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The Wave-Lengths of the Silver, Molybdenum, Copper, Iron and Chromium $K\alpha_1$ Lines

J. A. BEARDEN, *Johns Hopkins University*

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It has been shown that a double crystal spectrometer can be used to measure x-ray wave-lengths with a precision as great or greater than that obtained by the usual methods. The purpose of the present work was to determine the x-ray wave-lengths of several important lines by using such a spectrometer, and to compare the results with the most precise values which have been obtained by other methods. From two to five orders have been measured in each case, but in the following table only the order which was given greatest weight has been listed. The results on the silver and molybdenum $K\alpha_1$ lines, which are symmetrical lines, agree satisfactorily with the results obtained by the photographic methods. The $K\alpha_1$ lines of copper, iron and chromium which were found to be asymmetrical differ considerably from the results of photographic methods. Most of the other lines of the copper, iron and chromium K series were also found to be asymmetrical. Thus it appears that the double crystal spectrometer has a decided advantage in the measurement of wave-lengths of such lines.

Line	Order	Diffraction angle, 18°C	Wave-length $d_\infty=3.02945\text{A}$	Wave-length $d_\infty=3.02810\text{A}$
Ag $K\alpha_1$	4th	21° 37′ 35.6″	0.558255A	0.558006A
Mo $K\alpha_1$	4th	27° 51′ 34.8″	0.707835	0.707520
Cu $K\alpha_1$	2nd	30° 29′ 51.0″	1.537392	1.536707
Fe $K\alpha_1$	2nd	39° 37′ 34.4″	1.932042	1.931181
Cr $K\alpha_1$	2nd	48° 57′ 45.3 ±.2″	2.284974	2.283955

INTRODUCTION

THE introduction of the double crystal x-ray spectrometer by Bergen Davis and his collaborators has given us an ionization method of measuring x-ray wave-lengths with great precision. It has been shown[1, 2, 3] that with a suitably designed instrument of this type the diffraction angles can be measured to a fraction of a second of arc. Thus, the precision of the divided circle is one of the principal limitations, but this is of course an important limitation of most photographic spectrometers. The chief advantages of the double crystal spectrometer are its high resolving power, and ability to measure the peak of an asymmetrical line which is difficult to accomplish by the usual photographic methods. In the present work the wave-lengths of the silver, molybdenum, copper, iron and chromium $K\alpha_1$ lines have been measured with a high precision double crystal spectrometer, and the results compared with the results obtained by other methods.

CORRECTIONS FOR TEMPERATURE AND HEIGHT OF SLITS

The most precise calculation of the correction that must be applied to reduce all measured diffraction angles to a common temperature has been made by C. D. and D. Cooksey.[4] They have calculated the expansion coefficient of calcite perpendicular to the cleavage plane and found a value $\alpha=1.02\times10^{-5}$ cm/°C. The correction to the measured angle of diffraction θ is then $d\theta''=2.10(t-18°\text{C})\tan\theta$, where t is the temperature of the crystal at the time of measurement. This is an additive correction.

The correction for the height of the slits has been given by Williams[5] in the form

$$d\theta_{\text{eff.}}=-[(a^2+b^2)/24L^2]\tan\theta,$$

where a is the height of one slit, b that of the other, and L their separation. This correction must be subtracted from the measured angle of diffraction.

GRATING CONSTANT OF CALCITE

In comparing the results of different investigators it is essential to know what variation in the grating constant of the crystals used is to be expected. Such a comparison of the grating constant of calcite has been made,[2] the results of which are shown in Table I. These values have been corrected by using the corrections for

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[1] A. H. Compton, Rev. Sci. Inst. **2**, 365 (1931).

[2] J. A. Bearden, Phys. Rev. **38**, 2092 (1931).

[3] J. A. Bearden, Phys. Rev. **41**, 399 (1932).

[4] C. D. and D. Cooksey, Phys. Rev. **36**, 85 (1930).

[5] J. H. Williams, Phys. Rev. **40**, 636 (1932).

TABLE I. *Comparison of grating constants of calcite.*

Origin	Diffraction angle 4th order of Mo $K\alpha_1$	Diffraction from mean
Iceland I	27° 51′ 34.4″	−0.4″
Iceland II	27° 51′ 34.4″	−0.4″
Montana I	27° 51′ 35.0″	+0.2″
Montana II	27° 51′ 35.1″	+0.3″
Argentina	27° 51′ 35.1″	+0.3″
Spain	27° 51′ 34.8″	0.0″
Mean	27° 51′ 34.8″	0.26″

temperature and height of slits given above instead of those in the original paper. The maximum difference in the results of Table I is about 1 part in 145,000 and the maximum difference from the mean value is about 1 part in 250,000.

In the calculation of the true grating constant from the structure of the crystal and chemical data it is apparent that the greatest errors are introduced by the uncertainty in the value of Avogadro's number and the density of the crystal. It has been pointed out by the writer[2] that the best value of N is probably obtained from the Faraday constant and the charge on the electron as obtained by Millikan. This gives the value $N = 6.067 \times 10^{23}$ molecules/mole. Tu[6] has recently reported two determinations of the density of calcite, and also a determination of the density of the crystals used by the writer[2] has been made by the Bureau of Standards. The average density of the crystals listed in Table I as found by the Bureau of Standards was $\rho = 2.71027$ g/cm^3 at 20°C, which is to be compared with $\rho = 2.71026$ g/cm^3 at 20°C reported by the writer.[2] The agreement is fortuitous as it is exceedingly difficult to make absolute density measurements of this type to better than 1 part in 50,000. The results of Tu[6] on two crystals were $\rho_1 = 2.71011$ g/cm^3 at 20°C (cleaved crystal); $\rho_2 = 2.71018$ g/cm^3 at 20°C (polished crystal).

Since an imperfection in the crystal will probably manifest itself as a lowering of the density, the crystals which give higher values of density should be given more weight. Thus it appears to the writer that the best value of the density to be used in calculating the grating constant is $\rho = 2.71030$ g/cm^3 at 20°C, which is the same as that previously given.[2]

Using these values of ρ and N one obtains for the true grating constant $d_\infty = 3.02810$A at 18°C.

Many experimenters have used a somewhat arbitrary value of d in calculating x-ray wave-lengths. The true value of d usually assumed has been $d_\infty = 3.02945$A at 18°C, which corresponds to an effective $d_1 = 3.02904$A for the first order diffraction. The difference between the measured d_∞ and the assumed d_∞ is about one part in 2000. In questions of relative wave-lengths it is immaterial which value we use, but for absolute wave-lengths the measured value is necessary. On account of this the wave-lengths in the present report have been calculated for both values.

APPARATUS AND METHOD

The apparatus used in the present work was essentially the same as that used for the x-ray comparison of the grating constant of calcite crystals.[2] The Coolidge water-cooled tube was mounted vertically and in such a manner that the targets could be easily replaced without disturbing the position of the focal spot. The target was cut at an angle of 12° with a horizontal plane which gave a small effective height of slit for a broad focal spot. The current through the tube was usually about 20 m.a. The voltage was varied from about 27 kv for chromium to 50 kv for silver. The method[7] of placing the first crystal on a slide midway between the focal spot and second crystal has been continued. Such an arrangement, when properly adjusted, allows one to change from one wave-length to another very rapidly. The ionization chamber which was 4 cm in diameter and 8 cm long was filled with methyl bromide. The ionization current was measured with an F P 54 vacuum tube and galvanometer.

In the case of symmetrical lines, two methods were employed for determining the position of the peak of the line. The first method was that of plotting the curves as described previously[2] and taking the average of the angles for positions of equal intensity. In the second method the slow motion screw was advanced until the intensity as shown by the galvanometer deflection was about 50 percent of the intensity at the peak of the line. The readings on the divided circle were recorded and then the slow motion screw advanced until a

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[6] Yuching Tu, Phys. Rev. **40**, 662 (1932).

[7] P. A. Ross, Rev. Sci. Inst. **3**, 253 (1932).

position of equal intensity was found on the other side of the peak. The mean angular position thus corresponds to the center or peak of the line. Five such points were usually recorded for intensities from 50 percent to 95 percent of the peak intensity. This, essentially, is the same as the method above, but is much more rapid.

In the case of the asymmetrical lines the method employed is shown graphically in Fig. 1.

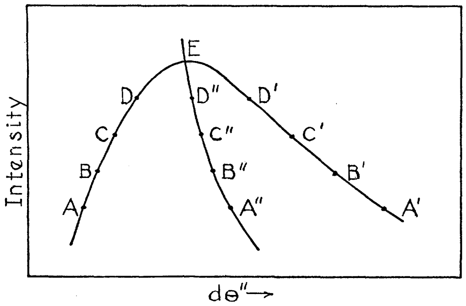

FIG. 1. Method of locating peaks of asymmetrical lines.

The points A'', B'', $\cdots$ are mean positions between the positions of equal intensity AA', BB', $\cdots$. The intersection of the extrapolated smooth curve $A''B''C''D''$ $\cdots$ with the ionization curve at E has been taken as the peak of the line.

The ± values given in Tables II, IV, VI and VIII are the average deviation of the results from the mean value. The column headed n shows the number of independent results included in the average value given.

RESULTS

Silver

Several sets of measurements were made in all orders up to the 5th. The position of the 4th order was more carefully determined than any other and has been given greater weight in the final estimate of the wave-length. A summary of the results is given in Table II. The x-ray tube broke down after the results of 4′ and 5′ had been obtained. When the new tube was aligned, the 4th order measurements were repeated in order to get a comparison of the results after such a complete realignment of the apparatus. The diffraction angles of Table II are compared with those obtained by other experimenters in Table III. In the early work of Lang and Leide, the probable error was rather large. Kellstrom's second order result agrees well with the writer's second order result, but the first order results differ considerably. From the work on the grating constant of calcite above, it would be almost impossible to account for the differences observed in the first three results of the first order of Table III as variations in the crystals used. If one calculates the expected first order diffraction from the present results of the second, third, fourth and fifth orders one obtains $\theta_1 = 5°\ 17'\ 14.4''$, which agrees with the measured value. It has been pointed out by C. D. and D. Cooksey that their results might have been in slight error if the beam diffracted by the crystal were not perfectly symmetrical. However the tests made failed to show an appreciable asymmetry. The consistency of the wave-lengths as calculated from various orders, and the fact that the double crystal spectrometer is free from many of the usual difficulties, lead one to believe that the present results are probably more precise than any previous determination.

TABLE II. *Silver $K\alpha_1$ line.*

Order	n	Diffraction angle 18°C	Wave-length $d_\infty = 3.02945$A	Wave-length $d_\infty = 3.02810$A	Weight
1	15	5° 17′ 14.5±.1″	0.558257A	0.558009A	1
2	8	10° 37′ 9.7±.1″	0.558257	0.558009	2
3	8	16° 2′ 47.9±.2″	0.558257	0.558008	3
4	17	21° 37′ 35.5±.2″	0.558254	0.558005	5
4′	14	21° 37′ 35.6±.2″	0.558255	0.558006	5
5′	9	27° 25′ 54.9±.3″	0.558256	0.558008	3
		Weighted mean	0.558255	0.558007	

TABLE III. *Comparison with other observations.*

Order	Present work	Cooksey's[4]	Kellstrom[8]	Lang[9]	Leide[10]
1	5° 17′ 14.5″	5° 17′ 13.8″	5° 17′ 15.2″	5° 17′ 13.1″	5° 17′ 13.0″
2	10° 37′ 9.7″		10° 37′ 9.8″		
3	16° 2′ 47.9″				
4	21° 37′ 35.5″				
5	27° 25′ 54.9″				

Molybdenum

The molybdenum $K\alpha_1$ line is apparently a symmetrical line, but slightly broader than the silver $K\alpha_1$ line. Typical curves for molybdenum have already been given.[2] The results are summarized in Table IV. Table V gives a com-

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[8] G. Kellström, Zeits. f. Physik **41**, 516 (1927).

[9] K. Lang, Ann. d. Physik **75**, 489 (1924).

[10] A. Leide, *Dissertation*, Lund (1925).

TABLE IV. *Molybdenum* $K\alpha_1$ *line.*

Order	n	Diffraction angle 18°C	Wave-length $d_\infty = 3.02945$A	Wave-length $d_\infty = 3.02810$A	Weight
1	11	6° 42′ 35.4 ± .2	0.707833A	0.707518A	1
2	9	13° 30′ 45.6 ± .2	0.707836	0.707521	2
3	9	20° 31′ 0.7 ± .2	0.707835	0.707520	3
4	28	27° 51′ 34.8 ± .2	0.707835	0.707520	5
5	10	35° 44′ 29.9 ± .3	0.707834	0.707519	3
		Weighted mean	0.707835	0.707520	

parison of these results with those of recent investigators for the same wave-length.

The present results are 0.1″, 0.7″, and 0.6″ higher in the first, second and third orders, respectively, than those of Larsson's. The second and third order differences are probably of no importance, as Larsson apparently made only two determinations in each case, which differed by about 1″. There is an appreciable difference between Compton's value of the first order and that of the writer. However Tu's result, which was obtained with Compton's spectrometer, is in close agreement with the writer's value. Thus it is probable that the average wave-lengths of Table IV are not in error by more than is indicated by the variation in the results of the different orders.

TABLE V. *Comparison with other observations.*

Observer	1st order	2nd order	3rd order	4th order
Leide[9]	6° 42′ 34.3″			
Allison and Armstrong[11]	6° 42′ 33.3″			
Larsson[12]	6° 42′ 35.3″	13° 30′ 44.9″	20° 31′ 0.1″	
Compton[1,5]	6° 42′ 35.9″			27° 51′ 35.0″
Tu[6]	6° 42′ 35.5″			
Present results	6° 42′ 35.4″	13° 30′ 45.6″	20° 31′ 0.7″	27° 51′ 34.8″

Copper and iron

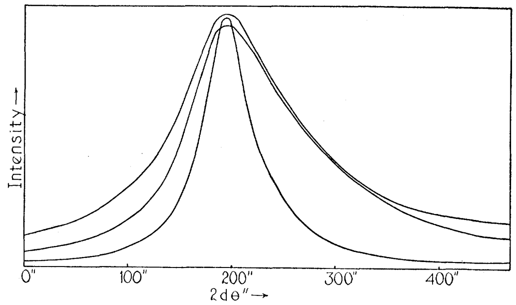

FIG. 2. Typical curves for the copper, iron, and chromium $K\alpha_1$ lines in the (1, +2) order.

Fig. 2 shows typical curves for the copper, iron and chromium $K\alpha_1$ lines in the (1, +2) order. It has been pointed out[3] that other lines of these series are more asymmetrical than the $K\alpha_1$ lines, but these and other lines of the elements from copper to chromium will be discussed later in a paper by the writer and Mr. C. H. Shaw. It is obvious that for such asymmetrical lines the usual photographic spectrometer would give different results for different lengths of exposures. Thus, as the asymmetry becomes greater one should expect the difference between the results of the two methods to become greater. This effect is shown by Tables VII, IX and XI. The results of the writer for the copper $K\alpha_1$ line are shown in Table VI and a comparison as above in Table VII.

TABLE VI. *Copper** $K\alpha_1$ *line.*

Order	n	Diffraction angle 18°C	Wave-length $d_\infty = 3.02945$A	Wave-length $d_\infty = 3.02810$A	Weight
1	10	14° 42′ 3.5 ± .2″	1.537385A	1.536700A	1
2	19	30° 29′ 51.0 ± .2″	1.537392	1.536707	3
		Weighted mean	1.537389	1.536704	

* It has been pointed out above that the preliminary results (Phys. Rev. **40**, 133 (1932)) were in error because of the correction formulae used for temperature and height of slits. Also in the case of copper and iron, two numerical errors of about 2″ each entered, which have been corrected in this report.

TABLE VII. *Comparison with other observations.*

Observer	1st order	2nd order
Siegbahn I[13]	14° 42′ 2.8″	30° 29′ 48.2″
Siegbahn II[14]	14° 42′ 0.6″	
Lang[9]	14° 42′ 1.5″	
Leide[10]	14° 42′ 0.3″	
Siegbahn III[15]	14° 42′ 3.8″	
Wennerlöf[16]	14° 42′ 3.8″	
Present results	14° 42′ 3.5″	30° 29′ 48.2″

The average deviation of the Siegbahn I and II results from the mean value was about 1 part in 17,000 and 35,000, respectively, whereas he gave as a value of the wave-length $\lambda_1 = 1.537358$A and $\lambda_2 = 1.537302$A. His recent result of $\lambda = 1.537396$A,

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[11] S. K. Allison and A. H. Armstrong, Phys. Rev. **26**, 701 (1925).

[12] A. Larsson, Zeits. f. Physik **41**, 507 (1927).

[13] M. Siegbahn, Ann. d. Physik **59**, 56 (1919).

[14] M. Siegbahn, Zeits. f. Physik **9**, 68 (1922).

[15] M. Siegbahn, Ark. Mat. Astr. O. Fys. **21**, No. 21 (1929).

[16] Ina Wennerlöf, Ark. Mat. Astr. O. Fys. **22**, No. 8 (1930).

which is in approximate agreement with the writer's results, is quite different from his previous values. The difference between the Siegbahn III and Wennerlöf results and those of the writer may be due to the slight asymmetry of the line, but a difference in crystals could also account for the results.

TABLE VIII. *Iron $K\alpha_1$ line.*

Order	Diffraction angle 18°C	Wave-length $d_\infty = 3.02945$A	Wave-length $d_\infty = 3.02810$A	Weight
1	18° 35′ 51.0±.3″	1.932031A	1.931170A	1
2	39° 37′ 34.4±.4″	1.932042	1.931181	1
	Weighted mean	1.932036	1.931175	

The results obtained on iron are shown in Table VIII and the comparison, with previous determinations, in Table IX.

Larsson's second order value agrees better with the present results than any of the others. However, Siegbahn[19] apparently disregards this value of Larsson's and uses only the first order result in his résumé of the wave-lengths of the iron K series. It is obvious that in the case of the iron $K\alpha_1$ line the asymmetry has made an appreciable difference between the results obtained by the double crystal spectrometer and the photographic spectrometer.

TABLE IX. *Comparison with other observations.*

Observer	1st order	2nd order
Siegbahn-Dolejsek[17]	18° 36′ 0.7″	
Lang[9]	18° 36′ 4.0″	
Larsson[12]	18° 35′ 52.3″	39° 37′ 34.8″
Eriksson[18]	18° 35′ 52.6″	
Present results	18° 35′ 51.0″	39° 37′ 34.4″

Chromium

The results on the chromium $K\alpha_1$ line were obtained by Mr. C. H. Shaw with the same apparatus described above. The shape of the line was shown in Fig. 2. The base line of each curve was obtained by placing a lead screen in the path of the x-rays and the base line of each curve was made to coincide in Fig. 2. Table X gives the diffraction angles and wave-lengths obtained.

TABLE X. *Chromium $K\alpha_1$ line.*

Order	n	Diffraction angle 18°C	Wave-length $d_\infty = 3.02945$A	Wave-length $d_\infty = 3.02810$A	Weight
1	10	22° 9′ 31.7±.2″	2.284956A	2.283938A	1
2	5	48° 57′ 45.3±.2″	2.284974	2.283955	1
		Weighted mean	2.284965	2.283947	

Table XI gives a comparison of the results with those obtained by previous experimenters. It will be noted that the first two results in Table XI were in almost identical agreement whereas the results of Eriksson differ by more than 7 seconds of arc from these. Such a large difference was probably due to an inaccurate centering of the effective crystal surface on the axis of rotation of the spectrometer in the earlier experiments. The use of the Seeman principal spectrograph (where the slit is placed between the crystal and photographic plate) reduces this effect and this probably accounts for the higher precision of Eriksson's results. The asymmetry of the line as found in the present results would indicate a wave-length, as measured photographically, of approximately that found by Eriksson.

TABLE XI. *Comparison with other observations.*

Observer	1st order	2nd order
Siegbahn-Dolejsek[17]	22° 9′ 26.9″	
Schrör[20]	22° 9′ 27.4″	
Eriksson[18]	22° 9′ 34.5″	
Present results	22° 9′ 31.7″	48° 57′ 45.3″

CONCLUSION

In the case of the molybdenum $K\alpha_1$ which is a symmetrical line, the agreement between the results obtained with a double crystal spectrometer and the recent results obtained by other methods leaves little to be desired. The differences observed in the silver $K\alpha_1$ line, for the three best determinations, appear to be greater than the experimental errors and also greater than can be accounted for by crystal imperfections.

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[17] M. Siegbahn and V. Dolejsek, Zeits. f. Physik **10**, 159 (1922).

[18] S. Eriksson, Zeits. f. Physik **48**, 360 (1928).

[19] M. Siegbahn, *Spektroskopie der Rontgenstrahlen*, Julius Springer (1931).

[20] J. Schrör, Ann. d. Physik **80**, 297 (1926).

The results on copper, iron and chromium indicate clearly the value of a double crystal spectrometer in studies of the shapes, relative intensities, and wave-lengths of x-ray lines. In the original curves the asymmetry of the copper $K\alpha_1$ line is very pronounced and the asymmetry of the iron and chromium lines is evident from Fig. 2. It can also be observed that the asymmetry is not strictly a function of the atomic number. Preliminary results also indicate that the asymmetry is not a function of the voltage applied to the x-ray tube. However, further work on this question is in progress with the use of a filtered d.c. source of potential.