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THE

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THE MAGNITUDE OF THE K-ABSORPTION DISCONTINUITY

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ABSTRACT

Mass absorption coefficients for wave-lengths on both sides of the K limit. (1) *Experimental results for six metals.* Using a water cooled Mo tube, absorption measurements were made for a sufficient range of wave-lengths in each case to determine the constants in the equations for the mass absorption coefficients above and below the K absorption discontinuity. $\mu_K/\rho = K_K\lambda^3 + \sigma/\rho$; $\mu_L/\rho = K_K\lambda^3 + \sigma/\rho$, in which σ/ρ is the scattering coefficient, with a value of 1 or less. λ is in angstrom units. τ_a is the atomic absorption coefficient at the K limit, corrected for scattering.

	Mo(42)	Ag(47)	Sn(50)	W(74)	Au(79)	Pb(82)
$k_K =$	375	545	595	1870	2230	2570
$k_L =$	50	70	90	330	395	476
$k_K/k_L =$	7.5	7.8	6.6	5.65	5.65	5.40
$\tau_a(10^{-21}) =$	13.3	11.0	8.90	3.19	2.57	2.37

(2) *Comparison with theories.* $(k_K/k_L - 1)$ is the ratio of the number of photoelectrons originating in the K and L levels for x-rays just shorter than the K limit. It is shown that the theories of Thomson, of Compton, and of de Broglie lead to the same values of k_K/k_L, which increase with decreasing atomic number in agreement with experiment except that they are about twice too large. Kramers' formula gives a value which does not vary with N and which agrees well with the experimental values for Mo to Pb, but it applies only to a single electron around the nucleus. A formula modified by use of Bohr's theory of energy levels to remove this restriction gives values nearly three times too large. No present theory, then, is supported by these experimental results.

INTRODUCTION

SEVERAL attempts[1,2,3,4] have been made to obtain, on theoretical grounds, the equation

$$\tau_a = CN^4\lambda^3 \tag{1}$$

which has been found by experiment to represent the relation between the atomic fluorescent absorption coefficient τ_a for x-rays of wave-length λ absorbed by a substance of atomic number N. C is a constant for all

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* This work has been made possible by a grant to the writer, from the Heckscher Research Council of Cornell University.

[1] J. J. Thomson, Conduction of Electricity through Gases, 2d. Ed., p. 321.

[2] L. de Broglie, Journ. de Phys. et Rad. **3,** 33 (1922).

[3] A. H. Compton, Nat. Res. Council, Bul. **20,** 37 (1922).

[4] H. A. Kramers, Phil. Mag. **46,** 836 (1923).

elements on the short wave-length side of the K absorption limit, and has a numerical value[5] of 22.4×10^{-27}, λ being expressed in angstrom units. At the K limit the value of C decreases abruptly. If we put

$$R_{\mathrm{L}}^{\mathrm{K}}=\frac{C_{\mathrm{K,L}\ldots}}{C_{\mathrm{L}\ldots\ldots}} \tag{2}$$

where $C_{\mathrm{K,L}\ldots}$ is the value of C on the short wave-length side of the K limit and $C_{\mathrm{L}\ldots}$ that on the long wave-length side, then the ratio $R_{\mathrm{L}}^{\mathrm{K}}$ of the two values of C depends on the atomic number of the absorber, being less for elements of higher atomic number. For example, for elements in the neighborhood of Ag $R_{\mathrm{L}}^{\mathrm{K}}$ is about 8. For elements in the neighborhood of Pt it is about 5.5.

The several theoretical formulas above referred to, although obtained on the basis of widely different considerations, agree with experiments in assigning 4 and 3 as the exponents of N and λ respectively in Eq. (1). There is a disagreement, however, with experiment, in respect to not only the magnitude of $R_{\mathrm{L}}^{\mathrm{K}}$ but also its variation with atomic number. The extent to which any theoretical formula agrees with experiment in predicting the correct value of $R_{\mathrm{L}}^{\mathrm{K}}$ is therefore a more discriminating test of the correctness of the formula than are the coefficient of N and λ.

A knowledge of the precise value of $R_{\mathrm{L}}^{\mathrm{K}}$ is of prime importance in connection with further extensions of our present very incomplete "picture" of the interaction between radiation and matter. So far as it goes this picture is quite precise with regard to the sequence of the main events in the (fluorescent) absorption of x-rays. Thus, if a monochromatic x-ray beam of frequency ν and of quantum energy $h\nu$ strikes an absorber the frequency of whose K absorption limit ν_{K} is less than ν, the first process is the photo-electric expulsion of electrons from the several electron levels[6] in the atom according to the well known equation

$$h\nu=W+h\nu_{\mathrm{K,L,M}}\ldots \tag{3}$$

where $h\nu_{\mathrm{K,L,M}\ldots}$ represents in turn the work necessary to remove electrons from the K, L, M . . . levels respectively and W is the residual kinetic energy of the photo-electron originating in the K, L, M. . . level. The vacant place in the atom is then filled by an electron from an outside level, or from infinity, and the K, L, M. . . fluorescent radiation results. It is to be remembered, however, that, irrespective either of what ultimately becomes of the energy given to the electron or whether a K, L or M electron is expelled, *each photo-electron removes from the incident beam*

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[5] F. K. Richtmyer and F. W. Warburton, Phys. Rev. **22**, 539 (1923).

[6] See, for example, the beautiful experiments of Robinson, Proc. Roy. Soc. **104**, 455 (Nov. 1923).

an amount of energy *hν*. By dividing by *hν* the total amount of energy removed by the absorber in this fluorescent process, the total *number* of photo-electrons produced under given conditions, may be obtained. We have at present no way of measuring with acceptable precision the actual magnitude of this absorbed energy, but by comparing the fluorescent absorption coefficient on the short wave-length side of the K absorption limit with that on the long wave-length side, it is possible to get the ratio of the total number of (K+L+M . . .) photo-electrons to the total number of (L+M. . .) photo-electrons. Thus

$$R_{\mathrm{L}}^{\mathrm{K}} = \frac{\text{total number of K+L+M+ . . . photo-electrons}}{\text{total number of L+M+. . . photo-electrons}} \qquad (4)$$

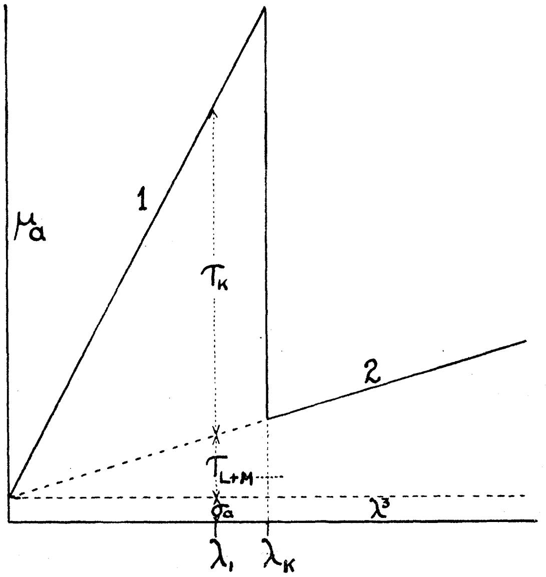

Fig. 1. Variation of the atomic absorption coefficient with the cube of the wave-length.

This relation is shown graphically in Fig. 1, which represents diagrammatically,[7] to approximate scale, the linear relation between the atomic absorption coefficient μ_a and the cube of the wave-length on both sides of the absorption limit. Thus, if radiation of wave-length $\lambda_1 < \lambda_K$ falls on the absorber, we may regard the atomic absorption coefficient at that wave-length as being made up of several parts: (1) a part τ_K due to the energy removed from the beam by the expulsion of K photo-electrons; (2) a part $\tau_{L+M+\ldots}$ due to the expulsion of L+M+. . . photo-electrons; and (3) a part σ_a due to the energy removed by scattering. Although σ_a and its variation with wave-length are of very great theoretical signifi-

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[7] F. K. Richtmyer, loc. cit. 10, p. 27.

cance, it is responsible for only a small proportion of the energy removed from the incident beam, especially in those elements and for those wavelengths for which R_L^K is known. Hence to a first approximation σ_a may be considered as constant and equal to the intercept on the μ_a axis, of the absorption curves on both sides of the K limit. Accordingly it is obvious that the ratio

$$(\tau_K+\tau_{L+M+}\ldots)/(\tau_{L+M+}\ldots) = R_K^L \tag{5}$$

gives the relative number of the several "kinds" of photo-electrons, and hence the relative probabilities of the expulsion of electrons from the several energy levels within the atom. It is this probability which has been computed by the several writers[1,2,3,4] and which it is desired to compare with experiment.

Data on the K Discontinuity

The experimental data on the magnitude of the K absorption discontinuity are very meager. Discarding, as of comparatively little value, the measurements with heterogeneous radiation, there are collected in columns 3, 4, and 5 of Table I data obtained by use of monochromatic radiation by Wingardh,[8] Allen,[9] and the writer.[10] At the December 1923 meeting of the American Physical Society, Mr. F. W. Warburton[11] in collaboration with the writer presented, in brief form, some data on the K discontinuities for several elements. The data were not regarded as very satisfactory, and publication of the results in full was delayed until further measurements could be made. Other investigations have pre-

Table I

Element	Atomic Number	Values of R_L^K			
		Wingardh[8]	Allen[9]	Richtmyer[10]	Richtmyer and Warburton[11]
Mo	42			8.7	7.5
Ag	47	8.0*	7.1*	7.3	7.8
Sn	50		8.9†		6.6
W	74		6.0		5.65
Pt	78		5.3		
Au	79		5.0		5.65
Pb	82		4.5		5.40
Bi	83		4.1		

* Computed from data given in reference.

† Computed by combining data given by Allen (loc. cit.[9]), with data given by Bragg and Pierce (Phil. Mag. **28**, 626, 1914).

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[8] K. A. Wingardh, Dissertation, Lund (1923).

[9] S. J. M. Allen, Phys. Rev. **24**, 1 (July 1924).

[10] F. K. Richtmyer, Phys. Rev. **18**, 13 (July 1921).

[11] F. W. Warburton and F. K. Richtmyer, Phys. Rev. **23**, 291 (Feb. 1924).

vented further progress on the work; so in this paper are presented the data of Warburton and Richtmyer, with some minor corrections.

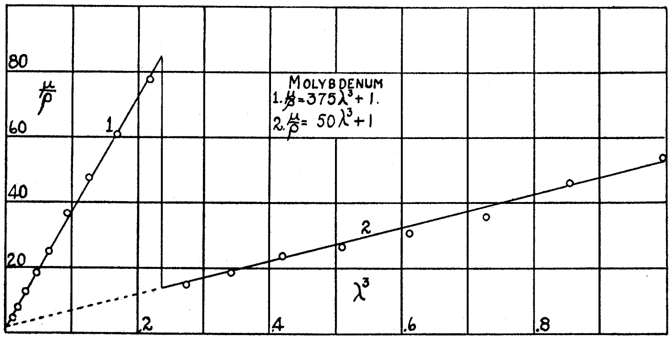

Fig. 2. Variation of the mass absorption coefficient of molybdenum with the cube of the wave-length.

The method of measuring coefficients of absorption of x-rays is too well known to require comment. The apparatus used for the present investigation has been previously described.[12] For obtaining sufficient energy at

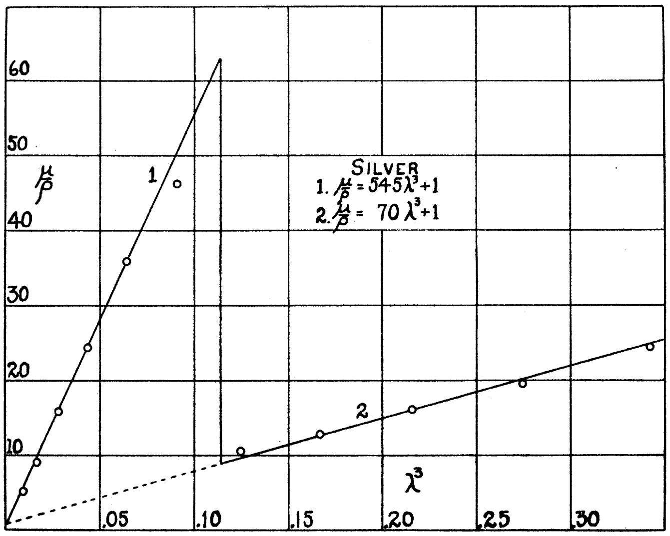

Fig. 3. Variation of the mass absorption coefficient of silver with the cube of the wave-length.

the longer wave-lengths herein reported, a water-cooled molybdenum tube was used. The writer is indebted to Dr. W. D. Collidge of the General Electric Company, for the use of this tube.

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[12] F. K. Richtmyer and F. W. Warburton, Phys. Rev. **22,** 539 (1923).

Observations were made through the K absorption limits of Mo, Ag, Sn, W, Au, and Pb. The data are shown in graphical form in Figs. 2-7, in which the mass absorption coefficients for the several elements are plotted as functions of the cube of the wave-length. In these graphs the K absorption discontinuity is represented by a vertical line, since, as has been recently shown by the writer,[13] the K discontinuity for silver shows no measurable structure and is sharp to at least .0001A. Since, to a very

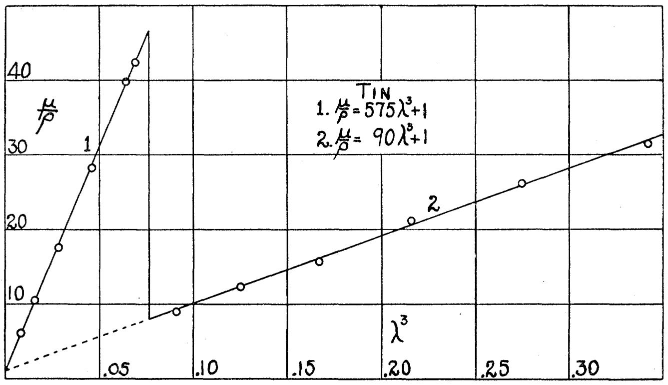

Fig. 4. Variation of the mass absorption coefficient of tin with the cube of the wave-length.

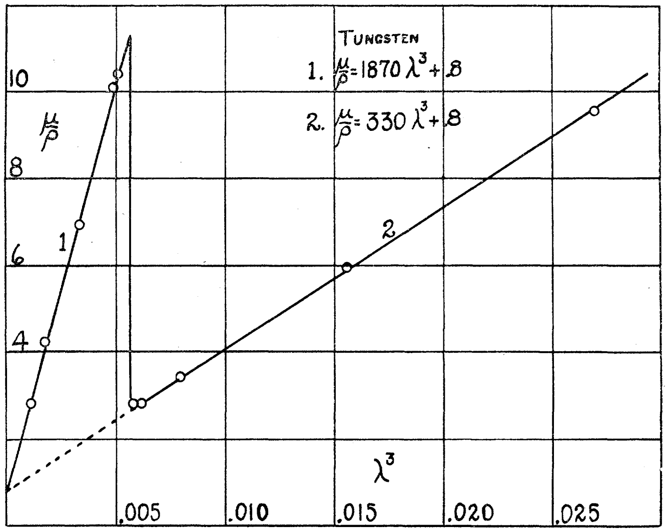

Fig. 5. Variation of the mass absorption coefficient of tungsten with the cube of the wave-length.

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[13] F. K. Richtmyer, Phys. Rev. **26**, 724 (Dec. 1925).

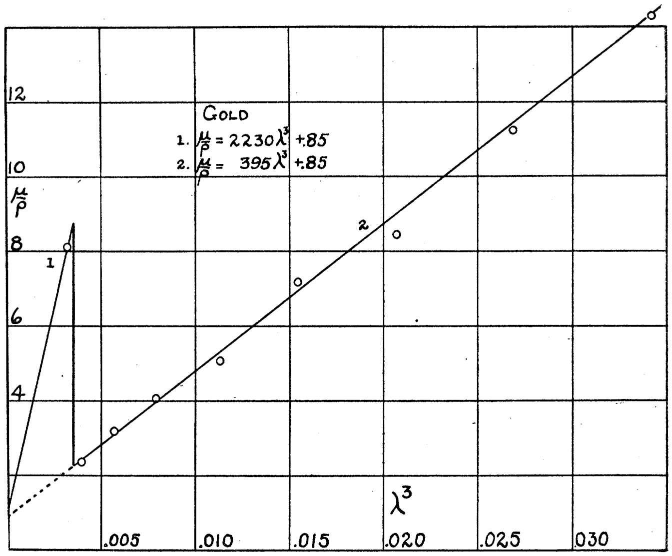

Fig. 6. Variation of the mass absorption coefficient of gold with the cube of the wave-length.

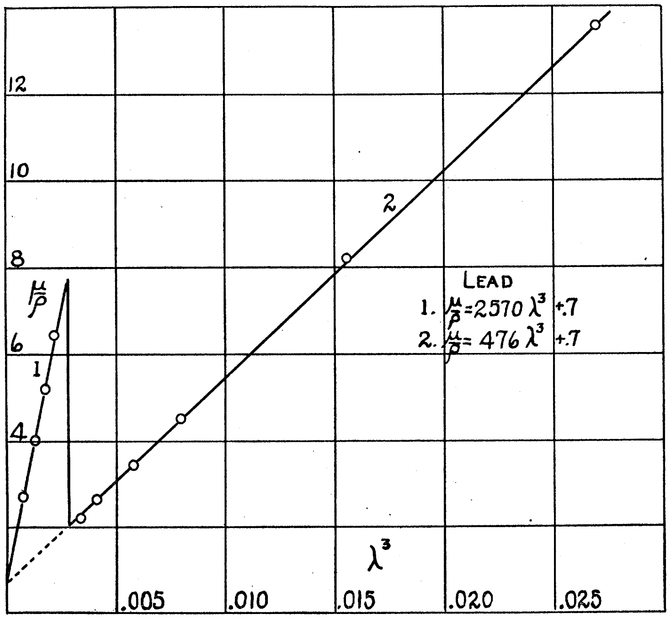

Fig. 7. Variation of the mass absorption coefficient of lead with the cube of the wave-length.

close approximation at least, the graphs, both above and below the K limit are straight lines, and have nearly, if not quite, identical intercepts on the μ/ρ axis, it is obvious that the values of R_L^K are given by the ratios of the slope of the graph on the short wave-length side of the limit to that on the long wave-length side. These slopes are collected in columns 2 and 3 of Table II, the values k_K and k_L being the values in the equations

$$\mu_K/\rho = k_K\lambda^3+\sigma/\rho \tag{6}$$

$$\mu_L/\rho = k_L\lambda^3+\sigma/\rho \tag{7}$$

TABLE II

The values of k_K and k_L are the slopes of the curves in figs. 2-7; $(\mu/\rho)_{max}$ is the maximum value reached by μ/ρ just at the short wave-length side of the K limit; $(\tau/\rho)_{max}$ is obtained by subtracting from $(\mu/\rho)_{max}$ the intercept on the μ/ρ axis; n gives the number of atoms per gram; $(\tau a)_{max}$ is obtained by dividing $(\tau/\rho)_{max}$ by n; R_L^K is the ratio k_K/k_L.

Element	k_K	k_L	$(\mu/\rho)_{max}$	$(\tau/\rho)_{max}$	n	$(\tau a)_{max}$	R_L^K
Mo 42	375	50	85.0	84.0	6.31×10^{21}	13.3×10^{-21}	7.5
Ag 47	545	70	63.0	62.0	5.61	11.0	7.8
Sn 50	595	90	46.5	45.5	5.11	8.90	6.6
W 74	1870	330	11.3	10.5	3.29	3.19	5.55
Aw 79	2230	395	8.8	7.9	3.07	2.57	5.65
Pb 82	2570	476	7.8	6.9	2.91	2.37	5.4

μ_K and k_K refer to the short wave-length side of the limit; μ_L and k_L to the long wave-length side. From what has been said before it is evident that the ratio R_L^K is given by

$$R_L^K = k_K/k_L$$

These ratios are tabulated in column 8 of Table II and also for comparison with results of others, in column 6 of Table I.

A glance at Table I makes it obvious that the data warrant only the general conclusions that there is agreement on the order of magnitude of the discontinuity and that the values of R_L^K range from around 5.5* for the heavier elements to 7.5 or 8 for elements in the neighborhood of silver.

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* A careful examination of Allen's data makes it seem probable that the values given by him for the heavier elements are too low. This statement is based on the circumstance that, beginning with tungsten, Allen's values of μ/ρ on the short wave-length side of the K limit *decrease*, at any given wave-length, with *increasing* atomic number, a result quite in opposition to data obtained by other investigators. Allen's curves reveal the fact that the *apparent* width of his K discontinuities from *silver* to lead, is the *same* for each element and is equal to approximately .02A. This defines his slit width, since the writer has shown[12] that for the K limit of the heavier elements, the apparent width of the discontinuity is due entirely to the finite width of slits. One suspects, therefore, that with a rather wide slit, when working near the absorption limit, there may have been a sufficient admixture of scattered radiation from the long wave-length side of the limit to reduce appreciably the observed mass absorption coefficient.

Discussion of Results

There are several points of passing interest, in connection with these results, which it may be not inappropriate to mention in order to call attention to the relative magnitude of the several discontinuities.

Fig. 8 shows to scale, each at the wave-length of its K absorption limit, the relative magnitudes of the K discontinuities for each of the six elements investigated. Here τ_a is the fluorescent atomic absorption coefficient* after making the rather unsatisfactory correction for scattering. It is to be noted that the *absolute* magnitude of the discontinuity increases rapidly with decreasing atomic number. That is, molybdenum, just at the short wave-length side of its absorption limit is a much better absorber than is lead at the short wave-length side of its limit.

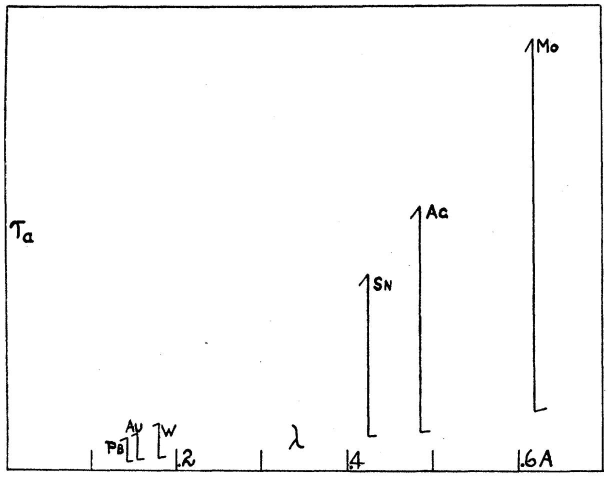

Fig. 8. Showing to scale the relative magnitudes of the K absorption discontinuities for the six elements investigated.

This result is of course to be anticipated from the well known laws of absorption, combined with Moseley's law, which, for the K absorption limit may be written in the form

$$\lambda_K = c'/(N-b)^2$$

where N is the atomic number, and b and c' are constants. If this value of λ_K be introduced into Eq. (1) there results

$$\tau_{\max} = c'' \, N^4/(N-b)^6 \qquad (8)$$

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* If the observed values of the mass absorption coefficient μ/ρ be corrected by subtracting the value of the mass scattering coefficient σ/ρ, as determined by the intercept on the μ/ρ axis in Figs. 2-7, one obtains τ/ρ the *fluorescent* mass absorption coefficient. Thus $\mu/\rho = \tau/\rho + \sigma/\rho$. If the values of τ/ρ be divided by the number of atoms per gram in each case, one obtains τ_a, the atomic fluorescent absorption coefficient. And as explained above $\tau_a = \tau_K + \tau_L + \tau_M + \ldots$

where $\tau_{\max}$ is the *maximum* value of the atomic absorption coefficient just at the short wave-length side of the K limit, and c'' is another constant, the assumption being made, of course, that Eq. (1) holds rigorously up to the K limit. If b be neglected in comparison with N, it follows that the maximum value of the atomic fluorescent absorption coefficient just at the short wave-length side of the K limit should be proportional to N^{-2}. A convenient check on Eq. (8) is the determination of b. This can be readily done by putting the equation in the form

$$(c''N^4/\tau_{\max})^{1/6} = N - b \tag{9}$$

and plotting a graph between $(N^4/\tau_{\max})^{1/6}$ and N.* This graph is shown in Fig. 9, from which it is seen that the value of b which best agrees with these data is about 7.5, much larger than the accepted value of b in Moseley's equation. The data are not sufficiently precise to determine whether this large value of b is due to experimental error, or whether it is due to the fact that Eq. (1), as is well known, is only a close approximation to the true formula.

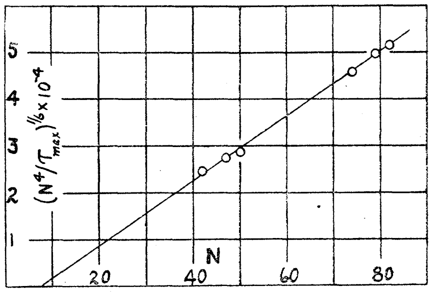

Fig. 9. Graphical determination of b in the term $(N-b)$ of Eq. (8).

COMPARISON WITH THEORY

The experimental values of R_L^K as a function of N are shown by the circles in Fig. 10. The points plotted for molybdenum and silver are the average of those given in Table I. The remaining points are those given in the last column of Table I. While it is obvious that the data do not warrant an attempt to ascertain an empirical relation between R_L^K and N, nevertheless they are sufficient to serve as a check, even though a rough one, on the several theories proposed.

Thomson's theory.[1] This well known theory was proposed by Thomson at least as early as 1903. It is based on the assumption that the electron

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* Values of $(N^4/\tau_{\max})^{1/6}$ were computed from the data given in columns 1, 4, 5, 6 and 7 of Table II, λ being expressed in angstroms.

is bound to a fixed position in the atom by simple harmonic forces. The displacement of the electron from this equilibrium position is then computed when a pair of rectangular but oppositely directed pulses, each of thickness d, passes over the electron. The potential energy stored up in this displacement is extracted from the pair of pulses and is emitted as fluorescent energy of wave-length λ_o after the pulse has passed. This leads to the following absorption coefficient per electron, τ_e, *for a single pair of pulses*

$$\tau_e = 4\pi^3 \frac{e^2}{mc^2} \frac{1}{\lambda_0{}^2} d^3 , \tag{10}$$

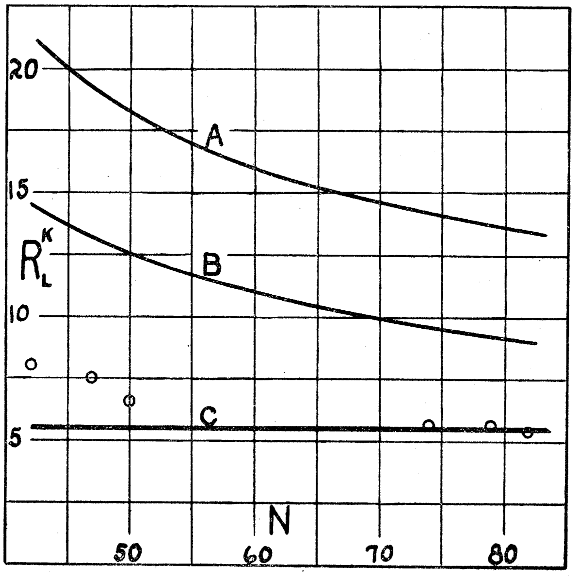

Fig. 10. Variation of the absorption discontinuity with atomic number. Curve A: Kramers' theory as modified by Eq. (26). Curve B: Theories of Thomson (Eq. (13)), of Compton (Eq. (15)), and of de Broglie (Eq. (21)). Curve C: Kramers' original theory (Eq. (24)). The circles represent actual observations.

or if we identify d with $\lambda/2$, where λ is the wave-length of the incident x-rays, we have

$$\tau_e = \frac{\pi^3}{2} \frac{e^2}{mc^2} \frac{1}{\lambda_0{}^2} \lambda^3 . \tag{11}$$

It is interesting to point out that on Thomson's theory the term d^3, or in more modern terms λ^3, is obtained by the following steps. (1) The electron experiences a uniform acceleration for a time which is proportional to d and is therefore displaced through a distance proportional to d^2. (2) The potential energy stored up against return forces is proportional to d^4; but the incident energy must be proportional to d. (3) The absorption coefficient, which is the ratio of absorbed to incident energy, is therefore proportional to d^3. The atomic absorption coefficient τ_a is obtained by summing up the term $1/\lambda_0^2$ for each electron in the atom, hence

$$\tau_a = \frac{\pi^3}{2}\,\frac{e^2}{mc^2}\sum\frac{n_0}{\lambda_0^2}\lambda^3 \tag{12}$$

where for the atom under consideration n_0 represents the number of electrons emitting characteristic radiation of wave-length λ_0. Eq. (12) can be put into a form to be compared with more recent formulas by using the relation

$$\frac{1}{\lambda_0^2} = \frac{h^2\nu_0^2}{h^2\,c^2} = \frac{E_0^2}{h^2\,c^2}$$

which gives

$$\tau_a = \frac{\pi^3}{2}\,\frac{e^2}{mh^2c^4}(n_K E_K^2 + n_L E_L^2 + \cdot\;\cdot\;\cdot)\lambda^3 \tag{13}$$

where, in modern notation, n_K, n_L . . . stand for the number of electrons in the K, L . . . levels respectively and E_K, E_L . . . are the corresponding binding energies. To check this with experiment, (13) gives for Bi in the K region, assuming $n_K = 2$, $n_L = 8$, $n_M = 18$ and averaging the multiple values of E_L and E_M usually found in tables,

$$\tau_a = 5.20 \times 10^6\ \lambda^3$$

whereas (1) gives for B_i

$$\tau_a = 1.06 \times 10^6\ \lambda^3$$

It appears therefore that Thomson's formula gives a value of τ_a about five times too large.

There are reasons why we might expect (13) to give too large values. The discussion is based on the passage of a *single* pair of pulses over the electron. If a *train* of pulses is considered, each succeeding pulse produces an additional displacement and an increased restoring force. The result is that less energy is removed per pulse the greater the displacement. For a large number of pulses it is obvious that the average energy removed per pulse would be less than for the first pulse; i.e. the absorption coefficient for a wave train should be less than for a single pulse.

It is observed* that the introduction into (13) of Moseley's approximate law $\nu \propto N^2$ for the relation between an absorption limit and atomic number leads directly to an equation of the form of (1).

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* See also A. H. Compton, Phys. Rev. **14,** 249 (1919).

Compton's theory. This is somewhat similar to Thomson's theory in that it applies the fundamental laws of dynamics to "electrically charged particles capable of executing damped harmonic oscillations." An equation for the absorption coefficient per electron is then derived which involves the damping coefficients of the forced and of the free vibrations and the corresponding frequencies. This equation is simplified by approximation, and the exponent of λ is determined by an empirical evaluation, the resulting expression for the *atomic* absorption coefficient being given by

$$\tau_a = 2\pi\frac{e^2}{mc^4}\left(n_K\frac{1}{\lambda_K{}^2} + n_L\frac{1}{\lambda_L{}^2} + \cdot\cdot\cdot\cdot\right)\lambda^3 \tag{14}$$

which, when put in the form

$$\tau_a = 2\pi\frac{e^2}{mh^2c^4}(n_K E_K{}^2 + n_L E_L{}^2 + \cdot\cdot\cdot)\lambda^3 \tag{15}$$

is identical with (13) except for the factor involving π.
For bismuth, this gives

$$\tau_a = 2.10 \times 10^6\ \lambda^3$$

a result approximately twice the experimental value. Compton's formula does not give an independent theoretical justification for the λ^3 term.

de Broglie's theory.[2] This theory is based on the assumption that it is possible to set up conditions of equilibrium between atoms and a radiation field such that the rate of absorption of energy by the atoms in the process of the *photo-electric emission of electrons* is just equal to the rate of emission of energy as a result of the converse process, namely the "de-ionizing" of atoms by the free electrons. The equation to express this fact assumes the following form

$$N_{i_p} A_{i_p}^{n} E_p dt = \frac{1}{\eta_p} N_n \int_{\nu_p}^{\infty} h\nu F(\nu)\ \rho(\nu\ ,\ T) d\nu\ dt \tag{16}$$

where $A_{i_p}^{n}\ dt$ represents the fraction of ionized atoms, N_{i_p} per cc which take up free electrons in time dt and return to the normal state n, from the ionized state i_p, giving out energy E_p per atom; N_n is the number of normal atoms per cc taking part in the equilibrium process; $F(\nu)$ is a function of the frequency which states the fraction of normal atoms which become ionized in unit time, for unit density of the radiation of frequency ν, the energy density being given by Wien's equation

$$\rho(\nu,\ T)d\nu = (8\pi h/c^3)\nu^3 e^{-h\nu/kT} d\nu. \tag{17}$$

$1/\eta_p$ represents the fractional part of the absorbed energy which is returned in the corresponding fluorescent radiation. If $F(\nu)$ be evaluated and multiplied successively by (1) the number of atoms $N\,dx$ per square centimeter of an absorbing material of thickness dx, (2) the energy *density* of the incident radiation of frequency ν, and (3) the energy $h\nu$ absorbed by each atom in the process of ionization, the result is the rate of absorption of energy. If this result be divided by the rate at which energy is incident on the square centimeter we have the absorption coefficient which is found to be

$$\tau_a = (1/8\pi ckT)\lambda^3 \sum A_{i_p}^{n}\, E_p \eta_p\,. \tag{18}$$

The summation is to be extended to all the electrons of the atom. It is assumed that

$$\eta_p A_{i_p}^{n} = KE_pT \tag{19}$$

K is evaluated and found to be

$$K = \frac{8\pi^2}{c^3}\,\frac{k}{h^2}\,\frac{e^2}{m} \tag{20}$$

If (19) and (20) be put in (16) and the result extended to all the electrons of the atom we have

$$\tau_a = \pi(e^2/mh^2c^4)(n_{\mathrm{K}}E_{\mathrm{K}}^2 + n_{\mathrm{L}}E_{\mathrm{L}}^2 \cdot\cdot\cdot\cdot)\,\lambda^3 \tag{21}$$

a result identical with Thomson's value, Eq. (13), except for the factor involving π. For bismuth Eq. (21) gives, for $\lambda < \lambda_{\mathrm{K}}$,

$$\tau_a = 1.14 \times 10^6 \lambda^3$$

in excellent agreement with experiment. It is to be observed that the λ^3 term appears in (18) because of the introduction of Wien's Eq. (17) in which appears the term ν^3.

Kramers' Theory. This has several points in common with deBroglie's theory. Both assume Wien's law of energy distribution and the possibility of thermodynamic equilibrium. Kramers then starts with the assumption that

$$NP_nQ_{n\rightarrow i} = NP_iQ_{i\rightarrow n} \tag{22}$$

where P_n represents the fraction of a total number N of atoms which are in an n or normal state and $Q_{n\rightarrow i}$ represents the fraction of these per second which pass from the normal to the ionized state i. Similarly P_i represents the fraction of N atoms which are in the ionized state, a fraction $Q_{i\rightarrow n}$ of which return per second to the n state. P_n and P_i are connected by Boltzman's probability principle. $Q_{n\rightarrow i}$ involves the spectral energy density of the exciting radiation (given by Wien's law) and the atomic absorption coefficient, τ_a' which, since τ_a' has the dimensions of an area, may be regarded as "the effective cross-section" of an atom for intercepting radiation. $Q_{i\rightarrow n}$ on the contrary involves the inverse process, namely the effective cross section τ_β of an ionized atom for intercepting electrons. A simple relation is thus established between τ_a' and τ_β. By aid of the correspondence principle and the classical laws of radiation of an electron describing an orbit *past a positively charged nucleus Ne*, the value of τ_β is determined. The final value of τ_a' may be put in the form

$$\tau_a' = \frac{64\pi^4}{3\sqrt{3}} \, \frac{e^{10}m}{c^4 \; h^6} g' \, \frac{1}{k^4(k+1)} N^4 \lambda^3 \tag{23}$$

where τ_a' refers to the absorption coefficient of a nucleus Ne, with a *single* electron in the k quantum orbit, and g' is a constant "which does not differ much from unity." If it be assumed that we can compute the *atomic* absorption coefficient τ_a by summing up (23) for all the electrons of a neutral atom of atomic number N we have

$$\tau_a = \frac{64\pi^4}{3\sqrt{3}} \, \frac{e^{10}m}{c^4 \; h^6} g' \left(\frac{2}{1.2} + \frac{8}{2^4 \; 3} + \frac{18}{3^4 \; 4} \right) N^4 \lambda^3 \tag{24}$$

where 2, 8, 18 . . . . represent the respective number of electrons in quantum rings 1, 2, 3. . . . .

Computing, as before, the absorption coefficient for bismuth we have (assuming $g' = 1$),

$$\tau_a = 60 \times 10^4 \lambda^3 \; ,$$

a value which is about half the experimental value.

Although difficult to trace, it appears that the term λ^3 appears in Kramers' formula on account of the introduction of Wien's law, and the term N^4 apparently comes from the application of classical electrodynamics to the radiation of an electron as it passes a nucleus of charge Ne.

As Kramers points out, Eq. (23) is derived for the case of a nucleus of charge Ne and a single electron. It can therefore be expected to be only an approximation when applied to all the electrons of an atom. The approximation may be expected to be of the same order as is found in the case of Bohr's theory of the hydrogen spectrum when applied to elements of higher atomic number. Indeed, by use of Bohr's equation for the energy of a given quantum orbit k, namely

$$E_k = h\nu_k = (2\pi^2 m N^2 e^4 / h^2) \; (1/k^2)$$

we can re-write (23) as follows

$$\tau_a{}'=\frac{16}{3\sqrt{3}}g'\frac{e^4}{mh^2c^4}\,\frac{E_k{}^2}{k+1}\lambda^3 \tag{25}$$

It seems reasonable to extend Eq. (24) so as to include all the electrons of a neutral atom by writing

$$\tau_a=\frac{16}{3\sqrt{3}}g'\frac{e^4}{mh^2c^4}\left(\frac{n_\mathrm{K}E_\mathrm{K}{}^2}{1+1}+\frac{n_\mathrm{L}E_\mathrm{L}{}^2}{2+1}\cdot\cdot\cdot\right)\lambda^3 \tag{26}$$

If now, in using (26) we put in the *experimental* values of E_K, E_L . . . the formula should be freed of the limitation of a *single* electron around a nucleus *Ne* and should apply generally. Computing τ_a for bismuth in this way gives

$$\tau_a=50\times10^4\lambda^3\,.$$

It is to be observed that (13), (15) and (21) are identical, except for the value of the factor involving π. However (26) differs from these three not only in the corresponding numerical factor, but in dividing each of the terms E^2 in the bracket by $(k+1)$. *It is in reality this factor $(k+1)$ which reduces the value of τ_a computed from (26) to about half the correct value.* If this factor be omitted the value of τ_a given by (22) is *correct within experimental error for $\lambda<\lambda_\mathrm{K}$.*

We are now in position to compare these several theories as regards their prediction of the magnitude of the K absorption discontinuity as expressed by the value of R^K_L. It is evident that Eqs. (13), (15), and (21) give identical values of R^K_L namely:

$$R^\mathrm{K}_\mathrm{L}=\frac{n_\mathrm{K}E_\mathrm{K}{}^2+n_\mathrm{L}E_\mathrm{L}{}^2+n_\mathrm{M}E_\mathrm{M}{}^2+\cdot\cdot\cdot}{n_\mathrm{L}E_\mathrm{L}{}^2+n_\mathrm{M}E_\mathrm{M}{}^2+\cdot\cdot\cdot} \tag{27}$$

while for (24) R^K_L is independent of N and is given by

$$R^\mathrm{K}_\mathrm{L}=\frac{1+1/6+1/18+\cdot\cdot\cdot}{1/6+1/18+\cdot\cdot\cdot}=5.5 \tag{28}$$

For (26) we have, on the contrary,

$$R^\mathrm{L}_\mathrm{K}=\frac{\dfrac{n_\mathrm{K}}{2}E_\mathrm{K}{}^2+\dfrac{n_\mathrm{L}}{3}E_\mathrm{L}{}^2+\dfrac{n_\mathrm{M}}{4}E_\mathrm{M}{}^2\cdot\cdot\cdot}{\dfrac{n_\mathrm{L}}{3}E_\mathrm{L}{}^2+\dfrac{n_\mathrm{M}}{4}E_\mathrm{M}{}^2\cdot\cdot\cdot} \tag{29}$$

In evaluating (27), (28) and (29) it is assumed that it is unnecessary to include limits beyond the M limits, and that the values of n_K, n_L and n_M

are respectively 2, 8 and 18. The values of E_K, E_L and E_M used are those obtained partly from Sommerfield's "Atomic Structure and Spectral Lines," and partly from Robinson (Proc. Roy. Soc. **104,** 455 (Nov. 1923). There has been no attempt to weight the multiple values of E_L and E_M; the average values of $E_L{}^2$ and $E_M{}^2$ have been used. The data are shown in Table III. The values of R_L^K given by the two equations are shown graphically in Fig. 10, curve A corresponding to Eq. (29) (Kramers' theory as modified in Eq. (26)), and curve B to Eq. (27). The line C in Fig. 10 gives the ratio predicted by Kramers' original Eq. (24). It is seen that the observed values correspond most closely to Kramers' Eq. (24), but this agreement must be regarded as fortuitous, since there can be no doubt that a multiple charged nucleus with a *single* electron behaves quite unlike such a nucleus with its normal quota of electrons. The step from Eq. (23) to (24) cannot therefore be made without some modification. The suggested modification (26) however, gives values of R_L^K (curve A) entirely too large.

TABLE III

Element		E_K	E_L*	E_M*	R_L^K Eq. (27)	R_L^K Eq. (29)
Pb	82	6463	1080	233	9.1	13.4
Au	79	5940	985	207	9.2	13.5
W	74	5114	833	170	9.6	14.2
Sn	50	2148	311	50	12.4	18.2
Ag	47	1879	263	36	13.3	19.7
Mo	42	1473	197	27	14.4	21.3

* "Root-mean-square" values.

Values of E are given in terms of ν/R, where ν is wave-number and R is the Rydberg constant.

While these equations, therefore, do not give values of R_L^K which check closely with experiment, it is very significant that they predict in a qualitative way the variation of R_L^K with N. The experimental data themselves are by no means satisfactory, although probably correct to ten or twenty percent.

It is hoped to improve the precision with which these measurements can be made, and to obtain values of R_L^K for a larger number of elements.

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