Dependence of the K x-ray energy upon the mode of excitation

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The energy of the Ta Kα x rays emitted after electron capture of $^{181}$W has been observed to be lower by 0.79 ± 0.06 eV compared to the fluorescent Ta Kα x rays. Similarly, it was found that the Ta Kα x rays emitted after internal conversion following β decay of $^{185}$Hf were higher by 0.7 ± 0.1 eV in energy compared to the same fluorescent Ta x rays. The observed effects cannot be explained by the known mechanisms of chemical shift, hyperfine effects, isomer shifts, and shake-off effects alone. Similar observations of the K x-ray energy shifts in the electron-capture decays of $^{157}$Gd and $^{187}$Hf with the corresponding fluorescent x rays in Eu and Lu, respectively, can be accounted for by the hyperfine effects, isotope shifts, and chemical shifts.

I. INTRODUCTION

In previous communications$^1,^2$ we presented evidence for the dependence of the energy of atomic K x rays upon the mode of excitation. For example, we observed that the Kα x-ray energies in Ta differ by as much as 0.8 eV depending on whether they are produced in association with electron capture, internal conversion, or fluorescence. Further systematic studies$^3$ of K x rays in several atoms corroborated this evidence. In addition, recent work by Borchert et al.$^{10}$ has lead to similar conclusions. The origin of this energy shift, however, is only partially understood. The known mechanisms of isotope and isomer shifts,$^7$ chemical shifts,$^7$ shake-off effects,$^5$ and hyperfine effects$^4$ are not able to account for the observations in the case of the Ta K x rays.

In this paper we present a full account of our experimental procedure and of the results. A discussion of several effects contributing to shift of inner atomic levels is presented. The motivation for our studies was the aim of establishing convenient x-ray energy standards for use in precision determinations of muonic x rays in the region of 50–100 keV. From our findings it becomes clear that reference values of x-ray energies, such as those listed in Ref. 8, may be meaningless in a given situation. Apart from this very practical goal, we became increasingly interested in exploring the atomic mechanisms responsible for the observed effects.

II. EXPERIMENTAL RESULTS

The x-ray wavelength measurements were performed with the help of the Caltech 2-m bent crystal spectrometer.$^9$ A (310) quartz crystal slab was used. Four sources whose K x-ray wavelengths were to be compared were mounted on a target wheel and could be turned into position with the help of a stepping motor. For each wavelength position of the spectrometer, the number of diffracted photons was counted sequentially for all four sources. The Kα x-ray lines were scanned in increments of 0.05 Å; 25 steps were chosen over the line profile. The data (in wavelength units) were analyzed by a fit to a Gaussian function with centroid, width, peak height, and slope and elevation of background as variable parameters. The differences of the centroid parameter, translated into energy units, are presented in Tables I and II. Both internal and external errors were calculated; the larger of the two was always assigned to the numbers quoted in the tables.

The $K\beta_{1,2}$ doublet was scanned in a similar fashion in 41 steps with 0.05 Å increments. The data were fitted to two Gaussians with a common linear background.

A. Ta x rays

Three modes of excitation of Ta x rays were investigated: electron capture of $^{181}$W, internal conversion in the decay of $^{185}$Hf, and fluorescence. Below we describe the preparation of the samples in each case and the experimental results.

Sources of 0.5-Ci strength of $^{181}$W and $^{185}$Hf were obtained by reactor irradiation (200 h at $2.5 \times 10^{14}$ thermal neutrons/cm$^2$ sec of enriched $^{180}$W and $^{184}$Hf. The samples were in form of $WO_3$, W metal, and HfO$_2$, respectively. The target material was in form of powder mixed with a similar volume of aluminum oxide powder to facilitate uniform distribution. The sources whose thicknesses were 70 mg/cm$^2$ were in the form of circular disks, 1 cm in diameter.

The fluorescent samples consisted of a Ta metal or oxide disk, 300 mg/cm$^2$ in thickness, backed by a 1.5-Ci $^{153}$Gd source, whose strong γ rays of 97 and 103 keV produced K-shell vacancies in Ta by photoeffect. In an early run (Ref. 1) $^{182}$Ta was
TABLE I. Comparison of experimental results of Ta K x-ray shifts from different runs.

<table>
<thead>
<tr>
<th>X-ray emitting source</th>
<th>Run No.</th>
<th>(K\alpha_1)</th>
<th>(K\alpha_2)</th>
<th>(E_A - E_B) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{181}\text{WO}_3)</td>
<td>1</td>
<td>-0.67 (0.13)</td>
<td>-0.96 (0.12)</td>
<td>-1.79 (0.52)</td>
</tr>
<tr>
<td>(^{181}\text{WO}_3)</td>
<td>2A</td>
<td>-0.78 (0.07)</td>
<td>-0.71 (0.09)</td>
<td>-1.06 (0.14)</td>
</tr>
<tr>
<td></td>
<td>2B</td>
<td>-0.81 (0.14)</td>
<td>-0.93 (0.20)</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>2C</td>
<td>-1.04 (0.24)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.59 (0.25)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(^{181}\text{WO}_3)</td>
<td>1</td>
<td>0.06 (0.27)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(^{181}\text{WO}_3)</td>
<td>2A</td>
<td>0.08 (0.27)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(^{181}\text{W})</td>
<td>2B</td>
<td>0.09 (0.11)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.23 (0.30)</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

*Run 1: Reference 1. Two sets of sources, and crystal No. 1 were used. Different positions of the crystal surface were exposed. Listed values are weighted means. Run 2: The spectrometer had been moved and reassembled before this run was taken. Crystal No. 2 and a third set of sources were used. Measurements 2A, 2B, and 2C were separated in time by several months while other lines (Table II) were studied. Run 3: A NaI detector was used instead of the Ge detector.

Fluoroscoped by radioactivity of \(^{181}\text{Ta}\) (Ref. 1).

Fluorosed by \(^{153}\text{Gd}_2\text{O}_3\) source.

used as a fluorescent (fl) source as indicated in Table I.

Three sets of data were taken, each involving a set of four targets measured simultaneously as described above. The first set contained targets of \(^{181}\text{W}\), \(^{181}\text{WO}_3\), TaO\(_2\)-(fl), and Ta metal (fl); the second set was \(^{181}\text{W}\), \(^{181}\text{WO}_3\), TaO\(_2\)-(fl), and \(^{181}\text{HfO}_2\); and the third set was \(^{181}\text{W}\), \(^{181}\text{WO}_3\), \(^{181}\text{HfO}_2\), and \(^{181}\text{HfO}_2\).

A summary of the experimental results of the first set of data \(^{181}\text{W}\) and Ta(fl)) from different runs is presented in Table I. Run 1 denotes the previously reported results. The other runs refer to recently acquired data under various experimental conditions (see references). We see that the relatively large shift in the Ta K x rays emitted from \(^{181}\text{W}\) compared to those produced by fluorescence is well confirmed. The chemical shift for W metal and \(^{181}\text{WO}_3\) source was reexamined and found small (last three lines in Table I), in agreement with the value obtained by Sumbaev et al.10

The averages of the individual runs of Table I are reported in Table II, lines 1 and 3. Table II also gives the results of the second and third set.

TABLE II. Experimental results of the K x-ray energy shifts.

<table>
<thead>
<tr>
<th>X-ray emitting source</th>
<th>(A)</th>
<th>(B)</th>
<th>(K\alpha_1)</th>
<th>(K\alpha_2)</th>
<th>(E_A - E_B) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta K x rays</td>
<td>(^{181}\text{WO}_3)</td>
<td>TaO(_2)(^b)</td>
<td>-0.77 (0.05)</td>
<td>-0.80 (0.07)</td>
<td>-1.13 (0.14)</td>
</tr>
<tr>
<td></td>
<td>(^{181}\text{W})</td>
<td>Ta(^a)</td>
<td>-0.81 (0.08)</td>
<td>-0.94 (0.30)</td>
<td>-1.06 (0.22)</td>
</tr>
<tr>
<td></td>
<td>(^{181}\text{W})</td>
<td>(^{181}\text{WO}_3)</td>
<td>0.07 (0.06)</td>
<td>-0.02 (0.24)</td>
<td>0.10 (0.23)</td>
</tr>
<tr>
<td></td>
<td>Ta(^a)</td>
<td>(^{181}\text{WO}_3)</td>
<td>0.10 (0.08)</td>
<td>-0.00 (0.34)</td>
<td>-0.03 (0.24)</td>
</tr>
<tr>
<td></td>
<td>(^{181}\text{W})</td>
<td>(^{181}\text{HfO}_2)</td>
<td>-1.27 (0.12)</td>
<td>...</td>
<td>-2.88 (0.58)</td>
</tr>
<tr>
<td></td>
<td>(^{181}\text{WO}_3)</td>
<td>(^{181}\text{HfO}_2)</td>
<td>-1.48 (0.12)</td>
<td>...</td>
<td>-2.17 (0.59)</td>
</tr>
<tr>
<td></td>
<td>(^{181}\text{WO}_3)</td>
<td>(^{181}\text{HfO}_2)</td>
<td>-0.70 (0.11)</td>
<td>...</td>
<td>-1.51 (0.44)</td>
</tr>
<tr>
<td>Eu K x rays</td>
<td>(^{152}\text{Gd}_2\text{O}_3)</td>
<td>EuO(_3)(^b)</td>
<td>0.09 (0.05)</td>
<td>0.11 (0.06)</td>
<td>0.60 (0.06)</td>
</tr>
<tr>
<td></td>
<td>(^{152}\text{Gd}_2\text{O}_3)</td>
<td>Eu(^b)</td>
<td>0.03 (0.03)</td>
<td>...</td>
<td>-0.60 (0.50)</td>
</tr>
<tr>
<td></td>
<td>(^{152}\text{Gd}_2\text{O}_3)</td>
<td>EuO(_3)(^b)</td>
<td>-0.03 (0.02)</td>
<td>...</td>
<td>-0.35 (0.25)</td>
</tr>
<tr>
<td>Lu K x rays</td>
<td>(^{176}\text{HfO}_2)</td>
<td>LuO(_2)(^a)</td>
<td>-0.43 (0.10)</td>
<td>-0.39 (0.17)</td>
<td>-0.20 (0.29)</td>
</tr>
<tr>
<td>Tm K x rays</td>
<td>(^{165}\text{HfO}_2)</td>
<td>TmO(_2)(^a)</td>
<td>...</td>
<td>...</td>
<td>-0.20 (0.29)</td>
</tr>
</tbody>
</table>

*Fluoroscoped by \(^{153}\text{Gd}_2\text{O}_3\) source (97.43- and 103.18-keV γ rays).

*Fluoroscoped by \(^{165}\text{Tb}_2\text{O}_3\) source (65.12-keV γ ray).

*Fluoroscoped by \(^{153}\text{Am}\) source (55.54-keV γ ray).
of data [\(^{150}\text{W}, \^{151}\text{Hf}, \text{Ta}(\text{II})\)] quoted on lines 2, 5, 6, and 7. As can be seen from Table II, there is a large energy shift in the Ta \(x\) rays between \({}^{150}\text{W}\) and \({}^{151}\text{Hf}\). For Ta(\(f\))–\({}^{151}\text{Hf}\) we observe a shift of the same magnitude and sign as for \({}^{150}\text{W}–\text{Ta}(\text{II})\). The results of a null experiment are presented on line 8 of Table II.

B. Eu \(x\) rays

We have examined the energies of the Eu \(K\) \(x\) rays emitted following electron capture of \(^{153}\text{Gd}\) and compared them to fluorescent \(K\) \(x\) rays. The \(^{153}\text{Gd}\) sources (1.5 Ci) were prepared by neutron irradiation of 80-mg-enriched \(^{153}\text{Gd}\) in form of \(\text{Gd}_2\text{O}_3\). The \(\text{Gd}_2\text{O}_3\) samples had a thickness of 150 mg/cm\(^2\). The fluorescence samples consisted of Eu metal (200 mg/cm\(^2\)) as well as \(\text{Eu}_2\text{O}_3\) (200 mg/cm\(^2\)) backed by a 3-Ci source of \(^{169}\text{Yb}\). The results given in Table II show a small energy shift for the oxide samples. The large shift between \(^{153}\text{Gd}_2\text{O}_3\) and Eu metal is attributed to the chemical shift caused by an additional 4\(f\) electron, as will be discussed below. The third entry for the Eu data represents a null experiment.

C. Lu \(x\) rays

In a similar fashion we compared the Lu \(K\) \(x\) rays associated with electron capture of \(^{177}\text{Hf}\) with the Lu fluorescent \(K\) \(x\) rays. The \(^{177}\text{Hf}\) source (0.2 Ci) was prepared by neutron irradiation of 5-mg-enriched \(^{177}\text{Hf}\) in form of \(\text{HfO}_2\). Fluorescent \(x\) rays were produced on a 300-mg/cm\(^2\) \(\text{Lu}_2\text{O}_3\) sample with the help of the aforementioned \(^{153}\text{Gd}\) source. The results are given in Table II.

D. Tm \(x\) rays

As a further test, the Tm \(K\alpha_1\) \(x\)-ray energy was measured for two fluorescent Tm samples excited with different \(\gamma\)-ray energies. The goal of that experiment was to study possible effects of deviation from the sudden approximation. The \(^{241}\text{Am} \gamma\) ray (59.54 keV) is only 150 eV above the \(K\) edge of Tm. The ejected electron will be still in the immediate vicinity of the atom when the \(x\) ray is emitted \((\tau \approx 10^{-17} \text{ sec})\). The results are given on the bottom line of Table II. No difference in energy is seen between the two situations. Our results may be compared with the results of Ref. 11, which showed that the differences between the \(L_\text{f}\) and \(K\) internal conversion electron lines in \(^{241}\text{Am}\) are constant within 5 eV for electron energies between 7 and 450 keV.

III. DISCUSSION

Let us briefly describe the known mechanisms that should be considered in an attempt to understand the observed energy differences. In Table III we include those effects that are expected to cause shifts larger than the experimental uncertainties of our measurements.

\(a\). Isotope shifts. The isotope shift (IS) affects the 1s electronic state, shifting all \(K\) \(x\) rays by the same amount. In the cases of \(\text{Ta}\) and \(\text{Lu}\), we compared \(x\) rays emitted by the identical isotopes. In Eu, however, the fluorescence data were obtained with the natural mixture of Eu isotopes, while the electron capture (EC) source contained only \(^{153}\text{Gd}\).

<table>
<thead>
<tr>
<th>Line</th>
<th>Sources</th>
<th>(\alpha) shift</th>
<th>Hyperfine (a) splitting shift</th>
<th>Isotope (b) shift</th>
<th>Chemical (c) shift</th>
<th>(\Delta E_{\text{corr}}) Corrected shift ^d</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ta} \text{K}\alpha_1)</td>
<td>(\text{WO}_2–\text{Ta}_2\text{O}_3)</td>
<td>(-0.77(0.05))</td>
<td>0.40</td>
<td>0</td>
<td>0</td>
<td>(-1.17(0.05))</td>
</tr>
<tr>
<td>(\text{W}–\text{Ta})</td>
<td>(-0.31(0.08))</td>
<td></td>
<td>0.40</td>
<td>0</td>
<td></td>
<td>(-1.21(0.08))</td>
</tr>
<tr>
<td>(\text{Ta}_2\text{O}_3–\text{HfO}_2)</td>
<td>(-0.70(0.11))</td>
<td>(-0.07)</td>
<td>0</td>
<td>0</td>
<td></td>
<td>(-0.03(0.07))</td>
</tr>
<tr>
<td>(\text{Eu} \text{K}\alpha_1)</td>
<td>(\text{Gd}_2\text{O}_3–\text{Eu}_2\text{O}_3)</td>
<td>(0.09(0.05))</td>
<td>(-0.35)</td>
<td>(-0.09)</td>
<td>(0.43(0.01))</td>
<td>(0.10(0.05))</td>
</tr>
<tr>
<td>(\text{K}\beta_1)</td>
<td>(0.11(0.06))</td>
<td>(-0.35)</td>
<td>(-0.09)</td>
<td></td>
<td>(0.39(0.01))</td>
<td></td>
</tr>
<tr>
<td>(\text{K}\beta_2)</td>
<td>(0.30(0.06))</td>
<td>(-0.35)</td>
<td>(-0.09)</td>
<td></td>
<td>(0.37(0.03))</td>
<td></td>
</tr>
<tr>
<td>(\text{K}\gamma)</td>
<td>(0.39(0.10))</td>
<td>(-0.35)</td>
<td>(-0.09)</td>
<td></td>
<td>(1.15(0.03))</td>
<td></td>
</tr>
<tr>
<td>(\text{Lu} \text{K}\alpha_1)</td>
<td>(^{175}\text{HfO}_2–\text{Lu}_2\text{O}_3)</td>
<td>(-0.43(0.10))</td>
<td>(-0.30)</td>
<td>0</td>
<td>0</td>
<td>(-0.13(0.10))</td>
</tr>
</tbody>
</table>

\(a\) Values from Table IV and the text.
\(b\) There are \(52.2\%\) \(^{152}\text{Eu}\) and \(47.8\%\) \(^{154}\text{Eu}\) in the \(\text{Eu}_2\text{O}_3\) fluorescence target. \(\Delta E_{\text{IS}} = 0.186\) eV (Ref. 12).
\(c\) Those \(32\%\) of the observed internal–conversion Eu \(K\) \(x\) rays do not have chemical shift (CS) (Ref. 15). The CS has been measured by Smirnov et al. (Ref. 16).
\(\Delta E_{\text{corr}}\) contains the contributions of shake-off effect, isomer shift, \(\lambda = 0\) electron–capture transitions, and “other” effects.
\(\Delta E_{\text{corr}}\) contains the contributions of shake-off effect, isomer shift, \(\lambda = 0\) electron–capture transitions, and “other” effects.
\(\gamma\%\) of the observed Eu \(K\) \(x\) rays are due to internal conversion.
\(\gamma\%\) of the observed Lu \(K\) \(x\) rays are due to internal conversion.
The experimental value\(^{12}\) of the Eu XS was used in Table III.

b. Isomer shifts. The known isomer shifts\(^{13}\) in Ta and Eu are considerably smaller than the isotope shifts and thus were not included in Table III.

c. Shake-off effects. As an electronic 1s vacancy is created, the atomic potential changes suddenly, causing partial ionization of the atom. The degree of ionization of the individual electron shells was calculated in Ref. 14. Generally, one expects larger shake-off effects when electron vacancies are produced by photoionization (fluorescence) or by internal conversion, and smaller shake-off effects in electron capture. The atom will remain partially ionized when the K X rays are emitted (in 10\(^{-17}\) sec).

It is straightforward to calculate the x-ray shift for the known degree of ionization. It is, however, important to use for such a calculation the complete self-consistent treatment. The "frozen orbital" calculation of the shake-off effect\(^4\) predicted 150–180 meV larger energy of the fluorescent source compared to the EC source. In the self-consistent treatment the predicted effect is, however, 2–3 times smaller\(^{16}\) and was, therefore, not included in Table III.

d. Chemical shift. The K x-ray energy is known\(^7\) to depend on the configuration of the outer atomic electrons. The 4f electrons are particularly effective in this respect. When comparing an EC x-ray source (element Z + 1) with a photoionization source (element Z) one often encounters a similar effect, because the K x-ray is emitted before the outer electron shell rearrangement takes place.\(^8,15\)

Among the sources we studied, a noticeable effect of this type is expected only for Eu. We assume that the Gd\(_2\)O\(_3\) has the valence electron configuration similar to the two-valent Eu (Eu metal). Thus we use the experimentally measured Eu x-ray chemical shift\(^6\) in column 6 of Table III. Note that the results in Table II imply the corresponding shift between the Eu metal and Eu\(_2\)O\(_3\).

e. Magnetic hyperfine interaction. This interaction leads to the shift of the electronic 1s state (and to the same shift of all K X rays) by the amount\(^17\)

\[
\Delta E = \frac{1}{2} A [I P(F_0 = I + \frac{1}{2}) - (I + 1) P(F_0 = I - \frac{1}{2})].
\]

Here \(A\) is the magnetic hyperfine interaction constant, for which we use the expression

\[
A = \frac{4}{3} I \mu_a \mu_B \alpha m e^2 \frac{(Za)^3}{\rho(2\rho - 1)},
\]

where \(\mu\) is the nuclear magnetic moment, \(I\) is the nuclear spin, \(\mu_B\) is the Bohr magneton, \(\alpha\) is the fine-structure constant, and \(\rho = [1 - (Za)^2]^{1/2}\). The quantity \(P(F)\) is the population of the hyperfine component with total angular momentum \(F\). Let us consider a nuclear transition (an electron capture or internal conversion) that begins with the nucleus with spin \(I\) and with the electron configuration (1s)\(^2\). Assume further that the final nuclear spin is \(I_f\), that the final electron configuration is (1s)\(^2\), that the transition operator has a multipolarity \(\lambda\), and that the ejected fermion (a neutrino for EC or an electron for internal conversion) has angular momentum \(S\). Considering the couplings of the angular momenta and summing over all projections one obtains

\[
P(F) = (2\lambda + 1)(2F + 1) \frac{\lambda F S}{\lambda F}.
\]

The population \(P(F)\) is not statistical, and thus the energy shift \(\Delta E\) is nonzero if \(\lambda = 1\) and if \(S = \frac{1}{2}\). In the electron capture this is the case for the allowed Gamow-Teller transitions and for some first forbidden transitions, as recognized and experimentally verified by Borchert et al.\(^5\) In the internal conversion, an x-ray shift is expected, and was observed in the M1 case.\(^18\) It is interesting to note that the nonstatistical population of hyperfine components was predicted already twenty years ago,\(^19\) and "rediscovered" within the last year.\(^6\)

The calculated magnetic hyperfine shifts for the EC sources are collected in Table IV. Moreover, the x rays emitted after M1 internal conversion will also be shifted. These additional shifts are, however, relatively small (\(-0.02\) eV for Eu x rays

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**TABLE IV. Calculated magnetic hyperfine shifts.**

<table>
<thead>
<tr>
<th>Transition</th>
<th>(I_i)</th>
<th>(I_f)</th>
<th>%</th>
<th>(\mu) (nm)</th>
<th>(\Delta E) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{181})W (\rightarrow) (^{181})Ta</td>
<td>(\frac{3}{2}^+)</td>
<td>(\frac{1}{2}^+)</td>
<td>65</td>
<td>2.36(^a)</td>
<td>0.84</td>
</tr>
<tr>
<td>(^{175})Hf (\rightarrow) (^{175})Lu</td>
<td>(\frac{5}{2}^-)</td>
<td>(\frac{3}{2}^-)</td>
<td>35</td>
<td>5.28(^a)</td>
<td>-0.42(^b)</td>
</tr>
<tr>
<td>(^{153})Gd (\rightarrow) (^{153})Eu</td>
<td>(\frac{1}{2}^-)</td>
<td>(\frac{1}{2}^+)</td>
<td>86</td>
<td>3.2(^c)</td>
<td>-0.20(^d)</td>
</tr>
<tr>
<td>(\frac{3}{2}^-)</td>
<td>(\frac{1}{2}^+)</td>
<td>14</td>
<td>3.1(^e)</td>
<td>-1.26</td>
<td></td>
</tr>
<tr>
<td>(^{153})Gd (\rightarrow) (^{153})Eu</td>
<td>(\frac{1}{2}^-)</td>
<td>(\frac{3}{2}^+)</td>
<td>24(^a)</td>
<td>1.53</td>
<td>0.42</td>
</tr>
<tr>
<td>(\frac{3}{2}^-)</td>
<td>(\frac{1}{2}^+)</td>
<td>30(^a)</td>
<td>3.2(^{1/2})</td>
<td>-0.37</td>
<td></td>
</tr>
<tr>
<td>(\frac{3}{2}^-)</td>
<td>(\frac{1}{2}^+)</td>
<td>32(^a)</td>
<td>2.0(^f)</td>
<td>-0.28(^g)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Nucl. Data Sheets 9, 347 (1973).
\(^b\) Pure \(\lambda = 1\) assumed, based on log\(f\) value.
\(^c\) Based on the Nilsson state assignment \(\frac{5}{2}^-\) [402].
\(^d\) Equal contribution of \(\lambda = 1, \lambda = 0\) assumed; based on log\(f\) in \(^{175}\)Hf and \(^{171}\)Er.
\(^f\) Nucl. Data Tables 5, 433 (1969).
\(^g\) Based on the Nilsson state assignment \(\frac{1}{2}^-\) [532].
\(^h\) Pure \(\lambda = 1\) assumed, based on the analysis of log\(f\) values in \(^{152}\)Eu and \(^{154}\)Tb.
from $^{152}$Gd, 0.002 eV for Lu $\times$ rays from $^{175}$Hf, and 0.07 eV for Ta $\times$ rays from $^{181}$Hf $\beta$ decay.

The last column of Table III shows that the above-mentioned effects are able to explain most of the observed shifts in Eu and Lu. One has to remember that the hyperfine correction has an inherent uncertainty caused by the unknown relative role of $\lambda = 1$, $\lambda = 0$ parts in $\Delta = 0$ first forbidden electron captures (particularly for Lu) and to the uncertainties of the EC feeding (particularly for Eu).

However, a surprisingly large shift remains in Ta, both for the $^{181}$W source, and for the $^{181}$Hf source. The accuracy of the $K_{\alpha}$ $\times$-ray shift $\Delta K_{\alpha}$ is insufficient, and one cannot decide whether it is more likely that $\Delta K_{\alpha} \approx \Delta K_{\beta}$ (suggesting a 1s electron shift), or whether $\Delta K_{\alpha} \approx -2\Delta K_{\beta}$ (suggesting an effect of 4f electrons).

It is perhaps possible to speculate that the observed shift may be related to the relatively large difference in mass density between Ta and W. The atomic radius of Ta is larger than that of W and the ionic radii increase from W$^{4+}$ to Ta$^{4+}$ and Hf$^{4+}$. Thus, the Ta atom from $^{181}$W EC is “squeezed” in the W lattice. Shaburov et al. observed that Ce and Sm $K$ $\times$ rays have lower energies when emitted from atoms in the lattices with smaller spacing. The effect was explained as “crowding out” of the 4f electrons.

While a similar mechanism may be responsible for the Ta $\times$-ray shift, there are, on the other hand, serious objections against such a hypothesis: (i) the ionic radii of Hf and Lu also differ, yet the Lu $\times$ rays are not shifted. (ii) Ta is not a rare-earth element and the 4f shell is assumed to be full. (iii) Borchert et al. did not observe W $\times$-ray shifts for a similar comparison of W photoionization with W $\times$ rays following Ta $\beta$ decay and internal conversion.

In conclusion, as a result of the present work and that of Refs. 4–6 and 18, several mechanisms of $\times$-ray shifts have been identified. The large shift in Ta, however, is not understood and further experimental and theoretical work is needed.

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