The True Absorption Coefficients for the Elements from Gold to Bismuth in the Neighborhood of the *L*-Absorption Edges

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The L x-ray absorption spectra of the metals gold to bismuth were examined with a calcite crystal spectrometer and ionization chamber. Thin films of thallium, lead and bismuth were evaporated onto very thin sheets of mica. The true absorption coefficients $\tau(L_{\mathrm{I}})$, $\tau(L_{\mathrm{II}})$, and $\tau(L_{\mathrm{III}})$ corresponding to the photoelectric absorption by the three types of L electrons were found to vary approximately as $\lambda^{2.56}$ for each of the five elements gold to bismuth. With this relation the coefficients were computed for a given wave-length. Their ratio $\tau(L_{\mathrm{I}}) : \tau(L_{\mathrm{II}}) : \tau(L_{\mathrm{III}})$ (which is therefore independent of the wave-length) was found to be constant over the range 0.5 to 1.5A and to have approximately the same value for each of the five elements. The value of the ratio was found to be 19 : 32 : 49. This ratio also gives the relative numbers of photoelectrons ejected from the three L shells by radiation of a given frequency. Ratios of $\tau(L_{\mathrm{I}})$, $\tau(L_{\mathrm{II}})$ and $\tau(L_{\mathrm{III}})$ which are evaluated at their respective absorption edges L_{I}, L_{II} and L_{III} were also determined. This ratio of $\tau(L_{\mathrm{II}})/\tau(L_{\mathrm{III}})$ was found to be approximately 0.45 for each element and is in good agreement with the value predicted by relativistic theory. The ratio $\tau(L_{\mathrm{I}})/[\tau(L_{\mathrm{II}})+\tau(L_{\mathrm{III}})]$ has been found theoretically only by means of a nonrelativistic treatment of absorption. The experimental value, 0.163, is not in good agreement with the predicted value.

INTRODUCTION

THE K region of the x-ray absorption spectrum has been investigated for a great number of elements by Richtmyer,[1] Allen,[2] Jönsson[3] and others. Comparatively little work, however, has been done in the L region. Very few elements have been studied and the results of different observers are not in good agreement. The object of this experimental work is to obtain more accurate values of the magnitudes of the discontinuities, to study the variation of the absorption coefficients with wave-length, and to compare the results with those obtained from theory.

APPARATUS

The high voltage was produced by a 5 kw 550 cycle motor-generator and transformer. The current was rectified by kenetrons and smoothed by a capacity of 0.025 microfarad. The field current in the generator was supplied by storage batteries. The voltage was measured to within 0.2 percent by a Taylor resistor stack of 50 megohms and a milliammeter.

The x-ray tube of Pyrex glass had removable electrodes. The copper filament holder gave a line focus on the tungsten target one centimeter long and one millimeter wide. The filament current was controlled by a continuously variable mercury resistance of the Kirkpatrick[4] type.

The x-ray spectrometer was the one used by Allison and Williams[5] and described by them in detail. The defining slits each 0.15 mm wide, 10 mm high were 35 cm apart thus giving an angular width to the beam of about 3′ of arc. This corresponds to about 5 X.U. or to a wave-length spread of 0.5 percent in the center of the group of wave-lengths 0.5 to 1.5A. Lead screens prevented the scattered and characteristic x-rays from the absorbing film from directly entering the ionization chamber.

The ionization chamber was of the cylindrical type with a potential of 315 volts applied between the nickel electrodes. The chamber was filled with a mixture of methyl iodide and argon at partial pressures of 14 and 62 cm of mercury, respectively.

The ionization currents were measured with a F.P. 54 Pliotron vacuum tube amplifier. The

[1] F. K. Richtmyer, Phys. Rev. **27**, 1 (1926); **30**, 755 (1927).

[2] S. J. M. Allen, Phys. Rev. **28**, 907 (1926).

[3] E. Jönsson, Dissertation, Upsala, 1928.

[4] P. Kirkpatrick, J. Opt. Soc. Am. **7**, 195 (1923).

[5] S. K. Allison and J. H. Williams, J. Opt. Soc. Am. **18**, 473 (1929).

Pliotron was mounted in a brass case which was attached directly to the case containing the ionization chamber.

Absorbing Films

The thin absorbing films were obtained by evaporation of the metals onto very thin sheets of mica. A nickel cover allowed the element to be deposited only on a strip of mica about 1 by 2 cm. Oxidation of the absorber was prevented by removing the nickel cover with an electromagnet and evaporating onto the whole sheet a very thin coat of aluminum. Films of thallium, lead and bismuth were made in this way.

Effects due to possible irregularities in the films were averaged out by keeping the film in constant motion before the slits. The film holder was mounted on a movable fulcrum allowing the film to be shifted in such a way that in one position the x-ray beam travelled through the mica and aluminum, and in the other position through the same thickness of mica and aluminum and the absorbing material. The actual path difference was therefore only the thickness of the element being examined.

Experimental Procedure

To assure constant working conditions the x-ray tube was operated for two or three hours before each set of readings. The voltage ranged from 18 to 38 kv, and was always at least 3 kv below the voltage required to excite second-order wave-lengths. The tube currents ranged from 20 to 40 m.a. The galvanometer deflections were always timed over a scale range of 30 cm. By adjusting the sensitivity of the galvanometer these deflections were made to extend over a period of about 60 seconds. Individual readings never varied from their average by more than one percent. The leakage rate was determined at the beginning and at the end of each set of readings, and was always between 2 and 7 percent of the value of the readings taken. Each reading was checked several times and the average of the readings was taken at each crystal setting.

Calculations and Results

The mass absorption coefficient μ/ρ is given by the equation

$$I = I_0 \exp(-\mu/\rho \cdot \rho x)$$

where I_0 is the original intensity of the monochromatic beam of x-rays and I is the intensity after penetrating to a depth x in an absorbing medium of density ρ. Within the limits of experimental error the mass absorption coefficients have been found to obey the empirical law:

$$\mu/\rho = A\lambda^c,$$

where A and c are constants whose values change from branch to branch of the absorption curve. The combining of these two equations gives:

$$\log \log I_0/I = c \log \lambda + \text{constant}.$$

Plots of $\log \log I_0/I$ against $\log \lambda$ yield straight lines the slopes of which give the values for c. The quantities I_0 and I are proportional to the rates of deflection of the galvanometer. I is obtained by passing the x-ray beam through the portion of the film covered with the absorbing material. I_0 is obtained when the x-ray beam passes through the portion of the film not covered with the absorber.

Fig. 1 shows plots of the $\log \log I_0/I : \log \lambda$ curves for the five elements gold, mercury, thallium, lead and bismuth. The data for gold were obtained by Uber and Patten[6] and the data for mercury were taken from a curve given by Uber.[7] The wave-lengths of the crystal settings were calculated by interpolation from tables of Siegbahn[8] and the wave-lengths of the absorption edges were taken from Sandström.[9] Following the customary nomenclature, that part of the curve which lies on the short wave-length side of the L_{I} discontinuity is referred to as the L_{I} branch. Similarly the segment of the curve between the L_{I} and L_{II} discontinuities is designated as the L_{II} branch, the segment between the L_{II} and L_{III} discontinuities as the L_{III} branch, and the part of the curve on the long wave-length side of the L_{III} discontinuity as the M_{I} branch.

The values of c for these branches are given in Table I together with some results of Back-

[6] F. M. Uber and C. G. Patten, Phys. Rev. **42**, 229 (1932).

[7] F. M. Uber, Phys. Rev. **38**, 217 (1931).

[8] Manne Siegbahn, *Spectroscopy of X-Rays*, 1st edition.

[9] Arne Sandström, Zeits. f. Physik **65**, 632 (1930).

TABLE I. *Values of c, the exponent of the wave-length.*

Element	Branch of the Absorption Curve L_I	L_{II}	L_{III}	M_I	Observer
Platinum (78)	2.6	2.6	2.6	2.64	Backhurst[10]
Gold (79)	2.91	2.91	2.64	2.61	Backhurst[10]
	2.55	2.94	2.64	2.78	Uber and Patten[6]
Mercury (80)	2.56	2.56	2.59	2.66	Uber[7]
Thallium (81)	2.64	2.50	2.35	2.57	Author
Lead (82)	2.62	2.54	2.46	2.69	Author
Bismuth (83)	2.56	2.54	2.52	2.60	Author
Thorium (90)	2.56	2.56	2.43	2.65	Küstner[11]

TABLE II. *Relative magnitudes of the L-absorption discontinuities.*

Element	δL_I	δL_{II}	δL_{III}	δL	$\nu L_I/\nu M_I$	Observer
79 Au	1.26	1.36	2.53	4.31	4.20	Backhurst[10]
	1.24	1.39	2.48	4.20		Dauvillier[12]
	1.15	1.35	2.45	3.85		Küstner[11]
	1.16	1.39	2.48	4.02		Uber and Patten[6]
	1.10	1.62	2.70	4.81		Wolf[13]
80 Hg	1.18	1.39	2.45	4.02	4.17	Uber[7]
81 Tl	1.16	1.34	2.36	3.64	4.14	Küstner[11]
	1.15	1.36	2.38	3.72		Author
82 Pb	1.15	1.35	2.38	3.70	4.12	Küstner[11]
	1.16	1.39	2.42	3.90		Author
83 Bi	1.16	1.38	2.38	3.81	4.10	Author

hurst[10] and Küstner[11] for comparison. The values accredited to Küstner have been interpolated from his graph. Because of the difficulty in determining the slope of the L_{II} branch it has been assigned a value equal to the average of the slopes of the L_I and L_{III} branches for each of the elements thallium, lead and bismuth. This seems to be justified in view of the fact that the slopes of all of the branches have very nearly the same value.

The relative magnitude of an absorption edge, δ, is defined as the ratio of the true mass absorption coefficients τ/ρ on the immediate short and long wave-length sides of the edge. The total magnitude of the L discontinuities, δL, is defined as the product of the individual magnitudes. That is:

$$\delta L = \delta L_I \cdot \delta L_{II} \cdot \delta L_{III}.$$

Jönsson[3] has found that δK and δL obey approximately the relation

$$\delta K = \nu K/\nu L_I \quad \text{and} \quad \delta L = \nu L_I/\nu M_I,$$

where ν represents the frequency of the designated absorption limit. In Table II are listed values of the relative magnitudes δ for the elements gold to bismuth and also the value of δL computed by the above frequency relation. It will be seen that the δL_{III} and δL magnitudes show a decrease in value with increasing atomic number. If δL_I and δL_{II} have similar decreases they are within the experimental uncertainty of the determination of the magnitudes. Also it may be noticed that the values for thallium are all lower than those for the neighboring metals. This irregularity is also shown in Küstner's data.

Every photoelectron produced in the absorption process removes from the incident beam an amount of energy equal to $h\nu$, or the number of quanta absorbed is equal to the number of photoelectrons produced. Hence the true absorption coefficient τ is the probability that a quantum of incident energy will produce one photoelectron per centimeter of path. This coefficient τ is made up of the absorption coefficients τL_I, τL_{II}, τL_{III}, τM_I, etc., which are the probabilities of ejecting L_I, L_{II}, L_{III}, M_I, etc., electrons, respectively. These coefficients are functions of the wave-length and have maximum values at their characteristic absorption edges. Theoretical calculations give values for ratios of these maximum values of the τ's as observed at the short wave-length side of the edges. Quantities proportional to these maximum values are found directly from Fig. 1 by taking the difference of the anti-logarithms of the points on the immediate sides of the edges.

In Table III values of the two ratios $\tau L_I/(\tau L_{II}+\tau L_{III})$ and $\tau L_{II}/\tau L_{III}$ are given where each coefficient has the value observed at the short wave-length side of the edge.

On the assumption of a relativistic wave-function Phillips[14] was able to make approxi-

[10] Ivor Backhurst, Phil. Mag. **7**, 353 (1929).
[11] H. Küstner, Phys. Zeits. **33**, 46 (1932).
[12] A. Dauvillier, Comptes Rendus **178**, 476 (1924).
[13] M. Wolf, Ann. d. Physik **16**, 973 (1933).
[14] Melba Phillips, Phys. Rev. **45**, 132 (1934).

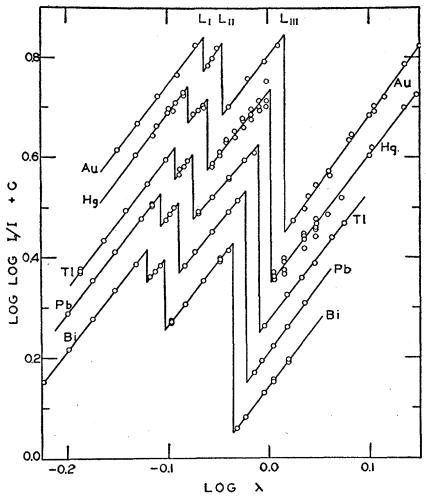

FIG. 1. The log log I_0/I : log λ curves for gold, mercury, thallium, lead and bismuth.

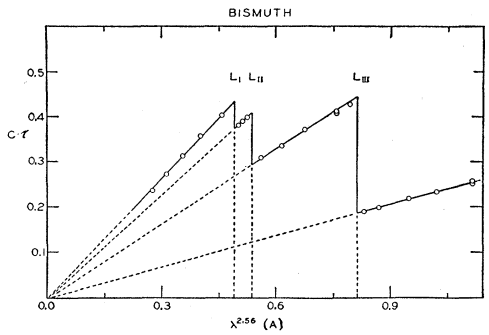

FIG. 2. $\tau L_I+\tau L_{II}+\tau L_{III}+\tau M_I+\cdots$ in arbitrary units as a function of $\lambda^{2.56}$ for bismuth.

mations which gave approximately 0.45 for $\tau L_{II}/\tau L_{III}$, each coefficient being evaluated at its absorption limit. The agreement with the experimental values in column 3 is seen to be exceedingly good.

Oppenheimer[15] has shown in a non-relativistic treatment of x-ray absorption that the absorption coefficients per electron at their absorption edges are approximately proportional to the wave-lengths of the edges. Hence the ratio $\tau L_{II}/\tau L_{III}$ is equal to $\frac{1}{2}(\lambda L_{II}/\lambda L_{III})$. The values of these λ ratios given in column 4 of Table III also agree remarkably well with those in column 3. As the atomic number decreases the ratio $\lambda L_{II}/\lambda L_{III}$ approaches unity. The experimental values of $\tau L_{II}/\tau L_{III}$ also show this increase with decreasing atomic number.

The ratios of the true absorption coefficients which have all been evaluated at the same wave-length give the relative numbers of photoelectrons ejected from the different electron shells. Ratios of this type are most commonly expressed in terms of the relative magnitudes δ. If the value of c in the expression $\tau=A\lambda^c$ is assumed to be the same for all of the τ's, as it approximately is (that is if an average value of c is taken), then any ratio of the τ's each measured at the same wave-length will be independent of the wave-length.

Since the thickness of the absorbing films is not known, the results of the measurements reported in this paper give not the values of the coefficients τ, but a value proportional to τ. This value has been plotted in Fig. 2 as a function of $\lambda^{2.56}$ for bismuth. 2.56 is the average value of the exponent of the wave-length for the four branches of the absorption curve. It will be seen from the geometry of the figure that any ratio of the coefficients τ (and therefore the relative magnitudes δ), will be independent of the wave-length, at least within the range of wave-lengths 0.5 to 1.5A. The ratios of the coefficients τL_I, τL_{II}, τL_{III}, τM_I, $\cdots$ may then be very simply expressed in terms of the δ's by the equation:

$$\tau L_I : \tau L_{II} : \tau L_{III} = (\delta L_I - 1)\cdot\delta L_{II}\cdot\delta L_{III} : (\delta L_{II}-1)\cdot\delta L_{III} : (\delta L_{III}-1).$$

Values of this ratio are given in Table IV.

The assumption of an equal probability of ionization for each of the L_I, L_{II} and L_{III} electrons would give a ratio proportional to the population of the levels, 25 : 25 : 50.

TABLE III. *Ratios with each coefficient evaluated at its absorption edge.*

Element	$\tau L_I/(\tau L_{II}+\tau L_{III})$	$\tau L_{II}/\tau L_{III}$	$\frac{1}{2}(\lambda L_{II}/\lambda L_{III})$
79 Au	0.159	0.454	0.432
80 Hg	0.180	0.450	0.431
81 Tl	0.155	0.435	0.430
82 Pb	0.164	0.450	0.429
83 Bi	0.159	0.440	0.428

[15] J. R. Oppenheimer, Zeits. f. Physik **41**, 268 (1926).

TABLE IV. *Ratios with each absorption coefficient evaluated at the same wave-length.*

Element	$\tau L_{\mathrm{I}} : \tau L_{\mathrm{II}} : \tau L_{\mathrm{III}}$	$\Sigma\tau L/\Sigma\tau$	$\tau L_{\mathrm{I}}/(\tau L_{\mathrm{II}}+\tau L_{\mathrm{III}})$
79 Au	0.185 : 0.322 : 0.493	0.750	0.231
80 Hg	0.203 : 0.317 : 0.480	0.750	0.254
81 Tl	0.177 : 0.315 : 0.508	0.730	0.218
82 Pb	0.186 : 0.325 : 0.489	0.745	0.228
83 Bi	0.187 : 0.322 : 0.491	0.738	0.230

The ratio $\Sigma\tau L/\Sigma\tau=(\delta L-1)/\delta L$, where $\Sigma\tau L=\tau L_{\mathrm{I}}+\tau L_{\mathrm{II}}+\tau L_{\mathrm{III}}$ and $\Sigma\tau=\tau L_{\mathrm{I}}+\tau L_{\mathrm{II}}+\tau L_{\mathrm{III}}+\tau M_{\mathrm{I}}+\cdots$ is given in column 5 of Table IV. This ratio indicates that for wave-lengths just shorter than the L_{I} absorption edge about 75 percent of the ejected photoelectrons come from the L shell.

In column 6 of Table IV are given values of the ratio

$$\frac{\tau L_{\mathrm{I}}}{\tau L_{\mathrm{II}}+\tau L_{\mathrm{III}}}=\frac{\delta L_{\mathrm{I}}-1}{\delta L_{\mathrm{II}}\cdot\delta L_{\mathrm{III}}-1}\cdot\delta L_{\mathrm{II}}\cdot\delta L_{\mathrm{III}}.$$

From nonrelativistic wave mechanics Stobbe[16] has derived expressions for the quantities τL_{I} and $\tau L_{\mathrm{II}}+\tau L_{\mathrm{III}}$. These quantities, when evaluated at a common L absorption limit, give the ratio $\tau L_{\mathrm{I}}/(\tau L_{\mathrm{II}}+\tau L_{\mathrm{III}})=0.182$. This theoretical value lies between the values given in Tables III and IV for this ratio. An assumption of equal probability of ejection of any of the L shell electrons would give $\tau L_{\mathrm{I}}/(\tau L_{\mathrm{II}}+\tau L_{\mathrm{III}})=0.33$.

In conclusion the author wishes to thank Professor R. B. Brode who suggested the problem for his kindly interest and many valuable suggestions throughout the course of the investigation.

[16] M. Stobbe, Ann. d. Physik **7**, 661 (1930).