THE K SERIES OF THE X-RAY SPECTRUM OF GALLIUM.

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1. *Introduction.*—The tables of wave-lengths of high frequency spectra contain no data for gallium, doubtless because this element is rare and usually very difficult to obtain. Since we had a sufficiently large amount of the metal at our disposal it seemed desirable to investigate its characteristic radiations and thus supply the missing data. As the experimental work progressed, the difficulties and sources of error inherent in the usual method became so prominent as to cause the senior author to make an analytical study of the general problem of determining glancing angles, and both of us to subject the old method and a new one to very thorough practical tests.

2. *Apparatus and Adjustments.*—The spectrograph consisted of a Hilger, type No. 2, spectrometer remodeled to meet the special requirements of the problem. The collimator was replaced by two slits, the one nearer the X-ray bulb being rigidly fastened to the original apparatus, while the slit nearer the crystal could be slid along ways and thus placed at different distances from the fixed slit. The distance between the centers of the slits was usually 10.5 cm., and that between the axis of rotation of the crystal table and the more remote slit was 13.9 cm. The jaws of both slits were made of lead 2.3 mm. thick, their opposing edges were carefully lapped plane and parallel, and they were so mounted as to open symmetrically and remain parallel to the axis of rotation. The frame diaphragmed the length of the fixed slit down to 3.25 mm. The original prism table was replaced by a triaxial crystal holder transferred from a goniometer. The telescope was superseded by a pair of parallel steel guides lying in a plane perpendicular to the fundamental axis. The rack for the plate-holder could be slid along this track, thus enabling the observer to vary at will the distance from the photographic plate to the chief axis. The vernier and tangent-screw associated with the telescope arm greatly facilitated the adjustment of the track parallel to the collimating axis, that is, to the line passing through the centers of the slits and intersecting the axis of rotation at right angles. In other words, the plate could be translated along the collimating axis. The plate-holder was removable, its incidence or front face

was covered with black paper (of the kind in which dry plates ordinarily come wrapped), and it accommodated plates 2 in. wide and 10 in. long.

The X-ray bulbs were very skilfully made by Mr. A. Greiner, vice-president of the Green and Bauer Company, Hartford, Conn. The anode target was water-cooled and its copper-tungsten surface was covered with a thin sheet of nickel to which the pure gallium, when liquefied in warm water, readily adhered. The tube was clamped in such a position as to cause the anticathode surface (which was inclined at 45° to the long axis of the tube) to be vertical and nearly edge-on to the collimating axis.

A very important item in the final assembling of the bulb consisted in the thin aluminium window (of thickness 0.012 mm.), through which the primary radiations passed with but slightly diminished intensity. To enable this foil to withstand the excess in pressure of the atmosphere over the low pressure inside the bulb, it was waxed over a small slot cut in a brass collar which covered the end of a lateral tube having the following approximate dimensions: length 5.5 cm., diameter 3 cm. The vertical and horizontal edges of the slot measured 3 mm. and 0.5 mm., respectively.

The pressure within the bulb was maintained at the best value by means of two mercury diffusion pumps in tandem. These pumps and their accessories were designed, made, and loaned to us by Professor B. B. Boltwood. The bulb was excited by an "Ideal Interrupterless" X-ray current generator purchased from the Kny-Scheerer Co. The alternative spark gap was usually set at 4 in., occasionally at 3 or 5 in. The current through the bulb averaged 5 milliamperes. Especial care was taken to line up the spectrograph both in altitude and azimuth so as to cause the collimating axis to coincide with the line passing through the center of the aluminium window and that of the focal spot. All final adjustments were based on photographic data.

3. *Methods and Measurements.*—(i) The "old" method consisted in keeping the plate-holder at a constant distance from the axis of rotation of the crystal while taking exposures both on the right and on the left of the direct or central image. This length was so chosen as to make the distance from the axis of rotation to the latent image equal to that from the axis to the center of the fixed slit. This slit was usually so narrow (0.02 mm.) that small, but arbitrarily made, changes in the position of the plate-holder seemed to exert an inappreciable influence on the width of the photographic lines.

In order to subject the old method to as fair a test as possible special attention was given to the determination of the length of the normal dropped from the axis of rotation O to the plane of the gelatin MN. A rectangular steel template $ABCD$ had one edge AD lapped plane so as to make good contact with the gelatin side of the developed plate. (The frame of the paper screen was removable.) This edge was longer than the distance between the extreme right and left spectral lines in the first order. (The plates were always clamped flat both in the plate-holder and on the comparator, since the glass usually had very noticeable curvature.) A fine fiducial line L was scratched on a piece of white celluloid which was inlaid flush with the upper surface of the steel at the side opposite to the straight edge. The reference line and edge were parallel, and their constant distance apart was measured on the same comparator as the spectrograms. To this distance must be added the length of the perpendicular between the fiducial line and the axis of rotation. This changeable length was measured by the aid of an auxiliary comparator having a travelling microscope with parallel lines in the focal plane of the eye-piece. The pitch of the screw of the latter comparator was calibrated in terms of that of the larger one first mentioned. The scale reading corresponding to the axis of rotation was found by making successive settings on a second fiducial line L' when in the two possible positions $(1, 1')$ parallel to the reference line on the steel template, that is, when the spectrometer table was turned through 180°. The fiducial line near the axis was marked in a bit of celluloid which was mounted on a special tripod replacing the crystal holder. To avoid gross errors several such lines were scratched on the white surface and different lines were used in successive measurements of the same length. All of the linear quantities could be determined to an unnecessarily high degree of accuracy (0.001 mm.).

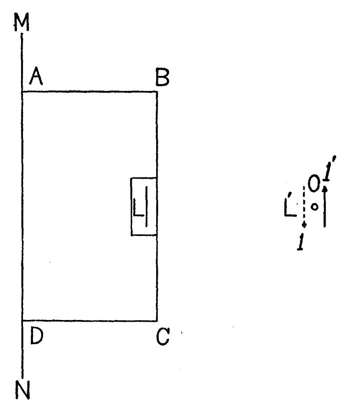

Fig. 1.

The crystals were adjusted, by the aid of a compound microscope, so that their front surfaces coincided as nearly as possible with the axis of rotation. These adjustments did not, of course, entirely eliminate the two fatal errors inherent in the present method: (*a*) the mean "reflecting" plane of the space grating does not coincide exactly with the outer surface of the crystal, and (*b*) the photographic plate does not return to precisely the same distance from the axis when removed from the plate-holder (for development or distance tests) and then returned to the same.

(ii) The new method consisted in taking two exposures (right and left) with the plate near the crystal and two more with the plate remote from the grating, the slits having *equal* widths. An accurate steel parallel with a suitable back-stop left no doubt concerning how far the plate had been translated along the collimating axis. By taking a short exposure for the lower half of the central image before putting the crystal tripod in place—the plate-holder being in one extreme position—and by making a like exposure for the upper half of the direct image after the characteristic radiations had been impressed and the crystal table removed—the plate-holder now occupying the other extreme position—a criterion for the adjustment of the plate-holder guides was obtained at once. A comparison of the distance apart of the two images of a given spectral line on the left with the homologous distance on the right indicated whether the plane of the plate-holder was normal to the direction of translation. The small errors in adjustment and construction of the apparatus were subjected to computation and found to be negligible, since the corrections never exceeded 0.2″.

It may not be inappropriate, at this juncture, to lay emphasis on some of the points of advantage of this method: (*a*) it is independent of the position of the mean "reflecting" plane of the crystal with respect to the axis of rotation, (*b*) it involves no uncertainty as to the amount of displacement of the plate, since the plate is constrained to move the same distance as its holder, (*c*) the numerator of the ratio for the tangent of twice the glancing angle is equal to the linear displacement of the spectral image of the same wave-length on the *same side* of the central image, hence by measuring the distance between homologous parts of the two images (on the same side) errors due to asymmetry in the distribution of radiation over the breadth of the image as well as to the depth of the silver grains in the gelatin are minimized, (*d*) the steel parallel or etalon can be measured on the same comparator as the plate, thus avoiding relative calibration of the pitches of different screws, (*e*) errors of adjustment and construction of the spectrograph can be readily determined and the corresponding corrections easily applied, (*f*) within certain limits, it does not matter where the back-stop is placed, in other words, the interval of displacement of the plate-holder may be at any reasonable but unknown distance from the crystal, and (*g*) within the same limits, the "focusing" is independent of the wave-length. It may also be added that we found the new method to be much easier and less time-consuming than the fixed-plate process. The chief disadvantage lies in the fact that the displacement of a given line (3.3 ± cm.) is much less than the distance (12.0 ± cm.) between the right and left images in the "old" method. This limitation can be removed by making the apparatus large enough. Since the exposure times for the comparatively soft radiations of gallium were usually 5 or 7 minutes, and never exceeded 15 minutes for the weak $K\beta_1$ line, the method should not require excessively long exposures for any of the radiations which do not necessitate the use of a vacuum spectrograph for their investigation.

4. *Experimental Results.*—The numerical data are given in full in Table I. The upper and lower sections of the table refer respectively to calcite and rock salt. The second, fifth, and sixth columns taken together indicate that the experimental conditions were varied as much

Table I.

Plate No.	Exposure Date.	Width of Fixed Slit. Mm.	Width of Movable Slit. Mm.	Distance from Plate to Axis. Mm.	Distance Plate was Translated. Mm.	γ_{α_2}.	γ_{α_1}.	γ_{β_1}.
20	May 29	0.04	0.04	125.71	0	$12^\circ\ 47'\ 21_5''$	$12^\circ\ 45'\ 19_5''$	
21	" 30	"	3.3	"	"			$11^\circ\ 28'\ 16_5''$
22	" 30	"	"	"	"	" " $3_6''$	" $44'\ 49_4''$	" " $14_5''$
32	June 28	0.02	"	125.43	"	" " $23_6''$	" $45'\ 11_6''$	
33	" 28	"	"	"	"	" ' $32_6''$	" " $19_6''$	" " $42_6''$
34	" 29	"	'	"	"	" " $25_8''$	" " $11_8''$	" " $37_5''$
35	" 29	'	"	"	"	" " $15_8''$	" $44'\ 59_8''$	" " $29_8''$
36	" 29	"	"	"	"			" " $29_9''$
37	" 29	"	"	123.38	"	" " $19_9''$	" $45'\ 2_9''$	" " $31_9''$
40	July 2	"	0.02	x	70.079	" " $11_9''$	" " $3_9''$	
41	" 3	"	"	x	"	" " $13_{10}''$	" " $3_{10}''$	
43	" 4	"	"	$x - 10$	"	" " $1_9''$	" $44'\ 59_9''$	
44	" 9	"	"	119.55	"	" " $7_{10}''$	" $45'\ 3_{10}''$	
45	" 9	"	"	"	"			" " $41_9''$
46	" 10	"	"	"	"			" " $28_{10}''$
26	June 16	"	"	119.65	0	$13^\circ\ 47'\ 22_2''$	$13^\circ\ 44'\ 57_2''$	
27	" 16	"	3.3	"	"	" " $34_3''$	" $45'\ 12_3''$	
28	" 26	"	"	123.13	"	" " $27_3''$	" " $3_3''$	
29	" 26	"	"	"	"			$12^\circ\ 22'\ 42''$
30	" 27	"	"	"	"	" " $26_3''$	" " $0_3''$	" " $23''$

as possible. Two calcite crystals and one rock salt crystal were used, and each one was removed from the holder and readjusted at least twice. The (100) cleavage faces were used in all cases. The former material gave perfect definition, but the latter produced slight irregularities in the images. Since the problem which we had set for ourselves was to determine the glancing angles with respect to calcite, we considered the very accurate determination of the ratio of the grating space of calcite to that of rock salt to be an entirely independent question. In other words, the rock salt was employed because a sufficiently satisfactory reduction factor, if present in the literature of the subject, has escaped our notice, and it was desirable to obtain wave-lengths on the same basis as the tables of Siegbahn and others.

The symbols γ_{α_2}, γ_{α_1}, and γ_{β_1} denote the glancing angles of the α_2, α_1, and β_1 lines of the K series of gallium, in the order named. The relative intensities of the α_1, α_2, and β_1 lines are roughly proportional to 5, 4, and 2, respectively. The subscripts in the last three columns are the weights assigned to the associated angles in forming the general mean values. The weights for the rock salt data are quite independent of the indices of relative importance for calcite. The $K\beta_2$ line must be very weak for gallium since we were unable to differentiate it (with short and long exposures) from the continuous background or "white radiation." This weakness of the $K\beta_2$ line seems to be fairly general since the corresponding wave-length is lacking for 24 irregularly distributed elements in Siegbahn's table of the K series. In this connection it may not be superfluous to call attention to the fact that with long exposures, narrow slits, and faint lines it is absolutely necessary to rotate the crystal, for we found it quite easy to arbitrarily produce spurious fine lines from the white radiation by keeping the space grating in a fixed position.

The data in Table I. lead to the following weighted mean values for the glancing angles of gallium:

$$\text{Calcite}\begin{cases}\gamma_{\alpha_2} = 12^\circ\, 47'\, 15'' \pm 2'' \\ \gamma_{\alpha_1} = 12^\circ\, 45'\, 5'' \pm 2'' \\ \gamma_{\beta_1} = 11^\circ\, 28'\, 30'' \pm 2''\end{cases}$$

$$\text{Rock salt}\begin{cases}\gamma_{\alpha_2} = 13^\circ\, 47'\, 28'' \\ \gamma_{\alpha_1} = 13^\circ\, 45'\, 4'' \\ \gamma_{\beta_1} = 12^\circ\, 22'\, 32''\end{cases}$$

Assuming the grating space of rock salt to be 2.814×10^{-8} cm. (E. Wagner) and weighting the preceding data we find the grating space of calcite to be 3.0307×10^{-8} cm.[1] From the 15 values of the wave-length of each of the α lines, and from the 11 determinations of that of the β_1 line, the unweighted mean wave-lengths are found to be

$$\lambda_{\alpha_2} = (1.34161 \pm 0.00004) \times 10^{-8}\text{ cm.},$$
$$\lambda_{\alpha_1} = (1.33785 \pm 0.00004) \times 10^{-8}\text{ cm.},$$
$$\lambda_{\beta_1} = (1.20591 \pm 0.00006) \times 10^{-8}\text{ cm.}$$

[1] While writing the present paper the July number of the PHYSICAL REVIEW was received. On page 95 we notice that F. C. Blake and William Duane take 3.027×10^{-8} cm. for calcite. The two values differ by 0.12 per cent., which seems quite satisfactory under the circumstances given in the above text. The value based on Millikan's datum for e is $(3.030 \pm 0.001) \times 10^{-8}$ cm., with which our value agrees absolutely.

As we are not aware of any reason why our data should be influenced by greater systematic errors than those given by other investigators, and since the wave-lengths heretofore published are usually carried out to three decimal places, but never to more than four (and even then for wave-lengths less than one angstrom), it seems just to conclude that the *relative* values of the three wave-lengths printed above are accurate to one or two more decimal places than have been previously attained. Be this as it may, the appreciably greater concordance of the seconds of arc obtained for the α_1 and α_2 calcite glancing angles (β_1 does not show enough contrast with the background to justify comparison) by the "method of displacement" as compared with the old method favors the opinion that imperfections in the space gratings will constitute the chief factor which will ultimately limit the precision of the determination of relative wave-lengths.

By applying the method of least squares to the calculation of the parameters of Moseley's linear law and interpolating for gallium ($N = 31$) the wave-lengths of the α_2, α_1, β_1, and β_2 lines are found to be 1.341 Å., 1.337 Å., 1.205 Å., and 1.191 Å., respectively. The data used in the computations were taken from one of Siegbahn's tables (based on the same grating space for rock salt), four elements above and below gallium being involved. As presupposed, this rare element falls in line perfectly with the other chemical elements and the laws discovered by Moseley. The agreement between our experimental wave-lengths and the predicted values is much closer than was expected, for the reason that the numbers from which the latter were calculated are decidedly irregular. The mutual inconsistencies of the borrowed data are shown by Table II.,

Table II.

El.	α_2.	α_1.	β_1.
Co	− 2′ 41″	− 3′ 6″	− 3′ 30″
Ni	− 0′ 43″	− 0′ 52″	− 0′ 8″
Cu	+ 1′ 17″	+ 1′ 20″	+ 1′ 20″
Zn	+ 0′ 45″	+ 0′ 56″	+ 1′ 15″
Ga	(+ 0′ 20″)	(+ 0′ 46″)	(+ 0′ 36″)
Ge	+ 3′ 31″	+ 3′ 51″	+ 2′ 52″
As	− 2′ 18″	− 1′ 56″	− 1′ 59″
Se	+ 1′ 16″	+ 1′ 2″	+ 1′ 30″
Br	− 1′ 31″	− 1′ 45″	− 1′ 44″

which gives the differences in the glancing angles obtained by subtracting the least square from the tabulated values. The range of elements involved is too small and the differences are too unsystematic to admit of the alternative inference that the linear law is at fault.

Again, in the vicinity of the atomic number 31, the published data satisfy the equation $\nu_{L\alpha_1} = \nu_{K\beta_1} - \nu_{K\alpha_1} + 0.0064$, which is Kossel's formula *with a correction term* added. Substitution of our data in this relation leads to the value 11.340 Å. for the wave-length of the α_1 line of the L series of gallium. Interpolation with the linear law for the square root of the frequency gives $\lambda_{L\alpha_1} = 11.353$ Å. The agreement between the numbers calculated by the two independent methods may be considered very satisfactory at the present time.

In conclusion the authors desire to express their deep appreciation of the assistance and counsel, with respect to pumps and vacuum difficulties, so gladly given by Professor B. B. Boltwood. It may also be mentioned that we have completed the working drawings for a large X-ray spectrograph with which apparatus we hope to attack a number of important problems depending in some cases on the highest attainable accuracy.

SUMMARY.

1. The glancing angles, with respect to calcite, of the K lines of gallium have been accurately determined.

2. A new method for measuring glancing angles has been devised, tested, and found superior to the older one.

3. A preliminary value for the grating space of calcite on the basis of 2.814×10^{-8} cm. for rock salt has been obtained experimentally.

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