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Energy-dispersive measurement of $K\alpha$ x-ray linewidths and relative intensities

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The natural linewidths Γ and component intensity ratios $K\alpha_2/K\alpha_1$ are determined using Ge(Li) spectroscopy for four $K\alpha$ x-ray doublets in the range $70 \leq Z \leq 82$. The necessary spectrum-fitting techniques employ two different approaches to convolute the intrinsic Lorentzian profiles with the detector resolution function. The forbidden $K\alpha_3$ transition is seen in Ge(Li) spectra for the first time. All results agree closely with Scofield's relativistic Hartree-Fock-Slater calculations.

I. INTRODUCTION

The available experimental data on K x-ray linewidths have been provided by crystal diffraction spectroscopy. They are critically reviewed by Salem and Lee[1] who performed least-squares fits in order to tabulate the most probable values based on all evidence at hand. For the $K\alpha$ lines at high Z, which are the subject of this paper, the uncertainties in the widths Γ ($\simeq$60 eV at Z=80) appear to be around 10%; this is deduced from the ~10% difference in tabulated $K\alpha_2$ and $K\alpha_1$ linewidths; in reality these can only differ from one another by about 1% since the K-level width $\Gamma(K)$ is responsible for over 90% of both x-ray widths via

$$\begin{aligned}\Gamma(K\alpha_1) &= \Gamma(K) + \Gamma(L_3)\,,\\ \Gamma(K\alpha_2) &= \Gamma(K) + \Gamma(L_2)\,,\end{aligned} \tag{1}$$

where $\Gamma(K)$ is the sum of radiative and nonradiative widths for the K level

$$\Gamma(K) = \Gamma_R(K) + \Gamma_{NR}(K)\,. \tag{2}$$

Theoretical calculations of the radiative widths for K and L_i vacancies have been reviewed by Scofield.[2] There are several Hartree-Slater calculations, but the most rigorous treatment is Scofield's own relativistic Hartree-Fock calculation.[3] Unlike earlier work, this recognizes that single-particle wave functions in initial and final states differ from one another and from the neutral atom, giving rise to exchange effects. Krause and Oliver[4] tabulate theoretical $K\alpha$ x-ray linewidths. They obtain $\Gamma(K)$ from Scofield's $\Gamma_R(K)$ and the experimental fluorescence yield ω_K[5], which at high Z is close to 1.0 and has uncertainty ~0.5%. $\Gamma(L_i)$ is obtained similarly and since it is 10 times smaller than $\Gamma(K)$, the greater uncertainty (10%) in ω_L is not important. A measurement of $\Gamma(K_\alpha)$ is therefore a test of Scofield's calculation of $\Gamma_R(K)$.

Salem and Lee's tabulated values of $\Gamma(K\alpha_1)$ agree quite well with Scofield's predictions in the $70<Z<90$ region, but their $\Gamma(K\alpha_2)$ follows a considerably steeper Z dependence than the theory, diverging from it by some 20% around Z=80.

Values of the intensity ratio $K\alpha_2/K\alpha_1$ at low Z derive from crystal spectroscopy and above Z=70 from energy-dispersive spectroscopy with Ge(Li) detectors. This area has been reviewed by Scofield[2] and by Salem *et al.*[6] Typical uncertainties in the Ge(Li) work are 2–5% up to Z=90 and 1–2% above that value. The large volume of data scatters around the theory by ±5%, the trend in good agreement, although Salem *et al.*[6] note that the experimental values tend to fall increasingly below theory at high Z.

The $K\alpha_3$ x ray is l forbidden and can only occur via spin-flip. The few measurements of the $K\alpha_3/K\alpha_1$ ratio (~10^{-3}), all by crystal spectroscopy, scatter widely,[2] ranging from 0.75 to 3 times the theoretical value.

Here we report the first extraction of $K\alpha$ x-ray linewidths from Ge(Li) spectra. The main objective is a more rigorous test of Scofield's $\Gamma(K)$ and $K\alpha_2/K\alpha_1$ values (in the range $70 \leq Z \leq 82$) than is afforded by previous work. In the present as in the previous work, the $K\alpha_2$ and $K\alpha_1$ lines overlap in Ge(Li) spectra, and their unravelling is the main source of error. In all of the previous energy-dispersive work this was done empirically or by fitting procedures where Gaussian shapes were used for the peaks. In the present work we represent the peaks correctly by convoluting the intrinsic Lorentzian line shape with the quasi-Gaussian spectrometer resolution. [This is normal procedure in wavelength-dispersive measurements (e.g. Ref. 7) with their much better resolution.] The fits also reveal, for the first time in Ge(Li) spectra, the forbidden $K\alpha_3$ x ray and permit measurement of the $K\alpha_3/K\alpha_1$ intensity ratio.

The obvious disadvantage of a Ge(Li) spectrometer relative to diffraction techniques is the much poorer energy resolution. In the Ge(Li) case the spectrometer FWHM is typically six times greater than the natural linewidth Γ, whereas with a bent

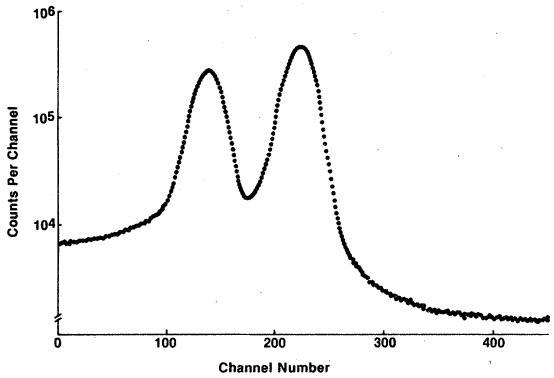

FIG. 1. Ge(Li) spectrum of Ta $K\alpha$ x-ray doublet.

crystal it can be of the same order or less depending on the degree of collimation. On the other hand, the Ge(Li) spectrometer accumulates the entire spectrum simultaneously while the crystal spectrometer involves scanning over wavelengths. Statistics of many million counts are then available in the Ge(Li) case from radioactive sources of a few microcuries, while even with the typical 100-curie sources, much poorer statistics are typical with a crystal spectrometer. In these circumstances Ge(Li) spectroscopy is fully competitive provided that a crucial criterion is met, viz, that the Ge(Li) resolution function for monoenergetic radiation is known very accurately.

II. EXPERIMENTAL

The Ge(Li) detector used was an Ortec LEPS of dimensions 5 mm × 80 mm^2; its energy resolution (FWHM) was 200 eV at 6.4 keV and 500 eV at 122 keV. It was used with a TC 205A amplifier (time-constant 2 μs) and an ND 2200 pulse height analyzer operated with conversion gain 4096. A digital stabilizer was set on each x- or gamma-ray peak of interest to minimize line broadening due to small electronic drifts. A slow-rise-time rejection system[8] and a pileup inspector gated the pulse height analyzer to reject imperfect pulses. Counting rates were kept below 400 cps.

$K\alpha$ x rays of Yb, Ta, Pt, and Pb were obtained from radionuclide sources having activities of a few microcuries, viz., ^{171}Tm, ^{181}W, ^{195}Au, and ^{207}Bi. These were prepared by allowing droplets of solution to evaporate on beryllium foils of 25 mm diameter and 0.05 mm thickness. Spectra were also recorded from a set of gamma rays spanning the same energy region, in order to determine the spectrometer's resolution function for monoenergetic photons. The gamma-ray sources were ^{210}Pb, ^{241}Am, ^{171}Tm, and ^{170}Tm. Since some of the radionuclides were beta emitters, a Lucite absorber covered the beryllium window of the detector.

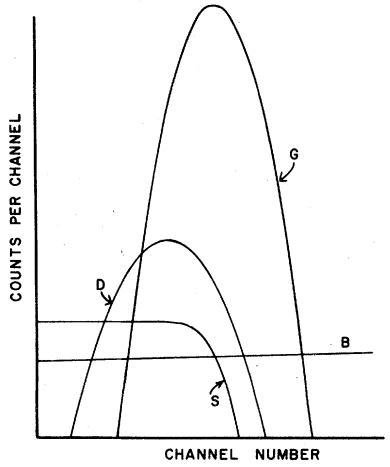

FIG. 2. Additive analytic components of spectral peak due to monoenergetic photons.

The gamma-ray spectra contained 6–7 million counts in the full energy peak and the x-ray spectra a similar number in the weaker $K\alpha_2$ line. Extensive background measurements ensured that the peaks were not contaminated by extraneous radiation of similar energy. Dispersions of ~20 eV/channel ensured broad peaks with typically 20 channels in the FWHM; this minimized histogram effects in subsequent peak fitting. The Ta $K\alpha$ doublet is shown in Fig. 1.

III. DATA ANALYSIS

Each gamma-ray peak was fitted with a resolution function $F(x)$ that is primarily due to Phillips and Marlowe[9] and has been extensively tested by others.[8] This has four additive components, i.e.,

$$F(x) = B(x) + G(x) + S(x) + D(x), \tag{3}$$

as shown in Fig. 2. The main ones are the linear background $B(x)$ and a Gaussian $G(x)$ which would represent the peak in a perfect detector subject only to statistical fluctuations in ionization. The step $S(x)$ and low-energy distortion $D(x)$ represent degraded pulses arising from incomplete collection of ionization, photoelectron escape, etc.; S has one free parameter, its height; D has two compo-

TABLE I. Reduced χ^2 for fits to monoenergetic gamma-ray spectra.

Energy (keV)	χ^2_ν
46.50	1.26
59.54	1.58
66.72	1.26
84.26	1.24

TABLE II. Reduced χ^2 for fits to $K\alpha$ x-ray doublets.

Z	Energy (keV) $K\alpha_2$	Energy (keV) $K\alpha_1$	Voigt approximation	Numerical convolution method χ_r^2 without $K\alpha_3$ component	Numerical convolution method χ_r^2 with $K\alpha_3$ component
70	51.354	52.389	1.79	1.69	
73	56.277	57.532	1.31	1.75	
78	65.122	66.832	1.39	1.66	1.50
82	72.804	74.969	2.39	2.14	1.78

nents, each an exponential of positive slope convoluted with the Gaussian, and thus has four free parameters. $F(x)$ has ten parameters in all. The mathematical details of D and S and their physical justification are given in detail in Refs. 8 and 9.

$F(x)$ was fitted to the data by Marquardt's nonlinear least-squares procedure.[10] Each region fitted spanned 300 channels centered on the peak (FWHM ~20 channels). The fits were excellent, the reduced χ^2 values (see Table I) being typically 1.25. The poorer ^{241}Am value is due to a small pileup contribution on the right of the peak, in whose absence the χ_r^2 would be approximately 1.25.

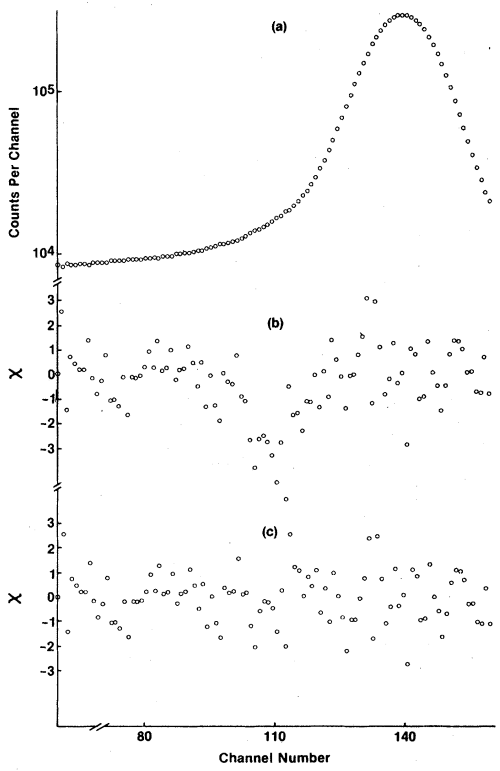

FIG. 3. Residuals from the fit to the Pb $K\alpha$ x-ray doublet, which is partly shown in (a), using the numerical convolution approach first (b) with 2 components and then (c) with 3 components.

The gamma-ray fits indicate then that $F(x)$ is an appropriate form for monoenergetic photons.

In the $K\alpha_1$ x-ray case the incident photons have a Lorentzian energy distribution

$$L(x)=\frac{\Gamma/2\pi}{(x-x_0)^2+(\Gamma/2)^2}\,, \tag{4}$$

which is convoluted by the detector response to produce the observed spectrum. This point has been ignored in work in this area. A simple means of recognizing it is simply to replace $G(x)$ in Eq. (3) by the analytic convolution of $G(x)$ with $L(x)$, which is the Voigt function $V(x)$; this can be evaluated through piecewise series approximations. The advantage of this is the ease of computation of $V(x)$ but the drawback is the neglect of convolution of the minor compontents $D(x)$ and $S(x)$. An alternative is to evaluate $P(x)=G(x)+S(x)+D(x)$ for the specific parameters at hand and then convolute $P(x)$ numerically with $L(x)$; this is more rigorous but very expensive in terms of computer time.

Technical details of these two computational techniques for fitting x-ray peaks are given elsewhere.[11] Both were employed here in fitting $K\alpha$ x-ray doublets over regions of 500 channels. In either, the Lorentzian width Γ was a variable to be determined in the fitting routine, and a common Γ was used for both $K\alpha_1$ and $K\alpha_2$ components; this is an acceptable approximation for the reasons given at the outset of this paper. For the two components, the three Gaussian parameters (position, height, width) for each, the common Γ,

TABLE III. Comparison of predicted and fitted Gaussian σ parameter for $K\alpha_1$ peaks.

Z	Eq. (5)	Voigt fit (eV)	Convolution fit (eV)
70	155.1±0.8	154.3±0.2	155.1±0.2
73	160.1	158.1	160.2
78	168.8	166.9	168.8
82	176.1	174.7	177.2

TABLE IV. Experimental and theoretical values of $K\alpha$ x-ray linewidth.

Z	$\Gamma(K\alpha)$ (eV) Voigt fit	$\Gamma(K\alpha)$ (eV) Convolution fit[a]	Theory (Ref. 3)	Empirical (Ref. 1) $K\alpha_1$	Empirical (Ref. 1) $K\alpha_2$
70	38.5	34.6±1.0	36.3	42.0	40.6
73	48.3	39.8±1.2	42.6	46.5	46.2
78	61.7	52.1±1.4	55.0	60.3	54.3
82	74.3	64.3±0.9	66.0	68.3	79.0

[a] The quoted error is ±3 standard deviations.

and the two background parameters add up to nine. The five parameters of $D(x)$ and $S(x)$ are expressed as multiples of those of G and, since as such they vary only slowly with energy, are common to both components, bringing the total parameter number to fourteen.

The resulting χ_ν^2 values are given in Table II, and indicate good fits by current standards in Ge(Li) spectroscopy.[8] Figure 3(b) displays the residuals for Z=82 and indicates the presence of a third component; inclusion of the $K\alpha_3$ component reduced the χ_ν^2 and produced a uniform residual plot [Fig. 3(c)] for Z=78 and 82. The χ_ν^2 values do not select one analysis technique as superior. We therefore compared the Gaussian width parameters σ for the $K\alpha$ x rays with those predicted by fitting

$$\sigma^2 = aE + b \tag{5}$$

(as required by the statistics of pulse formation) to the results of the gamma-ray fits. In Table III the predictions of Eq. (5) for the $K\alpha_1$ lines are compared with the σ values actually produced by the two fitting techniques. Although the comparison tends to favor the numerical convolution approach, the differences are not large.

IV. RESULTS AND DISCUSSION

Table IV compares the $K\alpha$ x-ray linewidths Γ derived from the two fitting procedures with the theoretical values and with the values resulting from Salem and Lee's fit to experimental data. As noted earlier, our Voigt fit, which yields $\Gamma(K\alpha)$ values 4–12% greater than theory, is the poorer approximation since it neglects convolution of the low-energy tail components. The full convolution treatment, which is the more rigorous approach, gives values of $\Gamma(K\alpha)$ that are on average 5% below the theoretical numbers, the 3σ error of the fit being typically 3%. The empirically derived $\Gamma(K\alpha)$ values of Salem and Lee[1] are on an average 10% higher than the theoretical numbers. The convolution fit to our data thus affords the closest approach to the predicted $K\alpha$ x-ray linewidths, but leaves room for the possibility of errors below the 5% level in the latter.

In extracting values of the $K\alpha_2/K\alpha_1$ ratio, the two fitting procedures agree closely. The second and third columns of Table V give the raw results; the fourth column gives the mean corrected for detector efficiency and with a 3σ error composed of roughly equal contributions from fit uncertainty and relative efficiency. We conclude that Scofield's predictions are confirmed within an uncertainty of about 1%. This is significantly more precise than the previous error estimates of 2–5% which were based on empirical data analysis or on Gaussian fitting.

In the Z=78 and 82 cases the fits were clearly improved by inclusion of the $K\alpha_3$ line. Table VI compares present $K\alpha_3/K\alpha_1$ intensity ratios with Scofield's Hartree-Slater predictions.[2] For consistency with the foregoing we quote ±3σ errors; this is perhaps pessimistic since the results agree within about 1σ with Scofield's calculations. We cite these results less as definitive data and more as an indication that this interesting quantity is measurable by energy-dispersive spectroscopy.

TABLE V. Experimental and theoretical values of $K\alpha_2/K\alpha_1$ intensity ratio.

Z	Uncorrected measurement Voigt	Uncorrected measurement Convolution	Corrected Mean[a]	Theory (Ref. 2)
70	0.5755	0.5765	0.576±0.006	0.567
73	0.5845	0.5854	0.582±0.006	0.574
78	0.6045	0.6045	0.591±0.015	0.585
82	0.6219	0.6217	0.597±0.010	0.595

[a] The quoted error is ±3 standard deviations.

TABLE VI. $K\alpha_3/K\alpha_1$ intensity ratios.

Z	$K\alpha_3/K\alpha_1$ (10^{-3}) Measured[a]	Theory (Ref. 2)
78	0.66±0.45	0.68
82	1.25±0.6	0.98

[a] Quoted error is ±3 standard deviations.

Large reductions in the uncertainty are available via three routes; first, at least ten times greater counting statistics are easily obtainable in reasonable time; use of higher $Z(Z\sim95)$ would at least double the ratio; and most important, an intrinsic Ge(I) detector would have more favorable low-energy tailing than our Ge(Li) detector. It should then be feasible to test Scofield's prediction of other values of $K\alpha_3/K\alpha_1$ with some 10% certainty.

V. CONCLUSIONS

This work provides support at the 5% uncertainty level for Scofield's Hartree-Fock calculations of atomic K-level linewidths and at the 1% level for his $K\alpha$ x-ray relative intensities. Sophisticated spectrum-fitting techniques afford significant improvement over earlier work and open up the possibility of future work on the forbidden $K\alpha_3$ transition.

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