It must be remembered, however, that the exact values of the short-wave limits are not the essential point of the theory by which I have attempted to explain these tertiary bands. As noted above, it is immaterial for this theory whether its basic hypothesis is so framed as to lead to the use of an emission line frequency in the calculation, or the frequency of an absorption limit. In other words, it is immaterial, so far as the essential point is concerned, whether the short-wave limits of the bands are where I estimated them or at the positions given by Clark and Duane.

The essential point is, first, that the unexpectedly high intensity and the narrow wave-length range of these bands are both inexplicable on the simple theory that the bands are ordinary continuous spectra, produced by the impacts of photoelectrons on atoms struck after leaving the atoms from which they are ejected; and furthermore, that both these characteristics of the bands are explained at once by the hypothesis outlined in my paper. As this point has not been discussed by Clark and Duane, one may infer that there is no disagreement about it.—D. L. W.

ON THE THEORY OF THE TERTIARY RADIATION PRODUCED BY IMPACTS OF PHOTO-ELECTRONS

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The authors have published[2] recently accounts of experiments in which the tertiary radiation due to the impacts of photo-electrons produced by primary X-rays has been discovered. The tertiary radiation appeared in some investigations of the spectrum of secondary rays coming from secondary radiators of various chemical elements under the influence of primary X-radiation. The tertiary radiation occupies certain bands in the spectra of the rays from the secondary radiators. The theory we proposed for the tertiary radiation assumed that it was due to the electrons emitted by the primary rays from certain atoms when these electrons impinged upon neighboring atoms. According to this theory, the short wave-length limit of a tertiary radiation band ought to be given by the equation

$$\nu = \nu_1 - \nu_2, \tag{1}$$

in which ν, ν_1 and ν_2 represent the frequencies of the limit of the tertiary band, the primary ray and the critical absorption of a chemical element in the secondary radiator, respectively. The experimental data agree with the equation to within errors of measurement.

In this number of these PROCEEDINGS, D. L. Webster, in an article submitted by him to us for comment, publishes a slightly different theory for the origin of the tertiary bands. According to his theory, the tertiary radiation arises from the impact of a photo-electron against a second electron in the very same atom from which it came. Assuming with Webster that the entire amount of energy of the photo-electron at the time it hits the second electron may appear as energy of radiation, the short wave-length limit of a tertiary band should be given by the equation

$$\nu' = \nu_1 - \nu_3 \qquad (2)$$

where ν_3 represents the frequency of vibration of an emission line in the X-ray spectrum of the chemical element, instead of a critical absorption frequency.

On account of the importance of this interesting idea the experimental data at hand should be examined with great care to see whether they fit one theory better than the other.

The difference between the high frequency limits of the tertiary band calculated on the two theories is the difference between a critical absorption frequency and that of an emission line. It is desirable, therefore, to choose as test data the results of the experiments in which this difference has its greatest value. The difference between the critical absorption frequency and that of a given emission line in its series increases rapidly with the atomic number of the chemical element. Silver has the highest atomic number of those chemical elements for which we have as yet observed the tertiary radiation. Let us, therefore, examine the theory as applied to the tertiary radiation from silver, and let us take the case in which the photo-electron is expelled from the K level of a silver atom by an X-ray belonging to the $K\alpha$ line of tungsten. Transforming equations 1 and 2 by introducing wave-lengths we find

$$\lambda = \frac{\lambda_1\lambda_2}{\lambda_2 - \lambda_1} \quad (3) \qquad \text{and} \qquad \lambda' = \frac{\lambda_1\lambda_3}{\lambda_3 - \lambda_1} \quad (4)$$

as the expressions for the short wave-length limits of the tertiary radiation band according to the two theories. In these expressions λ_2 signifies the K critical absorption wave-length of silver and λ_3, the wave-length of the $K\alpha$ doublet of silver. Putting their known values into the equation and that of the $K\alpha_1$ line of tungsten, we find for the short wave-length limit $\lambda = .366$ Å according to our theory and $\lambda' = .330$ Å according to Webster's. The short wave-length limit of the tertiary band as determined by experiment is contained in table II of our note to which Webster refers. It is $\lambda = .365$. It appears, therefore, that the experimental wave-length agrees very closely with its value calculated according to our theory and does not agree at all with that predicted by Webster's theory. In fact, the wave-length calculated according to Webster's theory lies about half way between the short wave-length limits of the tertiary bands due to the radiation from the $K\alpha$ line of tungsten and the $K\beta$ line of tungsten. As these differ from each other by as much as .07 Å, it is impossible that we could have made an error as great as that of the difference between Webster's theoretical value and the experimentally observed value. These wave-lengths can be measured to within about .002 Å.

A similar calculation of the short wave-length limit of the tertiary radiation due to the $K\beta$ line of tungsten gives $\lambda = .297$ according to our theory and $\lambda = .274$ according to Webster's. The value determined by our experiments is $\lambda = .296$, which agrees with our theoretical value to within $^1/_2\%$ but differs from Webster's by 8%, which is an impossible error.

An examination of the curve representing our experimental data for silver, published in the March number of these PROCEEDINGS, on page 92, shows clearly that the tertiary humps are very sharply marked on their short wave-length sides and that they are separated from each other by a considerable interval.

If we calculate the angles corresponding to the short wave-length limits, we find that the humps representing tertiary radiation due to the tungsten $K\alpha$ line should begin to rise at the angle 197°45′ according to our theory and 198°5′ according to Webster's. The position 197°45′ appears to be exactly correct, whereas the value 198°5′ lies half way between the short wave-length limits of the two tertiary radiation humps. The line between the two humps is substantially a smooth curve and shows no indication of any excess radiation at a point half way between the two limits. Similarly, the short wave-length limit of the hump representing tertiary radiation due to the tungsten $K\beta$ line ought to lie at the angle 198°24$^1/_2$′ according to our theory and 198°38′ according to Webster's. It appears from the curve that the hump begins at 198°26′ which agrees with our theoretical value and there is no excess radiation indicated at 198°38′. In making these calculations, a slit correction has been added amounting to about 5′. Even though this slit correction were entirely neglected, the positions of the two limits of the tertiary radiation, according to Webster's theory would be shifted only a very short distance on the curve and would not approach the experimentally determined positions to within anything like experimental errors. Hence, there is not the slightest evidence for any radiation that could be attributed to the impact of photoelectrons against other electrons in the atoms from which they come, as assumed by Webster.

Passing now to the data for the experiments with molybdenum reported in our note in these PROCEEDINGS for January, 1924, we find that Webster's theory predicts that the hump representing tertiary radiation from the tungsten $K\beta$ line should begin at 203°10′ whereas our theory predicts that it should begin at 203°25′. The actual beginning as nearly as can be estimated on the curve lies at 203°24′ and agrees therefore, much more closely with our theory than with Webster's. Similarly, the observed position for the short wave-length limit for the hump representing tertiary radiation from the tungsten $K\alpha$ line, lies at 203°54′. The value calculated by our theory is 203°55′ and by Webster's 203°44$^1/_2$′. Evidently in this case also, our theory represents experimental values far more closely than Webster's.

The difference between the calculated values of the short wave-length limits of the tertiary radiation according to the two theories grows smaller and smaller as we proceed to chemical elements of lower atomic number, for the difference between the critical absorption frequency and that of an emission line in its series decreases as the atomic number decreases. Even for the germanium experiment, described in the March number of these PROCEEDINGS, the two theories agree with each other quite closely. When we reach the chemical elements from carbon to chlorine, the difference between the two theories becomes inappreciable. Both theories predict tertiary radiation substantially as we have found it in our experiments described in the April number of these PROCEEDINGS. In these experiments, we used a molybdenum target tube and secondary radiators containing lithium, carbon, oxygen, sodium, aluminium, sulphur and chlorine. The experiments with carbon were very similar to the well-known experiments by A. H. Compton. In every case we found evidence of tertiary radiation substantially in the position predicted by our theory and, therefore, also substantially in the position predicted by Webster's modification of it.

The extremely interesting and painstaking experiments performed by Ross with molybdenum primary rays and a carbon secondary radiator supply photographic evidence of radiation having wave-lengths longer than those of the characteristic lines of molybdenum. Evidently the photographic plate registers the *tops* only of the peaks obtained by ionization experiments. It would require a very much longer time of exposure to obtain the position of the short wave-length limits of the tertiary radiation. To make sure that a limit was recorded the exposure should be long enough to record the continuous spectrum. In particular the photograph indicates the shift in the position of the short wave-length limit of tertiary radiation as the angle between the primary and secondary rays decreases. Such a shift for tertiary radiation has been observed by us in our experiments with both tungsten rays and molybdenum rays.

In the December, 1923, number of these PROCEEDINGS, we published accounts of experiments with the K series lines from a tungsten target as the primary radiation and with a secondary radiator of carbon. In these experiments scattered radiation from the carbon appeared with wave-lengths precisely equal to those of the primary K series lines of tungsten, but no evidence of radiation comparable in intensity with the scattered rays and having wave-lengths somewhat longer than the tungsten lines was detected. The last number of the Comptes Rendus to reach us contains a note by M. de Broglie, in which he describes similar experiments with a tungsten target tube but with a secondary radiator consisting of a combination of carbon and tungsten. He employed the photographic method of registering the secondary radiation, and on the photographic plate appeared a line separated from that representing the fluorescent radiation of tungsten, on its long wave-length side. The two experiments together suggest that this radiation with shifted wave-length comes from the tungsten and not from the carbon. As a matter of fact, our theory of tertiary radiation predicts that, in this case, there should be radiation of somewhat longer wave-length than the primary radiation, due to the impact of electrons ejected by the primary K series lines of tungsten from the L levels of the tungsten atoms in the secondary radiator. If we substitute in formula 3, which represents our theory, the known values for the wave-length of the $K\alpha$ doublet of tungsten and for the $L1$ and $L2$ critical absorption wave-lengths of tungsten, we find that the short wave-length limit of the tertiary radiation should lie at the wave-lengths .2521 and .2601, respectively. There should, therefore, be radiation coming from the carbon-tungsten secondary radiator having maxima of intensity at wave-lengths slightly longer than these values. This radiation lies precisely in the region of the spectrum occupied by the line with shifted wave-length mentioned in de Broglie's note.

Although the experiments carried on so far with chemical elements of low atomic number cannot furnish decisive evidence between our theory and Webster's modification of it, the experiments with chemical elements of higher atomic number show clearly that there is no perceptible radiation which has the wave-lengths predicted by this modification. On the other hand definite evidence appears in our experiments of radiation having the short wave-length limits predicted by our theory that it arises from the impacts of photo-electrons against neighboring atoms.

It would, of course, be possible to devise a theory somewhat different from Webster's and consistent with equation I, which represents experimental facts. We might assume, for instance, that either the electron directly acted upon by the primary radiation or the electron in its own atom that it impinges against must get completely outside of the atom in order that tertiary radiation shall take place. In this case the minimum amount of energy absorbed by the atom would be $h\nu_2$, and, equating this to the differences between the $h\nu$ values of the primary and tertiary radiation, we get

$$h\nu_2 = h\nu_1 - h\nu,$$

which reduces immediately to equation I. This hypothesis, however, seems somewhat artificial, unless in the future it becomes advisable to assume in general that an atom cannot radiate even continuous spectrum radiation without changing or being changed from one stable state to another.

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[2] These PROCEEDINGS, Jan., March and April, 1924.

ABSORPTION MEASUREMENTS OF CERTAIN CHANGES IN THE AVERAGE WAVE-LENGTH OF TERTIARY X-RAYS

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In a series of experiments by G. L. Clark and William Duane[2] on the wave-lengths of secondary X-rays, the radiation from the secondary radiators has been found to contain tertiary radiation with a high frequency limit ν given by the equation

$$\nu = \nu_1 - \nu_2$$

where ν_1 is the frequency of the primary radiation and ν_2 a critical absorption frequency of the secondary radiator. The experiments on the spectrum of secondary X-rays at different angles from the primary beam showed that, while the short wave-length limit of the tertiary radiation remained fixed, the maximum of the "hump" shifted toward longer wave-lengths with increasing angle. This effect is known to occur in the primary general radiation when examined at various angles from the incident cathode rays.[3] The radiation resulting when ν_1 is the frequency of the $K\alpha$ doublet of the target substance and ν_2 the K critical absorption frequency of the secondary radiator has a greater intensity than any other and our experiments are limited to this case.

We have examined the shift of the maximum of the tertiary radiation by the ingenious method described by Ross.[4] A beam of X-rays entering through the usual slits fell upon the secondary radiator, placed in the center of the spectrometer table. A screen was selected with a K critical absorption wave-length slightly longer than the short wave-length limit of the tertiary radiation under consideration. This screen was placed between the ionization chamber and the secondary radiator, and the ionization current examined at various angles with the direct beam. The shift of the maximum of the tertiary is indicated by an increase, rapid at first and then slow, of the fraction of the radiation transmitted by the screen as the angle increases. The wave-length width of the tertiary radiation is fairly narrow, but still broad enough; so that the effect should not be