Widths of the L x-ray lines of the rare-earth elements

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An improved version of a single-crystal high-angle goniometer and a NaI scintillation detector were used to measure the widths of the $L\alpha_{1,2}$, $L\beta_{1-4}$, and $L\gamma_1$ x-ray lines of the elements $58 \leq Z \leq 74$ and the widths of the less prominent lines $L\beta_{15}$, Ll, $L\eta$, and $L\gamma_1'$ of several elements in the same group. The x-ray spectrum of these elements was produced by bombarding them with an electron beam of constant energy and flux, and a computer program was used to unfold the physical widths of their emission lines. These results, as well as the previously reported values of linewidths of the higher-Z elements, are compared with the most recent theoretical predictions.

INTRODUCTION

Experimental measurements of total L-level widths were previously reported for elements of atomic number $Z \geq 73$.[1-4] These results were tabulated by Blokhin.[5] Values of linewidths of several elements of lower atomic numbers were also reported: Parratt studied $_{47}$Ag,[6] Wuilleumier studied $_{36}$Kr and $_{54}$Xe,[7] Krause *et al.* studied $_{40}$Zr,[8] and Yin *et al.* studied several elements between $_{29}$Cu and $_{48}$Cd.[9] Sevier[10] collected most of the experimental data available up until 1969. But no measurements of L-level widths of the rare-earth elements have been previously reported.

Two atomic levels are involved in the production of each x-ray line. If X and Y are the two levels and their level widths are $\Gamma(x)$ and $\Gamma(y)$, respectively, the width of the x-ray line will then be given by

$$\Gamma(x-y) = \Gamma(x) + \Gamma(y). \tag{1}$$

The total natural linewidth is the sum of three components:

$$\Gamma = \Gamma_R + \Gamma_A + \Gamma_C, \tag{2}$$

where Γ_R is the radiative width, Γ_A the Auger width, and Γ_C the Coster-Kronig width. These processes compete in filling a hole in a given level. The lifetime of the hole is related to the natural linewidth by Heisenberg uncertainty,

$$\Gamma\tau \simeq \hbar. \tag{3}$$

Thus, while experimentally one measures Γ, the natural linewidth, theoretical calculations are generally performed separately for each partial level width, and for comparison with experiments one has to sum the three partial widths of each of the two levels involved in the transition.

Radiative widths Γ_R were calculated by Scofield[11] and by Rosner and Bhalla.[12] The Auger widths of the L_1 shell $\Gamma_A(L_1)$ were calculated by McGuire[13] and by Crasemann *et al.*[14] The Auger widths $\Gamma_A(L_2)$ and $\Gamma_A(L_3)$ were calculated by McGuire[13] and by Chen *et al.*[15] The Coster-Kronig partial widths $\Gamma_C(L_1)$ were also calculated by McGuire[13] and by Crasemann *et al.*,[14] and values of $\Gamma_C(L_2)$ were reported in Refs. 13 and 15.

The total widths of the M subshells were calculated by McGuire,[16] and several of their partial widths were reported by Bhalla[17] and by Manson.[18] For lower-Z elements $22 \leq Z \leq 36$, the total widths of the M_1, M_2, and M_3 subshells were calculated by Yin *et al.*[19] The only available theoretical values of the N-subshells widths are those recently reported by Manson[18] and McGuire.[20]

All the previously mentioned theoretical values were collected, analyzed, and presented in graph forms by Rahkonen and Krause.[21] These graphs exhibit values of total and partial widths of the K level, L and M sublevels and several of the N sublevels. Values of level widths were extracted from these graphs and added as indicated in Eq. (1) to obtain theoretical values of total linewidths, which are later compared with the results of this experiment.

EXPERIMENTAL

All the studied elements were metallic foils about 0.13 mm thick and about 99.9% pure. A groove about 0.13 mm deep and about 1 cm wide was milled out of a thick Cu anode, and the studied samples were placed in the groove and secured to the Cu anode by a set-screw arrangement. The design is such that the surface of the sample under investigation and that of the Cu anode are in the same plane and are simultaneously exposed to the exciting electron beam. Thus the L x-ray spectrum of each of the elements studied and the $K\alpha_1$ and $K\alpha_2$ emission lines of Cu were measured under the same experimental conditions. This arrangement enables one to precisely determine any

change in the instrumental response from one setting to the other, while the bulk of the instrumental response at any given wavelength was taken from the most probable values given by the straight line in Fig. 2 of the preceding paper.[22] If in any one measurement the instrumental widths of the Cu $K\alpha_1$ and $K\alpha_2$ slightly differ from their values given in Fig. 2 of Ref. 22, the instrumental width is normalized over the total spectrum of the element studied to account for that difference.

Once the width of the Gaussian instrumental response is obtained, the unfolding of the width of the emission lines was performed by a least-square fitting program similar to the one used in the preceding paper.[22] Thus the experimental line contour is fitted by a five-parameter expression:

$$f(\nu_i) = P_1 + P_2\nu_i + P_3 \int_{-\infty}^{\infty} \int_{\nu_i - s/2}^{\nu_i + s/2} \frac{\exp[-4\ln 2(\xi/\sigma)^2]}{(\nu_i' - P_4 + \xi)^2 + (\frac{1}{2}P_5)^2}\, d\nu'\, d\xi\,, \tag{4}$$

where P_1 is the background, P_2 its slope, P_3 the peak height, P_4 the peak center, and P_5 the linewidth. The slit width s and the instrumental response σ are known quantities.

In cases where two emission lines are close together, the lines were fitted simultaneously by two expressions similar to that given by Eq. (4) and characterized by the same P_1 and P_2. A typical

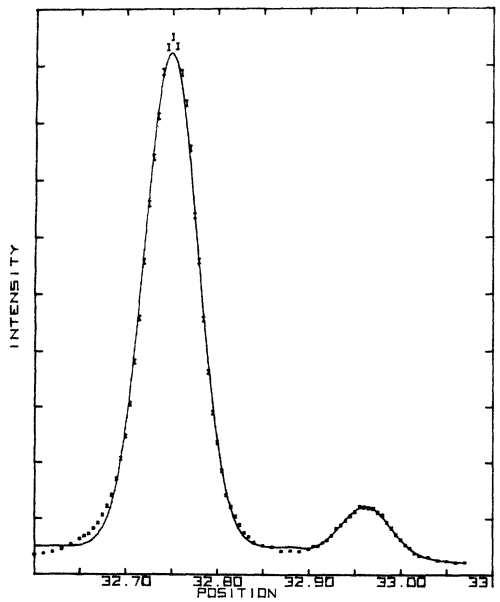

FIG. 1. $L\alpha_1$ and $L\alpha_2$ lines of $_{69}$Tm. The error bars represent statistical errors and the smooth curve is from Eq. (4).

TABLE I. L x-ray linewidths (in eV) of the rare-earth elements.

Elements	$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\beta_3$	$L\beta_4$	$L\gamma_1$	$L1$	$L\eta$	$L\beta_{15}$	$L\gamma_1'$
$_{58}$Ce	3.90±0.31	4.0±0.40	3.27±0.26	7.50±0.75	8.72±0.87	6.76±0.73	6.19±0.62				
$_{59}$Pr	4.21±0.34	4.4±0.44	4.18±0.33	7.60±0.76	9.33±0.93	8.03±0.88	6.50±0.65				
$_{60}$Nd	3.72±0.30	3.96±0.40	3.79±0.30	7.47±0.75	10.9±1.09	7.58±0.83	8.50±0.85				
$_{62}$Sm	3.54±0.28	4.48±0.45	4.20±0.34	7.40±0.74	10.7±1.07		9.54±0.95			17.6±2.64	19.6±2.94
$_{63}$Eu	4.10±0.33	4.06±0.40	4.56±0.36	6.11±0.61	12.2±1.22		8.52±0.85			11.7±1.76	19.6±2.94
$_{64}$Gd	4.87±0.39	4.38±0.44	4.04±0.32	7.26±0.73	11.8±1.18	10.0±1.10	8.42±0.84			10.3±1.03	9.50±1.43
$_{65}$Tb	4.17±0.33	5.03±0.50	4.78±0.38	6.91±0.69	12.0±1.20	9.3±1.02	8.75±0.88		10.9±2.18	8.47±0.85	9.50±1.43
$_{66}$Dy	4.82±0.39	5.03±0.50	5.60±0.45	6.48±0.65		10.8±1.19	6.44±0.64			9.20±1.44	10.0±2.00
$_{67}$Ho	4.86±0.39	5.63±0.56	5.12±0.41	7.75±0.78	11.2±1.12	10.8±1.19	5.70±0.57			8.27±1.65	9.54±1.91
$_{68}$Er	5.13±0.41	5.65±0.45	5.29±0.42	7.41±0.74	12.5±1.25	8.45±0.93	7.28±0.73				
$_{69}$Tm	5.28±0.42	5.83±0.58	5.04±0.40	8.63±0.86	12.3±1.23	10.5±1.16	10.0±1.20	8.1±1.62			
$_{70}$Yb	6.33±0.50	7.50±0.75	6.44±0.52	9.56±0.96	12.7±1.27	9.45±1.04	9.60±1.20	11.1±2.22	9.0±1.80		
$_{71}$Lu	4.59±0.37	6.40±0.64	6.69±0.54	8.52±0.85	11.1±1.11	12.3±1.35	7.32±0.73	9.8±1.96	8.4±1.68		
$_{72}$Hf	5.67±0.45	5.59±0.56	7.68±0.61	8.75±0.88	12.2±1.22	10.2±1.12	7.42±0.74	11.9±2.38	15.3±3.06		
$_{73}$Ta	5.20±0.42	5.41±0.54	7.62±0.61	8.54±0.85	11.0±1.10	12.3±1.35	8.34±0.83	10.9±2.18	11.2±2.24		
$_{74}$W	7.89±0.63	5.27±0.53	7.82±0.63	9.26±0.93	12.6±1.26	13.2±1.45	10.2±1.02	13.9±2.78	14.0±2.8		

spectrum is shown in Fig. 1. The rest of the experimental setup and experimental techniques are those described in the preceding paper.[22]

RESULTS AND DISCUSSIONS

The measured values of linewidths are given in Table I. Values reported in the first seven columns of this table are plotted as functions of atomic numbers in Fig. 2. They are presented in this format for comparison and to avoid confusion. Also plotted in this figure are the experimental values from Blokhin's tables[5] for elements with $Z \geq 73$. The few values reported for lower-Z elements were excluded, but the extrapolations of Sevier,[10] which are based on the experimental values that were available to him (1969), are shown as dashed lines. The theoretical values shown in this diagram (solid line) are those tabulated by Keski-Rahkonen and Krause.[21]

The errors quoted in Table I and shown as error bars in Fig. 2 are statistical errors obtained from the error matrix of the least-squares-fit program. These vary from a low of about 8% in the case of $L\alpha_1$ and $L\beta_1$ to as much as 20% for some of the values quoted for $L\beta_{15}$ and $L\gamma_1'$.

Our experimental values and those tabulated by Blokhin generally are in agreement except in the case of $L\beta_4$ where our values and the extrapolation of Sevier agree within experimental error, but are generally lower than Blokhin's. Sevier's extrapolated values[10] generally agree with the results of this experiment: The values of the $L\beta_3$ linewidths obtained in this experiment are lower than Sevier's values. Of significance is the deviation between the extrapolated values and the present experimental results in the case of $L\beta_2$ and $L\gamma_1$ in the neighborhood of $Z = 60$, where our experimental values are considerably higher. Here the $L\beta_2$ and $L\beta_{15}$ as well as the $L\gamma_1$ and $L\gamma_1'$ begin to merge together and become hard to resolve. Although similar physical conditions exist around $Z = 70$, here the deviation between Sevier's values and actual experimental values is not as pronounced as that observed at lower Z.

The values reported in the last four columns of Table I were not plotted. The widths of these lines were measured for a few elements and these were too close together to establish with any certainty the dependence of these values on atomic number. One should note the abnormally large values of the widths of the recently observed[23,24] $L\beta_{15}$ and $L\gamma_1'$ emission lines for the elements $_{62}$Sm and $_{63}$Eu. It is quite possible that each one of these structures includes more than one emission line.[24]

Except for values of $L\alpha_1$ linewidths, the theoretical predictions are considerably higher than the experimental values; for example, they are twice as large in the case of $L\beta_2$ and $L\gamma_1$ around $Z = 70$. Although the theoretical values presented in Fig. 2 by solid lines are the sums of partial widths calculated by several different authors using different approaches, it is possible that the disagreement between theory and experiment is to a large extent the result of the large values of M- and N-subshells partial widths reported in the extensive work of McGuire.

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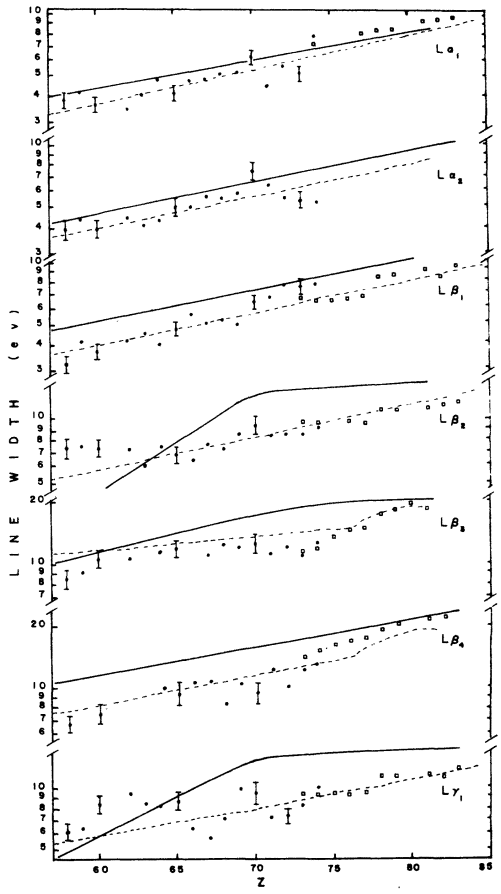

FIG. 2. Widths of the indicated L emission lines plotted as functions of atomic numbers. The open squares are from Ref. 5. The dashed lines are from Ref. 10. The solid lines are from Ref. 21, and the solid dots are the results of the present work.

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