SPECTROSCOPY OF SOFT X-RAYS

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I. Introduction

EVER since x-rays were recognised to be of the same nature as visible light, efforts have been made to explore, by photographic means, the unknown intervening region. Progress was rapid from both ends of the scale. Poineer work by Schumann[1] and Lyman[2] paved the way for the comprehensive experiments of Millikan[3] and his collaborators who, in 1921, extended the region of known optical spectra to wave-lengths as short as 136A. Meanwhile, the limit to which x-ray spectra from crystal gratings could be photographed was being pushed to longer wave-lengths, until, in 1925, Siegbahn and Thoraeus[4] successfully recorded lines at about 25A, —an important extension, as is easily realised by considering not wave-lengths, but frequencies. There remained a gap of about two and one-half octaves which defied exploration by standard methods. Further progress from the optical side was impossible on account of the extremely small reflecting power of gratings (used at normal incidence) for short waves; x-ray spectroscopists required crystals with very large grating spaces which were not readily obtainable; and in both cases were added the experimental difficulties of working in a high vacuum, for these x-radiations have very feeble penetrating power. Indirectly, spectrum lines and absorption edges in this intervening region had been detected by photoelectric methods,[5] but these were capable of no great accuracy in determining the positions of lines and could give, at the best, but vague information as to their intensity. It was not until a new technique was established that this last gap—the soft x-ray region, as it is called,—yielded satisfactory spectrum photographs. The soft x-ray region has no definite limits, merging into the extreme ultra-violet on the one hand, and into the domain of standard x-ray crystal spectroscopy on the other. It will be convenient, however, to restrict the spectra considered in this article to wave-lengths longer than about 15A. The experimental and theoretical basis of the new technique will be discussed in Section III.

II. Dauvillier's Exferiments

No account of soft x-ray spectroscopy would be complete without reference to the work of Dauvillier,[6] who was the first to carry out a successful

[1] Schumann, Wien. Ber. **202,** 625 (1893).

[2] Lyman, Spectroscopy of the Extreme Ultra-Violet, Longmans, London, 1914.

[3] Millikan, Proc. Nat. Acad. Sci. **7,** 289 (1921). Millikan and Bowen, Phys. Rev. **23,** 1 (1924).

[4] Siegbahn and Thoraeus, J. O. S. A. **13,** 235 (1926). Thoraeus, Phil. Mag. **2,** 1007 (1926).

[5] Holweck, De la Lumière aux Rayons X, Conférences Rapports, 1927.

[6] Dauvillier, Jour. de Phys. et le Rad. **8,** 1 (1927).

exploration of this region by photographic means. Although his experimental methods have been superseded by more accurate and less difficult ones, his work presents many points of interest which make it worthy of consideration here. It was, essentially, an extension of the standard methods of x-ray crystal spectroscopy, one of the chief problems being the preparation of a crystal of sufficiently large grating space. Soft x-rays are very readily absorbed by matter, so that a thick crystal is unnecessary. Dauvillier's solution of the problem was to deposit a thin layer of melissic acid (C_{29} H_{59} COOH) only a few hundred molecules thick on a flat lead plate. Under these conditions the long-chain molecules arrange themselves in a regular fashion, somewhat like the pile of a carpet. (Compare, for example, the experiments of Hardy and Miss Doubleday[7] on lubrication.) The resulting structure has the properties of a crystal. In the particular case of melissic acid, the grating space was found to be 73.5A, and of its lead soap 87.5A, which should reflect spectrum lines up to a theoretical limit of about 175A, which, however, cannot be reached in practice.

The Schumann plates which were used were easily fogged by scattered light from the filament of the x-ray tube. To prevent this, a very thin screen of magnesium oxide was interposed in the path of the radiation. This was made by depositing the oxide from a magnesium filament on a thin film of collodion stretched on a wire frame. The screen, although practically opaque to visible light, transmitted about 30 percent of a radiation of wave-length 40A, the 70 percent absorption being due about equally to the collodion and the magnesium oxide. The thinnest foils of gold and aluminum which were opaque to light transmitted only a few percent of this soft x-radiation.

The measurement of his plates was difficult on account of the diffuseness of many of the lines (due in part to imperfections of the crystal); at the same time refraction of the rays in the acid film displaced the spectra by varying amounts almost impossible to estimate. The numerical results of Dauvillier's work, therefore, have no great value. He recorded, however, for the first time, a few lines of oxygen, carbon, boron and thorium between 20 and 120A. His papers also give some rough estimates of the absorbability of these soft radiations in thin foils. These are the only measurements of this kind which have been made for soft x-rays.

III. The Refractive Index of X-Rays and its Significance

Until a few years ago optical gratings in vacuum spectrographs were invariably used at nearly normal incidence. The new technique for the exploration of the soft x-ray region consists in allowing radiation to fall on the grating at angles of incidence which are greater than 80°, and usually almost 90°. Under these conditions, the soft x-rays are reflected and spectra are formed. We shall proceed to discuss the principles which underlie this modification of the regular procedure.

The experimental basis is to be found in a paper by A. H. Compton,[8]

[7] Hardy and Miss Doubleday, Proc. Roy. Soc. **A101,** 487 (1922).

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

in which that author describes experiments on the reflection of x-rays from plane surfaces of glass and silver. A beam of x-rays of a definite wave-length of the order of 1A, selected by reflection from a crystal, was allowed to fall at a glancing angle of a few minutes of arc on a polished plate of glass, mounted on the turntable of an ionization spectrometer. The intensity of the reflected beam was measured in the usual way by an ionization chamber. By progressively varying the glancing angle and changing appropriately the position of the ionization chamber, a limiting angle was found at which the x-rays ceased to be reflected from the plane glass mirror. The experiments were carried out for more than one wave-length, and the significant facts emerged that the critical glancing angle increased with the wave-length and was different for different mirrors; in general, the more dense the substance of the mirror, the greater the critical angle.

Professor Puccianti,[9] of the University of Pisa, seems to have been the first to suggest that replacing the mirror by a plane optical grating and recording the reflected beam photographically should produce a diffraction pattern corresponding to the wave-length of the incident x-ray beam. His idea was tested by Carrara[9] who obtained, however, a negative result, though he verified the metallic reflection of x-rays. Unaware of Carrara's work, A. H. Compton and Doan,[10] a year later, carried out the same experiment; they were successful in recording a diffraction pattern in three orders, from a speculum grating. The diffraction and total reflection of x-rays were thus definitely established, and at the same time a valuable check was provided of the wave-length measurements of x-rays by crystal methods. It appears probable, indeed, that this method will, in a short time, become the most accurate at our disposal for the measurement of wave-lengths, and, indirectly, for the determination of Avogadro's and related constants.[10]

In A. H. Compton and Doan's work no data for wave-length calculations involved derived constants, such as the grating space of a crystal. A short time afterwards, in describing similar experiments, Thibaud[11] reported the important fact that glass gratings give greater intensity of reflection, less fogging of plates and sharper lines than those of speculum metal, as indeed Wood and Lyman[12] also showed in the extreme ultra-violet. This has been the general experience of later investigators.

Since x-rays in air (or in a vacuum) can be totally reflected from a polished surface, it follows that their refractive index μ is less than unity, but by a very small amount, since the critical glancing angles are small. Hence the velocity of an individual x-ray in (say) glass or speculum metal is greater than the velocity of light. There is, however, no contradiction of the special theory of relativity, since the group velocity remains less than that of light.

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

[10] A. H. Compton and Doan, Proc. Nat. Acad. Sci. **11**, 598 (1925). Bearden, Amer. Phys. Soc., Washington Meeting, April 1929, Phys. Rev. **33**, 1088 (1929). Bäcklin, Nature, March 16, 1929.

[11] Thibaud, Comptes rendus, Jan., 1926. Thibaud, Jour. de Phys. et le Rad. **1**, 13 (1927).

[12] Wood and Lyman, Phil. Mag. **2**, 310 (1926).

The refractive index of crystals for x-rays has been calculated by Stenström[13] and by Larsson[14] from the deviations from Bragg's Law ($n\lambda = 2d \sin\theta$) in high orders of reflection; it has been measured more directly for crystals by B. Davis[15] and his collaborators; and in Siegbahn's[16] laboratory the direct deviation of x-rays by a glass prism has been observed. The result in all cases is a value for μ slightly less than unity. There is thus a wealth of concordant experimental evidence.

From the theoretical side this is well supported. The expression for the refractive index of x-rays of frequency ν may be written[17]

$$\delta = 1 - \mu = \frac{e^2}{2\pi m} \sum_1^N \frac{n_s}{(\nu^2 - \nu_s^2)}.$$

Here, since the right-hand member is essentially positive ($\nu > \nu_s$), the refractive index μ is less than unity, but by a small amount only, so that it is convenient to consider its difference δ from unity; e, m, are the charge and mass of an electron; N is the number of electrons per unit volume of the refracting substance, comprising several groups, each containing n_s electrons whose natural frequency is ν_s. The formula can be derived by purely classical methods, starting from Maxwell's equations. It involves the assumption that the magnetic permeability of matter for high frequencies (of the order of 10^{17} per second) is unity to a very close approximation. On theoretical grounds this is justifiable since our ideas of permeability involve the orientation of magnetic units (molecules, atoms, electrons) which would be impossible at such great frequencies. There is, however, a dearth of experimental confirmation.

In the case of the reflection of ordinary x-rays from glass, the frequency ν of the incident beam is large compared with the natural frequencies ν_s of any of the electron groups. Hence the formula may be simplified to

$$\delta = 1 - \mu = \frac{Ne^2}{2\pi m \nu^2}.$$

If θ_c be the critical glancing angle for total reflection, then

$$\sin\left(\tfrac{1}{2}\pi - \theta_c\right) = \cos\theta_c = \mu\ ;$$

or, since θ_c is small,

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

This relation affords a convenient method of comparing experimental results with theory. In spite of occasional slight uncertainties as to the exact chemical composition of the glass mirrors, theory and experiment show agree-

[13] See A. H. Compton, Ref. 8.

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

[15] v. Nardroff, Phys. Rev. **24**, 143 (1924). Hatley, Phys. Rev. **24**, 486 (1924). Davis and Slack, Phys. Rev. **27**, 18 (1926). Slack, Phys. Rev. **27**, 691 (1926).

[16] Larsson, Siegbahn and Waller, Naturwiss. **52**, 1212 (1924).

[17] Darwin, Phil. Mag. **27**, 315 (1914). Ewald, Ann. d. Physik **54**, 519 (1918). Ehrenberg and Mark, Zeits. f. Physik **38**, 129 (1926). Kallmann and Mark, Ann. d. Physik **82**, 585 (1927). A. H. Compton, "X-Rays, and Electrons," Chap. VII.

ment to within a few percent. It follows from the formula that δ is to a first approximation proportional to the square of the wave-length. Hence, wave-lengths of soft x-rays obtained by crystal methods cannot be expected to have a high accuracy. Thibaud and Soltan[18] have, in fact, shown that some of Dauvillier's results are in error by nearly 8 percent.

Since $\sin\theta_c$, is approximately proportional to λ, larger glancing angles can be employed for x-rays of longer wave-length. For $\theta = 10°$, all radiations softer than about 40A are reflected from a glass grating. In many cases larger glancing angles simplify the experimental procedure.

IV. The Use of Gratings at Large Angles of Incidence

In the soft x-ray region, as in optics, concave and plane gratings may be used for spectrum work. Each has its special advantages which recommend it for some particular investigation. The Rowland (concave) mounting requires that the slit, the center of the grating and the photographic plate lie on the circumference of a circle whose diameter is equal to the radius of curvature of the grating. This circle must be tangential to the grating, as in Fig. 1, where S is the slit, P the plate and G the concave grating. R is

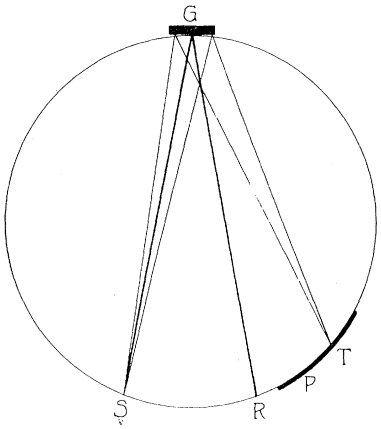

Fig. 1. Standard Rowland mounting for a concave grating.

the directly reflected beam. Under these conditions the spectra are in correct focus. For soft x-rays the glancing angle must be small; hence S and P must be moved along the circumference towards G. The resulting configuration is as shown[19] in Fig. 2, on a much larger scale than Fig. 1. The dotted arc represents part of the circle of reference. C is the source of radiation. If the grating is suitably adjusted an image of the slit, by direct reflection is formed at R, where $SG = GR$, and spectra are found between R and the outer end of the photographic plate, for example, at T. Since the angle of incidence is so large, the problem of housing even a two-metre grating in a vacuum spectrograph is not so formidable as might appear at first sight.

[18] Thibaud and Soltan, Jour. de Phys. et le Rad. **8,** 484 (1927).
[19] Osgood, Phys. Rev. **30,** 567 (1927).

This arrangement was used by Osgood[20] in the first successful exploration of the soft x-ray region from 40A to about 200A, overlapping considerably the extreme ultra-violet of Millikan.

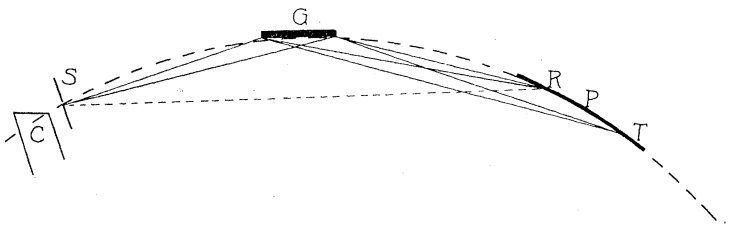

Fig. 2. Rowland mounting for large angles of incidence.

Almost at the same time, Thibaud,[21] who had already recorded lines at about 50A, reported x-ray spectra from a plane grating up to about 170A. These two researches of Thibaud and Osgood definitely closed the gap between x-ray and optical spectra, and illustrated the power of the new methods. The plane grating arrangement is explained[22] by Fig. 3. A pencil of radiation from an anticathode C is selected by parallel slits S_1, S_2 and

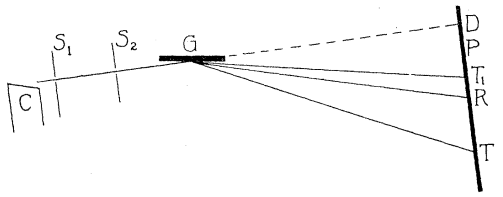

Fig. 3. Plane grating arrangement for large angles of incidence.

allowed to fall at a small glancing angle (perhaps 2°) on the grating at G. A reflected image is obtained on the plate at R, and spectra are found outside at T and inside at T_1. Since spectra cannot be formed behind the grating, those inside are limited. The distance GR is usually of the order of 50 cm. The slits S_1, S_2 may be made longer than the grating so that a reference line is produced at D while spectra are being recorded at T, T_1.

Up to the present time most investigators of the soft x-ray region have used plane gratings. They possess the following advantages over concave gratings: (1) measurements are accurate, approaching 0.1 percent; (2) spetrum lines are sharp[22] even with moderately wide slits; (3) adjustment is easy; (4) only a small grating is required. If a grating of the usual optical size were used, there would be uncertainty as to the exact part of it which was effective; that is, the point G, Fig. 3, would be indeterminate. For exact measurements, the position of this point must be known to a fraction

[20] Osgood, Nature, June 4, 1927.
[21] Thibaud, Comptes rendus, July 4, 1927.
[22] Thibaud, Jour. de Phys. et le Rad. **8**, 13 (1927).

of a millimetre. There are two ways of overcoming the difficulty. Either all the grating except a narrow strip 1 or 2 mm wide is masked by a thin film of collodion, or two photographs are taken simultaneously with plates at different distances from the grating.[23] The latter method is preferable, though, at the best, not more than a 10 mm strip of the grating is effective. Hence the intensity is limited. A concave grating, on the other hand, automatically focusses the spectra, and makes use of the whole surface of the grating. It is, unfortunately, difficult to adjust, and the wave-length measurements derived from it are lacking in accuracy.[19] There seems no reason to doubt, however, that it will develop into a valuable instrument for the study of soft x-rays as soon as a number of reference lines have been accurately measured by plane grating methods. The two types of grating are thus to be regarded as complementary instruments of research in the soft x-ray region. As regards dispersive power, for example, a good plane grating gives about 4A per mm at 100A, whereas a 2-metre concave grating with the same ruling gives 1A per mm if used at a glancing angle of roughly 10°. In neither case is the dispersion uniform. For a plane grating it is very great when the angle of diffraction is almost 90°, corresponding to a position on the photographic plate just outside the intersection of the planes of the grating and the plate, and decreases rapidly as the angle of diffraction decreases. (See Fig. 4 (c), 2).

The diagrams in Figs. 2 and 3 are schematic. For the detailed construction and adjustment of suitable vacuum spectrographs the reader must be referred to the original papers. In all cases wave-lengths are computed from a relation equivalent to

$$n\lambda = e(\cos\theta - \cos\phi),$$

which refers to a radiation of wave-length λ incident at a glancing angle θ on a grating whose constant is e, and diffracted in the n^{th} order at an angle ϕ. In the case of a concave grating, Fig. 2., the quantities necessary for the computation are: SR (straight line distance); RT, along the arc, i.e. along the plate; the grating space e; and the radius of curvature of the grating. For the plane grating, Fig. 3, the calculation requires, if the angle GDR is 90°: GD; DR; RT; and the grating space e.

In Fig. 4 are reproduced some typical soft x-ray spectrograms, taken with a plane grating. These I owe to the courtesy of Mr. Carl E. Howe, of Oberlin College, at present working at the University of Chicago. The strong lines D and R on all the photographs are the direct and reflected images of the slit system as in Fig. 3. X is due to diffraction of optical light (from the filament of the x-ray tube) past the straight edge of the grating. Spectra are formed on both sides of R. The interesting features of each photograph are enumerated below. All were taken with a plane glass grating of 6000 lines per cm; distance, plate to grating, about 25 cm; glancing angles from 1° to 5°.

[23] Thibaud, Jour. de Phys. et le Rad. **8**, 447 (1927). Howe, Proc. Nat. Acad. Sci., March, 1929.

V. Sources of Radiation, etc.

In a vacuum spectrograph for soft x-ray work, the source of radiation is a Coolidge x-ray tube, attached directly to the body of the instrument so that no material screen intervenes between the anticathode and the grating. As it is operated at a comparatively low potential—of the order of 1 kv.—it may be made small, thus bringing the target close to the slit system, and

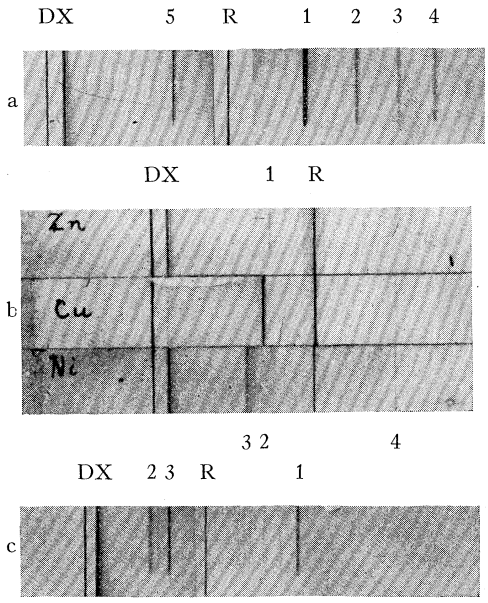

Fig. 4. (a) Anticathode, cobalt. Exposure 8 hours. 1, 2, 3, 4, Carbon K_α line, 44.6A, in four orders. This line is wide and diffuse. 5. Cobalt, $L_\alpha L_\beta$ overlapping; 16A.

(b) Anticathodes, zinc, copper, nickel. Exposures, 6, 1, 6 hours. 1. Zn, $L_\alpha L_\beta$ overlapping; 12A: 2. Cu, $L_\alpha L_\beta$ overlapping; 13A: 3. Ni, $L_\alpha L_\beta$ overlapping; 15A: 4. O, K_α; 24A.

(c) Anticathode, aluminum. Exposure, 12 hours. 1. Carbon K_α. 2. Al, K_α (strong); K_β (faint). 3. Si, $K_\alpha K_\beta$ overlapping. The dispersion of Al $K_\alpha K_\beta$ is much larger than of Si $K_\alpha K_\beta$ on account of the geometrical arrangement of the grating and plate, which produces non-uniform dispersion. The actual wave-length difference is only very slightly less for Si $K_\alpha K_\beta$ than for Al $K_\alpha K_\beta$. See Howe, Ref. 30.

thereby increasing the effective intensity of the x-rays. If the tube be made of metal and be water-cooled, it can carry large currents, 50–100 milliamperes, with safety. The brightness of the tungsten filament need cause no trouble if the anticathode be so shaped and orientated that it does not reflect light directly on to the slit of the spectrograph. Many tubes which fulfill these conditions are described in the literature.[24]

In the case of x-rays from an ordinary Coolidge tube, the fraction of the power input which reappears as x-rays is very small—about 0.1 percent. For x-rays of long wave-length, the value of this fraction is extremely uncertain. Thibaud,[23] from a consideration of the short exposures necessary

[24] Thoraeus, Phil. Mag. **1**, 312 (1926). Thibaud, Ref. 23.

to give good photographs, suggests that the conversion of the kinetic energy of electrons into radiation proceeds more economically in the soft x-ray than in the Roentgen region. On the other hand, Richardson[25] quotes the efficiency of soft x-ray excitation as being of the order of 10^{-6}, a figure based on the detection of these radiations by photoelectric methods. It is natural to expect that this efficiency should vary from element to element, and there is good evidence[26] that the variation is of a periodic character. Experiments of the photoelectric type are difficult to interpret since two transformations are involved; the primary electron-energy at the anticathode is partially converted into radiation which in turn causes the emission of electrons from another plate. There is no reason the problem should not be attacked by a spectrographic method. This should provide valuable information of a relative nature, at least. Whether absolute values of the efficiency of soft x-ray emission could be obtained is more doubtful, for it is well-nigh impossible to attain as good a vacuum in a spectrograph as in, say, the quartz apparatus employed by Richardson and his associates. The whole question is intimately bound up with the penetration of the cathode electrons through the surface layers of the target and the absorption by these layers of the radiation which is produced. A comparison of the absorption coefficients of slow-moving electrons and of their corresponding x-rays might lead to interesting results. Figures for the former, if we admit the mass-absorption law, are already available.

Early workers in this field used either Schumann plates, or x-ray plates smeared with a minute amount of fluorescent oil. With improved technique and more powerful sources of radiation, it has been found that ordinary untreated x-ray plates serve admirably, giving clear and sharp pictures. The first attempts at soft x-ray photography were made with speculum gratings, and met with varying success. The general characteristic of these gratings is to produce plates which are partially fogged, as though the grating scattered, rather than reflected, the radiation. As in optics, some gratings give better results than others apparently similar. Glass gratings give much better photographs; a light ruling seems to produce as intense spectra as a heavy ruling. It is rather remarkable that a grating, accurate perhaps to one-tenth of a wave-length of visible light, should reflect and diffract so well these short wave-length radiations.

VI. Interpretation of Soft X-Ray Spectra

In the early infancy of soft x-ray spectroscopy, there was little ordered investigation; the difficulty was to obtain spectra at all; subsequent improvements in technique have now reduced this almost to a routine performance; and in the last eighteen months a few systematic investigations have provided enough material for a study of the regularities in the spectra. One of the chief interests lies in the transition from x-ray to optical spectra. The regularity in x-ray spectra, first demonstrated by Moseley[27] for the K

[25] Richardson, Proc. Roy. Soc. **A119,** 538 (1928).

[26] Richardson and Robertson, Proc. Roy. Soc. **A115,** 280 (1927).

[27] Moseley, Phil. Mag. **26,** 1024, (1913); **27,** 703 (1914).

series, is that the square root of the wave-number of a particular line varies linearly with the atomic number of the element by which it is emitted. This may be expressed as

$$(\nu/R)^{1/2} = k(Z - k_1),$$

where ν is the wave-number of the line, R is Rydberg's constant, Z the atomic number, and k, k_1 are constants depending on the series (K, L, M, etc.) to which the line belongs and on the particular line of that series which is being considered. If the small relativity correction be ignored, this law represents faithfully all experimental wave-length observations, except for light elements. For the K series, the formula fails only in the case of hydrogen; for the L series, there is a break at neon ($Z=10$); for the M series, at argon ($Z=18$).[28] For lighter elements our knowledge is fragmentary and approximate. It is here that the importance of soft x-ray spectra is apparent.

Söderman[29] has recently published for soft x-rays the wave-lengths of the K_α lines of the elements from Be to Mg (excepting Ne), using the K_α line of Al as a standard, and deriving therefrom the constants of his spectrograph. His measurements overlap and extend the range covered by the earlier ones of Thibaud and Soltan,[18] and of Siegbahn and Thoreaus; among all three there is good agreement. The $(\nu/R)^{1/2}$ values for these K_α lines are plotted in Fig. 5 as a function of the atomic number of the corresponding elements. The curve has been completed by the points for

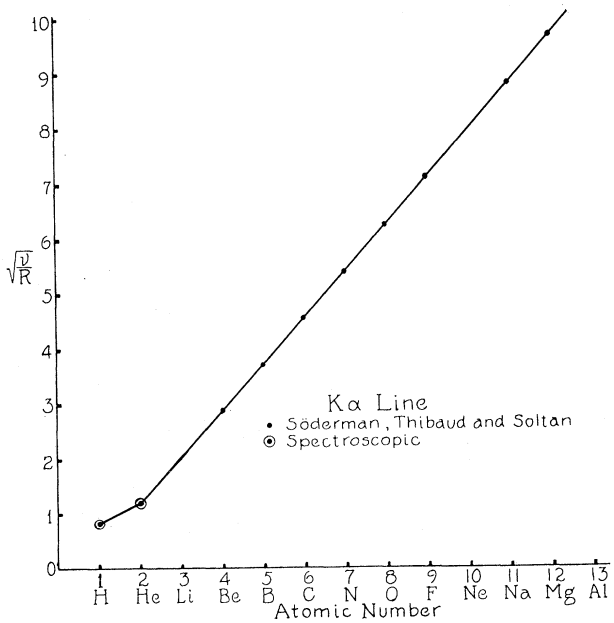

Fig. 5.

[28] Kossel, Zeits. f. Physik **2**, 470 (1920).

[29] Söderman, Zeits. f. Physik **52**, 795 (1929).

hydrogen and helium obtained from spectroscopic data. As predicted by Kossel, and in accordance with Moseley's law, the graph is straight as far as He, where the K shell of electrons is first completed. For hydrogen it is not complete, and the deviation of the curve from linearity is explained. Spectra of the L radiations of most of the elements from Ca(20) to Zn(30). have been photographed by Howe,[30] thus checking and amplifying the results already obtained by Thoraeus[4] by crystal methods. As is to be expected, their frequencies show a regular progression from one element to the next. The appearance of new lines in the L series as the atomic number increases indicates the building up of new groups of electrons in the atom, for, of course, an x-ray line cannot be emitted unless there is present in that atom at least one electron in the appropriate initial "stationary state." The evidence from observations of this nature by Thoraeus and Howe lends strong support to the accepted[31] grouping of the external electrons, at least as far as the low energy levels are concerned. The regular doublets of the N series (c. 50A) have been measured with some accuracy by Thibaud and Soltan[18] for the elements Ta (73), W (74), Pt (78) and Au (79). Apart from all these, our present knowledge of x-ray wave-lengths greater than 25A is extremely fragmentary.

The energies corresponding to the x-ray lines provide information only as to the relative amounts of energy associated with electron groups in the atom. The absolute values are derived from absorption discontinuities. These can be recorded with comparative ease in the Roentgen region, but in photographs of the longer wave-length region they are, in general, conspicuously absent. There are two reasons for this: (1) an x-ray tube operated at a low voltage appears to emit very little continuous radiation; (2) the radiation has very slight penetrating power. In spite of (2), one might expect to find on a photograph absorption edges characteristic of the material of the emulsion of the plate. There has been, however, one success. Using an anticathode of high atomic weight, Thibaud[32] demonstrated the emission of a continuous spectrum between 15A and 250A. In a metal spectrograph such as he used there are always present small quantities of carbon (vapors of grease, etc.), oxygen and nitrogen. These produced K absorption bands in several orders with sharp edges on the high-frequency side, so that the plate had a fluted appearance. The edges had wave-lengths as follows: C, 43.5A; N_2, 31.1A; O_2, 23.5A, as compared with the corresponding K_α lines, 44.9, 31.8, 23.8A. These figures permit an evaluation of the absolute energy of the $L_{II, III}$ levels in these atoms, since the sum of the energies of the K_α line and the $L_{II, III}$ level amounts to the energy of the K absorption edge. We are concerned here, however, with the differences between approximately equal numbers, as the energy of this level for these light elements is only a few electron volts. For elements heavier than Ne (10) the Moseley graph for the $L_{II, III}$ level is linear, as is to be expected (Fig.

[30] Howe, Amer. Phys. Soc., Washington Meeting, April 1929, Phys. Rev. **33,** 1088 (1929).
[31] Stoner, Phil. Mag. **48,** 419 (1924).
[32] Thibaud, Nature, March 3, 1928.

6.) For lighter elements, the available measurements indicate irregularities and a change in the slope of the graph, but their accuracy and completeness are scarcely adequate to determine definitely the nature of these irregularities. On theoretical grounds a break in the curve should occur at Ne (10). Precision measurements of lines and of absorption edges throughout this region are urgently required.

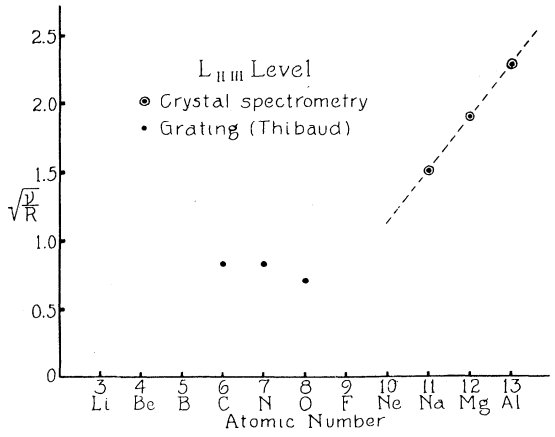

Fig. 6.

Already a beginning has been made in the accurate measurement of the carbon K_α line. This appears strongly on all plates, and is therefore a convenient reference line, although its diffuseness (about 1A wide) is a disadvantage. Thibaud[21] first gave its wave-length as 44.9A, with a possible error of two or three tenths of an Angstrom. A year later, Weatherby[33] arrived at the result 45.4 ± 0.2A but this appears to be much too high. In the summer of 1927 the writer, believing that an accuracy of 0.1 percent could be attained, found[34] the value $44.52 \pm$ 0.05A, but unfortunately his experiments had to be discontinued before the data were ample enough to justify publication. They were resumed by Howe,[35] who recently completed a careful measurement of this line, giving as his final value 44.60 ± 0.04A. This seems to be the most reliable determination up to the present time. It agrees well with Söderman's[29] figure of 44.70 ± 0.09A. Other measurements have been made by Hunt[36] (with a grating) and Dauvillier[6] (with a crystal) but their probable error is large.

VII. Conclusion

This review has been concerned with x-ray spectroscopy by grating methods. There is a mass of information, obtained from crystal spectrom-

[33] Weatherby, Phys. Rev. **32,** 707 (1928).
[34] Osgood, Dissertation, Chicago, 1927.
[35] Howe, Ref. 23.
[36] Hunt, Phys. Rev. **30,** 227 (1927).

etry, which overlaps the beginning of the soft x-ray region, but this has been referred to only in so far as it has a direct bearing on the immediate subject. Interesting problems arise also in connection with the refractive index of soft x-rays. For these, μ is less than unity, while for the ultra-violet, the value is much greater than unity. Already observations have shown that in the Roentgen region there occur phenomena analogous to anomalous dispersion in optics. It is not inapt to quote the words of Lorentz, who, with Drude, developed the theory which predicts the total reflection of x-rays. "It is remarkably interesting that with x-rays, one finds near an absorption edge phenomena similar to those which, in classical optics, occur near an absorption band. There is, however, a profound difference between these two cases, as the absorption edge does not correspond to a frequency which actually exists in the particles." Up to the present time much of the soft x-ray work has aimed at verifying or improving the accuracy of crystal measurements, which, for long wave-lengths, are complicated by refraction and uncertainty as to the exact grating space of crystals. Comparatively few observations have been made for very long wave-lengths. This is natural. To provide an adequate and unequivocal interpretation of results, progress must be gradual, advancing by small steps from known to unknown territory. We may confidently look forward to obtaining from the spectroscopy of soft x-rays a complete understanding of the transition from x-ray to optical spectra, and accurate measurements of the absolute values of the low energy levels in the atom, which will, at the same time, show how the extra-nuclear structure is altered as the atomic number changes. This change is periodic. Harder x-ray spectra, considered as a function of atomic number, give no indication of periodicity, since the shells of electrons near the nucleus are little affected by changes in the nuclear charge.

Note added in proof: Since this article was written, Bazzoni, Faust and Weatherby (Nature, May 11, 1929, p. 717) have succeeded in resolving the carbon K_α line into four components. This explains the divergent values obtained earlier for the wave-length of this line, for the prominence of any particular component appears to depend on the potential applied to the x-ray tube.

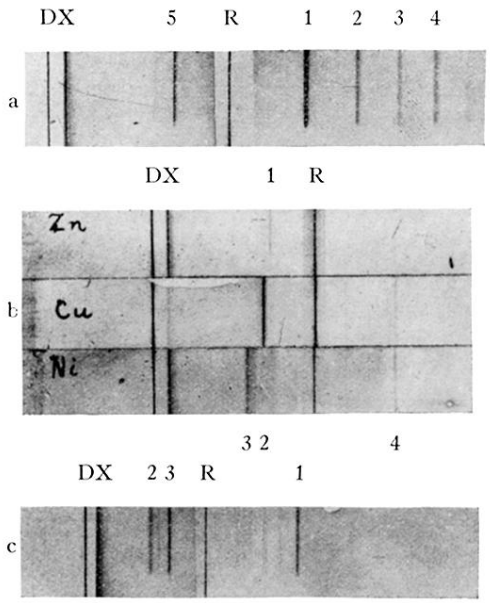

Fig. 4. (a) Anticathode, cobalt. Exposure 8 hours. 1, 2, 3, 4, Carbon K_α line, 44.6A, in four orders. This line is wide and diffuse. 5. Cobalt, $L_\alpha L_\beta$ overlapping; 16A.

(b) Anticathodes, zinc, copper, nickel. Exposures, 6, 1, 6 hours. 1. Zn, $L_\alpha L_\beta$ overlapping; 12A: 2. Cu, $L_\alpha L_\beta$ overlapping; 13A: 3. Ni, $L_\alpha L_\beta$ overlapping; 15A: 4. O, K_α; 24A.

(c) Anticathode, aluminum. Exposure, 12 hours. 1. Carbon K_α. 2. Al, K_α (strong); K_β (faint). 3. Si, $K_\alpha K_\beta$ overlapping. The dispersion of Al $K_\alpha K_\beta$ is much larger than of Si $K_\alpha K_\beta$ on account of the geometrical arrangement of the grating and plate, which produces non-uniform dispersion. The actual wave-length difference is only very slightly less for Si $K_\alpha K_\beta$ than for Al $K_\alpha K_\beta$. See Howe, Ref. 30.