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UNITED STATES ATOMIC ENERGY COMMISSION OAK RIDGE TEWNESSEE

THE X-RAY SPECTRA OF THE LAST-ROW ELEPENTS

by

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ABSTRACT

X-ray energy level diagrams as given in the literature are tabulated for radium, thorium and manium. A level scheme for protoactinium is derived from the published data. After a brief review of the use of X-ray data in studying outer electronic structure, it is pointed out that differences in the X-ray spectra should exist depending on whether the outer electrons are in \underline{f} or \underline{d} orbitals. The observed separation of the $O_{\underline{I}}$ and $O_{\underline{II}}$ levels in thorium and uranium indicate that the \underline{f} levels lie lower than the \underline{d} . This hypothesis also provides a reasonable explanation for the observed differences between the $M_{\underline{IV}}$ and $M_{\underline{V}}$ absorption edges and $M_{\underline{IV}}$ and $M_{\underline{V}}$ levels calculated from the emission spectra and the LIII edge.

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THE X-RAY SPECTRA OF THE LAST-ROW ELEMENTS

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INTRODUCTION

If the X-ray spectra of the last-row elements were completely and accurately known, they would furnish important information as to the electronic structure of these elements. In particular the X-ray spectra might reveal whether the \underline{f} or \underline{d} valence levels lie lowest. This summary has been prepared to review the existing data and to see what explanations of these data can be given in the light of present knowledge.

ENERGY LEVEL TABLES

A complete X-ray energy level table is the first goal of an X-ray study. Data have been reported for radium, thorium, protoactinium, and uranium; the resulting energy level schemes are given in Tables I and II. All values given in the tables are based on the L_{III} absorption edge. The values of V/R for radium, thorium, and uranium should be accurate to ± 0.2 relative to that edge. The probable error in the L_{III} edge itself is about ± 0.3 .

The available data for protoactinium are tabulated in Table III; from the values in that table an energy level scheme has been compiled as shown in Table IV. The data are fairly consistent except for the lines leading to levels N_{II} , O_I and $P_{II,III}$ which may be in error by 1 to 2 units.

INTERPRETATION BY MEANS OF ELECTRONIC STRUCTURE

The present outstanding problem in connection with these metals is the electronic structure. We do not know whether the outer valence electrons are f or d electrons or mixtures of the two. If they are f electrons we have the beginning of a second rare earth series and our interpretations of chemical and physical properties must be radically altered from the present interpretations which generally assume the outer electrons to be <u>d</u> electrons.

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X-ray spectra have not yet been very fruitful in providing information of electronic structure which is directly useful to chemists. However, a number of approaches have yielded information of great importance and promise to yield more as the experimental technique and theoretical understanding improve. We may summarize these approaches as follows:

1. Bohr-Coster Diagrams and Calculation of Screening Constants

This work is discussed by Fauling and Goudsmit, "The Structure of Line Spectra", McGraw-Hill Co., 1930, and Sommerfeld, "Atombau and Spectrallinion" 5 Aufl. Bd. 1. It is found that the X-ray energy levels can be expressed to an excellent approximation by a hydrogen-like energy expression used with suitable screening constants. A Bohr-Coster plot (Moseley diagram) of $\sqrt{\nu/R}$ for the various levels versus the atomic number gives therefore a smooth curve which is almost a straight line for the deep K and L levels. For the higher levels significant changes in slope occur which are related to the outer electronic structure. There is a slight change in slope when a d shell begins, but by far the largest change occurs when the 4f shell begins to fill. Hore the slope abruptly decreases because the added electron penetrates deeply and shields the electrons concerned more effectively than a d electron. The change in slope is found to be most pronounced in the N and O levels. The phenomenon may be treated in a semi-quantitative fashion by the use of screening constants. The treatment is given in some detail in Pauling

and Goudsmit (p. 180) where it is shown that the principle term in the energy expression may be considered to involve two screening constants, one for the inner and one for the outer electrons. By making approximate quantum-mechanical calculations of the average radii of the outer orbitals Fauling was able to separate the two effects and evaluate the inner screening constant. It was found that the inner screening constant for a given level was practically a constant for elements of atomic number 44 to 57 but that it rose abruptly for the $N_{\rm I}$, $N_{\rm II}$ and $N_{\rm AII}$ levels when the 4f shells started to fill, increasing by about 0.86 units per atomic number. However the rise for the M levels is very small. This result is significant in that it shows that a 4f orbital is penetrating enough to shield both the 4s and 4p electrons to a high degree but that it does not penetrate much inside the 3s or 3p levels. Pauling's calculations are less exact for elements of high atomic number and have little significance for the last row elements.

At first sight these methods would appear best adapted for studying the heavy metals; however a number of difficulties became apparent on closer examination. Absolute term values are needed and the recorded values for the outer levels are somewhat uncertain because of the questions as to eractly what transition is involved in the L_{III} absorption edge on which the values are based. The calculations of outer orbital radii are difficult and uncertain especially for heavy elements. Also the number of elements in which a 5<u>f</u> electron might appear are so few that a slight break in a function is difficult to determine. For these reasons no detailed application of Pauling's method has been tried. 2. Soft X-ray Spectroscopy of the Solid State.

The application of soft X-ray measurements to the determinations

of electronic energy level density in solids is a relatively new one but offers great promise. A summary of the work to 1938 is given by H. W. B Skinner, "Progress in Physics", Vol. 5, The Physical Society, London, 1939. So far only light elements have been studied and there are no data for the heavy elements.

3. X-ray Satellite Lines.

A number of lines are observed in X-ray spectrs which cannot be represented as transitions between known energy levels. These lines are called non-diagram or satellite lines and arise from either double ionization or combination of a non-radiative transition with a regular transition. The satellites are structure sensitive as shown, for example, by measurements of F. R. Hirsh, [Phys. Rev., <u>38</u>, 914 (1931)] on M_al, M_{a2} and M_β satellites of the heavy metals. He found a break at element 70 in the curve of <u>A</u> E between the main line and the satellite line versus the atomic number. Thorium and uranium show a continuum underlying the satellites. However the interpretation of the satellite lines is not yet definite enough to utilize the existing data. A summary of the work on satellite lines is given by F. R. Hirsh [Rev. Yod. Phys., 14, 45 (1942)].

STRUCTURE OF THE LAST ROW ELEMENTS

There are some qualitative arguments based on the X-ray spectra which we may present in regard to the electronic structure of the last row elements. A marked difference between an <u>f</u> and a <u>d</u> orbit is that the <u>f</u> orbit penetrates more deeply into the inner core of electrons. This is shown clearly by the calculations of N. Goeppert Mayer / Phys.

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Rev., 60, 184 (1941) and by the observed optical and magnetic properties of the rare earth elements as contrasted to those of the transition elements. From this evidence and from the screening constant curves shown in Pauling and Goudsmit, p.189, it seems likely that an nf orbit penetrates inside both the ns and np orbits a considerable fraction of the time. We would expect a (n+1)d orbit to penetrate the np orbit only slightly and the ns orbit oven less. If these expectations are realized it would mean that the ns and np Z-ray levels (e.g. MI and and My, or NI and NII) would have smaller absolute values if an nf rather than an (n+1)d electron were added and would also have a smaller separation. It is difficult to say much about the absolute values, but the separations shown in Table V support the assumptions. Addition of a d electron in either the Y-Pd series or the Hf-Pt series increases the s and p separation in the electron shell below by $\Delta (\nu/R) = 0.2$ to 0.4. The addition of an f electron in the rare earths however does not yield as nearly steady an increase in the separation but a fluctuating value with a much smaller average increase in the separation. The separation is less for the rare earth series that for elements adding a d electron. The fluctuations in the rare earth series may be in part attributed to the experimental error in the measurements due to the difficulties of gotting pure materials. The fact that the difference in screening constants for s and p levels is less for an added f than for an added d electron is best seen in the values of A ' 1' /R which are related to the screening constants by the approximate formula:

a v/R = a Th

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where A . is the difference between the ns and np screening constants.

Then we apply these considerations to the last-row elements we note first that the O_{I} , O_{II} separation in radium is about equal to N_{I} , N_{II} separation in barium. (Table V). This shows that the screening perturbations of the <u>s</u> and <u>p</u> levels are very similar in the N and O shells and that we are fairly safe in using the N shell as a criterion for the O shell. If we do this we see (Table V) that the elements therium and uranium behave like rare earths rather than the elements completing a <u>d</u> shell. The O_{I} , O_{II} separation in protocotinium is not sufficiently, well known to use. These considerations therefore indicate that the <u>f</u> shell begins to fill at therium, although the systems are too complex for this evidence to be conclusive.

It may be pointed out also that if the considerations given are true and if the interactions are of the order indicated in Table V, i.e. 1 to 2 units of V/R additional data might be obtained from measurements on the elements containing the <u>f</u> electrons in various chemical states. For example the N₁, N_{II} separation in CoO₂ should be somewhat different from that in the metal or in CoF_g; it may also be expected that the absorption edges will vary more than is customary in different compounds. Such differences may tell something of the solid structure. For example, the density of therium is rather low for a tetravalent metal of its atomic weight. This may be explained qualitatively by assuming that one valence electron is in an stomic <u>f</u> orbital and does not contribute much to the cohesion. The O₂ however probably does not have a S<u>f</u> electron concentrated about the therium stam so much of the time and there should be differences between the X-ray spectra of the metal exide.

Anothor experimental fact can be presented to support the hypothesis that the 5f shell starts to fill with thorium. It has been known for some time that the values of the My and My absorption edges differ from the calculated levels based on the LIT edge and the emission spectre by amounts considerably outside the experimental error. Siegbahn Zoit. f. Physik, 67, 567 (1931) explained this by assuming that the solection rules hold for absorption as woll as emission. For the clomonts 74 to 77 the Lypy absorption transition is probably made to the incomplete Orv. V levels but the corresponding MIV or My transition would be forbidden and its end level must be a higher one of the correct symmetry. The obsorved differences for Mry and My are shown in Table VI, in which the recent data for thorium, protoactinium and uranium have been included. "To note that the differences for the last row elements are not only much less in magnitude but are also of opposite sign! This is readily explained if we assume the edges to correspond to transitions LIII to PIV.V and MIV. or My to CVI, VII and assume that the OVI, VII levels lie lower than the Prv y levels. For lack of a better measure we may even take about 5 electron volts (0.37 in MR) as a rough value for the difference in stability between the f lovels and the d lovels in solid compounds of clovents 90, 91 and 92.

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In conclusion we may say that the X-ray spectra offers confirmatory though not decisive evidence for the hypothesis that the 5<u>f</u> electron shall begins to fill as therium.

TABLE I

X-RAY ENTRGY LEVELS OF RADIUM, THORIUM, PROTOACTINIUM AND URANIUM VALUES OF V/R ARE LISTED

| Leve 1 | Re 88 | Th 90 | Pa 91 | n 85 |
|-----------|---------|---------|---------|--------|
| | | | | |
| K | | 8075.9 | | 8474 |
| LT | 1416.80 | 1507.22 | 1554.6 | 1602.5 |
| LT | 1361.39 | 1450.31 | 1496.2 | 1542.7 |
| LTTT | 1137.54 | 1200.48 | 1232.5 | 1264.2 |
| Mr | 355.12 | 381.63 | 395.3 | 403.6 |
| MTT | 330.62 | 355.14 | 368.2 | 381.7 |
| Mara | 279.24 | 207.48 | 307.6 | 317.0 |
| MTW | 239.24 | 256.93 | 266.0 | 274.5 |
| MV | 218.68 | 245.32 | 253.7 | 261.5 |
| NT | 89.06 | 97.44 | 102.3 | 106.0 |
| NTT | 77.84 | 85.43 | 90.5 | 93.7 |
| NTTT | 64.73 | 70.63 | 74.2 | 76.7 |
| NTV | 46.82 | 52.40 | 54.9 | 57.4 |
| N. | 44.42. | 42.77 | 52.2 | 54.4 |
| NVUT | 122.02 | 24.69 | 27.3 | 128.3 |
| NUTT | \$ | 2 | 26.6 | }. |
| OT | 18.74 | 321.35 | 24.2(?) | 123.9 |
| OTT | 14.76 | 16.49 | 18.6 | 18.9 |
| 0 | 11.17 | 12.77 | | 14.8 |
| OIN | 2 5.01 | 16.39 | 17.0 |)7.6 |
| OV | | 1 | (| \$ |
| P. | 3.22 | Jr.4 | 5 | 1(5.3) |
| PII, PIII | 1.32 | 3.05 | 1.1(?) | 2.9 |

TABLE II

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VALUES OF V/R FOR THE

X-RAY ENERGY LEVELS OF RADIUM, THORIUM, PROTOACTINIUM AND URANIUM

| Level | Ra 88 | Th 90 | - | Pa 91 | U 92 |
|--|-------|-------|-----------|---------|-------|
| ĸ | | 89.87 | | | 92.05 |
| I.I | 37.64 | 38.82 | 10- 1 | 39.43 | 40.03 |
| 1 | 36.90 | 38.03 | | 38.68 | 39.28 |
| | 33.73 | 34.65 | | 35.17 | 35.56 |
| 111 | 18.85 | 19.54 | | 19.89 | 20.21 |
| 1 | 18.18 | 18.85 | | 19.19 | 19.54 |
| 11 | 16.71 | 17.25 | 14 States | 17.54 | 17.81 |
| MIN | 15.47 | 16.03 | 1274 | 16.31 | 16.57 |
| in the second se | 15.12 | 15.66 | 7 | 15.93 | 16.17 |
| N- | 9.44 | 9.87 | | 10.12 | 10.30 |
| N | 8.82 | 9.24 | | 9.51 | 9.68 |
| N ^{II} | 8.02 | 8.40 | | 8.61 | 8.76 |
| NTUII | 6.84 | 7.24 | | 7.41 | 7.58 |
| N., | 6.67 | 7.05 | | 7.23 | 7.38 |
| N _{WT} | 4.69 | 4.97 | | 5.23 | 5.32 |
| WUTT | | | | 5.16 | |
| DT | 4.33 | 4.62 | | 4.92(?) | 4.88 |
| DTT | 3.84 | 4.06 | | 4.31 | 4.35 |
| OTTT | 3.34 | 3.57 | | | 3.85 |
| DTV OV | 2.24 | 2.53 | | 2.65 | 2.76 |
| PI | 1.73 | 2.10 | | | 2.30 |
| PII, PIII | 1.15 | 1.75 | 144 | 1.05(?) | 1.70 |
| , | | | | | |

REFERENCES TO TABLES I AND II

- 11 ----

ALL AND A

Radium:

·14. (3.15)

Horia Hulubei, J. Phys. Radium, 8, 260 (1937)

· . 60 1492 1

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Thorium:

Y. Cauchois and L. Allais, J. Phys. Radium, I, 44 (1940)

Protoactinium:

Compiled from various data as shown in Tables 3 and 4.

Uranium:

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The levels to L_{III} are taken from Siegbahn, "Spectroskopie der Röntgenstrahlen", ^Springer, 1931. The rest are from H. Claesson, Zeit. f. Fhysik, <u>101</u>, 499 (1936) except P_I which is quoted by Cauchois and Allais.

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TABLE III

X-RAY DATA FOR PROTOACTINIUM

Absorption Edges

| Edge | 7 in X | V/R | | |
|------|--------|-------|--------|--|
| LIII | 739.4 | 10.1 | 1232.5 | |
| LII | 608.9 | \$0.1 | 1496.7 | |
| LI | 585.6 | ±0.2 | 1566.2 | |
| MV | 3601 | | 253.1 | |
| MIV | 3429 | | 265.8 | |

Emission Spectra

L Series

(Most lines + 0.1 X. U. The starred lines are less accurate)

| Transition | 7 in X.U. | ٧/R | Transition | ▶ in X.U. | V/R |
|------------|-----------|--------|------------|-----------|--------|
| MILIII | 1088.5 | 937.20 | MIIILI | 730.75 | 1247.0 |
| MIVLIII | 942.75 | 966.60 | MIVLI | 707.3 * | 1288.4 |
| MyLIII | 930.91 | 978.90 | MyLI | 700.3 * | 1301.3 |
| MILII | 827.8 | 1100.8 | NILII | 653.6 | 1394.3 |
| MILIII | 806.2 | 1130.4 | NIVLII | 632.5 | 1440.8 |
| NyLIII | 772.1 | 1180.3 | NIILI | 622.6 | 1453.7 |
| MIILI | 768.3 | 1186.1 | NIIILI | 615.6 | 1480.3 |
| NVIILIII | 755.3 * | 1206.5 | OIVLII | 612.0 | 1489.0 |
| OILIII | 753.0 | 1210.2 | OII.IIIL | 592.5 | 1538.0 |
| OIV.V LIII | 743.7 | 1225.3 | PII.IIILI | 586.6 * | 1553.5 |
| MIVLII | 740.75 | 1230.2 | | | |

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TABLE III (continued)

. . .

V/R Transition > in X. U. V/R Transition Nin X.U. NVIMIV 2386. OIVMII 2522 361.3 3819 NIVMII NVIIMV 227.0 2904 313.8 4014 NVIMV OVMIII 3032 300.6 4027 226.3 OINIII NIMIII 3238 4441 205.2 281.4 NIIIMY NIMII (?) (5081 3434 265.4 179.4 NVMIII 15066 3570 255.3 179.9 5182 NIVMIII 3607 252.6 175.9 NIIMIV OIIMIN 3683 257.4

M Series

to the set

100 100

TABLE IV.

X-RAY TERM VALUES FOR PROTOACTINIUM

Values of V/R are listed.

| LIII = | 1232.5 | Experimentally | determined | absorption | edge. |
|--------------------------|--|-------------------------|------------|------------|-------|
| LI . LIII | Mui - Mulin = | 322.40 | | | |
| 2% | MIVLI * - MyLIII Average | = <u>321.8</u> 322.1 | A | - | |
| LI = 1554.6 | Absorption ed | ge = 1556.2 | | | |
| LII-LIII | MILII-MILIII = | 263.6 | | | |
| C. 105 | MINTII-BINTIII : | 263.6 | | | |
| 9.95 | N _I L _{II} =N _I L _{III} : Average | 263.9 | | • | |
| L _{II} = 1496.2 | Absorption edge | = 1496.7 | | | |
| LIII-MI | MILIII | : 837.2 | | | |
| | MILII-(LII-LIII |) = 837.1 | | i. | |
| | verage | 837.2 | | | |
| M _T = 395.3 | | | | | |
| LIII - HII | MIILI-(LI- LI | 11) = 864.1 | | | |

 $N_{I}L_{II} - N_{I}M_{II} = (L_{II} - L_{III}) = 865.2$ $N_{IV}L_{II} - N_{IV}M_{II} - (L_{II} - L_{III}) = 863.3$ $O_{IV}L_{II} - O_{IV}M_{II} - (L_{II} - L_{III}) = \frac{864.4}{864.3}$ Average 864.3

MII = 368.2

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TABLE IV (CONTINUED)

LIII-MIII

No- Sub-

| WIIITI-(FI-FIII) | = 924.9 |
|---------------------------|----------|
| OVLIII-OVMIII | = 924.7 |
| OITIII* - OIMIII | =(928.8) |
| NyLIII - NyMIII | = 925.0 |
| NIATTI-NIAMIII-(TII-TIII) | = 924.5 |
| NILII-NIWIII-(LII-LIII) | = 925.4 |
| Average | 924.9 |

1

MIII = 307.6

LIII - MIV

| Average | 966.5 |
|-----------------------------|----------|
| NIILI-NIIMIN-(LI-TIII) | =(965.7) |
| OII, IIILI-OIIMIN-(LI-LIII) | =(968.5) |
| MINTLA - (TI-TIII) | = 966.3 |
| MINTII - (TII-TIII) | = 966.5 |
| WINTIII | = 966.6 |

Mry = 266 0

LIII-My

| MyLIII | = 978.90 |
|-------------------------------|-----------------|
| $M_V L_I^* - (L_I - L_{III})$ | = 979.2 |
| NIIILI-NIIIMV-(LI-LIII) | = 978.8, (978.3 |
| Average | 978.9 |

My = 253.7

TABLE IV (CONTINUED)

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| TIII -NI | NILIII | = 1130.4 |
|----------------------|---|----------|
| | NILII - (LII-LIII) | = 1130.6 |
| | NIHII*+ (LIII-HII) | : 1129.7 |
| | NIWIII + (LIII-WIII) | = 1129.9 |
| | Average | 1130.2 |
| N I = 102.1 | 5 | |
| LTTT-NII | N ₁₁ L ₁ -(L ₁ -L ₁₁₁) | = 1141.6 |
| | NIIMIA+(TIII-WIA) | = 1142.4 |
| | Average | 1142.0 |
| NII : 9 | 0.5 | |
| LIII-NIII | NIIILI-(LI -LIII) | • 1158.2 |
| · · · · | NIIIMy + LIII-My | = 1158.3 |
| | Average | 1158.3 |
| EIII = 74 | .2 | |
| rill-R ^{IA} | NINTII-(TII-TIII) | = 1177.1 |
| | NINNII + LIII-MII | = 1178.1 |
| - | NINWIII+ LIII-MIII | : 1177.5 |
| | Average | 1177.6 |
| | | |

f

NIV = 54.9

= 1205.2

= 1205.1

1205.1

= 1205.9

1213.9

| | TABLE | IV | (CCNTINUED) | |
|--|-------|----|-------------|--|
|--|-------|----|-------------|--|

LIII - NV

- 510F

 NyLIII
 = 1180.3

 NyMIIILIII -MIII
 = 1180.2

 Average
 1180.3

N_V = <u>52.2</u>

LIII - NVI

1.000 2

NVIMU + LLLL - MV NVIMIV + LIII - MIV Average

100 - 2 T - F -

NVIIMy +LIII - My

OIIMIN+LIII - MIN

- N_{VI} = <u>27.3</u> L_{III} - N_{VII} L_{VII} = 26.6
- LIII 0I

OILIII* = 1510.2 OINIII+TIII - MIII = 1506.3 1508.3

 $O_{I} = 24.2$

LIII - OII

OII, IIILI - (LI - LIII) =(1215.9)

 $O_{II} = 18.6$ $L_{III} - O_{III}$ $L_{III} - O_{IV}$

No data $O_{IV}L_{II} - (L_{II} - L_{III}) = 1225.3$ $O_{IV}M_{II} + L_{III} - M_{II} = \frac{1225.6}{1225.5}$

OIV = 7.0

. "

TABLE IV (CONTINUED)

L_{III} - 0_V 0_{IV}V_{III} = 1226.3 0_VM_{III}+ L_{III} - M_{III} = <u>1225.5</u> 1225.4

0v = 7.1

LIII= PI

No data

L_{III} - P_{II,III} P_{II,III}L_{I*} -(L_I · L_{III}) = 1231.4

PII,III = 1.1

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L Absorption edges: V. Dobejsek and J. Marek, Zeit. P. Physik, <u>97</u>, 97 (1935)
M Absorption edges: V. Dobejsek and V. Kunzl, Mature, <u>138</u>, 590 (1936)
L Series: H. Bouthe and A. V. Crosse, Zeit. f. Physik, <u>61</u>, 170 (1930)
M Series: Pierce and A. V. Grosse, Phys. Rev., <u>47</u>, 532 (1935)

TABLE V

| Mr · | MII | | NI - NII | | . 0I - 0II | | | | |
|---------|-----------------|------|----------------|-----|------------|--------|----|-----|------|
| 0(| 0 (v /R) 4/2/R | | 0 (v /R) 4/2/R | | 40 | A DIVA | | | |
| 38 Sr | 5.8 | 0.50 | 56 Ba | 4.2 | 0.52 | 88 | Re | 4.0 | 0.49 |
| 39 Y | 6.1 | .58 | 57 La | 5.6 | .67 | 89 | Ac | | |
| | | | 58 Ce | 4.7 | . 54 | 90 | Th | 4.9 | . 56 |
| | | | 59 Pr | 5.2 | .58 | 91 | Pa | | |
| | | | 60 Hd | 5.3 | .58 | 92 | U | 5.0 | .53 |
| | | | 61 | | | | | | |
| | | | 62 Sm | 5.7 | .60 | | | | |
| | | | 63 Eu | 5.3 | .54 | | | | |
| | | | 64 Gd | 6.3 | .63 | | | | |
| | | | 65 Tb | 5.9 | .57 | | | | |
| | | | 66 Dy | 5.9 | .56 | | | | |
| | | | 67 Ho | 6.4 | .60 | | | | |
| | | | 68 Er | 5.9 | .54 | | | | |
| | | | 69 Tm | | - | | | | |
| | | | 70 Yb | 7.8 | .60 | | | | |
| | | * | 71 La: | 6.3 | .54 | | | | |
| 40 Zr | 6.4 | .60 | 72 Hf | 7.4 | .61 | | | | |
| 41 Cb | 6.6 | .59 | 73 Ta | 7.6 | .62 | 6 | | | |
| 42 Mo | 7.0 | .60 | 74. 17 | 7.3 | .58 | | | | |
| 43 I'm | | | 75 Re | 8.0 | .61 | | | | |
| 44 Ru | 7.3 | .59 | 76 Os | | | | | | |
| 45 Rh | 7.7 | .61 | 77 Ir | 8.3 | .61 | | | | |
| 46 Pd | 8.0 | .59 | 78 Pt | 8.3 | .60 | | | | |
| 47 A.E. | 8.6 | .61 | 79 Au | 8.5 | . 59 | | | | |

REFERENCES FOR TAPLE V.

All data are for Siegbahn, "Spectroskopie der Roentgenstrahlen", 2nd Ed., Springer, Berlin, 1931, except for the last row elements which are from Tables I and II, and rhenium which are from Y. Cauchois, J. Phys. Radium, 8, 267 (1937).

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100 M

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TABLE VI

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DIFFERENCES BETTEEN OBSERVED AND CALCULATED MIN AND MN EDGES.

| Values | of | 2/ | R | are | list | ted. |
|--------|----|----|---|-----|------|------|
|--------|----|----|---|-----|------|------|

| Ele | ement | MIV Edge observed | [MIV] Edge Calc. from LIII edge | | Wy Edge | [My] edge calc. fr LIII ed | $\Delta(\nu/R)$ from $M_V = [M_V]$ ige |
|-----|-------|----------------------|---------------------------------------|------|---------|----------------------------------|--|
| 73 | Ta - | | | | 130.2 | 128.1 | +2.1 |
| 74 | W | 140.5 | 137.5 | .3.0 | 136.0 | 132.9 | 3.1 |
| 76 | Os | 152.5 | 1 | | 146.1 | 149.4 | 3.3 |
| 77 | If | 158.4 | 155.3 | 3.1 | 152.9 | 149.8 | 3.1 |
| 78 | Pt | 164.4 | 161.2 | 3.2 | 158.6 | 155.3 | 3.3 |
| • | | • | | | | | |
| _ | | | | | | | |
| 90 | Th | 256.7 | 256.9 | -0.2 | 244.3 | 245.3 | -0.5 |
| 91 | Pa | 265.8 | 266.0 | -0.2 | 253.1 | 253.7 | -0.6 |
| .95 | U . | 273.9 | 274.5 | -0.6 | 261.0 | 261.6 | -0.6 |
| | | | | | | | |



Elements 74-77

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Elements 90-92

(Sketch added by Ed.)

