Precise measurements of $K\alpha$ x-ray linewidths in Eu, Tm, and Ta

K.-C. Wang, A. A. Hahn, and F. Boehm
California Institute of Technology, Pasadena, California 91125
(Received 14 December 1977)

The widths of $K\alpha_1$ and $K\alpha_2$ x rays in Eu, Tm, and Ta have been measured to an accuracy of (2–4)% with a high-resolution spectrometer by means of third- and fourth-order diffraction from the (111) crystalline planes of a bent silicon crystal. The measured values confirm the results from calculations of the radiative, Auger, and Coster-Kronig widths. Possible effects from hyperfine interaction, Coulomb exchange interaction, and chemical shift are discussed.

I. INTRODUCTION

It is well known that the atomic-level width, constituting a measure of the refilling rates of an electron hole, can be separated into radiative width, Auger width, and Coster-Kronig width. In recent years several calculations for these partial widths have been published.[1-5] Only few precise measurements of atomic-level widths[6-8] are available to serve as critical tests of the calculations. As the width of an x-ray line is the sum of the widths of the two levels connected by the transition, a careful study of x-ray linewidths provides a direct way to test the calculations of the partial widths.

Investigations of the linewidths can be accomplished with the help of a high-resolution diffraction crystal spectrometer. It should be remembered that the diffraction profile is a convolution of the Lorentzian x-ray profile and the instrumental response.[9,10] In a Cauchois-type spectrometer the instrumental width, in wavelength units, stemming from the crystal resolution and the size of the detector slit, is the same for different orders n of diffraction. On the other hand, the width of the Lorentzian x-ray profile is proportional to the order n. This renders the unfolded Lorentzian width relatively insensitive to the exact instrumental line profile and thus allows a precise determination of the x-ray width. Dannhäuser and Wiech[11] have previously used the method of different orders to determine the wavelengths and linewidths of the $M\xi$ x rays ($M_{4,5}N_{2,3}$) of elements ^{38}Sr to ^{47}Ag.

In the present paper we describe linewidth measurements of the $K\alpha_1$ $K\alpha_2$ x rays in three medium heavy atoms, Eu, Tm, and Ta. These atoms were selected for reasons of convenience. In each case a long-lived strong radioactive source can be prepared emitting x rays, and in the case of Eu and Tm also γ rays. The γ rays may serve as a convenient probe for obtaining the instrumental resolutions.

II. EXPERIMENT

The experimental setup shown schematically in Fig. 1 has been described in Ref. 12. A Si monocrystal was cut, ground, and polished with the (111) planes perpendicular to the surface. The interplaner spacing is 3135 mÅ. The finished slab had a size of 5×4 cm^2 and a thickness of 1.4 mm. It was imprisoned between two bending blocks and bent to a radius of 2 m.

For the Eu measurements a 1.5-Ci ^{153}Gd (oxide) electron-capture source was used, emitting both Eu K x rays and a calibrating γ ray of 97.43 keV. This γ ray is reflected in seventh order at a Bragg angle of 8.17°, which is very close to the $n=3$ Bragg angles of Eu $K\alpha_1$ and $K\alpha_2$ x rays (8.21° and 8.34°, respectively). The use of the same source at a fixed position for both, the spectrometer linewidth calibration and the x-ray linewidth determination, completely eliminates aberrational errors (vertical divergence and crystal irregularities).

To obtain the instrumental width the γ-ray data were computer fitted to a Gaussian function with centroid, peak height, and width as variable parameters. In the fit (and also in the x-ray data fit) we assumed a linear background with variable elevation and slope. The x-ray data were then fitted by the convolution of a Lorentzian function and a Gaussian function with the Gaussian width fixed as determined by γ-ray calibration. From the fit the Lorentzian width was extracted.

In the Tm measurements a 1.5-Ci ^{169}Yb (oxide)

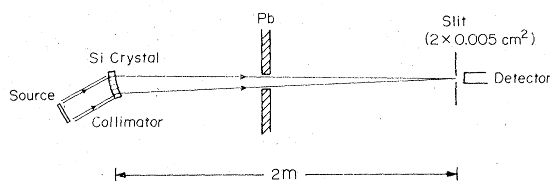

FIG. 1. Diagram of setup.

© 1978 The American Physical Society

TABLE I. Measured linewidths and comparisons (in eV).

	$K\alpha_1$				$K\alpha_2$			
Element	Present	Expt. Ref. 10 [a]	Least-squares-fitted values Ref. 13 [b]	Calc.	Present	Expt. Ref. 10 [a]	Least-squares-fitted values Ref. 13 [b]	Calc.
$_{63}$Eu	24.8(0.4)	···	27.7	24.96	26.3(0.5)	22.2	26.3	25.22
$_{69}$Tm	34.4(0.7)	···	39.7	34.64	35.6(0.8)	36.9	38.0	34.85
$_{73}$Ta	42.9(1.1)	42.4	46.5	42.60	43.4(1.9)	36.4	46.1	42.83

[a] Errors were given as ±6 %.
[b] Errors were estimated to be about ±10 %.

electron-capture source produced both x rays and γ ray. In a similar manner to the Eu case the fourth-order diffraction peak of the 63.119-keV γ ray was used to calibrate the instrumental width, while the x-ray lines were measured in third order.

The Ta K x rays were obtained with a 0.2-Ci ^{181}W (metal) electron-capture source. The x rays were measured in fourth order and compared with a 59.537-keV γ ray from a 0.3-Ci ^{241}Am source, also reflected at $n=4$. Since two different sources were used in this case, the active source position was defined with the help of a lead diaphragm, 0.95 cm in diameter.

The results are shown in Table I. The quoted errors consist of the fitting error of the Lorentzian width as well as that of instrumental width. All these line fits have χ^2 values of about 1 per degree of freedom except for the γ-ray line in Tm where the statistical accuracy was so high that a χ^2 value of 25 per degree of freedom was obtained.

To test the dependence of the measured x-ray line widths on the γ-ray line shape we also fitted the γ-line profile in Tm to the sum of two Gaussian functions, whereby the relative amplitudes, separation, and common width were allowed to vary. The χ^2 value decreased to 6 per degree of freedom. However, the unfolded Tm $K\alpha_1$ x-ray linewidth changed only by 0.1% which is negligible compared with the quoted errors in Table I. Therefore, we conclude that a single Gaussian line fit gives an adequate description of the instrumental response.

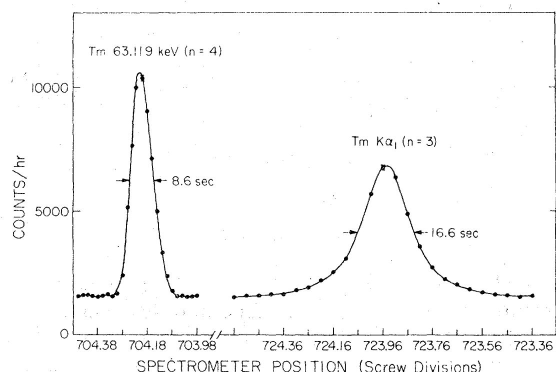

FIG. 2. Data run and fit for the Tm $K\alpha_1$ case. Points represent data. Solid line represents fitted function.

A data run and a fit for the Tm $K\alpha_1$ case are shown in Fig. 2. Here the instrumental width is $\Delta\theta = 8.6$ sec arc, and the unfolded Lorentzian width is $\Delta\theta = 16.6$ sec arc.

III. COMPARISONS AND DISCUSSION

The x-ray linewidths measured by Nelson *et al.*,[10] the least-squares-fit values by Salem and Lee,[13] and the calculated values are shown in Table I for comparisons.

Nelson *et al.*, using a Cauchois-type 2-m-radius bent crystal spectrometer, have measured the first-order diffraction peaks off the (310) planes of a quartz crystal. Their instrumental resolution was roughly equal to the x-ray linewidth. The errors in their measurement were estimated to be ±6%. Our results agree well with theirs for Ta $K\alpha_1$ and Tm $K\alpha_2$, but do not agree for Eu and Ta $K\alpha_2$ lines.

Salem and Lee have determined the K and L x-ray linewidths for elements from $Z=20$ to $Z=96$ by constructing least-squares computer fits to the available experimental points. The errors of their results were estimated to be about 10%. Our values agree with theirs within the 10% error.

The calculated values in Table I are combinations of theoretical calculations and empirically fitted results. We used the K, L_2, and L_3 emission rates calculated by Scofield[1,2] and the L-level radiationless widths calculated by Chen *et al.*,[4] and interpolated for our Z values. The K fluorescence yields used were determined empirically by Bambynek *et al.*[14] Details are shown in Table II.

TABLE II. Details for calculated linewidths (in eV).

Element	Radiative width $\Gamma_{K,R}$ (Ref. 1)	$\Gamma_{L2,R}$ (Ref. 2)	$\Gamma_{L3,R}$ (Ref. 2)	Auger width $\Gamma_{L2,A}$ (Ref. 4)	$\Gamma_{L3,A}$ (Ref. 4)	C-K width $\Gamma_{L2,C}$ (Ref. 4)	K fluorescence yield ω_K (Ref. 14)	K x-ray $\Gamma_{K\alpha_1}$	Width [a] $\Gamma_{K\alpha_2}$
$_{63}$Eu	19.55	0.636	0.581	3.02	3.38	0.57	0.931	24.96	25.22
$_{69}$Tm	28.60	1.003	0.908	3.10	3.56	0.58	0.948	34.64	34.85
$_{73}$Ta	36.10	1.328	1.186	3.14	3.65	0.60	0.956	42.60	42.83

[a] $\Gamma_{K\alpha_1}=\Gamma_{K,R}/\omega_K+\Gamma_{L3,R}+\Gamma_{L3,A}$; $\Gamma_{K\alpha_2}=\Gamma_{K,R}/\omega_K+\Gamma_{L2,R}+\Gamma_{L2,A}+\Gamma_{L2,C}$.

In deriving x-ray linewidths with high accuracy from the experimental profiles, it is necessary to give consideration to several effects that cause line broadening. These effects and their magnitudes are discussed below.

A. Hyperfine interaction

After generation of a 1s hole the energy level of the remaining 1s electron will split into two components due to the magnetic hyperfine interaction. The 1s level splitting causes the emission of K x rays of two slightly different energies, thus broadening the measured x-ray line.[15,16] In our measurements the K x rays are emitted following electron capture. A rough estimate of the difference δ of the hyperfine levels gives $\delta\sim 1-2$ eV. It is found numerically that the width of the sum of two Lorentzian functions, with a common width Γ and a separation δ ($\delta/\Gamma \ll 1$) is larger than Γ by about δ^2/Γ which amounts to less than 0.1 eV in our case.

B. Coulomb exchange interaction

Measurements of $K\alpha$ and $K\beta$ x rays (in Refs. 17–19) of 3d transition metals are known to exhibit a pronounced asymmetry of the line profile. The reason for this asymmetry has not been fully understood yet.[17-20] Tsutsumi[18] has attributed this asymmetry to the exchange interaction of 3d and 3p (or 2p) electrons, splitting the final state by an amount ΔE. His calculations agree with the observed values for the elements Mn, Fe, and Co where this asymmetry effects are largest. In a similar manner we have calculated the exchange integral

$$\langle 4f(1)2p(2)|e^2/r_{12}|4f(2)2p(1)\rangle$$

for Eu and found the energy split ΔE to be less than 0.01 eV. Furthermore, by examining the difference between data points and (symmetric) fit function along the Eu $K\alpha_1$ profile, we could rule out a significant asymmetry of the line profile.

C. Chemical and isotope shifts

If the sources contain different chemical compounds or nuclear isotopes, the energy shift[21] of x rays may also broaden the measured x-ray linewidth. The sources we used are all single chemical compounds (oxide in Eu, Tm, and metal in Ta) and single isotopes (^{153}Eu, ^{169}Tm, and ^{181}Ta), and it seems at first that these effects do not exist in our cases. However, a closer look reveals the following complications:

In the Eu case, we note that about 50% of electron capture of Gd_2O_3 is accompanied by internal conversion. While ^{153}Gd is three valent, immediately following electron capture, the resulting Eu K x ray is emitted while the Eu atom is in a two-valent state. The Eu K x ray accompanying the internal conversion however is emitted after the Eu atom has returned to its normal three-valent oxide state, and thus is shifted with respect to the former x ray as confirmed by recent experiment.[22] The contribution from this chemical shift which was measured[23] to be 0.64 eV gives rise to a line broading of $\delta^2/\Gamma\approx 0.02$ eV. Similar arguments can be made for the other lines. However, the direct influence on the transition rates due to chemical structure and nuclear charge distribution needs further investigation.[24]

We conclude that there is excellent agreement to within our accuracy of (2–4)% between the present results and the calculations. Broadening effects have been shown to be negligible. Comparisons with the measurements of Nelson and co-workers and with least-squares-fit values by Salem and Lee are given.

ACKNOWLEDGMENTS

We wish to thank H. Henrikson for helping in the experiment and Professor P. Lee and Professor P. Vogel for valuable discussions. We also wish to thank Professor P. Van Assche for generously providing the silicon crystal. This work was supported by the Department of Energy under Grant No. EY-76-C-03-0063.

[1]J. H. Scofield, Phys. Rev. A 9, 1041 (1974); At. Data Nucl. Data Tables 14, 121 (1974).
[2]J. H. Scofield, Phys. Rev. A 10, 1057 (1974).
[3]V. O. Kostroun, M. S. Chen, and B. Crasemann, Phys. Rev. A 3, 533 (1971).
[4]M. H. Chen, B. Crasemann, and V. O. Kostroun, Phys. Rev. A 4, 1 (1971).
[5]E. J. McGuire, Phys. Rev. A 3, 587 (1971); in *Atomic Inner Shell Processes*, edited by B. Crasemann, (Academic, New York, 1975), Vol. I, p. 317.
[6]L. I. Yin, I. Adler, T. Tsang, M. H. Chen, D. A. Ringers, and B. Crasemann, Phys. Rev. A 9, 1070 (1974).
[7]M. H. Chen, B. Crasemann, L. I. Yin, T. Tsang, and I. Adler, Phys. Rev. A 13, 1435 (1976).
[8]M. O. Krause, in *Atomic Inner Shell Processes*, edited by B. Crasemann (Academic, New York, 1975), Vol. II, p. 33.
[9]P. L. Lee, Nucl. Instrum. Meth. 144, 363 (1977).
[10]G. C. Nelson and B. G. Saunders, J. Phys. Suppl. No. 10, 32, C4-97 (1971); Phys. Rev. 187, 1 (1969); Phys. Rev. A 2, 542 (1970).
[11]G. Danhaüser and G. Wiech, Phys. Lett. 35A, 208 (1971).
[12]R. B. Chesler and F. Boehm, Phys. Rev. 166, 1202 (1968); S. K. Bhattacherjee, F. Boehm, and P. L. Lee, *ibid.* 188, 1919 (1968); P. L. Lee and F. Boehm, Phys. Lett. 35B, 33 (1971).
[13]S. I. Salem and P. L. Lee, At. Data Nucl. Data Tables 18, 233 (1976).
[14]W. Bambynek, B. Crasemann, R. W. Fink, H.-U. Freund, H. Mark, C. D. Swift, R. E. Price, and P. V. Rao, Rev. Mod. Phys. 44, 716 (1972).
[15]G. L. Borchert, P. G. Hansen, B. Jonson, H. L. Ravn, O. W. B. Schult, P. Tidemand-Petersson, and the ISOLDE collaboration, Phys. Lett. 63A, 15 (1977).
[16]A. S. Ryl'nikov, A. I. Egorov, G. A. Ivanov, V. I. Marusenko, A. F. Mezentsev, A. I. Smirnov, O. I. Sumbaev, and V. V. Fedorov, Sov. Phys. JETP 36, 27 (1973).
[17]P. L. Lee and S. I. Salem, Phys. Rev. A 10, 2027 (1974).
[18]K. Tsutsumi, J. Phys. Soc. Jpn. 14, 1696 (1959).
[19]B. Ekstig, E. Källne, E. Noreland, and R. Manne, Phys. Scr. 2, 38 (1970).
[20]V. I. Nefedov, Bull. Acad. Sci. USSR, Phys. Ser. 28, 724 (1964); J. Struct. Chem. 5, 603 (1964); 7, 672 (1966).
[21]F. Boehm, in *Atomic Inner-Shell Processes*, edited by B. Crasemann (Academic, New York, 1975), Vol. I, p. 411.
[22]A. A. Hahn, K.-C. Wang. F. Boehm, and P. Vogel (unpublished).
[23]E. V. Petrovich, Y. P. Smirnov, V. S. Zykov, A. I. Grushko, O. I. Šumbaev, I. M. Band, and M. B. Trzhaskovskaya, Sov. Phys. JETP, 34, 935 (1972).
[24]K. D. Sevier, *Low Energy Electron Spectrometry* (Wiley, New York, 1972), p. 236.