THE L SERIES SPECTRA OF THE ELEMENTS FROM CALCIUM TO ZINC

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ABSTRACT

Using the first inside order of a plane grating (600 lines per millimeter) L lines of the elements Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Ti and Ca have been measured. Separation of the $L\alpha$ and $L\beta$ lines as well as the L_l and L_η is attained by adjusting the grating so that the angle between the inside order and the plane of the grating is small. Under this condition the angular dispersion is given by $(d\alpha/d\lambda) = (1/D\beta)$, where D is the grating space and β the small angle between the plane of the grating and the first inside order. The results obtained are somewhat higher than those obtained by crystal measurements but are entirely consistent with the work of other experimenters. The failure of the $L\alpha$ and the $L\beta$ lines to appear in the case of calcium is in accord with Foote's extension of Stoner's arrangement of the electrons. All measurements are absolute.

THE study and measurement of x-rays of long wave-length have been handicapped by the extensive absorption in air of the rays and by the lack of satisfactory gratings, the grating spaces of ordinary crystals being much too small. The former difficulty has been overcome by the use of vacuum spectrographs; the latter to a certain extent by the use of organic crystals of large grating space. Extensive measurements of L lines in this region have been made by Thoraeus.[1] His work was done with a vacuum spectrograph using crystals of lauric acid $(2d = 54.536A)$ and palmitic acid $(2d = 70.98A)$. The wave-lengths given in his report are based on the sodium K_α line (11.884A). Shearer[2] has measured the nickel L_α line using the 100 face of a crystal of cane sugar $(2d = 21.1519A)$. Unfortunately, however, absorption in the crystal causes a considerable broadening of the spectral lines. It is also quite conceivable that the index of refraction might take on anomalous values due to a resonance frequency of the electrons in the crystal being near the frequency of the x-rays. Under these conditions the application of Bragg's law becomes uncertain even in its corrected form. For these reasons it seems advisable to apply the recently developed method of measuring x-ray wave-lengths from spectra obtained by reflection from a ruled grating to the study of the L lines under discussion.

When Professor A. H. Compton[3] showed in 1923 that x-rays could be reflected from plane surfaces at grazing angles smaller than a certain critical angle determined by the index of refraction of the x-rays reflected, he opened

[1] R. Thoraeus, Phil. Mag. **1**, 312 (1926); Phil. Mag. **2**, 1007 (1926).

[2] J. Shearer, Phil. Mag. **4**, 745 (1927).

[3] A. H. Compton, Phil. Mag. **45**, 1121 (1923).

up the possibility of using a ruled surface as a grating. Two years later Compton and Doan[4] obtained x-ray spectra from a ruled reflection grating. In 1926 and 1927 Thibaud,[5] Osgood,[6] and Hunt[7] applied the ruled grating to the study of the spectral region between x-rays and the ultra-violet, Osgood using a concave grating with a Rowland mounting. Since then the grating has been used by a number of investigators[8] in this field, some making the wave-length determinations from the constants of the apparatus, others by comparison with lines of known wave-length. This method has been used[9] to compare wave-lengths as measured by crystals with those measured by gratings. The measurements from gratings, using the constants of the apparatus, have been found slightly greater than the crystal measurements.

The general method used in the spectroscopy of soft x-rays has been reviewed by Osgood.[10] The general methods and results of this experiment were briefly presented by the author[11] to the American Physical Society. Kellström[12] has reported on measurements of the lines in this same region using outside orders of the spectral lines, comparing them with the K_α line of aluminum.

Theory of the Experiment

In making wave-length measurements in the optical region using a plane reflection grating the formula $n\lambda = D(\sin \phi - \sin \phi')$ is used, n being the order observed, λ the wave-length in centimeters, D the grating space in centimeters, ϕ the angle of incidence and ϕ' the angle of diffraction. In using the plane grating for measurements in the x-ray region it is more convenient to express the wave-length in terms of the grazing angle of incidence θ and the grazing angle of diffraction $\theta \pm \alpha$, the negative sign referring to inside orders, in which case,

$$n\lambda = D[\cos \theta - \cos (\theta \pm \alpha)].\tag{1}$$

By a simple trigonometric transformation this becomes

$$n\lambda = 2D \sin \frac{2\theta \pm \alpha}{2} \sin \frac{\alpha}{2}.\tag{2}$$

[4] A. H. Compton and R. L. Doan, Proc. Nat. Acad. Sci. **11**, 598 (1925).

[5] J. Thibaud, Comptes Rendus **182**, 55 (1926); Comptes Rendus **185**, 62 (1927); Journ. Op. Soc. **17**, 145 (1928).

[6] T. H. Osgood, Phys. Rev. **30**, 567 (1927); Dissertation, Chicago (1927).

[7] F. L. Hunt, Phys. Rev. **30**, 227 (1927).

[8] B. B. Weatherby, Phys. Rev. **32**, 707 (1928). E. Bäcklin, Inaugurald Dissertation, Uppsala Universitets Arsskrift (1928). M. Söderman, Zeits. f. Physik **52**, 795 (1929). C. E. Howe, Proc. Nat. Acad. Sci. **15**, 251 (1929).

[9] C. P. R. Wadlund, Phys. Rev. **32**, 841 (1928); J. A. Bearden, Proc. Nat. Acad. Sci. **15**, 528 (1929).

[10] T. H. Osgood, Phys. Rev. Supp. **1**, 228 (1929).

[11] C. E. Howe, Phys. Rev. **33**, 1088 (1929).

[12] G. Kellström, Zeits. f. Physik **58**, 511 (1929).

Reference to Fig. 1 will help to visualize these angles. The beam of x-rays collimated by the slits, falls on the grating. The zero order is reflected to the point R, the first outside order to the point O and the first inside order to the point I. P is in the extended plane of the grating, while D is the position of the direct beam when the grating is removed.

It should be noted that the position of the inside order is farther removed from the zero order than is that of the first outside order, indicating greater angular dispersion for the inside order. Differentiating Eq. (1) with respect
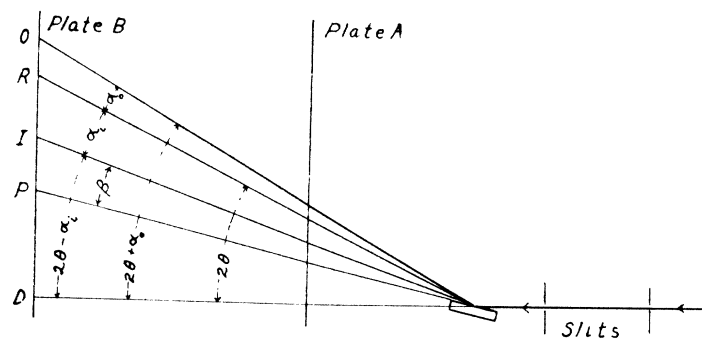

Fig. 1.

to α there is obtained the expression $n(d\lambda/d\alpha) = D \sin (\theta \pm \alpha)$where, as before, the plus sign refers to outside orders and the minus sign to inside orders. The angular dispersion may be written as

$$\frac{d\alpha}{d\lambda} = \frac{n}{D} \frac{1}{\sin (\theta \pm \alpha)} .$$

It is thus seen that the dispersion is greater for inside orders than for outside orders. By varying θ the position I of the inside order may be made as close as desired to the extended plane of the grating. In this way the angle $\theta - \alpha$, which we shall call β, can be made very small, resulting in a large dispersion. For the first inside order

$$\frac{d\alpha}{d\lambda} = \frac{1}{D\beta} . \tag{3}$$

Experimentally it has been found that there is a practical lower limit to the value of β; otherwise the dispersion could be made greater without limit as the angle β decreases. It is of interest to note that the dispersion is independent of both λ and θ.

For outside orders the theoretical maximum dispersion is obtained when $\sin (\theta + \alpha)$ is a minimum. This is the case when $\theta = 0$. The dispersion for outside orders then becomes (neglecting higher powers of $n\lambda/D$)

$$\frac{d\alpha}{d\lambda} = \frac{1}{D}\left(\frac{D}{2\lambda}\right)^{1/2} n^{1/2}.$$

If r represents the ratio between the dispersion of the first inside order and that of the maximum theoretical value of the nth outside order, then

$$r = \frac{1}{\beta}\left(\frac{2\lambda}{D}\right)^{1/2}\frac{1}{n^{1/2}}.$$

Actually the ratio will be larger than this since it is not possible to make $\theta = 0$. In some cases in this experiment the dispersion obtained with the first inside order was equal to twelve times the theoretical maximum for the first outside order. To obtain the same dispersion in an outside order would require going to the 150th order.

THE X-RAY SPECTROGRAPH

Fig. 2 shows a horizontal cross section of the spectrograph and x-ray tube. The body of the spectrograph consisted of a brass tube 8 inches in diameter and 40 inches long. To one end-plate was attached the water-
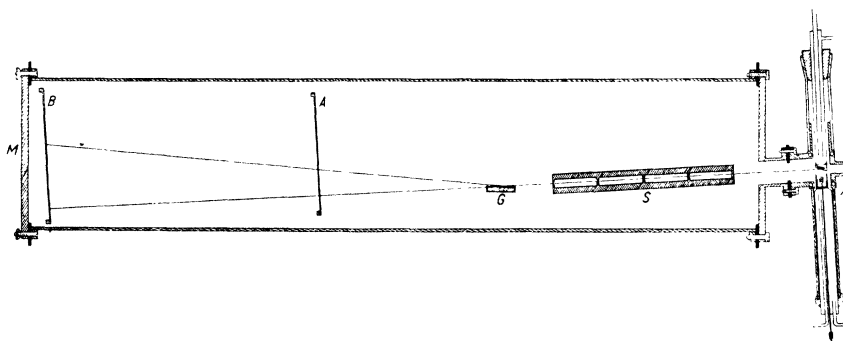

Fig. 2. Horizontal cross-section of the spectrograph and x-ray tube.

cooled metal x-ray tube X. The targets used consisted of small slabs of metal dove-tailed into the face of a water-cooled copper support. The tungsten filament was supported in the center of a water-cooled iron focusing cup.

To the same end-plate was attached a bed-plate on which the slit system, grating support, plate holders etc. were fastened. In order to collimate the rays and to exclude as much of the light from the incandescent tungsten filament as possible, the slit system S consisted of five slits. The two end slits, separated by a distance of 18 centimeters, were 0.05 mm wide; the three intermediate ones, 0.10 mm. By the passage through these slits the intensity of the light was so greatly diminished that it gave little difficulty. No trouble was experienced in the alignment of the slits in as much as the system consisted of two halves, half of each of the several slits being care-

fully machined into each metal piece, the two separate pieces then being clamped together.

The glass grating G, ruled 600 lines per millimeter, was mounted on a table which could be turned through any desired angle by means of a train of gears controlled from the rear end of the spectrograph near the end-plate M. This table, in turn, was mounted on a slide so that the grating could be removed from the path of the x-rays, this movement also being controlled from the rear end. The mechanism was so constructed that either operation could be performed without disturbing the setting of the other, and also so that definite settings could be reestablished with sufficient accuracy.

The plate holder A served to hold a plate which intercepted the lower half of the radiation coming from the grating. The upper half was recorded on a plate placed in the holder B. Plate A was made perpendicular to the direct beam as follows. One side of the slit system was removed, and a straight iron bar carefully clamped to the other half. With a precision square, A was made perpendicular to the bar within a few minutes of arc. B was then made parallel to A by means of an inside micrometer, this operation serving also to obtain the distance between the two plate holders. This distance was 37.982 cm.

All of the apparatus described thus far was mounted as one unit. It could be removed from the main body of the spectrograph at any time for purposes of adjustment.

After adjustment this unit was placed in the spectrograph, a sulphur-free rubber gasket being placed between the end-plate and the body. Plates (Eastman process) were put in holders A and B, and the spectrograph evacuated to a pressure of about 2×10^{-4} mm. A pressure considerably lower than this was maintained in the x-ray tube by means of a separate set of mercury vapor pumps. An exposure of from one to twelve hours was made, depending on the intensity of the radiation. After about twenty minutes exposure the reflected beam was covered with a small screen (operated by an electromagnet) to prevent over exposure and fogging. The exposure being completed, air was admitted, the end-plate M taken off and the grating removed from the path of the beam. After reevacuation the direct beam was exposed for a minute or two.

A small vessel containing phosphorus pentoxide was kept inside the spectrograph to absorb water vapor. The life of the tungsten filament was increased greatly by having a liquid air trap close to the x-ray tube to take up moisture.

The current through the x-ray tube varied from 15 to 40 milliamperes. Because a transformer having rather high secondary resistance was used it was not practicable to attempt to measure the effective voltage on the target, which was much lower than the inverse voltage across the self rectifying tube. It may be estimated that the effective voltage varied from 4000 to 12000 volts.

The Spectra

Fig. 3 shows typical spectra obtained. These particular spectrograms, having nearly equal values of θ, were selected to show the relative displacement of corresponding lines and the increased dispersion with smaller values of β. The L_α and L_β lines of zinc are not resolved. The corresponding lines
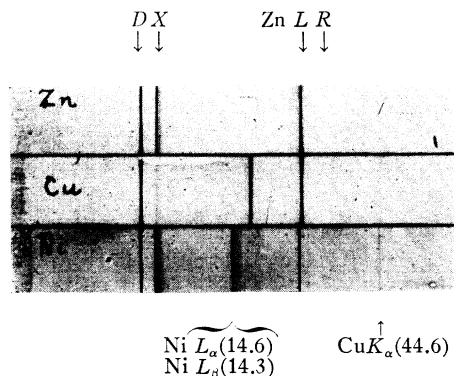

Fig. 3. Typical L series spectra of Zn, Cu and Ni. D is the direct beam, R the reflected beam and X is light diffracted past edge of grating.

of copper overlap, the more intense L_α line being to the left. The lines of nickel are resolved. Since about the same wave-length difference exists between these lines, the spectra show the increase in dispersion as the inside order approaches the plane of the grating. Of the three spectrograms shown only that of nickel is useful in making measurements on the L_β line.

$$\tan 2\theta = \frac{a}{e} \text{ or } \frac{b}{d+e}, \quad \tan (2\theta-\alpha) = \frac{a'}{e} \text{ or } \frac{b'}{d+e}, \quad e = \frac{a}{b-a}d.$$
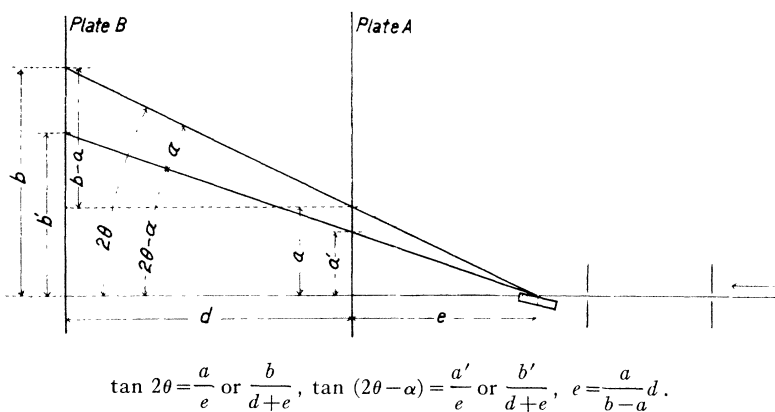
Fig. 4.

It was found that the first inside order from the grating used was much greater in intensity than the outside orders. This fact, combined with the great dispersion obtained with inside orders, contributed greatly to the success of the work. It was also found that the intensity of the L radiation from

the elements studied depended greatly upon the operating conditions of the tube. It was most intense when the temperature of the focal spot was maintained very close to the melting point. With this condition the spot was kept very clean.

The measurement of the plates and the calculation of results can best be described with reference to Fig. 4. The size of the ruled surface (2 cm × 2 cm), the width of the x-ray beam (approx. 0.1 mm) and the magnitude of the grazing angle (more than 2°25′) make it possible to have the entire beam "reflected" from the ruled surface of the grating. Hence all measurements may be made to the centers of the recorded lines. The positions of the lines on the plates were taken as a mean of at least ten independent settings on a Gaertner comparator. The probable error in the readings was usually less than 0.003 mm. The distance e of plate A from the grating and the angles 2θ and $2\theta - \alpha$ were obtained as indicated. By subtraction α was found and substitution made in Eq. (2) to obtain the wave-length.

The results of the measurements are shown in Table I, which gives both the wave-length in angstroms and the value of $(\nu/R)^{1/2}$.

TABLE I.

Element	$L\alpha_{12}$ λ	$(\nu/R)^{\frac{1}{2}}$	$L\beta$ λ	$(\nu/R)^{\frac{1}{2}}$	Ll λ	$(\nu/R)^{\frac{1}{2}}$	$L\eta$ λ	$(\nu/R)^{\frac{1}{2}}$
30 Zn	12.25	8.63	11.96	8.73	14.02	8.06		
29 Cu	13.37	8.26			15.33	7.71	14.95	7.81
28 Ni	14.62	7.90	14.28	8.00	16.73	7.38	16.36	7.47
27 Co	15.99	7.55	15.64	7.64	18.34	7.05		
26 Fe	17.66	7.18	17.29	7.26	20.25	6.71		
25 Mn	19.55	6.82	19.17	6.89	22.34	6.39		
24 Cr	21.73	6.48						
23 V	24.31	6.12			27.70	5.73		
22 Ti	27.48	5.76						
20 Ca					39.63	4.79		

DISCUSSION

Fig. 5 is a Moseley diagram of the results. The results here given are all higher than those obtained by Thoraeus[1] and Shearer.[2] This is in accord with the results obtained by other experimenters.[13] Kellström has reported measurements on most of these lines, using outside orders which did not permit the resolution of the α and β lines or of the l and η lines. His values for the α and l lines are less than those reported here. This is, of course, due in part to the added weight of the unresolved β and η lines. However, in the case of the β line at least, the relative intensity is so much smaller than that of the α line that the wave-length determined from the measurement of the unresolved lines is far from the mean of the two component wave-lengths. Comparison of the results of the two experiments is therefore limited. This is further complicated by the fact that Kellström has made his measurements by comparison with the K_α line of aluminum as obtained from crystal

[13] A. H. Compton, Jour. Franklin Inst. 208, 605 (1929).

measurements. This would also make his measurements lower. In view of these considerations the agreement between the two experiments is very satisfactory, with the exception of the *l* line of calcium for which Kellström
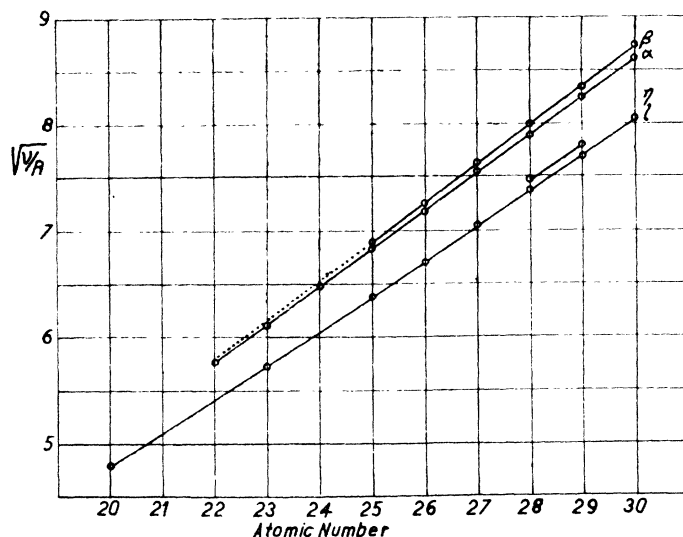

Fig. 5. Moseley diagram for *L*-series lines.

finds a value three percent higher than the value here given. Unfortunately the author recorded this line on but one plate and could not therefore check this wave-length carefully. In all but a few cases, however, sufficient values were obtained to give a probable error less than 0.01A.
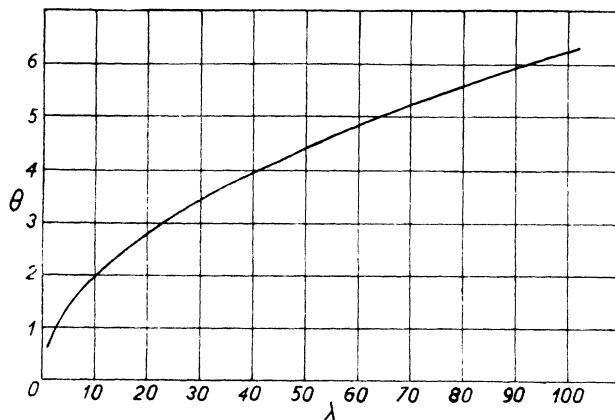

Fig. 6. Values of θ for which the inside order should be in the plane of the grating.

In order to resolve the α and β lines as well as the l and η lines it was necessary to rotate the grating so that the inside orders occurred close to the plane of the grating. Consequently each element required at least two

independent settings; one to resolve the α and β lines, the other to resolve the l and β lines. In order to facilitate this operation the angle θ was calculated for which the inside order should be in the plane of the grating. Fig. 6 shows this value of θ in degrees plotted against the corresponding value of λ in angstrom units. In actual practice θ was made a little larger than this critical value.

For most of the elements in this region the L_α line is really two lines, the $L\alpha_1(M_{33} - L_{22})$ and the $L\alpha_2(M_{32} - L_{22})$. According to Foote's extension of Stoner's arrangement of the electrons the M_{33} level disappears with vanadium and the M_3 level with calcium. This means that neither of the two components of the $L\alpha_{12}$ line should be observed for calcium. Reference to Fig. 1 shows that it was not observed in this experiment although Kellström[12] finds it present. The $L\beta_1(M_{32} - L_{21})$ line should also disappear with calcium.

In conclusion I wish to express my indebtedness to Professor A. H. Compton of the University of Chicago under whose direction the experimental work was done.
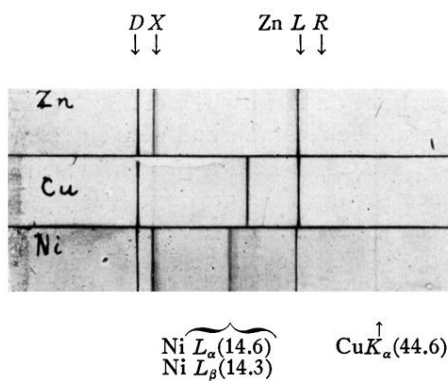
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