X-RAY SPECTRA OF LONG WAVE-LENGTH

By T. H. Osgood[1]

Abstract

Method of obtaining x-ray spectra by reflection from a concave grating.—The paper describes a photographic method of obtaining x-ray spectra of long wave-length, based on the experimental fact that x-rays are totally reflected from a mirror (or grating) provided the angle of incidence is sufficiently large. Details are given of a *vacuum spectrograph* employing an x-ray tube as a source of radiation, in conjunction with a two-metre concave grating. About fifteen lines have been measured between 40 and 200A. As it has not yet been possible to obtain a pure spectrum of any one element, the interpretation of these lines is a matter of considerable uncertainty. Nearly half of them appear to be due to strontium and barium deposited on the anti-cathode from the oxide coated filament of the x-ray tube. The method is applicable to all wave-lengths greater than about 20A.

DURING the last few years the unexplored region between x-ray spectra and optical spectra has grown rapidly smaller, yielding under optical methods on the one hand and under x-ray methods on the other. Millikan[2] and his collaborators have photographed spectra down to a wave-length of 136A, while Siegbahn and Thoraeus[3] have extended the x-ray region up to 27A. The gap separating these two limits has, until very recently, defied all investigation by direct spectroscopic means. Indirectly, characteristic line radiations have been detected[4] by their photo-electric effects. This method, however, is capable of no great accuracy in determining the positions of the lines, and can give, at the best, but vague information as to their intensity. The need for spectroscopic investigation of the soft x-ray region is therefore apparent. Previous experiments on shorter and on longer wave-lengths suggest that the gap might be filled up by a modification of the usual grating method or by an extension of the standard methods of x-ray spectrometry. Dauvillier,[5] in a recent paper, describes a successful application of the latter method by which he has obtained photographs of a few lines of oxygen, carbon, boron and thorium between 20 and 125A. The present paper describes an investigation which employs a combination of the x-ray and optical methods; it covers the region 40 to 200A.

The Refractive Index of X-rays

According to the Drude-Lorentz theory of dispersion, the refractive index μ, for a radiation of frequency ν, of a substance containing n_r electrons per unit volume, which have a natural frequency ν_r, is given by

[1] Commonwealth Fund Fellow.

[2] R. A. Millikan and I. S. Bowen, Phys. Rev. **23,** 1 (1924).

[3] M. Siegbahn and R. Thoraeus, Jour. Opt. Soc. Amer. **13,** 235 (1926); R. Thoraeus, Phil. Mag. **1,** 312 (1926).

[4] The work on this subject is too extensive to refer to in detail.

[5] A. Dauvillier, Jour. de phys. et le rad. **8,** 1 (1927).

$$\delta = 1 - \mu = \sum_{1}^{r} \frac{n_r e^2}{2\pi m(\nu^2 - \nu_r^2)}$$

where e and m have the usual significance. As far as x-rays are concerned, this may be written approximately as

$$\delta = 1 - \mu = ne^2/2\pi m\nu^2$$

since ν_r is very small in comparison with ν. Here n is the total number of electrons per unit volume. Since the right hand term is positive, μ is less than unity. A beam of x-rays falling on a polished metal plate should therefore show the same behavior as a beam of light at a glass-air interface; at a certain critical angle total reflection should occur. Elementary optical considerations indicate that total reflection will take place when $\sin i = \mu$, where i is the angle of incidence. For x-rays, however, μ differs from unity by only a very small amount; hence the relation may be more conveniently written $\cos\theta = \mu$, where θ is the glancing angle; or

$$\sin\theta = [2(1-\mu)]^{1/2} = (2\delta)^{1/2}.$$

The experiments of A. H. Compton[6] in 1923 showed that these formulas could be used with considerable confidence, and that the total reflection of x-rays could be observed for wave-lengths as short as 1.28A. The agreement of the theory with experiment has also been confimred by other methods.[7]

This at once opens up the possibility of obtaining spectra by reflecting a beam of x-rays at a small glancing angle from an ordinary diffraction grating. The first suggestion of thus employing a grating (to give an absolute determination of the wave-length of a beam of x-rays) seems to have come from Professor Puccianti[8] of the University of Pisa. On carrying out his idea, however, Carrara[8] obtained merely a totally reflected image, with no diffraction pattern. A year later, and independently, A. H. Compton and Doan[9] obtained diffraction patterns (in three orders) from a speculum grating, of the $K\alpha_1$ line of molybdenum; from the measurement of their photographs a value for the wave-length was obtained in very good agreement with that found by the usual crystal methods. In these experiments the glancing angle was about 10 minutes.

Since $\sin\theta$ is proportional to λ, larger glancing angles can be employed for x-rays of longer wave-length. For $\theta = 10°$, all radiations softer than 40A should be reflected from a speculum grating. Larger angles simplify the experimental procedure—except that everything has now to be done in a vacuum.

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

[7] Larsson, Siegbahn and Waller, Naturwiss. **52,** 1212 (1924); R. von Nardroff, Phys. Rev. **24,** 149 (1924); C. C. Hatley, Phys. Rev. **24,** 486 (1924).

[8] N. Carrara, Il Nuovo Cimento **1,** 107 (1924).

[9] A. H. Compton and R. L. Doan, Proc. Nat. Acad. Sci. **11,** 598 (1925). Similar spectra have also been obtained by J. Thibaud, Comptes rendus, Jan., 1926.

The Spectrograph and its Adjustment

Two concave gratings were used in this investigation; the first, of speculum metal with a ruled surface (8.4 cms by 5 cms) having 580 lines per mm. and a radius of curvature of 205.2 cms; the second, of glass, of the same size, but with 800 lines per mm, and a radius of curvature of 215 cms. The latter was used almost exclusively; plates taken with the speculum grating were almost invariably fogged, and never showed more than two or three spectral lines. With the glass grating the photographs were comparatively clean. Though the mounting was of the standard Rowland type, the angle of incidence was so large that the problem of housing a two-metre grating in a vacuum was less formidable than appears at first sight. Fig. 1 illustrates the essential features of the spectrograph. The grating G and plate-holder P were mounted on a heavy steel base-plate A, 102 cms long, which was rigidly attached to a circular brass plate B, 1 cm thick and 24.5 cms in diameter. This slid into the brass tube C, 103 cms long and 20.4 cms inside diameter, the plate B thus forming a cover plate for one end of C. In order that the joint between A and B might be subject to no undue strain the base-plate was arranged to rest on the walls of C. The slit S was mounted in a wide

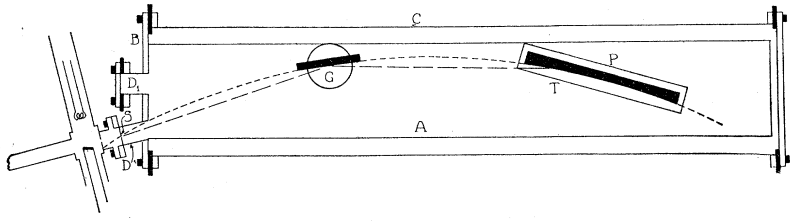


Fig. 1. The vacuum spectrograph.

brass ring fitting snugly inside the projecting tube D, to which a small metal x-ray tube was bolted. A second tube D_1 was provided so that by using one or the other, the glancing angle could be varied from 10° to as near 0° as might be required. The junctions between the end-plates and C were made vacuum tight by gaskets of sulphur-free rubber, 3 mms thick, and drawn together by twelve bolts. The alternative slit-tube D_1 was sealed in the same way.

In Fig. 1 the dotted arc is part of the circle of reference for the Rowland mounting. It passes through the slit S, and is tangential to the grating at its mid-point. Such an arc was scratched on the base-plate by an accurate beam compass, and the plate holder screwed down so that the surface of the plate would lie along the circle. This could be done with no greater error than 0.2 or 0.3 mm. By means of an electrical control, not shown in the diagram, the plate in its carriage could be raised while an experiment was in progress, enabling three exposures to be made without breaking the vacuum. The grating mounting had to be screwed down only in approximately the correct position, as it was provided with several independent adjusting screws.

Since any filter placed in the path of the radiation to prevent fogging of the photographic plate by scattered light from the filament would also absorb the soft x-rays just as effectively,[10] the tube was operated to give a minimum of light. This was accomplished by using a low-temperature oxide-coated filament, and by setting the face of the anticathode so that it did not reflect light directly on to the slit. Both the tube and anticathode were water-cooled. In operating the tube it was found convenient to earth the filament and the tube, applying the high potential to the anticathode, which thus received all, instead of a fraction of the electrons from the filament.

The source of high potential was a half-kilowatt Thordarson wireless transformer providing an alternating p.d. of about 5000 volts. The current through the tube was generally 25 m.a.

A pressure of less than 0.0002 mm was maintained in the spectrograph by a set of three condensation pumps in series, backed by a water aspirator; the x-ray tube, which communicated with the body of the spectrograph only by the slit S, was provided with a separate pump backed by the same aspirator. The pressure in the x-ray tube, though not measured, was certainly much less than in the rest of the apparatus.

One of the greatest difficulties encountered was that the coating of the filament was very soon destroyed. Some of this deposited on the cold anticathode, which also became blackened, due apparently to the destruction of residual gases and vapors in the tube. This meant that any spectrum obtained could not be ascribed to the substance of the anticathode alone; its interpretation was therefore difficult. Dauvillier[5] mentions the same effect.

The procedure in adjusting the instrument was as follows: A vertical scratch was made on the mask of the plate-holder at T. The grating mounting was then bolted to the base plate A with the center of the grating approximately equidistant from the slit and from T; by adjusting the grating, the reflected image of the slit, illuminated by a mercury arc, was brought to a focus at T.

Wave-lengths were computed directly from the constants of the apparatus, as the only reference line on each plate was the direct image of the slit at T. From the distance of any other line from this image, the corresponding angle of diffraction could be calculated, knowing the radius of the circle of reference and the distance ST. Thence the unknown wave-length follows easily from the relation $\lambda = e\ (\mathrm{Sin}\ i - \mathrm{Sin}\ \phi)$ where i and ϕ are the angles of incidence and diffraction, and e is the grating space. Higher orders of spectra were obtained only on one or two plates; with a grating used at such a large angle of incidence, the dispersion is, of course, far from normal; it varied from about 1A per mm at 50A to nearly 2A per mm at 200A. Schumann films on thick celluloid, made by Adam Hilger, Ltd., were used, and proved very satisfactory, being very slightly sensitive to the yellow light from the low-temperature filament. Computations from different films taken under apparently identical conditions (the only change being the

[10] J. J. Thomson, Phil. Mag. **49**, 761 (1925). See also, R. Thoraeus, Nature, Nov. 27, 1926; and A. Dauvillier, Ref. 5.

readjustment of the instrument) showed discrepancies up to about 3 percent. Where several measurements have been made, the error of the average should be much less. The whole investigation up to the present has been designed to give general information as to the character of soft x-ray spectra, rather than to determine wave-lengths with precision. For exact measurements it would be necessary to determine a few wave-lengths with considerable accuracy—by means of a plane grating—and to measure films from such lines as standards.

Results of the Experiments

It will be convenient first to make a few remarks about the spectrograms which are reproduced in Fig. 2. No great significance can be attached to the relative times of exposure, which are stated alongside each photograph, for other factors, such as the pressure in the tube and the condition of the anti-cathode seemed to influence the production of lines to an equal extent. In general, the spectrum obtained was independent of the substance of the anticathode, and was therefore ascribed to impurities in the tube. The carbon K line at 44A appeared on practically every photograph, though in varying intensity; the L lines of carbon, oxygen and nitrogen fall at longer wave-lengths than were covered by the plate; the K lines of nitrogen and

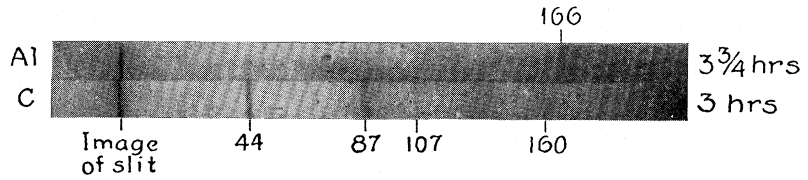


Fig. 2. Typical spectrograms with Al and C anticathodes. Glancing angle 9° 30′, glass grating, one-third actual size.

oxygen were not recorded when the grating was set at an angle small enough to allow them to be reflected. There remain, therefore, as possible sources of the line radiations, barium, strontium and nickel from the coating of the filament, deposited on the cold anticathode, and the substance of the anticathode itself. No absorption edges would have been photographed.

Plate I, where carbon and aluminium were in turn the anticathode substances, shows four strong lines in the carbon spectrogram; two of these, at 107 and 160A, clearly extend over the aluminium spectrum; the others, at 44 and 87A, do not appear to do so, though they were easily visible on the original film. The most curious feature of the aluminium spectrum is a continuous band, with a sharp limit at 166A, shading off towards longer wave-lengths. It appears to be not without structure, though no definite assertion can be made on this point until further experiments have been carried out.

In Table I are listed all the lines which have been measured in these experiments; no lines of doubtful existence have been included. Care has been taken to exclude second-order lines, which were occasionally obtained,

especially with the speculum grating. The strong line previously referred to at 160A is a doublet. Little seems to be gained by measuring exactly the relative intensities of the lines, since the values depend so much on the nature of the anticathode; they have therefore been designated approximately as strong, moderate or faint. The assignment of lines to transitions between particular atomic levels is a matter of considerable uncertainty, since at least half of them appear to be due to strontium and barium, of the low energy

TABLE I

List of lines observed.

No. of obs.	Wave-length	Int.	Volts	ν/R	$(\nu/R)^{1/2}$	Ascribed to	
13	43.96	s	281	20.54	4.53	C	$L_{II,III} - K$
5	86.9	s	142.3	10.49	3.24	Sr	$N_{II,III} - M_{IV,V}$
2	101.5	f	121.6	9.00	3.00	Sr	$N_{II,III} - M_{IV,V}$
6	107.0	s	115.3	8.52	2.92	Sr	$N_{II,III} - M_{IV,V}$
3	75.7	m	163	12.05	3.47	Ba	$O_I - N_{II}$
3	154	f	80.3	5.92	2.43	Ba	$O_{II,III} - N_{IV,V}$
7	159.0	s	77.8	5.74	2.40	Ba	$O_{II,III} - N_{IV,V}$
7	160.1	s	77.2	5.71	2.39	Ba	$O_{II,III} - N_{IV,V}$
5	66.9	m	185	13.62	3.69		?
5	81.8	s	151	11.16	3.34		?
2	111.5	f	111	8.18	2.86		?
1	133.5	f	92.6	6.84	2.62	Zn	?
1	150.5	f	82.2	6.06	2.46	Zn	$N_I - M_{II,III}$
1	164	f	75.4	5.56	2.35	Cu	$N_I - M_{II,III}$
1	215	f	57.5	4.24	2.06	Fe	$N_I - M_{II,III}$
2	166.6	edge	74.4	5.48	2.34	Al	band.

levels of which very little accurate information is available. Thoraeus[11] has, however, recently published a table of energy values of the elements chromium (24) to bromine (35), which can be extrapolated with some confidence up to strontium (38). The transitions given in the last column of the table are therefore little better than probable guesses, except in the case of the first line (carbon K) and the last three which are definitely ascribable to the elements zinc, copper and iron. They are consistent with the values for the $M_{II, III}$ levels given by Thoraeus except in the case of iron, where the measured line was a ν/R value of 4.24 as compared with the value 4.17 for the level itself. For these elements the N_I level has an energy of only a few volts. The continuous band shown in the spectrogram of aluminium is difficult to account for; the experiments give no clue as to its origin. It may be that its occurrence depends on the presence of a film of oxide on the aluminium target.

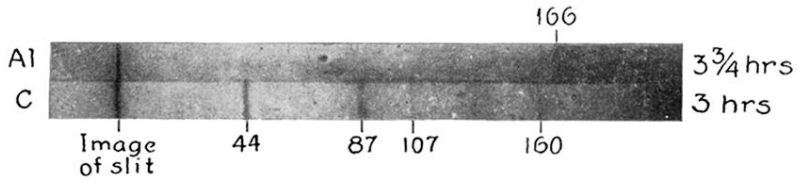
The data set forth in Table I are so fragmentary, and their interpretation so uncertain, that there seems to be no advantage in discussing them further; nor does it appear worth while to state in detail the correspondences which

[11] R. Thoraeus, Phil. Mag. **2**, 1007 (1926); see also E. C. Stoner, Phil. Mag. **2**, 97 (1926).

have been found to exist between the energies, of some of the measured line and published values of critical potentials, determined by photoelectric methods, for these show none too good agreement among themselves. The value of these experiments, admittedly of a preliminary character, lies in the fact that they have opened up a simple method of studying x-ray spectra of long wave-length.

I wish to thank my friends in the Ryerson Physical Laboratory for the interest they have taken in the work; and especially Professor A. H. Compton, at whose suggestion the problem was undertaken.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
August 1 1927.



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