The Natural Widths of the L-Series Lines in the X-Ray Spectra of Elements 74 to 83

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The full widths at half-maximum of the $L\alpha_1$, $L\beta_1$, $L\beta_2$ and $L\gamma_1$ lines of Bi, Pb, Tl, Au, Pt, Ir and W have been measured with Allison's double spectrometer in the (1, +1) position equipped with previously calibrated calcite crystals of high perfection. The results in X.U. are given in the table. The widths are uncorrected for the finite resolving power of the crystals or for the geometrical divergence of the x-ray beam. Approximate small corrections have been made for interfering lines. Relative wave-lengths of neighboring lines are given. Empirical relations between the energy widths of the lines investigated and the atomic number and the electron transitions involved are suggested. The effects of alloys of the elements on the widths observed are discussed.

Line	74 W	77 Ir	78 Pt	79 Au	81 Tl	82 Pb	83 Bi
$L\alpha_1$	1.26	1.19	1.17	1.13	1.11	1.05	1.03
$L\beta_1$	0.943	0.822	0.804	0.785	0.743		0.700
$L\beta_2$	1.38	1.17	1.14	1.06	1.00		.895
$L\gamma_1$	1.01	0.923	0.837	0.791	0.741	0.698	.669

INTRODUCTION

AN empirical knowledge of the natural widths of x-ray lines has been attained in the past few years by the use of the double crystal x-ray spectrometer devised by Ehrenberg and Mark[1] and Davis and Purks.[2] Many investigators have measured the widths of the K-series lines of various elements[3] but little is known about the widths of the lines in the L-series. Preliminary experiments on the widths of a few lines in the L-series of lead and thallium performed by Allison[4] and in tungsten by Ehrenberg and von Susich[5] showed that L-series lines were much wider than K-series lines of the same wave-length. The widths of twelve lines in the L-series spectrum of uranium were investigated by the author[6] in a study of possible correlations between the widths and the transitions involved. Spencer[7] studied the width of Ag $L\alpha_1$ with a "universal" double spectrometer and obtained the large value of 4.5 X.U. for the width at half-maximum.

The present experiments investigated the widths of the $L\alpha_1$, $L\beta_1$, $L\beta_2$ and $L\gamma_1$ lines of W(74), Ir(77), Pt(78), Au(79), Tl(81), Pb(82) and Bi(83).

The measurements were all obtained with the crystals in the (1, +1) position (in the notation of Allison and Williams[8]). In this position, where the crystal faces are not parallel, the dispersion of the instrument is finite. Widths are obtained for the lines that are much greater than those expected from the diffraction pattern of the crystals and hence must be attributed principally to the natural widths of the lines themselves.

APPARATUS AND OPERATING CONDITIONS

The double crystal x-ray spectrometer used in this research has been described previously.[9, 10] The slits limiting the vertical and horizontal divergence of the x-ray beam were 49.6 and 14.5 cm apart, respectively. Table I gives the experimental conditions. α_m is the maximum horizontal divergence of the x-ray beam passing through two slits of equal width a that are L_H cm apart and is equal to a/L_H. ϕ_m is the maximum vertical divergence and is similarily equal to b/L_V.

The crystals used in this investigation were

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[1] Ehrenberg and Mark, Zeits. f. Physik **42**, 807 (1927).

[2] Davis and Purks, Proc. Nat. Acad. Sci. **13**, 419 (1927).

[3] See reference 1 in Allison, Phys. Rev. **44**, 63 (1933).

[4] S. K. Allison, Phys. Rev. **34**, 176 (1929).

[5] Ehrenberg and von Susich, Zeits. f. Physik **42**, 823 (1927).

[6] J. H. Williams, Phys. Rev. **37**, 1431 (1931).

[7] R. C. Spencer, Phys. Rev. **38**, 630 (1931).

[8] Allison and Williams, Phys. Rev. **35**, 149 (1930).

[9] S. K. Allison, Phys. Rev. **44**, 63 (1933).

[10] S. K. Allison, Phys. Rev. **41**, 1 (1932).

TABLE I. *Experimental conditions.*

Element	Line	Voltage (kv)	Current (m.a.)	α_m $\times 10^{-3}$	ϕ_m $\times 10^{-2}$
83 Bi	$L\alpha_1$	36.5	3.1	6.9	1.2
	β_1	"	3.0	"	1.1
	β_2	"	"	"	1.2
	γ_1	41.0	4.1	"	1.4
82 Pb	$L\alpha_1$	36.5	4.0	5.5	1.4
	γ_1	42.5	8.0	6.9	1.2
81 Tl	$L\alpha_1$	36.5	2.5	6.9	1.2
	β_1	"	2.6	"	1.4
	β_2	"	2.5	"	"
	γ_1	39.5	2.0	"	"
79 Au	$L\alpha_1$	36.5	3.0	7.4	1.4
	β_1	"	3.3	8.3	1.2
	β_2	"	3.4	"	1.4
	γ_1	39.5	3.3	"	"
78 Pt	$L\alpha_1$	36.5	3.3	8.3	1.1
	β_1	"	"	"	1.2
	β_2	38.2	3.5	"	1.4
	γ_1	39.5	3.1	"	"
77 Ir	$L\alpha_1$	36.5	3.3	8.3	1.4
	β_1	"	3.6	"	"
	β_2	38.6	3.8	"	"
	γ_1	39.5	"	"	"
74 W	$L\alpha_1$	36.5	3.0	8.3	1.4
	β_1	"	3.3	"	"
	β_2	39.5	3.4	"	"
	γ_1	"	"	"	"

Allison's[10] calcites III*A* and III*B* which had been shown to approximate closely the theory of reflection by perfect calcite crystals. Measurements with Pt $L\alpha_1$ and Pb $L\alpha_1$ reflected from the crystals in the (1, −1) position showed that the crystals had not deteriorated during the course of this investigation.

The x-ray tube and targets were of a design previously described by Allison.[9] Bi, Pb and Tl were melted into circular cavities in the faces of standard copper base targets. In the case of Tl the surface was filed and then covered with naphthalene to prevent oxidization. The naphthalene evaporated quickly when the tube was evacuated. Au and Pt sheets were soft-soldered to a flat copper face. Ir was silver-soldered into the cavity and W was first spot-welded with nickel and then silver-soldered to a standard base target.

EXPERIMENTAL PROCEDURE

The curves were taken by rotating crystal *B* about a vertical axis lying in the plane of its reflecting face while crystal *A* remained stationary. DuMond and Hoyt[11] have pointed out that this method may introduce errors because, as crystal *B* is rotated through small steps, the x-ray beam is reflected from different parts of the crystals and also, the central beam comes from different parts of the focal spot of the tube. By rotating both crystals simultaneously in a manner that satisfies the geometrical conditions, Allison[9] has shown that for the Co $K\alpha$ lines, which have an angular width of 0.82 and 0.94 X.U., widths are obtained which agree with those obtained by the former method of operation. Since the widths of the lines observed in the present experiment were of the same order of magnitude as those examined by Allison, the method of rotating crystal *B* alone is justified. A further test of the method was made with Tl $L\beta_1$, $L\beta_2$ lines of wave-lengths 1012.99 and 1008.22 X.U., respectively. The width of either $L\beta_1$ or $L\beta_2$ was found to be independent of the setting of crystal *A* at values between the limiting reflection angles imposed by the above wave-lengths. Thus it is felt that the method of single rotation will yield curves that are not influenced by the movements of the observed beam over the focal spot or the reflecting crystal faces.

CORRECTIONS TO THE OBSERVED WIDTHS

The three factors that may be considered to affect the observed widths are: the horizontal and vertical divergence of the x-ray beam and the finite resolving power of the calcite crystals. Allison[9] has discussed the question of these corrections for *small* values of α_m and ϕ_m and has shown that the geometrical divergence of the incident beam contributes a negligible amount to the width calculated for monochromatic radiation. In the case of real line radiation possessing a finite wave-length spread, with the limits on α_m and ϕ_m of the order of magnitude of those given in Table I, geometrical contributions may be neglected. The contributions of the finite resolving power of the crystals to the observed widths are not so well known. The widths observed when the crystals are in the (1, −1) position[10] show that this width is from 8 to 12 percent of the widths of the lines examined here in the

[11] DuMond and Hoyt, Phys. Rev. **36**, 1702 (1930).

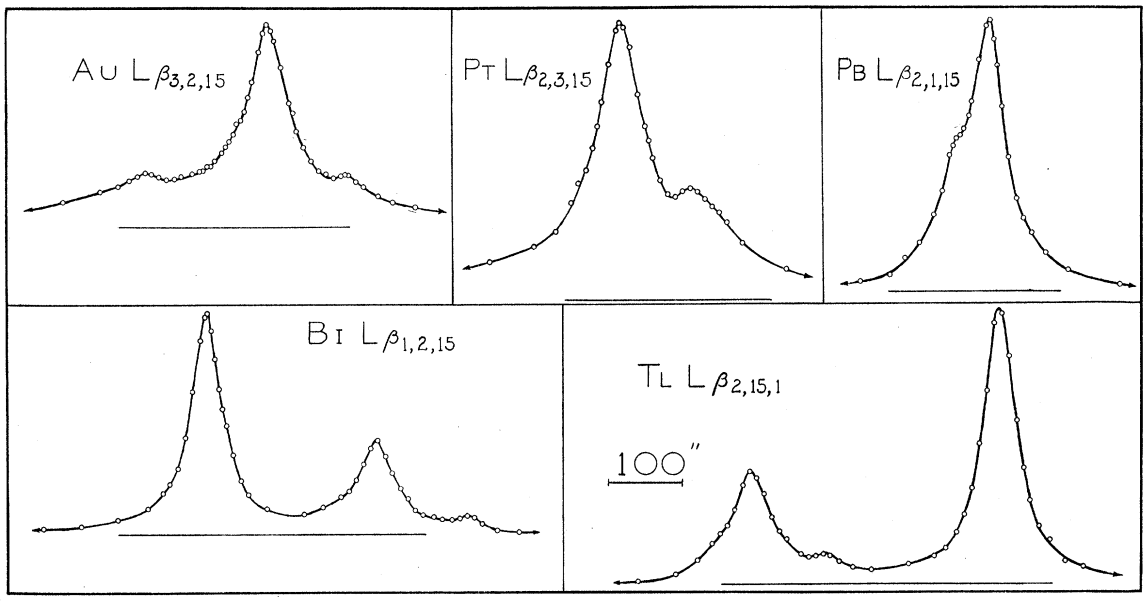

FIG. 1. Curves of L-series lines obtained in the (1, +1) position by rotating crystal B alone. The vertical scale of intensity is not the same for all the curves. The horizontal scale of angular rotation of crystal B from an arbitrary zero is the same for all the curves. The horizontal lines beneath the curves are the base line intensities measured at least 500″ on either side of the peaks.

(1, +1) position. Laue[12] has shown that the actual shape of a single crystal diffraction pattern cannot be obtained from the (1, −1) curve and so any treatment is necessarily handicapped by the assumption of an arbitrary function for this shape, even if empirical functions are known[13] for the (1, −1) rocking curve shape. The results of this experiment are therefore uncorrected for the three possible effects.

The widths of most of the lines examined are not influenced by neighboring lines except in the case of the doublet $L\beta_2$, $L\beta_{15}$ in all the elements, the neighboring lines $L\beta_2$, $L\beta_3$ in Au, $L\beta_2$, $L\beta_3$ in Pt, and the coincident lines $L\beta_1$, $L\beta_2$ in Pb. The doublet $L\beta_2$, $L\beta_{15}$ has a relative intensity of 9 to 1 predicted by an extension of the Burger and Dorgelo[14] sum rules and experimentally proven by measurements on uranium and thorium by Allison.[4] The relative intensity $L\beta_2/L\beta_{15}$ for Au, Tl and Bi was here estimated to be 10, 9 and 8.5, respectively. Considerations of the curves showed that the influence of $L\beta_{15}$ on the width of $L\beta_2$ was negligible. Estimates were made from large scale plots of the small contribution of $L\beta_3$ to Au $L\beta_2$ and Pt $L\beta_2$. Curves of the interfering lines and of the group $L\beta_1$, $L\beta_2$, $L\beta_{15}$ in Tl, Pb and Bi are shown in Fig. 1.

All the principal lines examined were symmetrical to within the accuracy of the measurements so that the ratio of the part of the width lying to the long wave-length side of the maximum ordinate to that part on the short wave-length side was 1.00 ± 0.05. In striking contrast to these results are the measurements of Allison[9] and others on Cu $K\alpha_1$ where the ratio is 1.4 although the wave-length is approximately the same as W $L\alpha_1$.

By assuming that the principal lines are perfectly symmetrical one can split the composite curve into its separate parts and obtain values for the relative wave-lengths of neighboring lines from the measured angular separation and the known dispersion of the instrument. By taking the most intense line as the reference line and assigning to it a wave-length given by Siegbahn,[15]

[12] Laue, Zeits. f. Physik **72**, 472 (1932).
[13] A. Hoyt, Phys. Rev. **40**, 477 (1932).
[14] Burger and Dorgelo, Zeits. f. Physik **23**, 258 (1924).
[15] M. Siegbahn, *Spektroskopie der Röntgenstrahlen*, second edition.

TABLE II. *Relative wave-lengths of overlapping lines in X.U.*

Element	$L\beta_1$	$L\beta_2$	$L\beta_{15}$	$L\beta_3$
Bi (83)	(950.02)	953.33 953.24*	955.14 955.08*	
Pb (82)	(980.83)	980.15 980.83*		
Tl (81)	(1012.99)	1008.14 1008.22*	1009.69 1010.0 *	
Au (79)		(1068.01)	1069.54 1069.9 *	1065.61 1065.50*
Pt (78)		(1099.74)	1101.34 1101.65*	

the relative wave-lengths shown in Table II have been obtained. Values of the wave-lengths of Ir $L\beta_{15}$ and W $L\beta_{15}$ are not given because $L\beta_2$ has become so wide that the derived values are unreliable. The values in parentheses are the reference wave-lengths and the starred values are Siegbahn's values for the wave-lengths.

RESULTS

Table III shows the values of the widths, $\Delta\theta$, in seconds of arc obtained for the full width at half maximum of the various lines in the (1, +1) position. From these the values of $\Delta\lambda$ in X.U., ΔV in volts and $(\Delta\nu/R)^{\frac{1}{2}}$ are calculated by the following equations:

$$\Delta\lambda = (\tfrac{1}{2})\lambda \cot\theta\Delta\theta \qquad (1)$$

$$(\Delta\nu/R)^{\frac{1}{2}} = 9.5460\times10^{2}\lambda^{-1}(\Delta\lambda)^{\frac{1}{2}} \qquad (2)$$

$$\Delta V = 1.2336\times10^{7}\Delta\lambda/\lambda^{2} \qquad (3)$$

where $\Delta\lambda$ and λ are in X.U.

TABLE III. *Experimental results on the natural widths.*

Line	λ (X.U.)[15]	$\Delta\theta$	$\Delta\lambda$ (X.U.)	$(\Delta\nu/R)^{\frac{1}{2}}$	$\Delta\nu$ (volts)
83 Bi $L\alpha_1$	1141.50	71.5″	1.03	0.849	9.76
$L\beta_1$	950.02	48.3	0.700	.841	9.57
$L\beta_2$	953.24	61.7	0.895	.947	12.1
$L\gamma_1$	811.43	46.0	0.669	.963	12.5
82 Pb $L\alpha_1$	1172.58	73.3	1.05	.837	9.47
$L\gamma_1$	838.01	48.0	0.698	.952	12.3
81 Tl $L\alpha_1$	1204.93	77.2	1.11	.834	9.41
$L\beta_1$	1012.99	51.3	0.743	.812	8.93
$L\beta_2$	1008.22	69.2	1.00	.948	12.2
$L\gamma_1$	865.71	51.0	0.741	.949	12.2
79 Au $L\alpha_1$	1273.77	78.4	1.13	.795	8.57
$L\beta_1$	1081.28	54.3	0.785	.782	8.28
$L\beta_2$	1068.01	73.2	1.06	.919	11.4
$L\gamma_1$	924.61	54.5	0.791	.918	11.4
78 Pt $L\alpha_1$	1310.33	81.5	1.17	.788	8.40
$L\beta_1$	1117.58	55.7	0.804	.766	7.94
$L\beta_2$	1099.74	79.0	1.14	.927	11.6
$L\gamma_1$	955.99	57.7	0.837	.913	11.3
77 Ir $L\alpha_1$	1348.47	83.2	1.19	.773	8.08
$L\beta_1$	1155.40	57.0	0.822	.749	7.59
$L\beta_2$	1132.97	81.3	1.17	.913	11.3
$L\gamma_1$	988.76	63.7	0.923	.927	11.6
74 W $L\alpha_1$	1473.36	88.5	1.26	.727	7.16
$L\beta_1$	1279.17	65.7	0.943	.725	7.11
$L\beta_2$	1242.03	95.8	1.38	.902	10.1
$L\gamma_1$	1096.30	70.0	1.01	.875	10.4
92 U[16] $L\alpha_1$	908.33	61.3	0.890	0.991	13.3
$L\beta_1$	718.07	42.0	.612	1.04	14.6
$L\beta_2$	752.68	53.1	.774	1.12	16.8
$L\gamma_1$	612.83	35.3	.516	1.12	16.9

The angular widths are estimated to be correct to within ±2 percent for $L\alpha_1$, ±3 percent for $L\beta_1$ and ±5 percent for $L\beta_2$ and $L\gamma_1$. In general three or more curves were taken of each line.

Fig. 2 and Fig. 3 show the variation of $\Delta\lambda$ and $(\Delta\nu/R)^{\frac{1}{2}}$ as a function of atomic number. The points in Fig. 3 lie on straight lines to within the

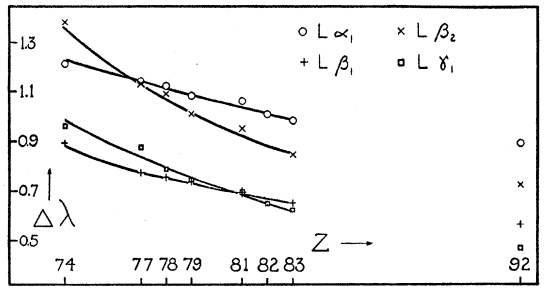

FIG. 2. The full width in X.U. at half-maximum of *L*-series lines as a function of atomic number.

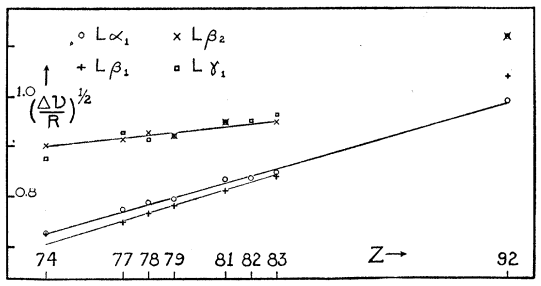

FIG. 3. The square root of the frequency width of *L*-series lines as a function of atomic number.

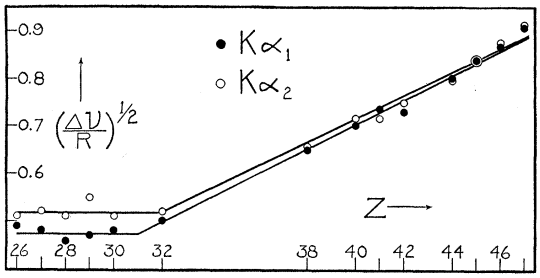

FIG. 4. The square root of the frequency width of the $K\alpha$ lines as a function of atomic number plotted from Allison's[9] data.

experimental error. In order to see if this empirical linear relationship existed in the K-series, Allison's[9] results were plotted with the same variables and are shown in Fig. 4. It is seen that straight lines may be drawn through the experimental points with a change in slope at Z equal to 31 or 32. Allison has pointed out that in this region the M_{IV}, M_V shells have just become filled and that in the solid state the distortion of the shells may extend above 29 Cu where the spectroscopic data give evidence of a complete $3d$ level. On this basis it is evident that the L transitions examined in this research are not affected by the filling of outer shells in the region 74 W to 83 Bi. The values[16] of $(\Delta\nu/R)^{\frac{1}{2}}$ for U $L\beta_1$, $L\beta_2$ and $L\gamma_1$ do not fall on the extrapolated lines. This might indicate changing conditions in the unexamined region which is unfortunately meager in elements easily available for solid x-ray targets.

The generalizations drawn by the author[6] from the voltage widths of the L-series lines of uranium are somewhat confirmed by the present results. The $L\beta_2$ and $L\gamma_1$ voltage widths agree and it may be more than fortuitous that these lines involve transitions from similar initial and final orbits and the eccentricities of these orbits on the Sommerfeld theory are the same as well as the changes in the quantum numbers. The neighboring values of the voltage widths of $L\alpha_1$ and $L\beta_1$ might be correlated with the fact that the lines involve transitions between energy levels differing only in the magnitude of j but agreeing in changes in quantum numbers and have the same ellipticity of the orbits. It should be pointed out that the conclusion of experimenters[17] working with the photographic method that $L\alpha_1$ is the narrowest L-series line on a wave-length scale is definitely in error.

Parratt[18] has reported changes in the width of Mn $K\alpha_1$ in alloys of Mn–Ni, Mn–Cu and Mn–Cr but no changes in a 50–50 Mn–Fe alloy. In order to see if this effect was evident in the L-series the width of Pb $L\alpha_1$ was examined from various alloys of Pb and Sb. No changes in the width were observed but this might well be due to the fact that the levels here involved are more deeply buried in the atom than the Mn levels investigated by Parratt. Also the alloy chosen might correspond to the Mn–Fe alloy which showed no effect on the width of Mn $K\alpha_1$. All the elements used in the determination of the natural widths shown in Table III were of sufficient purity not to be influenced by this effect except that a layer of oxide might have been on the Tl despite the precautions.

The agreement between the present results and the previous meager results[4, 5] on the natural widths of the L-series lines is not at all good. However, the previous measurements were obtained when the technique of the instrument was just being acquired and it is felt that the disagreement is not to be taken seriously. The better crystals and the more accurate adjustments of the instrument in the present experiments are certain to yield more accurate values for the widths.

In conclusion I wish to express my sincere thanks to Professor S. K. Allison for placing his laboratory at my disposal and for the many favors extended by him in the past few years. I am also indebted to the members of Ryerson Laboratory for the use of their many laboratory facilities and for their helpful interest.

[16] The values for uranium have been recalculated from reference 6 by the same method as the above.

[17] Coster, Zeits. f. Physik **45**, 797 (1927).

[18] L. G. Parratt, Phys. Rev. **44**, 328 (1933).