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NOTE ON X-RAY SPECTRA

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In previous papers¹ the authors have presented measurements of the critical absorption wave-lengths belonging to the *L* series of nine of the heavy elements (27 wave-lengths in all). We have also discussed the bearing of these data on theoretical matters, and their relation to other available measurements of X-ray spectra. Since these papers were published, many accurate measurements have been made of the emission spectra in both the *L* and *M* series for the heavy elements.

Coster,² working in Siegbahn's laboratory, has accurately measured the *L* series emission lines for eleven heavy elements. He has extended the three known *M* absorption limits to five for uranium and thorium, and has measured the first three *M* limits for bismuth.

De Broglie and Dauvillier³ have studied in detail the *L* series emission spectra for six heavy elements.

With these new, accurate data, Smekal,⁴ Coster,² Dauvillier³ and Wentzel⁵ have constructed atomic systems to explain the source of each known emission line. The systems are based on the Bohr-Sommerfeld theory of the origin of characteristic X-radiation. In developing and discussing their systems, these investigators have used the values of the *L* absorption limits measured by us. Certain criticisms have been made of a few of our values. It has therefore seemed desirable to measure some of the limits again.

Coster⁶ has suggested a possible source of error in our values for the absorption limits of tungsten on the ground that we used an X-ray tube equipped with a tungsten anticathode, and that therefore we would get an effect not due to absorption alone but also to the neighboring emission lines. We wish to call attention to the fact (stated on page 534 of our paper in the *Physical Review*, Dec. 1920) that we took⁷ the precaution

of using an X-ray tube with a molybdenum target to avoid exactly this difficulty. If there had been an appreciable amount of tungsten on the anticathode due to sputtering, we would have detected the presence of the strong emission lines of the L series. In a more recent paper Coster⁸ states that he has measured the L_1 and L_2 absorption limits of tungsten and obtained essentially the same wave-lengths as those given by us.

Table I contains our new values for the L_2 and L_3 absorption limits of Pt, Au and Bi. These measurements were taken with almost the same arrangement of apparatus as before. The X-ray tube was provided with an arm which reached nearly to the first slit of the spectrometer, thus reducing the absorption of X-rays by air. At the end of this arm and also on the front of the ionization chamber thin mica windows were employed which still further reduced the absorption of X-radiation. Finally the sensitivity of our electrometer had been increased many times. We were thus supplied with a much more sensitive detector of X-ray spectra than in our earlier measurements. This enabled us to use narrower slits and to obtain at the same time greater drops in our ionization currents for the absorption limits.

TABLE I
CRITICAL ABSORPTION. L SERIES OF X-RAYS
GRATING SPACE FOR CALCITE, $2d = (6.056 \pm 0.004) \times 10^{-8}$ CM.

CHEMICAL ELEMENT	$\lambda \times 10^8$ cm.	L_2	ν/ν_{∞}	$\lambda \times 10^8$ cm.	L_3	ν/ν_{∞}
Pt	.9318 \pm 3		0.9779	.8918 \pm 9		1.022
Au	.9008 \pm 4		1.0116	.8610 \pm 9		1.058
Bi	.7871 \pm 4		1.1578	.7562 \pm 9		1.205

In the first column for each limit is given the wave-length in Ångstrom units; in the second, the wave number divided by the Rydberg constant.

Our new value for L_2 of Au differs from our previous one by 0.17 per cent. The error in our previous work was due to the proximity of the bromine ionization limit, which has a wave-length = 0.91796×10^{-8} cm. In our new measurements it was unnecessary to have ethyl bromide in the ionization chamber.

For the L_3 limits to Pt and Bi the new values differ from the old ones by a considerable amount in excess of our then estimated error. These errors were undoubtedly inherent in the faintness of the effect which we were endeavoring to measure.

The other three values are substantially the same as we gave before. We do not find the error in L_3 for Au suggested by Dauvillier.

At the time of our previous investigation, the available evidence seemed to indicate that the β_5 and γ_2 emission lines belonged, respectively, to the L_1 and L_2 groups—i.e., that β_5 was emitted when an electron fell into the L_1 orbit, and γ_2 when an electron fell into the L_2 orbit. As we definitely proved that the L_1 and L_2 absorption limits for tungsten were of lower

frequency than β_5 and γ_2 (a fact since verified by Coster), the idea of absorption limits being "limiting frequencies" for groups of emission lines was confronted with an anomaly. We proposed an explanation of this apparent anomaly that was in accord with the Bohr theory. Since then, however, Hoyt⁹ and Dauvillier³ have pointed out that the W emission line at $\lambda 1.212$ should be taken as β_5 instead of the one at $\lambda 1.203$ as before. This suggestion has been confirmed by the more accurate measurements of the corresponding line for the other heavy elements. When the square root of the frequency is plotted against atomic number for the β_5 lines, the points all lie on a smooth curve. Furthermore, in place of γ_2 , the work of Dauvillier and Coster indicates that a new γ line, γ_6 , at $\lambda = 1.072$, is the result of an electron falling into the L_2 orbit, and therefore belongs to the L_2 group. Both the old β_5 line for W and the γ_2 lines have been assigned to the L_3 group.

Consequently, we now take β_5 , γ_6 and γ_4 to be the shortest emission wave-lengths in the L_1 , L_2 and L_3 groups, respectively.

Coster has compared his new values for the wave-lengths of each of these emission lines with our values of the corresponding absorption limits, and has concluded that the absorption limits are in general somewhat shorter in wave-length than the emission lines associated with them. Table II gives this comparison using our new values for L_2 and L_3 .

ELEMENT	L_2	γ_6	L_3	γ_4
Pt	.9318 \pm 3	.9317	.8918 \pm 9	.8950
Au	.9008 \pm 4	.90125	.8610 \pm 9	.8663
Bi	.7871 \pm 4	.7874	.7562 \pm 9	.7610

Within experimental error the wave-lengths of the absorption limits are shorter than the wave-lengths of the shortest emission lines associated with them.

Coster² now places the number of L doublets at four, $\eta-l$, $\beta_2-\alpha_2$, $\gamma_5-\beta_6$, $\gamma_6-\beta_5$. The $\gamma_1-\beta_2$ doublet has been eliminated which is in accord with our suggestion that the electrons responsible for these two lines do not appear to start from the same orbit but different ones. He has also found and measured the two M absorption limits predicted by us for U and Th in order to explain the existence of the $\eta-l$ doublet. His values are in close agreement with our predicted ones.

According to Smekal,⁴ the $M\gamma$ line is due to the passage of an electron from an N_3 orbit to an M_3 orbit. If this is true, the following relation between frequencies should hold:

$$(L_3 - L_1) - M\gamma = L\beta_3 - L\beta_2$$

Coster has tested this relation using his new values for β_2 and β_3 , Stenstrom's value for $M\gamma$ and our values of L_1 and L_3 . He finds it confirmed by the available experimental data except in the cases of Pt and Bi. Our

new values bring Pt into line. For Bi, however, our correction is in the right sense but far too large. We cannot at present explain this discrepancy. Table III gives our new values for this relation.

ELEMENT	$L_2 - L_1$	$M\gamma$	$(L_3 - L_1) - M$	$\beta_3 - \beta$
Pt	.1706	.17158	-.0010	.0000
Bi	.2163	.20144	+ .0149	+ .0176

The lines β_7 and γ_4 have been assigned by Coster to electrons which start from *different* outer orbits and fall, respectively, into L_1 and L_3 orbits. Assuming the γ_4 electron to start from a higher orbit than β_7 , we should then expect $\gamma_4 - (L_3 - L_1)$ to be greater than β_7 . Coster shows this to be the case except for Pt and Bi. Our new measurements bring both Pt and Bi into line with the other elements. Table IV contains values for these quantities in the cases of Pt and Bi.

ELEMENT	$\lambda_4 - (L_3 - L_1)$	β_7	Δ
Pt	847.8	844.9	+2.9
Bi	980.6	(977.2)	+3.4

The value of β_7 for Bi was obtained, as suggested by Coster, by interpolation based upon the constant difference in wave-length exhibited by the elements for $\beta_2 - \beta_7$, the wave-length for β_2 being known. The differences in the fourth column are in the same sense and of the same magnitude as those found by Coster for Ta, W, Au, Tl and Pb. Moreover, if we estimate a value for the wave-length of γ_4 for U based upon our value of L_3 for the same element, we obtain a difference greater than those above and also in the same sense. It is therefore quite well established that the β_7 and γ_4 electrons start from orbits which maintain approximately the same difference in energy level as we go from Ta to U.

The authors in 1920 compared the frequencies of certain L emission lines with the differences in frequency between corresponding L and M absorption limits.¹ Kossel first pointed out that these quantities should be equal on Bohr's theory. At that time we found each L emission frequency to be equal to a corresponding difference in absorption frequencies within the limits of experimental error. Coster^{2,3} has recently extended this comparison with his new and more accurate measurements to in-

ELEMENT	l	$L_1 - M_3$	η	$L_2 - M_3$	α_1	$L_1 - M_1$	α_2	$L_1 - M_2$
U	855.84	855.1	1134.95	1131.8	1003.23	1002.17	990.37	989.21
Th	819.19	818.8	-----	-----	955.78	954.80	944.08	943.15
Bi	-----	-----	-----	-----	798.54	797.43	790.20	789.35
	β_1	$L_2 - M_2$	β_3	$L_3 - N_3$	β_4	$L_3 - M_4$		
U	1269.08	1265.87	1286.29	1285.78	1222.53	1220.86		
Th	1194.94	1193.15	1211.67	1209.77	1155.00	1151.86		
Bi	959.93	958.16	973.85	971.2	-----	-----		

clude two more M absorption frequencies for U and Th, and the first three M limits for Bi. Table V contains his values with the exception of $L_3 - M_3$ for Bi which we have corrected to accord with our new value of L_3 for that element.

In each case the emission frequency exceeds the difference in absorption frequencies, but by an amount that is less than 0.3 of a per cent.

The K Series of Molybdenum.—The authors have also measured the emission and absorption spectra for the K series of molybdenum. The apparatus and method used are described in previous papers.⁷ A Coolidge tube equipped with a molybdenum target and an extra arm at the end of which happened to be a thin glass window served as the source of radiation.

Table VI contains the results of these measurements.

TABLE VI
K SERIES OF MOLYBDENUM
GRATING SPACE OF CALCITE = $2d = 6.056 (10)^{-8}$ CM.

LINE	NO.	GLANCING ANGLE	WAVE-LENGTH $\times (10)^8$ CM.	ORDER
α_2	3	13°-36'-08"	0.71213 \pm 8	2d
α_1	3	13°-31'-07"	0.70783 \pm 7	2d
β'	3	12°-02'-50"	0.6320 \pm 2	2d
β	6	12°-01'-50"	0.63114 \pm 7	2d
$\beta\beta'$	1	5°-59'-05"	0.6314 \pm 3	1st
γ	3	11°-48'-32"	0.6197 \pm 2	2d
γ	1	5°-52'-30"	0.6199 \pm 3	1st
K	1	5°-51'-40"	0.6184 \pm 2	1st

In the second column the number is the number of actual measurements made.

In the second order, the β line was markedly asymmetrical and we were able to estimate the position of its weaker component, β' , predicted by Sommerfeld. The wave-length difference between these two lines is of the same order of magnitude as that found in the case of other elements. The wave-lengths of β and γ found in the first order are definitely longer than those found in the second order. This is chiefly due to the complex structure of both of these lines, although several investigators including the authors have found a similar but smaller effect in the case of emission lines supposed to be single.

In a recent paper Overn¹⁰ has also given wave-lengths for these same emission lines. His values, however, do not agree with ours even when corrected for the difference between the rock salt grating space used by him and the calcite grating space used by us. The discrepancy between his values and ours seems to increase as we go farther from the "white line" used as a reference line by him.

As we determined these wave-lengths by the ionization method, we are also able to give the ratio of the intensities of α_1 and α_2 . From three de-

terminations in the second order we obtain for this ratio 1.97 as compared with 2.00 predicted by Bohr.

The ratio of the intensities of β to γ in the first order is 6.3 (one determination) and in the second order is 5.46 (two determinations).

¹ Duane and Patterson, *Proc. Nat. Acad. Sci., Washington*, Sept. 1920; *Phys. Rev.*, Dec. 1920, p. 526.

² Coster, *Z. Phys.*, **5**, 1921 (139); also **6**, 1921 (185).

³ De Broglie and Dauvillier, *Paris, C. R.*, **173**, p. 137. Dauvillier, *Ibid.*, **172**, also **173**, p. 647, also other papers in this volume.

⁴ Smekal, *Z. Phys.*, **5**, 1921 (91, 121). Also **4**, 1921.

⁵ Wentzel, *Ibid.*, **6**, 1921 (2).

⁶ Coster, *Ibid.*, **5**, 1921 (147). Also *Physic Rev.*, Sept. 1921.

⁷ Duane and Patterson, *Physic Rev.*, **16**, 1920 (534).

⁸ Coster, *Ibid.*, Jan. 1922.

⁹ Hoyt, *Proc. Nat. Acad. Sci., Washington*, Nov. 1920.

¹⁰ Overn, *Physic. Rev.*, Nov. 1921, p. 350.

A NEW METHOD OF USING X-RAYS IN CRYSTAL ANALYSIS

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The procedure described in this paper differs in some fundamental details from the elegant methods of analyzing crystals by means of X-rays developed by Laue, the Braggs and others.

The substance to be examined may be in the form of powder or of whole crystals. In the latter case the crystal need not be large. One having a volume of only .25 cubic mm. suffices, although slightly more accurate data may be obtained, if it has a somewhat larger volume.

In our method we employ X-rays belonging to the continuous spectrum, and therefore containing rays of a great variety of wave-lengths, and not the line spectra of definite wave-lengths, as in most other methods. This procedure has certain advantages. An ordinary X-ray tube with a tungsten target may be used, and high voltages may be applied to it. More intense X-radiation can be obtained from tungsten than from such chemical elements as rhodium and molybdenum. Further in some cases it is desirable to employ X-rays of shorter wave-lengths than those in the *K* series of rhodium and molybdenum, for these shorter rays are more penetrating than the longer ones. As a rule we use the spectrum between .12 and .80 Ångström.

In making an analysis of a small crystal we place it at the center of an X-ray spectrometer, provided with an ionization chamber and a quadrant electrometer. The slits of the instrument should be fairly narrow, and