THE CRITICAL ABSORPTION OF SOME OF THE CHEMICAL ELEMENTS FOR HIGH FREQUENCY X-RAYS.

By F. C. Blake and William Duane.

It has been known for a long time that marked increases in the absorption of X-rays by a chemical element take place at frequencies close to the frequencies of the characteristic X-rays of that element. The coefficient of absorption of the element is much greater on the high-frequency side of the characteristic X-radiation than on the low frequency side. In the K series of the characteristic rays of an element the α lines are much stronger than the β and γ lines, but the frequencies of the β and γ lines lie above those of the α lines. It would be natural to suppose that a marked change in the absorption would occur near the frequencies of the α lines, for most of the energy of the characteristic rays is radiated in these lines. Such, however, does not appear to be the case. The curves representing the relation between the coefficient of absorption of a few of the elements and the frequency of the X-rays presented by one of us[1] to the American Physical Society in October, 1914, showed that marked increases in the absorption occurred at frequencies considerably above those of the α lines and near those of the β lines. Subsequently Bragg[2] made some more accurate measurements of the absorption of X-rays by different elements, and came to the conclusion that the critical absorption frequency lay at or above that of the γ line in the K series. The γ line has a frequency about 1 per cent. higher than that of the β line.

Marked increases in the absorption of the X-rays by a chemical element also occur in the neighborhood of the L characteristic lines of the element. Here, however (as de Broglie has shown), there are three characteristic frequencies at which sharp changes in the absorption occur. These appear to correspond to the three critical emission frequencies recently observed by Dr. Webster and Dr. Clark.[3]

We recently made an accurate measurement of the value of h by means of X-radiation.[4] One of the chief sources of error (amounting in some

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[1] William Duane, The Relations between the Wave-Length and Absorption of X-Rays.

[2] Phil. Mag., March, 1915, p. 407.

[3] Physical Review, June, 1917, p. 571.

[4] Blake and Duane, Phys. Rev., Dec., 1917, p. 624.

cases to 2 per cent.) which we found in measuring the X-ray wave-lengths arose from the penetration of the X-rays into the crystal. The correction for this penetration must be made, if the method of using the X-ray spectrometer involves the measurement of the angle made by the reflected beam with the zero line or with its position on the other side of the zero. In the methods in which the positions of the reflected beam are determined by the marks it makes on a photographic plate this correction must be made. It must be applied, also, in some, but not necessarily all of the ways of using the spectrometer in which the ionization currents due to the reflected rays are measured, as Blake and Duane pointed out (l. c.).

If the square roots of the frequencies of the characteristic lines in the K series of different elements are plotted against the atomic numbers of the elements, the points lie on curves which in certain regions approximate to straight lines. They become markedly curved, however, in the neighborhood of the K radiation of bromine. The plots published by Moseley in his classical paper on this subject indicate this curvature very clearly. It appeared from our work on the value of h that the absorption of X-rays by the crystal itself, if not corrected for, would produce a curvature of these plots in the observed direction and of about the observed order of magnitude. Partly on this account, and partly on account of the great importance of measuring the highest frequencies that are known to be characteristic of the elements as accurately as possible, we undertook the research recorded in this paper.

We began by measuring the K characteristic absorption frequencies of the elements from bromine to cerium. The characteristic rays of cerium have frequencies that are nearly as high as the maximum frequencies of the X-rays that we can produce by means of the storage battery of 20,000 cells, which we have used to generate the X-rays. In measuring the frequencies we have employed the spectrometer which we used in measuring the value of h, when we obtained the value of $h = 6.555 \times 10^{-27}$.

Since in this work we have to measure X-rays of widely different wave-lengths, and, therefore, of widely different coefficients of absorption, and, since the correction for the penetration into the crystal depends upon the wave-length, we adopted the method of using the spectrometer which gives readings that are independent of this penetration. In this method the X-rays pass through two narrow slits in lead disks before they reach the reflecting crystal of the spectrometer. These slits determine the breadth of the beam of the X-rays, and, therefore, the variation in the wave-lengths of the rays in the beam reflected from the crystal.

A third slit lies in front of the ionization chamber, and must be broad enough to allow the entire reflected beam of X-rays to enter the chamber. Evidently in this case the ionization current does not depend upon the position of the ionization chamber, provided, only, that the entire X-ray beam passes through the slit. The angle between the two positions of the crystal planes for reflection on both sides of the zero line gives us twice the glancing angle of incidence, θ, which is used in calculating the wave-lengths by means of the formula

$$\lambda = 2a \sin \theta = 6.056 \times 10^{-8} \sin \theta \text{ cm.}$$

If we make measurements of the ionization current for different settings of the crystal, and if we plot these currents as a function of the readings of the verniers, we get a curve that rises from zero at a certain point, reaches a maximum and then descends again. Such a curve representing the general X-radiation was published in the original paper by Duane and Hunt,[1] in which they showed that the point at which the curve begins to rise fulfills the quantum relation

$$Ve = h\nu,$$

V being the constant potential applied to the tube, e the elementary charge, h Planck's action constant and ν the frequency.

If we place a thin sheet of some chemical element in the path of the X-ray beam, the ionization current corresponding to every position of the crystal will be reduced. At a certain angle, however, corresponding to the characteristic absorption of the element a marked change in the ionization appears; for at frequencies above this characteristic frequency the thin sheet of the element absorbs much more of the radiation than at frequencies below it. Further, if the gas in the ionization chamber happens to have a characteristic X-ray frequency in the region covered by the curve, there will also be a marked change in the ionization current at the angle corresponding to this frequency: for, as is well known, ionization produced by X-rays having a frequency just above the characteristic lines is much greater than that due to X-rays having a frequency just below it.

The curve of Fig. 1 represents the ionization current in methyl iodide as a function of the reading of one of the verniers attached to the crystal table, and therefore, approximately of the wave-length. In this case a thin sheet of antimony was interposed in the path of the beam. The zero reading lies to the left of the portion of the curve shown. Near the angle 286° 50′ the curve begins to rise and this is the point for which the quantum relation holds

$$Ve = h\nu.$$

[1] Duane and Hunt, Phys. Rev., Aug., 1915, p. 166.

As the reading of the vernier decreases corresponding to an increase in the angle measured from the zero, the wave-length of the reflected beam of X-rays increases, and the curve rises, indicating that X-rays of these wave-lengths are produced. As we pass across the frequency of the characteristic rays of iodine a sharp drop occurs in the ionization current. The X-rays of longer wave-lengths than this characteristic wave-length do not excite as much ionization as those of shorter wave-lengths. Proceeding further we come to the point representing the critical absorption of antimony. Here there is a marked increase in the value of the current, because X-rays of longer wave-lengths than this characteristic wave-length are not absorbed as much as those of shorter wave-lengths.

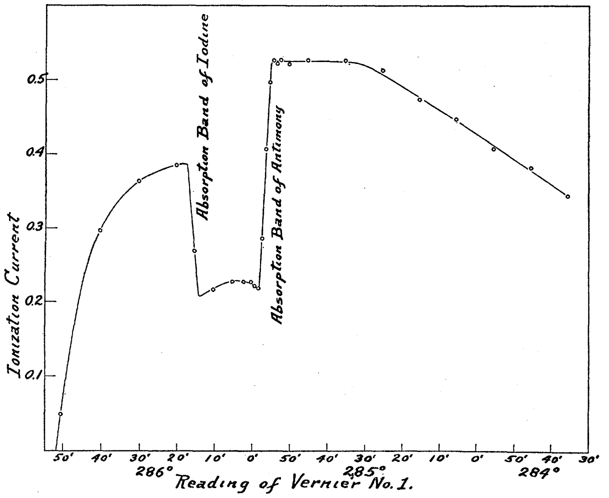

Fig. 1.

Evidently these marked changes in the ionization current furnish a means of accurately estimating the characteristic absorption frequencies of the elements for X-rays.

In practise we did not measure the angle from the zero of the instrument but we took curves on both sides of it, and measured the crystal table angles from one side to the other, thus eliminating the determination of the zero and increasing the accuracy of the measurements.

Fig. 2 represents a number of such measurements. The readings were taken in the immediate neighborhood of the characteristic absorption. The two slits between the X-ray tube and the spectrometer crystal were so narrow, and consequently the range of the wave-lengths in the beam was so small that the entire change in the ionization current representing the change in absorption took place within a variation of the angle θ of less than $3'$ of arc.

We have assumed that the center of the rapidly rising portion of the curve corresponds to the characteristic absorption for the X-rays at the center of the X-ray beam. By drawing curves on a sufficiently large scale we think that we have been able to determine the angle corresponding to the center of this line to within about one sixth of 1′. This represents an error of one part in 1,100 about for barium, of one part in 2,300 about for zirconium, etc.

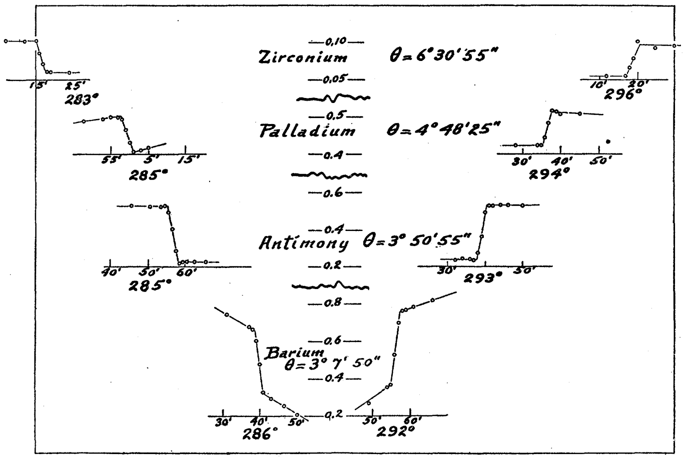

Fig. 2.

The table contains the results of our measurements for all the known elements between bromine and cerium, both inclusive, with the exception of the two gases xenon and krypton.

The values for bromine and iodine were obtained not by using bromides and iodides as absorbing materials, but by putting ethyl bromide and methyl iodide in the ionization chamber and measuring the ionization current without any absorbing material. The fact that the values obtained fall accurately on the curve proves that this is a legitimate method of procedure within the limits of error of our measurements.

The curve of Fig. 3 represents the square root of the characteristic absorption frequency as a function of the atomic number plotted from our measurements. The values obtained by de Broglie[1] and by Wagner[2] are also plotted in the figure. We think that the difference between de Broglie's values and ours is due to the fact that no corrections for the penetration of the rays into the crystal are necessary in our method of measurement. In de Broglie's method, on the other hand, in which

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[1] Comp. Rendu, July, 1916, p. 87.

[2] Ann. d. Phys. 46, 1915, p. 868.

TABLE I.

Element.	Atomic Number.	θ.	λ (Wagner) Ä. U.	λ (de Broglie) Ä. U.	λ Observed Ä. U.	λ Calculated Ä. U.	Per Cent. Difference.
		° ′ ″					
Cerium........	58	2–54–30		.2979	.3073	.3070	+.10
Lanthanum....	57	3– 1– 5			.3188	.3186	+.06
Barium.......	56	3– 7–50		.3249	.3307	.3308	−.03
Caesium.......	55	3–15–35			.3444	.3438	+.17
Xenon........	54					.3575	
Iodine.........	53	3–31–40		.3666	.3727	.3721	+.16
Tellurium.....	52	3–41–20		.3829	.3896	.3876	+.51
Antimony.....	51	3–50–55		.3985	.4065	.4041	+.59
Tin...........	50	4– 1– 0	.425	.4188	.4242	.4217	+.59
Indium........	49	4–11–55			.4434	.4404	+.68
Cadmium......	48	4–23–10	.468	.4580	.4632	.4604	+.60
Silver.........	47	4–35–35	.490	.4793	.4850	.4819	+.64
Palladium.....	46	4–48–25	.513	.5029	.5075	.5048	+.53
Rhodium......	45	5– 2–40			.5324	.5294	+.56
Ruthenium....	44	5–17–25			.5584	.5559	+.45
——..........	43					.5844	
Molybdenum ..	42	5–51–25		.6113	.6180	.6151	+.47
Neobium......	41	6– 9–50		.6455	.6503	.6484	+.29
Zirconium	40	6–30–55		.6813	.6872	.6844	+.41
Yttrium.......	39	6–52–50			.7255	.7235	+.28
Strontium.....	38	7–18– 5		.7641	.7696	.7660	+.47
Rubidium.....	37	7–43–40		.8095	.8143	.8125	+.22
Krypton.......	36					.8632	
Bromine.......	35	8–43– 5	.926	.9139	.9179	.9189	−.11

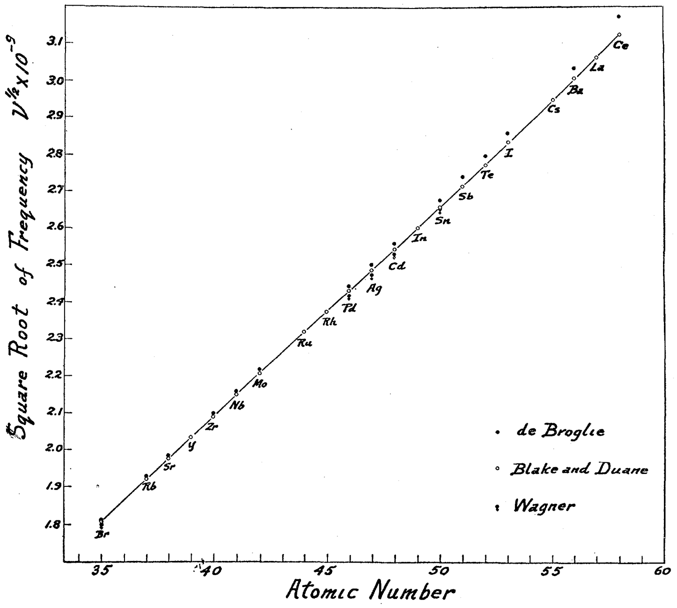

Fig. 3.

the wave-length is calculated from the angle made by the reflected beam measured to a line on a photographic plate, such a correction must be made (at least for X-ray wave-lengths lying in the region under consideration). The magnitude of the difference between our values and those of de Broglie is just about the correction that would have to be applied, if the crystal face lay in the axis of rotation of the spectrometer. This correction has been fully explained in the article by Blake and Duane referred to. The increase in the difference between the two sets of values with increasing frequencies of the X-rays is what one would expect, for the high frequency X-rays penetrate further into the crystal than the low frequency ones, and therefore a larger correction must be made for them.

The relation between the square root of the frequency of the characteristic rays and the atomic number is approximately a straight line relation. Moseley's original measurements of the α and β wave-lengths indicate this. As stated above, however, they also show a departure from the straight line relation in a certain region. This departure occurs exactly where one would expect it to, if no correction were made for the penetration of the rays into the crystal.

Our values of the critical absorption frequencies, which are the highest frequencies known to be characteristic of the elements (higher even than the frequencies of the α and β lines measured by Moseley) fall more nearly on a straight line than Moseley's values do. It is possible to draw a straight line near the points representing our data such that no point will lie as far from it as one fifth of one per cent. of its ordinate. There is, however, a systematic variation of the points from this straight line, which indicates that our values really lie on a line that is very slightly curved.

The fact that after using our method of automatic correction for the penetration of the rays into the crystal we get points that lie so nearly on a straight line raises the question as to whether there may not be some other correction, which we have not thought of, and which, if applied, would make the line perfectly straight.

As is well known equations can be written out containing Rydberg's fundamental frequency as a coefficient, that approximately represent the frequencies of the characteristic lines of the elements as functions of the atomic numbers. It is interesting to note (see next-to-last column of the table) that the equation

$$\nu = \nu_0(N - 3.5)^2$$

in which ν_0 is the Rydberg fundamental frequency (namely 109,675 multiplied by the velocity of light), represents with considerable accuracy our experimental results. In this equation N stands for the atomic number of the element, and the only constant determined by the X-ray experiments is that in the parenthesis, namely 3.5. It is interesting, too, to note that this equation gives us the correct value for the nuclear charge as worked out by Sanford[1] from the assumption of equality between orbital and vibration frequencies. For we have

$$\nu = \frac{2\pi^2 e^4 m}{h^3}(N - 3.5)^2$$

and Q, the nuclear charge, fulfills the equation

$$Q^2 = \frac{v^2 h^2}{\pi^2 e^2} = \frac{2h^3 \nu}{\pi^2 e^2 m}.$$

Eliminating ν we get at once $Q = 2e(N - 3.5)$, an equation that manifestly holds to the accuracy shown in the table for the elements there shown. Thus it would appear that a knowledge of the position of the X-ray absorption lines, which corresponds to the head of the emission line series leads to results that are more fundamental than a knowledge of the position of the principal emission lines can.

It is hoped to extend the measurement to elements of higher and lower atomic number than those included in this paper.

HARVARD UNIVERSITY.

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[1] PHYSICAL REVIEW, May, 1917, p. 383.