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Structure and Width of the L_{III} Absorption Limits of Tantalum, Tungsten and Gold

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The double crystal spectrometer was used to investigate the structure and widths of the L_{III} absorption limits of the elements Ta, W and Au, in the free metal and in compounds. Curves of these absorption limits are presented. Tables are given of the measured values of the wave-lengths and of the widths of these limits, and also the relative displacement of these limits in compounds. The widths, in volts, of the L_{III} absorption limits increase with atomic number. There is a decrease in absorption on the short wave-length side of the main edge for these elements corresponding to an absorption line on the short wave-length side of the main edge. Evidence is given to support the hypothesis that x-ray energy levels have definite energy widths.

THE double x-ray spectrometer has been used recently by Barnes,[1] Ross,[2] and Richtmyer and Barnes,[3] for investigating the structure and width of the *K* absorption limits, and by Hull,[4] for the L_{II} and L_{III} absorption limits of mercury. The single crystal spectrograph has been used for studying the secondary structure on the short wave-length side of the main *K* and *L* edges. In particular, Hanawalt[5] has examined the secondary structure of the L_{III} absorption limits of xenon and mercury, and Coster and Veldkamp[6] have examined the secondary structure of the L_{III} limits of gold and platinum.

In the present work, the double x-ray spectrometer was used to investigate the structure and widths of the L_{III} absorption limits of the elements tantalum (73), tungsten (74), and gold (79), and also the structure and relative positions of these limits in chemical compounds containing these elements. The compounds used were Ta_2O_5, K_2TaF_7, H_2WO_4, Au_2O_3 and $KAu(CN)_2$.

APPARATUS AND EXPERIMENTAL PROCEDURE

The double x-ray spectrometer used in this investigation is identical with that used by Hull[4] and described by Davis and Purks.[7] The ionization current was amplified by an FP-54 pliotron, and read on a Leeds and Northrup Type R galvanometer. Methyl bromide at atmospheric pressure was used in the ionization chamber.

The x-ray tube used in the investigation of the L_{III} limits of tantalum and gold had a standard tungsten target; the filament was made of 10 mil tungsten wire wound in the form of a helix about 7 mm long and 1 mm in diameter. The filament was mounted in a cylindrical cathode made of molybdenum. This type of filament construction gives a large focal spot approximately rectangular in shape, and is well adapted for work with the double x-ray spectrometer. A tungsten x-ray tube could not be used in the study of the L_{III} absorption limit of tungsten because the strong $WL\beta_5$ line is present at about the position of the main edge. Instead, a tube with a gold target and a tantalum filament was used in the investigation of this tungsten absorption limit. The x-ray tubes were generally operated at 40–50 m.a. and 30 kv.

All the substances used in this investigation were in powder form except the free metal gold. Thin absorbing screens of each substance were made by dusting the powder through heavy silk or cotton cloth on to thin paper moistened with castor oil. The gold absorbing screen was made of sheets of gold leaf. Screens of various thicknesses were tried, and the ones finally used were those which gave maximum contrast in transmitted energy on the short and long wave-length sides of the absorption limit. The screens were placed before the first crystal, and were oscillated several times per second in horizontal guides perpendicular to the x-ray beam to smooth out any effects due to the non-uniformities in the screens.

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[1] A. H. Barnes, Phys. Rev. **44**, 141 (1933).
[2] P. A. Ross, Phys. Rev. **44**, 977 (1933).
[3] F. K. Richtmyer and S. W. Barnes, Science **77**, 459 (1933).
[4] H. L. Hull, Phys. Rev. **40**, 676 (1932).
[5] J. D. Hanawalt, Phys. Rev. **37**, 715 (1931).
[6] D. Coster and J. Veldkamp, Zeits. f. Physik **74**, 191 (1932).
[7] Bergen Davis and H. Purks, Proc. Nat. Acad. Sci. **13**, 419 (1927).

The procedure in obtaining the curves was as follows: for any given wave-length, as determined by the position of the second crystal, three readings of the ionization current were taken without an absorbing screen, then three readings were taken with an absorbing screen in place. Corrections could then be made for any variations in the background energy. Each point on a curve represents the average of three such readings. Several curves were obtained for each substance investigated.

The positions of the L_{III} limits were determined with reference to neighboring lines in the L series of tungsten. The Ta limit was determined with reference to the β_1, β_2 and β_3 lines, the W limit with reference to the β_5, β_7 and β_{10} lines, and the Au limit with reference to the γ_2, γ_3 and γ_4 lines. The relative displacement of the L_{III} edge in a compound with respect to the edge in the free metal was determined by taking readings, at each setting of the second crystal, of the background energy, the energy transmitted through the free metal, and the energy transmitted through the compound.

EXPERIMENTAL RESULTS

The structures and widths of the absorption limits of the substances investigated are shown in Figs. 1, 2 and 3. While these curves are the results of individual runs, they are typical of several curves obtained for each substance. The curves are plotted with transmitted energy as ordinates, and wave-lengths in X.U. as abscissae. The values of the abscissae in volts and in seconds of arc are also indicated on the graphs.

The width of the main absorption edge was measured by drawing a straight line tangent to the curve, and determining its intersections with the ordinates of maximum and minimum energy. (See Fig. 1.) Corrections to these observed widths due to the crystals, as calculated by means of the formula developed by Schwarzschild,[8] are negligible. The width of the rocking curve for the crystals in the (1, −1) position is 12 seconds of arc. The wave-length of the absorption limit is taken as that of the midpoint of the main edge. Table I gives the values of the wave-lengths of the absorption limits, and also their widths, in volts and in X-units. The values for Ta and Au are averaged from ten curves, the values for W from five curves. It will be noticed that the widths, in volts, of the L_{III} absorption limits of these elements increase with the atomic number. Fig. 4 shows that in the region of atomic numbers 74–80, these widths lie on a straight line. The width of the L_{III} edge of Hg (80) is that obtained by Hull.[4]

TABLE I. L_{III} *absorption limits.*

Atomic number	Element	Wave-length (X-units)	Width of absorption edge (volts)	(X-units)
73	Ta	1252.9±0.2	10.8±1.0	1.36±0.13
74	W	1213.4±0.1	11.6±0.5	1.41±0.06
79	Au	1037.8±0.2	14.6±0.7	1.21±0.06

The curves for tantalum and tungsten show certain similarities. In particular there is a slight decrease in absorption for the free metals on the short wave-length side of the main edge. This corresponds to an absorption line on the short wave-length side of the absorption edge. Sandstrom[9] using the single crystal photographic method, shows a microphotometer curve of the tungsten L_{III} edge which exhibits this same effect. This decrease in absorption on the short wave-length side becomes much more pronounced in the compounds containing these elements. Furthermore, the main edges of these elements in the compounds investigated are all displaced towards the short wave-length side with respect to the main edge of the free metal. It is interesting to note that both of these elements belong to the group in which an inner level, the $O_{\text{IV, V}}$ or $5d$ level is not filled.

Fig. 3 shows that the shape of the L_{III} edge of gold is different from that of Ta and W. While the curve for gold also shows an absorption line on the short wave-length side of the absorption limit, it differs from the curves for Ta and W in that the absorption begins to increase at about 17 volts from the center of the main edge and reaches a maximum value about 26 volts from the main edge. Furthermore, the displacement of the edge in a compound is very small; in the case of AuO_3 it is negative, that is, towards longer wave-lengths, and in the case of $KAu(CN)_2$ it is practically zero within the limits of

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[8] M. Schwarzschild, Phys. Rev. **32**, 162 (1928).

[9] A. Sandstrom, Zeits. f. Physik **66**, 784 (1930).

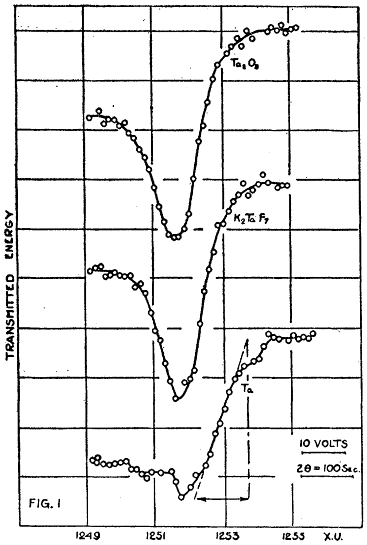

FIG. 1.

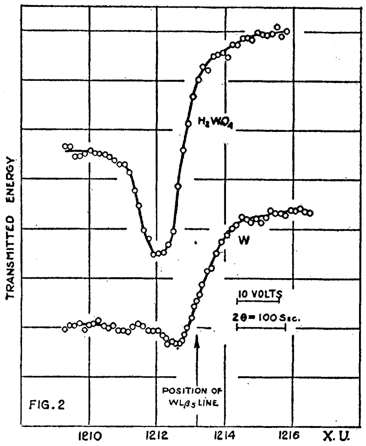

FIG. 2.

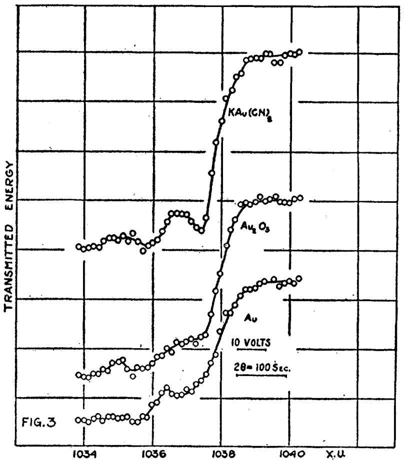

FIG. 3.

FIG. 1. Tantalum L_{III} absorption limit in the free metal and in compounds.
FIG. 2. Tungsten L_{III} absorption limit in the free metal and in a compound.
FIG. 3. Gold L_{III} absorption limit in the free metal and in compounds.

experimental error. It is interesting to note that gold is the first element in which the $5d$ level is complete as shown by Allison[10] in his investigation of the intensity ratio of the $L\beta_5$ line to the $L\beta_1$ line for the elements from atomic number 74 to 83. (See Table II.)

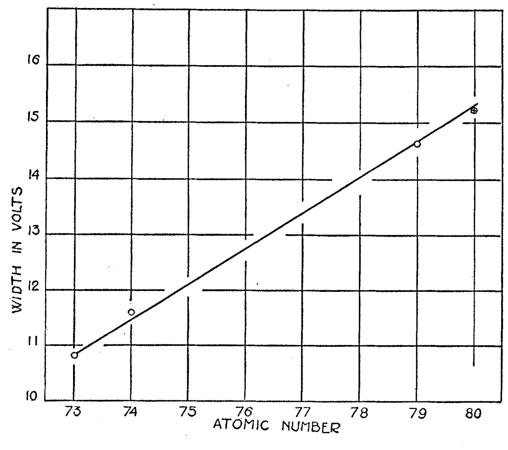

FIG. 4. Width of L_{III} absorption limit plotted against atomic number.

TABLE II. *Displacement of the L_{III} edges in compounds relative to the edges in the free metal.*

Element	Compound	Relative displacement in volts
Ta	Ta_2O_5	3.8±0.2
	K_2TaF_7	3.6±0.3
W	H_2WO_4	4.8±0.4
Au	Au_2O_3	−1.4±0.7
	$KAu(CN)_2$	0

DISCUSSION

Tables of wave-lengths of absorption limits usually give several different values for the same limit for a single element. Frequently this is due to the fact that compounds were used in determining the wave-length of the absorption limit. Nishina[11] measured the wave-lengths of the L_{III} absorption limits of Ta and W using Ta_2O_5 and WO_3, respectively, and obtained values smaller than those given in Table I. This is in agreement with the result that the edges of these compounds are displaced towards shorter wave-lengths.

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[10] S. K. Allison, Phys. Rev. **34**, 7 (1929).

[11] Y. Nishina, Phil. Mag. **49**, 521 (1925).

A comparison of the data on the widths of the K and L absorption limits of the same element leads to the conclusion that x-ray energy levels are of finite energy width. For example, Richtmyer and Barnes[3] found the width of the K limit of tungsten to be 133 volts, and that of gold to be 160 volts. These values are more than ten times the widths of the L_{III} limits of the corresponding elements. Since the process of absorption consists essentially in the removal of an electron from an inner x-ray level to one of the optical levels or completely outside the atom, the difference between the widths of the K and L_{III} absorption limits must be due to the difference in the widths of the K and L_{III} energy levels themselves.

Let us assume that the width of the main absorption limit is due to two terms, (1) the energy width of the x-ray level from which the electron is removed, and (2) the energy width of the combined optical levels to which the electron may be raised. Thus, if A represents the width of the K level, and B the width of the L_{III} level, and C the width of the combined optical levels, then the width of the main K absorption limit is $A+C$, and the width of the L_{III} absorption limit is $B+C$. The magnitude of C for an element of atomic number Z may be taken as the ionization potential of the element of atomic number $Z+1$. In accordance with the conclusions of Weisskopf[12] and Weisskopf and Wigner,[13] an x-ray spectral line should be the sum of the widths of the energy levels involved in the transition. Thus the width of the K line should be $A+B$, since this line is due to a transition from the L_{III} level to the K level. The magnitude of B is of the order of a few volts, of the same order of magnitude as C. Hence the width of the $K\alpha_1$ line should be approximately equal to the width of the K limit for any one element. Furthermore, the width of the $K\alpha_1$ line and the width of the K absorption limit should vary in a similar manner with atomic number.

It must be emphasized that the method used in measuring the width of an absorption limit is entirely arbitrary. It might also be noted that the width of an absorption limit is not necessarily the width of an atomic energy level. For a comparison of the widths of absorption limits and of lines, the recent data of Ross[2] on the K absorption limits and Allison's[14] data on the widths of the $K\alpha_1$ lines for the same elements may be used. We get good quantitative agreement if we compare twice the width at half maximum of a $K\alpha_1$ line with the measured width of the K absorption limit of the same element. Zinn [15] presents a curve giving the width of the K absorption limit as a function of atomic number and shows that above atomic number 32, the width of the K absorption limit increases as the fourth power of the atomic number, while for elements of lower atomic number the widths are practically constant. The curve given by Allison[14] for the width of the $K\alpha_1$ line as a function of atomic number is very similar to that given by Zinn,[15] and follows a fourth power law for atomic numbers greater than 32. The fact that the widths of the K absorption limits all have practically the same value for elements below atomic number 32 is to be expected on the basis of the above assumption since the width of an absorption edge cannot be less than C. In a similar manner the widths of the L_{III} absorption limits should reach a limiting value for elements below atomic number 73.

The writer is indebted to Professor Bergen Davis for having suggested this investigation, and for his continued interest and encouragement throughout the progress of this work.

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[12] V. Weisskopf, Ann. d. Physik **9**, 23 (1931).

[13] V. Weisskopf and E. Wigner, Zeits. f. Physik **63**, 54 (1930).

[14] S. K. Allison, Phys. Rev. **44**, 63 (1933).

[15] W. H. Zinn, Phys. Rev. **46**, 659 (1934).