^{-3} \frac{\sin^2\theta}{\lambda^2} . T, \quad . \quad . \quad . \quad (11)$$

λ being expressed, as before, in Ångström units. For (300) this reduces to

$$-M = 1{\cdot}39 \times 10^{-3} T. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

TABLE II.

T.	$\frac{R_T}{R_1}$ (calc.).	$\frac{R_T}{R_1}$ (obs.).
300°	·973	·98
400°	·846	·79
500°	·735	·60
600°	·640	·42
700°	·558	·27
800°	·486	·17
900°	·422	·10

Table II. shows the values of $\frac{R_T}{R_1}$ calculated from this formula compared with those actually observed. It is evident that the intensity of the spectrum falls off far more rapidly with increasing temperature than theory indicates. The difference between the observed and calculated figures is much greater than could be accounted for by experimental errors, and there must therefore be some factor which diminishes the intensity as the temperature rises which has not been allowed for in the theory.

One possibility which might be worth examining is that the value of the factor F may depend on the temperature. The theory treats the atoms as diffracting points. Now we know that the atom does not diffract even approximately as a point, particularly for large values of θ. The electrons are distributed around the atomic nuclei throughout a region whose dimensions are comparable with the spacing of the crystal planes; this causes a rapid decrease in the effective scattering power of the atom as it increases, and the factor F is introduced to allow for this. If, owing to the temperature vibration and the consequent jostling of atom against atom, the electron orbits were caused to vibrate about their mean positions, this would cause a change in the factor F in such a direction as to increase the falling-off of intensity with temperature.

Another possibility, although it seems very unlikely that it could account for such a large effect as that observed, is that the crystal may become softer as the temperature rises, so that an atom is more easily displaced from its position of rest. This would be equivalent to supposing that the characteristic temperature Θ depends on the temperature—an hypothesis which might be investigated by examining the Reststrahlen at different temperatures. To account for the T^2 law on this hypothesis alone, it would have to be assumed that Θ varied as $\frac{1}{\sqrt{T}}$. This seems highly improbable, and it is more likely that several factors work together and produce, over the range of temperature used, a law approximating closely to the T^2 law.

It is evidently desirable to extend the measurement to low temperatures, and experiments by means of which it is hoped to measure the intensity of reflexion at liquid-air temperature are already in progress.

Another point to be noticed is that in rocksalt we have two different kinds of atom—sodium and chlorine. In all the spectra so far examined we are dealing with the sum of the contributions from Na and Cl. In the case of spectra such as (111), (333), (311), (555), and so on we are, however, dealing with the difference of the contributions from

Na and Cl. It is proposed, therefore, to make a set of observations using the (333) spectrum, in order to see whether the law still holds good in this case.

In conclusion, I wish to express my thanks to Professor W. L. Bragg, F.R.S., for his interest and advice during the course of the work, and to Mr. W. A. Wood, B.Sc., for help with a number of the observations. My thanks are also due to Mr. W. Kay and Mr. W. Reynolds for much assistance in the design and construction of the apparatus. The X-ray bulb used in this research was very kindly presented to the laboratory by the General Electric Company of Schenectady, New York, and the alternator was purchased with the aid of a grant made by Messrs. Brunner Mond, Ltd.

Snmmary.

1. A series of measurements of the intensity of reflexion of X-rays from the (100) face of a rocksalt crystal at temperatures between 19° C. and 650° C. are described. The spectra investigated were the 2nd, 3rd, and 4th orders, using molybdenum Kα radiation, and the 3rd order, using rhodium Kα radiation.

2. A theoretical formula obtained by Debye shows that if R_T is the intensity of a spectrum reflected at a glancing angle θ at absolute temperature T ; R_0 that at absolute zero :

$$R_T = R_0 e^{-bf(T)\frac{\sin^2\theta}{\lambda^2}} = e^{-M} ,$$

where b is a constant and $f(T)$ is some function of the temperature. The theory indicates further that over the range of temperature employed, M is of the form

$$-aT\frac{\sin^2\theta}{\lambda^2}.$$

3. The experiments show that M is proportional to $\frac{\sin^2\theta}{\lambda^2}$ for all the spectra investigated, but that instead of being proportional to T it is proportional to T^2. The results obtained may be expressed by the empirical formula

$$R_T = R_0 e^{-1{\cdot}162\times10^{-5}\frac{\sin^2\theta}{\lambda^2}T^2},$$

where λ is expressed in Ångström units.

The intensity diminishes as the temperature rises much more rapidly than theory indicates.

The University, Manchester,
Jan. 28, 1925.