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Precise measurement of the widths of some L x-ray lines of tungsten

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The widths of the L x-ray lines $L\alpha_1$, $L\alpha_2$, $L\beta_1$, and $L\gamma_1$ of tungsten have been measured to an accuracy of 4—6 % with a high-resolution 90-cm-radius bent crystal Cauchois spectrograph, with the use of the photographic-photometric method. The measured values have been compared with those of earlier workers as well as with those obtained from theoretical self-consistent-field calculations. Our values of the $L\alpha_1$ and $L\alpha_2$ widths are in good agreement with those deduced from the recent Dirac-Hartree-Slater estimates of Chen *et al.* for the L and M subshells. Contrary to results of earlier workers, the width in eV of the $L\beta_1$ line is found to be larger than that of the $L\alpha_1$ line, a result which is in conformity with theoretical predictions. On the other hand, our measured value of the width of the $L\gamma_1(L_2N_4)$ line does not agree with the results of earlier workers, but is in fair agreement with the nonrelativistic estimate of McGuire. The need for a relativistic calculation of the N subshell widths therefore seems to be indicated.

I. INTRODUCTION

Apart from apparatus broadening which, depending upon the case, can be corrected for, or reduced to negligible proportions, the full width at half maximum (FWHM) of an x-ray spectrum line, as it is experimentally observed, arises from (i) lifetime broadening, (ii) hyperfine interactions, (iii) multiplet splitting, and (iv) solid-state and chemical effects. Of these, lifetime broadening is the most important and the largest contributory factor. Hyperfine effects are extremely small and have been successfully measured only recently using very sophisticated instrumentation.[1,2] Except for light elements, solid-state and chemical effects are unimportant for lines arising from transitions involving inner atomic levels. Broadening effects due to multiplet splitting become negligible for the deeper levels in heavy atoms. Thus for suitably chosen x-ray lines, the width arises mainly from lifetime broadening and is equal to the sum of the widths of the participating levels. The width of a level is a direct consequence of the Heisenberg uncertainty relation $\Gamma\tau=\hbar$, where τ is the lifetime of the level and is equal to the reciprocal of the total transition rate of filling the hole characterizing the level. Neglecting the "exotic" decay modes such as two-photon emission and radiative and double Auger processes[3] for which the transition rates are very small, the total transition rate may be written as the sum of the radiative, Auger, and Coster-Kronig transition rates. One can therefore write for the width of a level

$$\Gamma=\Gamma_R+\Gamma_A+\Gamma_C ,$$

where Γ_R is the radiative width, Γ_A is the Auger width, and Γ_C is the Coster-Kronig width.

In recent years, considerable progress has been made in the self-consistent-field (SCF) calculation of transition rates, both radiative as well as nonradiative, in atoms having an inner-shell vacancy. Thus radiative transition rates in atoms having vacancies in K, L, and M shells have been calculated using the relativistic Hartree-Slater model.[4–6] Although nonradiative SCF transition rates have been calculated by several authors,[7] only a few relativistic calculations of these rates[8,9] were available so far. However, a series of papers[10–14] have recently appeared dealing with the calculation of Auger and Coster-Kronig transition rates using the Dirac-Hartree-Slater (DHS) approach.

Now it is well known that nonradiative transition rates are very sensitive to the choice of the wave function and the energy of the emitted electron, the type of coupling assumed, and neglect or otherwise of relativity. In this context, the importance of experimentally measuring x-ray linewidths has been repeatedly stressed,[7,15] because linewidth measurements can constitute a valuable check on the correctness or otherwise of the various assumptions made in the theoretical calculation of different types of transition rates.

With a 1-m-radius bent crystal spectrograph constructed by Frilley[16] at the Laboratoire Curie, Paris, and using the photographic-photometric method, Gokhale[17] measured in 1950 the FWHM of the $K\alpha_1$ and $K\alpha_2$ lines of elements $_{37}$Rb to $_{50}$Sn. He showed that this method gives widths which are actually smaller than those given by the two-crystal spectrometer. This was confirmed subsequently by the work of Meisel and Nefedow.[18] Chen *et al.*[19] used the widths measured by Gokhale to obtain semiempirical estimates of the L_2- and L_3-shell fluorescence yields which were found to be in excellent agreement with purely theoretical estimates of these quantities. These experimental widths also agree well with the "most probable values" published by Salem and Lee,[20] with the semiempirical widths reported by Krause and Oliver,[21] and with the recent relativistic estimates of Chen *et al.*[11,14]

With a view to extending the domain of comparison between theory and experiment, it was thought interesting to use the bent-crystal method for measuring the L-series linewidths in heavy elements for some of which detailed relativistic SCF calculations[13,14] have recently become available. As part of this program, we report in the present paper the results of our measurement of the widths of the $L\alpha_1$, $L\alpha_2$, $L\beta_1$, and $L\gamma_1$ lines of tungsten.

II. EXPERIMENTAL DETAILS AND RESULTS

We use a Beaudouin B-80 demountable x-ray tube with a tungsten target as the source of radiation and a 90-cm-radius curved mica (100) crystal spectrograph in Cauchois geometry, giving a dispersion of about 5.5 mÅ/mm. The convex and concave blocks of the crystal holder of our spectrograph were machined at the workshop of the California Institute of Technology, and the curvature of the convex block was optically found to be uniform correct to one fringe width when it was used to form straight Newton's fringes.

The details of the spectrograph and its adjustments have been described earlier.[22]

The density of blackening of the photographic film is not linearly related to the exposure. Therefore in the photographic-photometric method for measuring the FWHM of a spectrum line, it is necessary to have a reference level of blackening which would correspond to half the intensity of the peak of the spectrum line so that its FWHM could be read off at this level on the microphotometer record. For the measurement of the FWHM of the $K\alpha_1$ line, for example, this reference level is provided by the peak of the $K\alpha_2$ line which, while lying sufficiently close to the $K\alpha_1$ line so as to have the same density-exposure relationship, is nevertheless not so close as to distort its intensity profile. No such reference is available for L-series lines. We therefore used the following method which has been briefly described earlier.[23]

The central part of the line is photographed on the single-coated x-ray film, which has a height of 2.5 cm. The total height of the line being 9 cm, its upper portion is made to enter a scintillation counter through a narrow slit. The counter is followed by a single-channel pulse-height analyzer (window corresponding to about 30 mÅ on either side of the line) and a scaler. With the x-ray tube operating at 30 kV, 5 mA, a suitable exposure is given, noting simultaneously the total number of counts, say N, in the scaler. The film holder is then displaced parallel to itself through a small distance, and the film is again exposed, at the same ratings of the x-ray tube, until the number of counts become $N/2$, so that we have side by side on the same film two impressions of the same line, one with half the intensity of the other, with both the lines standing on the same background. This procedure eliminates the errors which could arise from fluctuations in the operating conditions of the x-ray tube in spite of the best manual efforts to keep the x-ray tube running at the same ratings throughout the experiment. The exposure time for the more intense line is chosen in such a way that the density of blackening for both the exposures lies in the linear part of the characteristic curve of the film. The film is then microphotometered with magnification $50\times$ and the width of the more intense profile is measured on the microphotometer record at the level of the peak of the less intense profile. For converting the width in mÅ the dispersion is measured in mÅ/mm on the same microphotometer record. Using this procedure we have measured the widths of the $L\alpha_1$, $L\alpha_2$, $L\beta_1$, and $L\gamma_1$ lines of $_{74}$W.

During the entire course of these measurements, care was taken to verify from time to time that the bent crystal remained at the best level of performance as regards its focusing characteristics. For this we periodically measured the FWHM of the $_{42}$Mo$K\alpha_1$ line. Each measurement gave a result closely agreeing with that obtained by Gokhale[17] ($\Delta\lambda = 0.26$ mÅ) in 1950.

For each of the lines, some eight to ten photographs were taken, and each photograph was microphotometered three times at different heights. Thus each of our results represents an average of at least 24 individual measurements. A typical microphotometer record, showing the profiles for the full- and half-intensity lines is shown in Fig. 1 for the W$L\alpha_1$ line. All the microphotometer records were taken with Carl Zeiss microphotometer model GII BII coupled with recorder GI BI. The width of the exploring slit was kept between 0.02 and 0.03 mm. The results of our measurements are given in Table I. The errors given are the standard deviations about the mean values.

Strictly speaking these widths ought to be corrected for the various instrumental broadening effects,

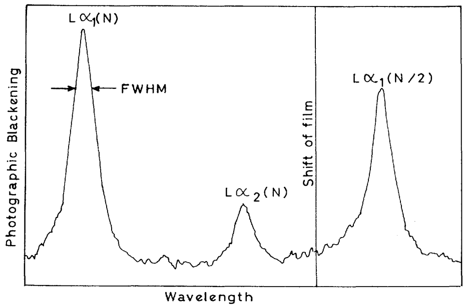

FIG. 1. Microphotometer record of the full-intensity $_{74}$W $L\alpha_1,\alpha_2$ lines and the half-intensity $_{74}$W $L\alpha_1$ line. N and $N/2$ refer, respectively, to the number of counts corresponding to the full- and half-intensity exposures.

namely, broadening due to crystal diffraction, the aperture and height of the crystal, etc. Using the expressions given by Cauchois,[24] we find that for our spectrograph the linear spread on the photographic film arising from the focusing defect due to the effective aperture of the crystal is equal to 4.19×10^{-5} mm, while that due to the effective height of the crystal is 1.65×10^{-3} mm for the wavelength of the $L\alpha_1$ line. These values are entirely negligible in comparison with the broadening due to crystal diffraction which, as calculated from Darwin's formula,[25] amounts to 0.012 mm or 0.07 mÅ. If it is assumed that the x-ray line and the broadening function for crystal diffraction both have the Gaussian shape, this would lead to an entirely negligible correction. On the other hand, if a Lorentzian shape is assumed for both, the correction would amount to 0.07 mÅ, which is about 6% of the width measured by us for the $L\alpha_1$ line. In the actual experimental situation, the correction is expected to lie in between these two extremes and should be very small. Finally, the width of the exploring slit of the microphotometer is some 2% of the width of the line which, in our instrument, is projected in the plane of the slit with magnification 6×. The additional broadening of the recorded microphotometric profile caused by microphotometer slit width is thus entirely negligible.[26] In view of the fact that the exact nature of the broadening function is not known for the method used by us, we have preferred to give in Table I our measured values *without any correction* for instrumental broadening effects which, in any case, are quite small. However, our value for $L\alpha_2$ has been corrected for the overlap of $L\alpha_1$ assuming both line shapes to be Lorentzian.

III. COMPARISON WITH OTHER MEASUREMENTS AND THEORETICAL CALCULATIONS

In Table II, we compare our results with those of earlier workers[23,27–29] as well as with theoretical estimates.[13,14,30–32]

(i) $L\alpha_1$ *line.* It is seen that our measured value of the width of this line is smaller than that reported by all the earlier workers. It is also smaller than that obtained earlier in this laboratory by Gokhale and Srivastava.[23] We attribute the improved result to the special care taken during the present investigation in mounting the bent crystal as well as to a more careful adjustment of the distance between the crystal and the photographic film. Our measured value is in good agreement with the theoretical relativistic estimate of Chen *et al.*[13,14] as well as with the nonrelativistic value of McGuire.[31]

(ii) $L\alpha_2$ *line.* The width of this line has been measured earlier only by Salem and Lee.[29] However, their value appears to be unrealistic inasmuch as the width of $L\alpha_2(L_3M_4)$ is expected to be larger than that of $L\alpha_1(L_3M_5)$ in view of the larger width of the M_4 level as compared to the M_5 level. A glance at the $L\alpha_1$ and $L\alpha_2$ widths measured by these authors for the elements $_{58}$Ce to $_{74}$W shows erratic trends as regards the relative magnitudes of the two widths. This is presumably due to the low resolution of the single crystal instrument used by them.

Our value of the $L\alpha_2$ width agrees exactly with the calculation of Chen *et al.*[13,14] While this exact agreement may be fortuitous, the difference of the

TABLE I. Measured widths of the L x-ray lines of tungsten.

Line	Transition	λ (mÅ)[a]	Δλ (mÅ)	Γ (eV)[b]
$L\alpha_1$	L_3M_5	1476.47	1.16±0.05	6.61±0.28
$L\alpha_2$	L_3M_4	1487.460	1.19±0.07	6.68±0.39
$L\beta_1$	L_2M_4	1281.841	0.97±0.04	7.33±0.30
$L\gamma_1$	L_2N_4	1098.61	1.29±0.07	13.28±0.72

[a]Reference 33.
[b]These values were obtained by applying the conversion factor recommended in Ref. 34, namely, $\Gamma(\text{eV})=12398520\ \Delta\lambda(\text{mÅ})/[\lambda(\text{mÅ})]^2$ to the actual values of Δλ (mÅ) and not to the rounded-off values given in column four.

TABLE II. Comparison of measured L x-ray linewidths of tungsten with earlier measurements and theoretical estimates. The units are eV.

Authors	$\Gamma(L\alpha_1)$	$\Gamma(L\alpha_2)$	$\Gamma(L\beta_1)$	$\Gamma(L\gamma_1)$
Williams[a]	7.16		7.11	10.4
Cooper[b]			6.5	9.3
Salem and Lee[c]	7.89±0.63	5.27±0.53	7.82±0.63	10.2±1.02
Gokhale and Srivastava[d]	6.83±0.11			
Present work	6.61±0.28	6.68±0.39	7.33±0.30	13.28±0.72
McGuire[e]	6.45[f]	7.86[g]	9.12[f]	13.80[h]
Chen *et al.*[i]	6.642[j]	6.680[k]	6.689[l]	

[a]Reference 27.
[b]Reference 28.
[c]Reference 29.
[d]Reference 23.
[e]References 30—32.
[f]From Ref. 31.
[g]Obtained from $\Gamma(L\alpha_2)=\Gamma(L\beta_1)-\Gamma(L_2)+\Gamma(L_3)$ with $\Gamma(L\beta_1)$ from Ref. 31 and $\Gamma(L_2)$, $\Gamma(L_3)$ from Ref. 30.
[h]Obtained by adding $\Gamma(L_2)$ from Ref. 30 and $\Gamma(N_4)$ from Ref. 32.
[i]References 13 and 14.
[j]Obtained by adding $\Gamma(L_3)$ from Ref. 14 and $\Gamma(M_5)$ from Ref. 13.
[k]Obtained by adding $\Gamma(L_3)$ from Ref. 14 and $\Gamma(M_4)$ from Ref. 13.
[l]Obtained by adding $\Gamma(L_2)$ from Ref. 14 and $\Gamma(M_4)$ from Ref. 13.

M_4 and M_5 level widths as deduced from the difference between our measured $L\alpha_1$ and $L\alpha_2$ widths (0.07 eV) is in good agreement with the relativistic calculation of Chen *et al.*[13] (0.038 eV). The difference of the M_4 and M_5 level widths can also be computed from McGuire's theoretical estimates for the widths of the L_2 and L_3 levels and $L\alpha_1$ and $L\beta_1$ linewidths for tungsten. According to McGuire,[31] $\Gamma(L\alpha_1)=6.45$ eV and $\Gamma(L\beta_1)=9.12$ eV, which gives

$$[\Gamma(L_2)+\Gamma(M_4)]-[\Gamma(L_3)+\Gamma(M_5)]=2.67$$

(in eV). But in another paper,[30] McGuire has calculated $\Gamma(L_2)=5.91$ eV and $\Gamma(L_3)=4.65$ eV. Combining these results we get 1.41 eV for the difference of M_4- and M_5-level widths. This is much larger than that deduced from our experimental values as well as from the theoretical values of Chen *et al.* It would thus appear that as far as the M_4 and M_5 levels are concerned, much better agreement with experiment is obtained when relativity is taken into account.

(iii) $L\beta_1$ *line.* On theoretical grounds, the width in eV of the $L\beta_1(L_2M_4)$ line should be larger than that of the $L\alpha_1(L_3M_5)$ line. Our experimental values corroborate this for the first time. All earlier workers have reported $\Gamma(L\beta_1)<\Gamma(L\alpha_1)$. This must of course be attributed to some unsuspected experimental errors in their measurements. In particular, it may be mentioned that as pointed out by Salem and Lee,[20] Cooper,[28] who has measured the widths with a two-crystal spectrometer, has overcorrected his observed widths for instrumental response.

The difference $\Gamma(L_2)-\Gamma(L_3)$ between the widths of the L_2 and L_3 levels, as deduced from our measured widths of the $L\beta_1(L_2M_4)$ and $L\alpha_2(L_3M_4)$ lines, comes out to be 0.65 eV. Compared to this the relativistic calculation of Chen *et al.*[14] leads to the surprisingly small value of 0.009 eV for this difference, while nonrelativistic calculations of McGuire[30] and Chen *et al.*[19] give 1.26 and 0.227 eV, respectively. Thus experiment, relativistic calculations, and nonrelativistic calculations do not agree with one another. In this connection, it would be interesting to obtain another experimental estimate of the $\Gamma(L_2)-\Gamma(L_3)$ difference through measurement of the widths of the $L\eta(L_2M_1)$ and $Ll(L_3M_1)$ lines. We plan to carry out these measurements in the near future.

(iv) $L\gamma_1$ *line.* Our value of the width of this line is distinctly larger than the values of all the earlier workers. When the first results were obtained, we suspected that the larger width might be due to an impairment in the focusing properties of the bent crystal. To check this, we measured the FWHM of Mo $K\alpha_1$, but we again obtained a value agreeing closely with our earlier measurement of 0.26 mÅ, thus showing that the focusing properties of the bent crystal had not deteriorated. Having ensured this, several more measurements of $\Gamma(L\gamma_1)$ were made. The result quoted in Table I is thus the mean of some 60 independent measurements. It would thus appear that some unsuspected errors have crept into the measurements of earlier workers. McGuire[32] has computed N subshell level widths. For tungsten he finds $\Gamma(N_4)=7.89$ eV. When this is added to his $\Gamma(L_2)=5.91$ eV[30] for $_{74}$W, one gets $\Gamma(L\gamma_1)=13.80$ eV, which is in fair agreement with our experimental value of 13.28 eV. In this connection the need for relativistic calculation of N subshell level widths seems to be definitely indicated.

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