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The Measurement of X-Ray Wavelengths by Large Ruled Gratings

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A plane ruled grating was placed between the crystals of a precision double crystal spectrometer for the determination of the diffraction angles and the absolute wavelengths of x-ray lines. This arrangement has two important advantages: (1) A large grating surface is employed and (2) the ionization chamber method for recording intensities permits an accurate location of the peak of the diffracted lines. The gratings were 75 mm long and were ruled with 100 and 300 lines per mm, respectively. The results on the copper $K\alpha$ line (1.54A) are in good agreement with previous ruled grating measurements. The differences between the ruled grating and crystal wavelengths as obtained by Backlin, Söderman and the writer have been recalculated using as the "true" value of the calcite grating constant $d=3.02810$Å and the most recent determinations of the calcite diffraction angles. There is excellent agreement among the various observations and the difference between the grating and crystal values is independent of wavelength. The results of two independent methods of measuring x-ray wavelengths are included and these agree with the ruled grating values. Calculations of the "true" grating constant of calcite d, Avogadro's number N, the charge on the electron e, and Planck's constant h were made. Some of the difficulties encountered if these values of e and h are used are pointed out.

ONE objection to the previous use of ruled gratings for measuring x-ray wavelengths is that one actually uses only a very few lines of the grating. Slight errors in the spacing of the ruled lines could produce relatively large effects in the measured wavelength. No arrangement has previously been used to determine accurately the shape of the diffracted line and consequently the position of the point of maximum intensity. In the present arrangement these difficulties have been overcome by placing the grating between the crystals of a double crystal spectrometer.

METHOD

The principle of the present method is shown schematically in Fig. 1. The ruled grating was placed between the crystals of a double crystal spectrometer and the second crystal C_2 used to determine the angular directions of the rays from the grating. The vertical projection of the x-ray focal spot (2 mm×2 mm) served as the first slit. This allowed both the α_1 and the α_2 lines to be reflected from the first crystal C_1 and to strike the grating at different angles of incidence θ (i.e., θ is the angle between the grating surface and the incident beam). Although the wavelength of the α_2 line is greater than that of α_1 this difference in the angle of incidence makes the diffracted α_2 line appear at a smaller angle from the direct beam than the α_1 line. Since the angle of incidence was only about 20′, a large part of the incident x-rays passed by the grating and were diffracted by the crystal C_2 in the usual $(1+1)$ position. If C_2 were rotated counterclockwise, from the peak position of the α_1 line in the $(1+1)$ position, through an angle (2θ) then the α_1 line reflected from the grating was diffracted by C_2. By continuing the rotation of

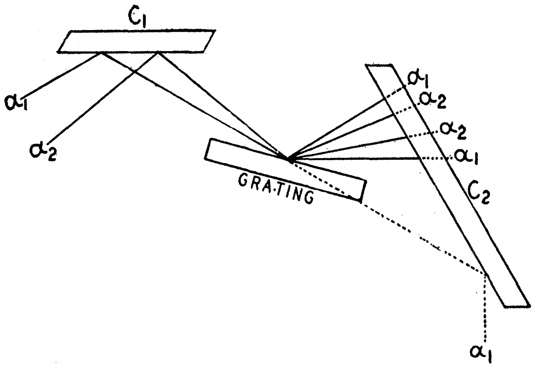

FIG. 1. The method used of placing the ruled grating between the crystals of a double crystal spectrometer.

C_2 the reflected α_2 was next recorded, then the α_2 which had been diffracted by the grating, and finally the diffracted α_1. A further rotation recorded the higher diffracted orders of the α_2 and the α_1 lines but in practice it was found that the intensity of the higher orders was so low that precise measurements were impossible.

Since an extended source of x-rays was used without any collimating slits, it is obvious that the entire length of the grating was effective in the x-ray diffraction. All the angles necessary for the calculation of the wavelengths were obtained from the precision divided circle on which C_2 rotated. The wavelengths were calculated from the usual grating formula which can be written in the following convenient form:

$$n\lambda = 2d\{\sin[(2\theta+\alpha)/2]\cdot\sin(\alpha/2)\}, \qquad (1)$$

where λ is the wavelength, d the grating constant, θ the angle of incidence and α is the angle between the reflected and the diffracted lines.

The crystals C_1 and C_2 were placed in the $(1+1)$ position (Fig. 1). From Eq. (1) it is obvious that the precision of the measured wavelength depends primarily on the accuracy with which the angle α can be determined. Therefore it was desirable to have the reflected and diffracted lines as narrow as possible so that their positions could be accurately determined. In the double crystal spectrometer a reflection from a surface between the crystals changes the effective positions from (1 ± 1) to (1 ∓ 1). By placing the crystals in the $(1+1)$ as shown in Fig. 1, the width of the reflected line is that of the $(1-1)$ width for the wavelength and the perfection of the crystals used (about $10''$). The width of the diffracted line is the $(1-1)$ width plus the width added by the dispersion of the grating ($13''$ to $16''$ total). The width of the direct line is the usual $(1+1)$ width.

Although this method makes use of a large grating the resolving power is not increased over that with a short grating. In the double crystal spectrometer a wide parallel bundle of rays is used but these rays originate at different points in the source. In order to increase the resolving power of a plane ruled grating by using a larger number of lines it is necessary that the wide bundle of rays originate from the same point. However, increased revolving power is not essential for x-ray measurements. It is more important to increase the number of lines per cm, but there are experimental limitations that prevent using finely ruled gratings.

Apparatus and Its Adjustment

The double crystal spectrometer was built by the Société Genevoise. The second crystal C_2 was mounted on a table attached to a high precision circle. Four carefully calibrated microscopes were used to read the divided circle. The micrometer settings (read to $0.1''$) were repeated three or four times and the average obtained. Since two lines, ten minutes apart, were read in each microscope, eight angular readings (or from 24 to 32 micrometer settings) were obtained for each individual setting of the circle. Two different parts of the circle were used in order to reduce any effects due to possible erratic rulings on the circle. The two parts of the circle used had proven to be particularly good when it was previously carefully calibrated.

The crystals C_1 and C_2 were accurately adjusted by the usual telescope and x-ray method. The surface of C_2 was not more than 0.01 mm from its axis of rotation. The surface of the ruled grating was placed accurately parallel to and on its axis of rotation by the use of a Michelson interferometer. This axis was then adjusted parallel to that of C_2 with the aid of two telescopes fitted with Gauss eyepieces. The accuracy of this adjustment was to within one minute of arc. The axis on which the ruled grating rotated was mounted on an adjustable horizontal slide so its position could be altered. This allowed the grating to be placed in the most intense portion of the x-ray beam.

The source of high voltage and the vacuum tube method of measuring the ionization currents were the same as previously described.[1] The x-ray source was a water-cooled copper target tube with a line focus cathode. The effective size of the focal spot, as viewed from the ionization chamber was about 2 mm×2 mm.

The calcite crystals were split from a block of Iceland calcite. The crystals gave the theoretical width of 9.8″ for the $(1-1)$ of the copper $K\alpha$ lines. The $(1+1)$ width for the copper $K\alpha_1$ line was 39.5″.

Since the reflections of the various lines from C_2 occurred at slightly different points on the crystal surface it was necessary to know that the atomic planes of the crystal continued in a geometrical plane over the total region used. The maximum distance on the crystal between the direct α_1 and the diffracted α_1 was 10 mm. The planeness of C_2 was tested by adjusting C_1 to diffract both the copper α and β lines at the same time and in such a direction that the lines would strike C_2 $(1-1)$ position on either side of the region of C_2 that was used when the grating was put in place. The ionization chamber was first set to receive the α lines only and the angular position of C_2 was carefully determined. The chamber was then adjusted to receive the β line only and the angular position of C_2 was again carefully determined. These angular positions agreed as closely as could be measured, which was within 0.1″ of arc. Thus between the places on C_2 where the α and β lines were reflected the crystal planes were parallel within the limits of measurement.

The lines of the grating were carefully ruled parallel to the edge of the grating blank (to within 1′ of arc) and this edge was then made parallel to the axis of rotation of the grating. The maximum error in the final value of λ due to this adjustment was less than one part in 10^5.

In making the angular measurements it was necessary that the temperature of both crystals remain constant during the entire time taken to make a complete determination of the wavelength. This time was about three hours. A thermometer was placed near each crystal and the temperature noted many times during the run. When the x-ray outfit was first started it required about two hours for the temperature of the crystals to reach an equilibrium temperature. Usually about three hours were allowed before an attempt was made to make measurements. After this time if no change were made in the x-ray load or no change in room temperature occurred, the temperature of the crystals remained constant to within 0.1°C.

GRATINGS

In choosing a suitable grating constant there are two important considerations. First the dispersion should be as large as possible; and second, the diffracted intensity must be easily measurable. One has to compromise in making a choice, for large dispersion and satisfactory intensity cannot be obtained simultaneously. From previous experience, grating constants were chosen corresponding to about 100 and 300 lines per mm.

Two gratings were ruled on the same optically flat blank which was 50 mm×75 mm. The actual ruled surfaces were each 18 mm×75 mm so that an unruled space existed between the rulings and also between each ruling and the edge of the blank. When the gratings were ruled the ruling engine was in very good condition, the Lyman ghost lines being less than 0.001 the intensity of the main line even for 6-inch gratings of 15,000 lines per inch. Optical examination of the gratings showed no detectable errors.

The grating constants were determined by directly measuring the distance between two lines from 10 mm to 40 mm apart and counting the number of spaces in the interval. Repeated measurements using different parts of the grating and different parts of the comparator disagreed in no case by more than one part in 50,000.

The gratings were sputtered with a layer of gold which reduced the intensity of transmitted light about 95 percent. This made it possible to use larger angles of incidence and also gave much greater intensity in the diffracted lines than could have been obtained with a glass surface.

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[1] J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).

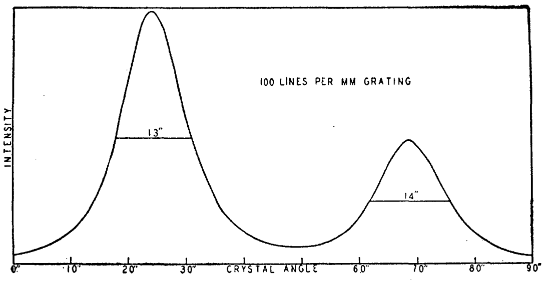

FIG. 2. The grating diffracted copper $K\alpha_1$, α_2 lines when using the 100 lines per mm grating.

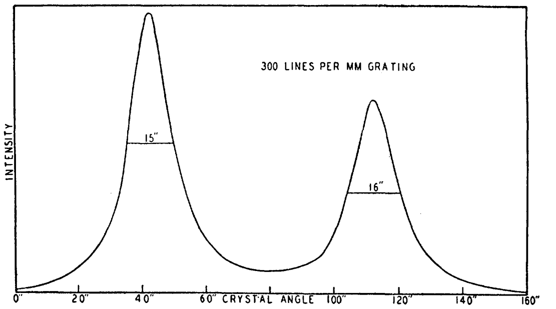

FIG. 3. The grating diffracted copper $K\alpha_1$, α_2 lines when using the 300 lines per mm grating.

RESULTS

A typical curve of the first order diffraction of the copper $K\alpha_{1,\,2}$ lines for each grating is shown in Fig. 2 and Fig. 3. Fig. 3 shows that the intensities of the α_1 and α_2 lines are not in the ratio of 2 to 1. The reason for this is not apparent but it is probably connected with the fact that the intensities of the diffracted lines are critically affected by variations in the angle of incidence. It is doubtful, however, that such effects could shift the peak of the line by a measurable amount. A further study of this is needed.

The method employed for determining the angles necessary for the calculation of the wavelengths was as follows: The position of the direct α_1 line was obtained, then the positions of the reflected and diffracted α_1 lines were recorded. The process was reversed and the diffracted, reflected and direct beams were recorded. This gave two determinations of each angle and the average was used as one independent value of α and θ. Sixteen circle readings or about 50 micrometer settings were contained in each angular determination.

A correction for the overlapping of the lines was made by using the classical equation[2] for the line shape as previously[3] described. In most cases this correction was negligible.

The second order was observed for both gratings and the third for the coarsely ruled grating. The intensity was very low in these cases and for this reason very accurate location of the lines could not be made. The second order from each grating was used and the resulting wavelengths agreed within 0.1 percent with those obtained when using the first order but since the results were much less accurate they have not been considered in the final average.

The results of 12 independent first order determinations of the wavelength of the copper $K\alpha_1$ line are shown in Table I. The first column gives the angle of incidence which is the measured angle divided by 2. The second column gives α the measured angle between the reflected and the diffracted beams. The third column gives the resulting wavelengths and the fourth the percent difference between these wavelengths and that obtained with calcite crystals. The maximum variation is about 0.04 percent and the probable error as calculated from consistency is 0.003 percent. It is possible that a constant error in the divided circle is present, but since six different angles and two entirely different parts of the circle have been used it is difficult to

TABLE I. *Twelve independent determinations of the wavelength of the copper $K\alpha_1$ line using two gratings.* The first six results were obtained using a grating with a constant of 2.03248×10^{-3} cm and the last six results with a grating whose constant was 0.67749×10^{-3} cm. The crystal value of λ was 1.53671A.

θ	α	λ_g	$(\lambda_g-\lambda_c)/\lambda_c$
15′ 10.43″	9′ 5.11″	1.5403A	0.234
15′ 10.30″	9′ 5.38″	1.5411	0.286
8′ 0.14″	12′ 32.85″	1.5403	0.234
7′ 59.91″	12′ 32.98″	1.5403	0.234
19′ 42.74″	7′ 37.10″	1.5405	0.247
19′ 43.75″	7′ 36.67″	1.5403	0.234
15′ 16.56″	20′ 53.64″	1.5405	0.247
15′ 16.57″	20′ 54.27″	1.5416	0.318
26′ 17.67″	15′ 44.19″	1.5409	0.273
26′ 18.14″	15′ 43.80″	1.5405	0.247
7′ 11.90″	26′ 22.06″	1.5404	0.241
7′ 11.79″	26′ 22.13″	1.5404	0.241
	Average	1.5406	0.253

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[2] A. Hoyt, Phys. Rev. **40**, 477 (1932).

[3] J. A. Bearden and C. H. Shaw, Phys. Rev. **46**, 761 (1934).

TABLE II. *The percent difference between the ruled grating and calcite crystal values of x-ray lines.* The numbers in parentheses are the numbers of independent values that entered into the recorded value.

Observer	*Grating*	Cu $K\beta$	Cu $K\alpha$	Cr $K\beta$	Cr $K\alpha$	Al $K\alpha$
Backlin (1928)[4]						0.17(31)
Bearden (1929)[7]	a, b, c	0.24 (10)	0.25 (10)			
Bearden (1931)[8]	1, 3	.241(26)	.229(46)	0.239(16)	0.245(28)	
Bearden (1931)[8]	4	.234(4)	.250(11)	.250(15)	.255(27)	
Bearden (1931)[8]	4′	.264(30)	.257(49)	.253(3)	.254(5)	
Bearden (1931)[8]	5	.246(41)	.234(73)	.235(32)	.239(51)	
Bearden (1931)[8]	5′	.259(49)	.250(82)	.256(44)	.255(67)	
Bearden (1931)[8]	6	.239(11)	.244(16)	.240(3)	.240(4)	
Backlin (1935)[5]						.249(56)
Söderman (1935)[6]			Cu $K\alpha_1$			.255(9)
Bearden (1935)[11]	100		0.245 (6)			
Bearden (1935)[11]	300		.261 (6)			
Bearden (1935)[12]	Refr.	0.260(25)				
		Weighted average $=0.248\pm0.0016\%$				

believe that an error of this type greater than 0.1″ to 0.2″ exists. The results are very consistent and agree excellently with previous photographic results. By using an entirely different grating technique for determining x-ray wavelengths we find again that the ruled grating measurements are correct.

COMPARISON OF PREVIOUS RESULTS

In Table II the differences between the ruled grating and crystal wavelengths as obtained by Backlin,[4, 5] Söderman,[6] and the writer[7, 8] have been recalculated using as the "true" value of the grating constant of calcite[9] $d=3.02810$A and the most recent determinations of the calcite diffraction angles. In the case of the aluminum $K\alpha$ line a gypsum crystal was used for determining the crystal wavelength but since Larsson[10] has measured by x-rays the ratio of the grating constant of gypsum to that of calcite, the gypsum value can be easily converted to the calcite scale.

In Table II the numbers in parentheses are the numbers of independent measurements that entered into each recorded value. The weighted average was obtained by giving each value a weight equal to the number of measurements that entered into that value, except in the case of Backlin's 1928 value. This was given zero weight in view of the fact that his latter repetition of the experiment with improved technique gave a very much higher value. The probable error was calculated by the method of least squares giving each value equal weight.

It will be noted that, with the exception of Backlin's 1928 result,[4] all the results using different gratings and different methods are in exceptionally good agreement. The differences between the ruled grating and the crystal results apparently do not depend at all on the wavelength in the range from 1.4A to 8.3A. This gives strong evidence in favor of the correctness of the ruled grating measurements, especially since in both theory and experiment there appears to be nothing wrong with the idea of using ruled gratings for this wavelength region.

In Table II there is also included the results of two methods[11, 12] of determining x-ray wavelengths that are independent of the usual absolute ruled grating methods. In the first method Söderman[11] has used a 5 m concave grating to compare a high order of the aluminum $K\alpha$ line with a spark line of known wavelength. This essentially measures the x-ray line in terms of the red cadmium line which Michelson has measured in terms of the standard meter. In the second method[12] the wavelength of the copper $K\beta$ line has been measured by its refraction in a

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[4] E. Backlin, Inaug. Diss. Uppsala (1928).
[5] E. Backlin, Zeits. f. Physik **93**, 450 (1935).
[6] M. Söderman, Nature **135**, 67 (1935).
[7] J. A. Bearden, Proc. Nat. Acad. Sci. **15**, 528 (1929).
[8] J. A. Bearden, Phys. Rev. **37**, 1210 (1931).
[9] J. A. Bearden, Phys. Rev. **38**, 2089 (1931).
[10] A. Larsson, Uppsala Univ. Arsskrift, 1929.
[11] J. A. Bearden, present paper.
[12] J. A. Bearden, Phys. Rev. **47**, 811 (1935).

diamond prism. Similar results have been obtained with a quartz prism by Shaw and the writer.[3] The good agreement between these and the other results of Table II also gives strong support to the conclusion that the ruled grating measurements are correct.

CALCULATION OF THE CONSTANTS d, N, e, AND h

In view of the apparent correctness of the ruled grating wavelengths one should be justified in using these wavelengths together with the known calcite crystal diffraction angles to calculate the true grating constant of calcite. By using the weighted average of Table II and the value of $d_\infty = 3.02810\text{A}$ which was used in the calculations for this table, one obtains for the true x-ray value of the grating constant

$$d_\infty = 3.02810 \times 1.00248 = 3.03560 \pm 0.00005\text{A}.$$

This value is independent of any theory of crystal imperfection.

Since the many tests made on crystals normally used in x-ray work have indicated no measurable mosaic structure it would appear that one should be able to use the x-ray data for calculating Avogadro's number N. This can be obtained from the usual crystallographic relation as

$$N = M/2\rho\varphi(\beta)d^3.$$

By using the following values of these constants

$M = 100.078$,[13]

$\rho = 2.71030$ g/cm^3 at 20°C,[9]

$\varphi(\beta) = 1.09594$ at 20°C,[9]

$d = 3.03566$A at 20°C,

one obtains

$$N = 6.0221 \pm 0.0005 \times 10^{23} \text{ mole}^{-1}.$$

If one can assume that the apparent accuracy of the Faraday is correct then by using $F = 9648.9 \pm 0.7$ abs. e.m. units one obtains for the charge on the electron

$$e = 4.8036 \pm 0.0005 \times 10^{-10} \text{ e.s.u.}$$

In the case of Planck's constant h there are two possible values. The first is to use the values of d and e from above in the high frequency relationship $Ve = h\nu$ in which case by using Kirkpatrick and Ross's[14] result for V/ν we obtain

$$h = 6.607 \times 10^{-27} \text{ erg}\cdot\text{sec.}$$

In the second case if we assume there is some difficulty in calculating e from the x-ray data, that is, that there is something wrong in the value of the Faraday or that there is present some undetected crystal phenomena, then Millikan's oil drop value of e equal to 4.768×10^{-10} e.s.u. can be used. This together with d and V/ν from above gives

$$h = 6.558 \times 10^{-27} \text{ erg}\cdot\text{sec.}$$

which is the smallest value of h that can be obtained from x-ray data.

While the above methods of determining e and h are apparently correct the results obtained are difficult to reconcile with existing data obtained by other methods. One of the principal difficulties encountered concerns the Rydberg constant which may be written in the form

$$R = 2\pi^2 e^5/c^2h^3 e/m.$$

If $e = 4.806 \times 10^{-10}$ e.s.u., $h = 6.607 \times 10^{-27}$ erg$\cdot$sec., $R = 109{,}737.4$ cm^{-1}, and $c = 2.99796 \times 10^{10}$ cm/sec. then $e/m = 1.774 \times 10^7$ e.m.u./g. This value is about 0.8 percent greater than the present accepted value. Other, but less serious, difficulties arise when one attempts to use the above high x-ray values in many of the interrelationships of the constants.

At the present time there appears to be no satisfactory explanation of this dilemma. If the accepted value of the Faraday were about 0.75 percent too high then the major difficulties would be removed. The difficulty of accurately determining F is well known but it would be very surprising if the error in its determination were 0.75 percent. In addition F enters into the x-ray refraction measurements and the use of a value of F 0.75 percent lower than the accepted value would raise the resulting x-ray wavelengths 0.50 percent above the average grating wavelengths. This seems impossible.

The writer is indebted to Professor R. W. Wood for his cooperation in allowing a modification of the ruling engine to be made so that the special gratings could be ruled on the best ruling engine.

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[13] R. T. Birge, Rev. Mod. Phys. **1**, 1 (1929).

[14] Kirkpatrick and P. A. Ross, Phys. Rev. **45**, 454 (1934).