A Summary of X-Ray Satellites

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I. INTRODUCTION

IN the past, several summary articles on x-ray satellites[1, 2, 68, 72] have been published. While they may have been up to date at the time, there has been no recent attempt to scrutinize the field. The late F. K. Richtmyer's article on "Multiple ionization of inner electron shells of atoms" presented, most beautifully, the Coster-Kronig theory of satellite origin and some of the immediately relevant facts. There has been no complete review of the entire subject and all the pertinent facts. "Rome was not built in a day," and the history of the study of x-ray satellites, which now extends back over the past quarter of a century, is a story of progress made step by step painstakingly, until at last the picture was clear and complete enough for those clear-sighted scientists, Coster and Kronig, to finish it at one master stroke. It is, therefore, the purpose of this essay to cover the field completely, and provide a present-day picture. It is not proposed to present tables of data already published, but rather to describe them and provide the means for locating them in the literature.

(A) Discovery of Satellites. Survey and Summary Articles

X-ray satellites were first observed, in the K series, by Siegbahn and Stenstrom,[3] who noted faint lines on the short wave-length side of $K\alpha_1$ extending from Na(11) to Zn(30).

Surveys have been made of the K, L, and M series of x-ray lines, with the purpose of determining the wave-lengths, number, and atomic number extent of satellites. The L series was first carefully scrutinized by F. K. and R. D. Richtmyer.[26] They found the satellites were much more numerous than was previously supposed, observing as many as eight satellites of $L\alpha$ of Mo(42). They found:

5 satellites when $37 \leq Z \leq 49$ for $L\alpha$
4 satellites when $42 \leq Z \leq 48$ for $L\beta_1$
3 satellites when $48 \leq Z \leq 50$ for $L\beta_1$
5 satellites when $42 \leq Z \leq 50$ for $L\beta_2$.

Wave-length measurements were given for satellites and parent line.

Next, the M series was studied by F. R. Hirsh, Jr.[39] who in 1931 gave wave-length separations for three satellites of $M\beta$, and wave-length separations for four satellites of $M\alpha_1$. It was noted that the superimposed "semi-Moseley" graphs were very similar for the two satellite groups; mention of this will be made later in this article.

In 1932 O. R. Ford[43] made a careful re-survey of the K-series satellites; he noted the following satellite lines:

Satellite	Atomic numbers of occurrence
α_3	12 to 32 (inclusive)
α_4	12 to 25 (inclusive)
α'	12 to 23 (inclusive)
α_5	12 to 14 (inclusive)
α_6	12 to 14 (inclusive)
α_3'	12 to 14 (inclusive)
β^{i}	26 to 28 (inclusive)
β^{ii}	17 to 24 (inclusive)
β^{iii}	19 to 27 (inclusive)
β^{iv}	19 to 21 (inclusive)
β^{v}	17 to 20 (inclusive)
β^{vi}	19 to 24 (inclusive).

Ford[43] attempted to refer the $K\beta$ satellites to $K\alpha_1$ as their parent line, noting the improvement in semi-Moseley graph data, as did Deodhar.[38] This reasoning has been shown to be fallacious by Hirsh.[41]

From time to time, summary articles have been written. While the articles by Siegbahn[1] and Lindh[2] were quite complete at their time of publication, they are far out-dated now. The article by Wisshak[68] gave nearly all the important methods of attacking the problem of satellite origin: λ and $\Delta\lambda$ measurement; observation of intensity *vs.* atomic number, I *vs.* Z; intensity of satellites with respect to parent line intensity, I_s/I_p; excitation potentials.

The only article which carefully discusses the final solution to the problem of satellite origin is that of Richtmyer[72] who discussed the Coster-

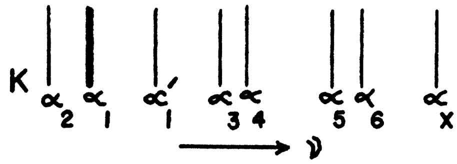

FIG. 1. $K\alpha_1$ satellites.

Kronig theory of satellite origin; he, however, made no pretense of covering the literature of this subject.

II. THEORIES OF ORIGIN AND RELEVANT DATA

(A) Wentzel-Druyvesteyn Theory

The successive attempts to account for the frequency separations of satellites and their parent line on the basis of the Wentzel-Druyvesteyn theory is an example of step by step progress—each worker benefiting by the results of his predecessors—until finally the exact nature of the multiple ionization was clear beyond all doubt.

Gregor Wentzel[6,17] in 1921 accounted for the frequency separations of the $K\alpha_1$ satellites by means of multiple atomic ionization. The $K\alpha_1$ satellites are simple to represent as shown in Fig. 1. Wentzel assigned the following energy separations to the given satellites:

$$(K\alpha_{1,2}=K-L) \text{ (Parent line)}$$
$$K\alpha_3=KL-L^2 \text{ Satellite}$$
$$K\alpha_4=K^2-KL \text{ Satellite}$$
$$K\alpha_5=KL^2-L^3 \text{ Satellite}$$
$$K\alpha_6=K^2L-KL^2 \text{ Satellite}$$
$$K\alpha_x=K^2-KL^2 \text{ Satellite.}$$

If we knock out one electron from the K shell, let the energy required be K_z; the energy to remove the next electron is then K_{z+1}; for the next electron the energy is L_{z+2}. Thus for KL ionization we write for the energy change K_z+L_{z+1}; for L^2 we write L_z+L_{z+1} that is, the energy required to remove two L electrons; for KL^2 we write $K_z+L_{z+1}+L_{z+2}$; for K^2L, $K_z+K_{z+1}+L_{z+2}$, and so on, realizing that these are all rough approximations. Performing these substitutions in the energy separations above, it is easy to prove that:

$$\nu\alpha_4-\nu\alpha_3=\nu\alpha_6-\nu\alpha_5 \qquad (1)$$

and

$$\nu\alpha_5-\nu\alpha_3=\nu\alpha_3-\nu\alpha_1. \qquad (2)$$

TABLE I. Differences $\Delta\nu/R$.

	Na(11)	Mg(12)	Al(13)	Si(14)
$\alpha_3-\alpha_1$	0.52	0.64	0.71	0.83
$\alpha_5-\alpha_3$	0.57	0.67	0.76	0.91
$\alpha_6-\alpha_4$	0.65	0.76	0.83	0.94

Transposing (1), we get:

$$\nu\alpha_5-\nu\alpha_3=\nu\alpha_6-\nu\alpha_4.$$

Combining this with (2) we have:

$$\nu\alpha_6-\nu\alpha_4=\nu\alpha_5-\nu\alpha_3=\nu\alpha_3-\nu\alpha_1. \qquad (3)$$

Wetterblad[19] has sought experimental verification of (3) in the spectrum of Na(11), Mg(12), Al(13), and Si(14), see Table I. The agreement is none too good, but we must remember that Eqs. (3) are approximations. Wetterblad[19] has shown that more precisely:

$$(\nu\alpha_6-\nu\alpha_4)_Z=(\nu\alpha_3-\nu\alpha_1)_{Z+1}.$$

This is quite well confirmed in Table I, as indicated by the last and first entries in each column.

Druyvesteyn[20,23] has compared theoretically the frequency separations for the satellites of $K\beta_1$, $L\beta_2$, $L\gamma_1$, and $L\gamma_{2,3}$ with the experimental data, and finds good agreement. He, however, does not study the satellites of $K\alpha$ and $L\alpha$, which constitute the most important groups.

B. B. Ray[27] next studied this problem, making a spectroscopic interpretation of lines on the basis of the Wentzel-Druyvesteyn theory. Wentzel, for example, interprets the $K\alpha_3$ satellite as $1K7L\rightarrow 2K6L$, neglecting multiplicity. Ray takes into account level multiplicity; an example of his interpretations, for $K\alpha_4$ is: $2K_1L_15L_2\leftarrow K_1L_16L_2$ or ${}^3P_{0,2}\leftarrow{}^3S_1{}^1S_1$ in spectroscopic notation. A multiplet of six lines results (see Table II).

Ray computes $\Delta\nu/R$ values for the combination ${}^1P-{}^3P$. Next, Langer[37] published a new interpretation; this was similar to the interpretation of Wolfe;[45] the combined interpretation is given in Table III. The calculation was for K(19), $K\alpha$ satellites. Wolfe's work[45] was an improvement over Langer's attempt[37] to account for these satellites.

TABLE II. Multiplet of six lines.

	${}^1P_1$	${}^3P_0$	${}^3P_1$	${}^3P_2$
${}^3S_1$	α_3	α_4	α_6	α_x
${}^1S_0$	α_1		α_5	

TABLE III. Interpretations of satellite lines.

Line	ν/R (obs.)	Transition (Wolfe)		ν/R (calc.) (Wolfe)	Transition (Langer)	
α'	245.05	$1s2p\,^1P$	$2p^2\,^1S$	245.05	$1s2s\,^1S$	$2s2p\,^1P$
α_3	245.56	$1s2s\,^3S$	$2s2p\,^3P$	245.63	$1s2p\,^3P$	$2p^2\,^3P$
α_4	245.69	$1s2s\,^1S$	$2s2p\,^1P$	245.53	$1s2s\,^3S$	$2s2p\,^3P$
α_5	—	$1s2p\,^3P$	$2p^2\,^3P$	246.38	$1s2p\,^1P$	$2p^2\,^1S$
α_6	—	$1s2p\,^1P$	$2p^2\,^1D$	246.15	$1s2s\,^1P$	$2p^2\,^1D$

Ramberg and Kennard[52] next studied the K-satellite origin, using the Hartree self-consistent field. Their calculated frequency separations were in excellent agreement with the observed separations. Their results and method used were certainly the best in this branch of the field of x-ray satellites. They definitely established KL ionization as the cause of $K\alpha'$, $K\alpha_3$, and $K\alpha_4$; KL^2 ionization as the cause for $K\alpha_{5,6}$ and $K\alpha_{7,8}$. By this result, we see that Langer[37] and Wolfe[45] were working in the right direction, but the configurations they used were not all correctly assigned (see Table IV). Table IV shows the assembled spectroscopic assignments for five workers on the problem of K-satellite origin. A peculiar fact, readily seen, is the nearly complete absence of correlation between the results of the different workers. There are but few permitted term differences (see Ray's work[27]) and the nearly complete absence of correlation is astounding. However, the careful and precise nature of Ramberg and Kennard's work[52] would lead one to place full confidence in their assignments.

R. D. Richtmyer[60] in 1936 published a paper on "The probability of KL ionization and x-ray satellites." He calculated the intensity of $K\alpha_{3,4}$ relative to $K\alpha_1$ as a function of atomic number, on the basis of the Wentzel-Druyvesteyn theory. He finds $I_{\text{Sat}}/I_{K\alpha_1}=C/(Z-\sigma)^3$, where $C=91$, and $\sigma=4.5$. This predicted atomic number trend of intensity is in good agreement with the results of Parratt;[63] however, it fails to agree with the later results of Shaw and Parratt.[66]

Recently Richtmyer and Ramberg[69] published frequency separations for the satellites of $L\alpha_1$ and $L\beta_2$ of Au(79). Using the theory of complex spectra, they calculated frequency separations and intensity profiles which, however, did not agree with the Wentzel-Druyvesteyn theory; rather they agreed with the results and predictions of Coster and Kronig,[58] which will be discussed later.

In passing, we must mention the theoretical work of R. D. Richtmyer[73] on LL (L^2) and LM x-ray lines. These lines have been detected for atomic number 47 by Burbank;[74] they have not been detected for atomic number 42 by Veith and Kirkpatrick,[75] who performed a painstaking search.

(B) Richtmyer Double-Jump Theory

For some time the theory of Wentzel and Druyvesteyn on satellite origin seemed to show small promise, partly at least, because of faulty work on excitation potentials (discussed in Section III-B), and it was entirely natural that an alternative theory should arise. F. K. Richtmyer[21] in 1928 proposed a new theory of satellite origin. He was aware that the square root of $\Delta\nu/R$, the frequency separation of satellite and parent line, was linear with atomic number: a similar fact was first noted by Coster,[9] (actually it is immaterial whether we plot it as the square root or the first power: this has been shown by Pincherle[82]). This immediately suggested to F. K. Richtmyer that this plotted *square root of the energy separation actually was a Moseley* (or "semi-Moseley," as he called it) *graph for an atomic energy difference, radiated jointly with the parent line quantum energy as a single quantum.* Thus he formulated in a later paper[25] that the two electron jumps occurred simultaneously in the atom: an inner jump and an outer jump, the *combined energy being radiated as a single quantum, or "satellite" quantum:*

$$h\nu_i+h\nu_0=h\nu_s \tag{5}$$

or

$$h\nu_s-h\nu_i=h\nu_0;$$

then

$$(\Delta\nu/R)^{\frac{1}{2}}=(\nu_0/R)^{\frac{1}{2}}. \tag{6}$$

Since ν_0 represented a semi-optical frequency, its $\Delta\nu/R$ value should be linear with Z, atomic

TABLE IV. Correlations in spectroscopic assignments.

Satellite	Wentzel-Druyvesteyn	Ray	Langer	Wolfe	Ramberg-Kennard
$K\alpha'$	—	—	$^1S\rightarrow{}^1P$	$^1P\rightarrow{}^1S$	$^1P\rightarrow{}^1S$
$K\alpha_3$	$KL-L^2$	$^3S_1\rightarrow{}^1P_1$	$^3P\rightarrow{}^3P$	$^3S\rightarrow{}^3P$	$^3P\rightarrow{}^3P$
$K\alpha_4$	K^2-KL	$^3S_1\rightarrow{}^3P_0$	$^3S\rightarrow{}^3P$	$^1S\rightarrow{}^1P$	$^1P\rightarrow{}^1D$
$K\alpha_5$	KL^2-L^3	$^1S_0\rightarrow{}^3P_1$	$^1P\rightarrow{}^1S$	$^3P\rightarrow{}^3P$	—
$K\alpha_6$	K^2L-KL^2	$^3S_1\rightarrow{}^3P_1$	$^1P\rightarrow{}^1D$	$^1P\rightarrow{}^1D$	—
$K\alpha_3$	K^2-KL^2	$^3S_1\rightarrow{}^3P_2$	—	—	$^3S\rightarrow{}^3P$

number, where outer shell electrons increase uniformly—which is just exactly what is observed.

In this same paper, with characteristic thoroughness, he also noted that K, L, and M satellites occurred in certain well-defined atomic number ranges: K, where $10 \leq Z \leq 30$; L, where $30 \leq Z \leq 52$; M, where $62 \leq Z \leq 92$.

It was at this time that DuMond[32] remarked that: "It would seem that all the known facts of x-ray satellites are explained qualitatively by Richtmyer's double-jump hypothesis, and only await further experimental work for a quantitative verification." He, quite evidently, was swept away by pardonable enthusiasm for the promise of the new theory.

About this time, Sawada[44] in Japan, published a "new theory" which was nothing more or less than plagiarism of the F. K. Richtmyer double-jump hypothesis. It is so obviously just that, that no further comment will be made.

E. G. Ramberg,[50] in 1934, cast considerable doubt on the validity of the double-jump hypothesis by theoretical calculations on "the validity of double-jumps in x-ray spectra." He computed the intensity of the $K\alpha_{3,4}$ satellite doublet relative to the intensity of the $K\alpha_{1,2}$ lines for Na(11).

$$K\alpha_3\text{: } I(2p4s \rightarrow 1s3s)/I(2p4s \rightarrow 1s4s) = 1 : 170,$$
$$K\alpha_4\text{: } I(2p3s \rightarrow 1s4s)/I(2p3s \rightarrow 1s3s) = 1 : 320.$$

The computed relative intensity for each is far too small when compared with the actual measured relative intensities. Ramberg pointed out that we should, on the basis of the double-jump hypothesis, expect long wave-length side satellites as well, which would represent subtraction (absorption) of the "semi-optical" shell ionization energy from the x-ray quantum in the process of ionizing the semi-optical shell by means of the x-ray quantum. For these hitherto unobserved lines, he computed the intensity ratios, with respect to $K\alpha_{1,2}$ of 1 : 4800 and 1 : 18,000—totally beyond the sensitivity of detection.

Pointing in exactly the opposite direction, are the results of Bloch[55] in "Double-electron transitions in x-ray spectra." He finds that the $K\alpha_{3,4}$ *doublet of Cu(29) could be due to double-electron transitions.* His calculated relative intensities agree well with experiment, in a careful wave-mechanical treatment. It is not within the provinces of the present author to decide between these apparently conflicting results.

(C) Coster-Kronig Auger Effect Theory

The first work which pointed in the direction of the Coster-Kronig theory, was done by Coster[8,9] who has pondered the satellite origin question for many years. He noted that the intensity of the $L\alpha$ satellites relative to their parent line decreased from Rh(45) to In(49); this is the first recognition of the upper atomic number side of the Auger intensity maximum for $L\alpha$. In this same work he also was looking for the radiation transitions $L_{\text{I}} \rightarrow L_{\text{III}}$ and $L_{\text{I}} \rightarrow L_{\text{II}}$, permitted by selection rules; he failed to find them and we now know why: they are the important radiationless transitions which give rise to the $L\alpha$ and $L\beta_2$ satellite, and the $L\beta_1$ satellite intensity maxima, respectively.

In the latter paper, Coster noted that the frequency of the satellite, minus the frequency of the parent line, is proportional to atomic number, an observation which F. K. Richtmyer modified, and used directly in formulating his double-jump hypothesis. Coster also remarked in the latter paper[9] that, according to his ideas, x-ray satellites should appear simultaneously in emission and absorption, an idea affirmed by Ramberg.[50]

In 1935, Coster and Kronig[58] published a paper which revolutionized ideas in the field of x-ray satellites. They pointed out the importance of the radiationless transition $L_{\text{I}} \rightarrow L_{\text{III}}$ in explaining certain satellite phenomena: (1) the abnormal weakness of the L_{I} emission lines for certain atomic numbers; (2) the intensity maxima (within certain atomic number ranges) for the $L\alpha_1$ and $L\beta_2$ satellites; (3) the broadness of the L_{I} emission lines, compared with the L_{II} and L_{III} emission lines, for certain atomic numbers. Coster and Kronig noticed that between roughly $Z=52$ and $Z=74$, $(\text{Energy})_{L_{\text{I}} \rightarrow L_{\text{III}}} < (\text{Ionization energy})_{M_{\text{IV,V}}}$, for $Z+1$. Elsewhere the inequality is reversed (see Coster-Kronig diagram, Fig. 2). This important observation fully explained facts: (1) The $L\alpha_1$ and $L\beta_2$ satellites show their maximum intensity relative to their parent lines at $Z=45$

and are extremely faint at $Z=52$ (references 51 and 56). (2) They increase markedly in intensity at $Z\sim 74$ (reference 46). (3) They exist, owing to double ionization by single electron impacts, between $Z=52$ and $Z=74$, but only with small intensity. Coster and Kronig point out[58] that this whole phenomenon can be explained by application of the Franck-Condon principle: if $E_{L_{\mathrm{I}}\rightarrow L_{\mathrm{III}}} \gtrsim (\text{Ionization energy})_{M_{\mathrm{IV,V}}}$ for $Z+1$, the normalized radial wave function for the ejected electron overlaps strongly the normalized radial wave function for the $M_{\mathrm{IV,V}}$ electron (taken for $Z+1$ as an L electron is already missing) and the radiationless transition $L_{\mathrm{I}}\rightarrow L_{\mathrm{III}}$ takes place with simultaneous ejection of an $M_{\mathrm{IV,V}}$ electron. Thus the atom is left doubly ionized in the state $L_{\mathrm{III}}M_{\mathrm{IV,V}}$, which is the initial state for the $L\alpha_1$ and $L\beta_2$ satellites.

Hirsh[57, 64] has shown the radiationless transition $L_{\mathrm{I}}\rightarrow L_{\mathrm{II}}$ accounts for the intensity behavior with atomic number of the $L\beta_1$ satellites. Thus the mean ionized life of the L_{II} and L_{III} shells is increased by the radiationless transitions $L_{\mathrm{I}}\rightarrow L_{\mathrm{II}}$ and $L_{\mathrm{I}}\rightarrow L_{\mathrm{III}}$, while the mean ionized life of the L_{I} shell is decreased by the same transitions. This very obviously will account for the great breadth of the L_{I} emission lines (and L_{I} level), for the shorter the mean ionized life is, the greater will be the breadth of the level concerned: this follows directly from the uncertainty principle of Heisenberg.

Hirsh[64] discusses the Auger effect in the M series and points out the probable origin of the $M\alpha_1$ and $M\beta$ satellites: $M\alpha_1$ satellites are due to the radiationless transition $M_{\mathrm{III}}\rightarrow M_{\mathrm{V}}$ with ejection of an $N_{\mathrm{IV,V}}$ electron, initiating the transition $M_{\mathrm{V}}N_{\mathrm{IV,V}}\rightarrow N_{\mathrm{VII}}N_{\mathrm{IV,V}}$; $M\beta$ satellites should be due to the radiationless transition $M_{\mathrm{III}}\rightarrow M_{\mathrm{IV}}$ with simultaneous ejection of an $N_{\mathrm{IV,V}}$ electron, initiating the transition $M_{\mathrm{IV}}N_{\mathrm{IV,V}}\rightarrow N_{\mathrm{VI}}N_{\mathrm{IV,V}}$. The great similarity of these two single electron transitions between doubly-ionized states accounts for the similarity of the $M\alpha_1$ and $M\beta$ satellite semi-Moseley graphs, over-all line shapes, etc.

Richtmyer and Ramberg[69] have calculated intensity shapes (profiles) of the $L\alpha_1$ and $L\beta_2$ satellite groups of Au(79), and have compared their results with their measurements on the two-crystal ionization spectrometer, finding agreement with the results of the Coster-Kronig theory.[58]

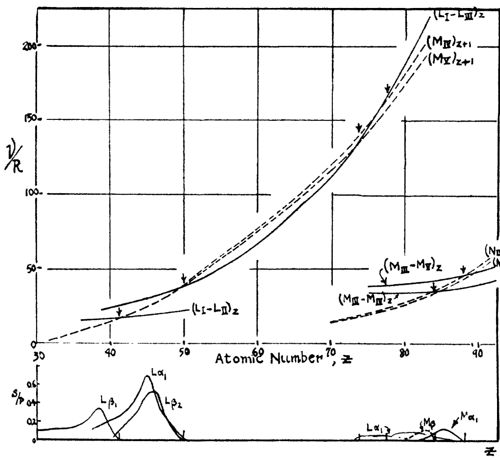

FIG. 2. Coster-Kronig diagram for all the known x-ray satellite intensity anomalies (maxima). At left, the $M_{\mathrm{IV,V}}$ level ionization energy curves are crossed over by the $L_{\mathrm{I}}\rightarrow L_{\mathrm{III}}$ and $L_{\mathrm{I}}\rightarrow L_{\mathrm{II}}$ radiationless transition energy yield curves to produce the $L\alpha_1$ and $L\beta_2$, and the $L\beta_1$ satellite intensity maxima, respectively. At right, above, the $M_{\mathrm{IV,V}}$ level ionization energy curve is crossed over by the radiationless transition energy yield for $L_{\mathrm{I}}\rightarrow L_{\mathrm{III}}$ to produce a double maximum for $L\alpha_1$, because of the high resolution of the $M_{\mathrm{IV,V}}$ levels at that atomic number. (Below, on an intensity scale, and the same atomic number scale, the maxima are represented.) At right, below, the $N_{\mathrm{IV,V}}$ level ionization energy curve is crossed over by the energy yield curves for $M_{\mathrm{III}}\rightarrow M_{\mathrm{IV}}$ and $M_{\mathrm{III}}\rightarrow M_{\mathrm{V}}$ to produce the $M\alpha_1$ satellite Auger intensity maximum in the case, of the latter radiationless transition; none is produced in the case of the former as another and more probable radiationless transition prevents the occurrence of the $M\beta$ satellites Auger intensity maximum. The $L\alpha_1$ and $L\beta_2$, and $L\beta_1$ Auger maxima, at low atomic numbers, are measured photographically; the $L\alpha_1$ for high atomic numbers is measured by ionization methods; the $M\alpha_1$ maximum is merely located photographically; the $M\beta$ maximum *does not exist.*

Ramberg and Richtmyer[70] have further confirmed the Coster-Kronig theory by finding that the total energy level width for Au(79) can be explained as due to the sum of contributions of Auger and radiation widths. The Auger width becomes increasingly important as we pass from the K to the L, M, and N levels.

DeLangen[76] corroborated the work of Hirsh[64] who found an intensity maximum for the satellites of $L\beta_1$, relative to their parent line, below $Z=40$. DeLangen, studying the intensities of $L\beta_1$, $L\beta_3$, and $L\beta_4$ photographically for Zr(40), Cb(41), and Mo(42), finds that $L\beta_3$ and $L\beta_4$ are more intense relative to $L\beta_1$, for Mo(42) than for Cb(41) and Zr(40); this agrees with the Auger transition $L_{\mathrm{I}}\rightarrow L_{\mathrm{II}}$ with ejection of an $M_{\mathrm{IV,V}}$

electron. $L\beta_4$ and $L\beta_3$ come from transitions ending in the L_I shell; $L\beta_1$ comes from a transition ending in the L_{II} shell. This means that $L\beta_4$ and $L\beta_3$ are being robbed of intensity by the Auger transition $L_I \rightarrow L_{II}$ for Cb(41) and Zr(40), showing that the Auger transition is improbable if $Z > 41$, in precise agreement with the predictions of Hirsh.[64]

Hirsh,[77] in 1940, corroborated his early ideas, patterned after Coster and Kronig,[58] on the existence of an intensity maximum for the satellites of $M\alpha_1$, showing photographically that at roughly $Z=82$ there existed a maximum of satellite intensity relative to the parent line. This was in substantial agreement with the results of the analysis[58] which showed the Auger effect to be probable below $Z=88$.

Later Hirsh[81] reported that the satellite intensity maximum for $M\beta$ did not exist, and briefly explained the absence.

As has been previously mentioned,[64] the $M\beta$ satellites are due to the transition $M_{IV}N_{IV,V} \rightarrow N_{VI}N_{IV,V}$ and the $M\alpha_1$ satellites to the transition $M_V N_{IV,V} \rightarrow N_{VII} N_{IV,V}$. Since the $M\alpha_1$ Auger intensity maximum has already been found[77] it was natural to look for the $M\beta$ intensity maximum which was found to be absent.[81, 84] The radiationless transitions which broaden the M_{III} shell are $M_{III} \rightarrow M_V$ which causes the $M\alpha_1$ satellites, and $M_{III} \rightarrow M_{IV}$ which should cause the $M\beta$ satellites. Contributing to the breadth of the M_{II} level is $M_{II} \rightarrow M_{IV}$. (A level is broadened when the mean ionized life is decreased by means of a radiationless transition.) If we should choose two radiation transitions ending in a common level, in one of which the electron comes from the M_{II} level, and in the other one of which the electron comes from the M_{III} level, we could tell the relative Auger probabilities for filling these two shells. (In the M series the Auger width comprises almost the entire line width.)[70] This is possible: in the case of $L\beta_4$ and $L\beta_3$ the widths have been measured by Cooper[83] for several atomic numbers disclosing that $M_{II} \rightarrow M_{IV}$ is more probable than $M_{III} \rightarrow M_{IV}$ and $M_{III} \rightarrow M_V$ combined. Since $M_{II} \rightarrow M_{IV}$ does not contribute to the satellites at all and $M_{III} \rightarrow M_{IV}$ alone should cause them, we can conclude that the high probability of the wrong radiationless transition effectively prevents the occurrence of the $M\beta$ satellite intensity anomaly.

The material now supporting the Auger-effect theory of Coster and Kronig is so convincing that all doubt in favor of old theories must be cast aside, as the new theory for all purposes is too well substantiated.

III. METHODS OF ATTACK ON PROBLEM OF SATELLITE ORIGIN

(A) 1. λ and $\Delta\nu/R$ Values, K Series

Dauvillier[7] has published a list of wave-lengths of $K\alpha_{3,4}$. Wetterblad[19] gives data on the K-spectrum spark lines of Na, Mg, Al, and Si. Dolejsek and Engelmanova[29] report values of λ and $\Delta\nu/R$ for $K\alpha_{3,4}$ and $K\alpha_{5,6}$ of V(23), Cr(24), and Mn(25). Valasek[34] reported the absence of fine structure in $K\alpha_{1,2}$ and $K\beta$ for Mo(42), Cu(29), and Ni(28). Ford[43] gives a complete survey of the K-satellite lines. Carlsson[42] gives the $K\alpha$-satellite lines of Al(13). Parratt[63] recently made a two-crystal spectrometer study of the $K\alpha$ satellites, giving ionization curves of the $K\alpha_{3,4}$ group of satellites from $Z=16$ to $Z=32$. He resolves them into five components $16 \leq Z \leq 28$ and four components $29 \leq Z \leq 32$. His tables include λ, $\Delta\nu/R$ values and relative intensities and widths. This ionization study is of extremely high caliber, and is the first of its kind. Shaw and Parratt[66] studied the K satellites, by the same ionization methods, from Zn(30) to Pd(46). They find:

four components, $\alpha_{3,4}$, α_3' and α' if $30 \leq Z \leq 33$;
three components, $\alpha_{3,4}$, α_3' if $34 \leq Z \leq 40$;
two components, α_4, α_3' if $41 \leq Z \leq 46$.

They give λ values, $\Delta\nu/R$ values, relative intensities and widths.

(A) 2. λ and $\Delta\nu/R$, L Series

The first work on the L series was done by Druyvesteyn[23] who reported in his thesis the existence of 5 satellites of $L\alpha$ from Cb(41) to Ag(47). Beuthe[22] reports some L satellites of Re(75). Richtmyer and Richtmyer[26] performed an important survey of the satellites of $L\alpha_1$, $L\beta_2$, and $L\beta_1$ which has been previously discussed under surveys. Parratt[65] has presented data on the $L\alpha$ satellites of Ag(47). Cauchois[67, 71] has studied the $L\alpha$ satellites of heavy elements and finds four satellites from U(92) to Sm(62).

(A) 3. λ and $\Delta\nu/R$, M Series

Stenstrom[4] makes the first mention of M-series satellites, reporting that the principle lines are diffuse and broad and hence "contain unresolved lines which cannot be determined." Hjalmar[5,12] made the first extensive M-series study, finding two satellites of $M\alpha$, $\alpha'+\alpha''$ from U(92) to Yb(70); three satellites of $M\beta$, β', β'', and β''' for U(92) and one from there to Ho(67); one satellite γ' of $M\gamma$ from U(92) to W(74). Beuthe[22] reports some satellites of Re(75), $M\alpha$. Lindberg[24,28] reported only two satellites of $M\alpha$ from U(92) to Cp(71); one satellite of $M\beta$ in the same range. Hirsh[39] made a complete survey of M satellites, already reported under surveys, and found four satellites of $M\alpha$; three of $M\beta$; none of $M\gamma$. Hirsh[84] has shown that there are actually four satellites of $M\beta$ and that the $M\alpha$ and $M\beta$ groups are very similar due to their similar origin.

(B) Excitation Potentials

If x-ray satellites are, as all theories agree, due to multiple ionization, it should be easy, with careful work, to distinguish between the excitation potential of the parent line and that of its satellites. Coster[9] did the first work on excitation potentials of satellites. Using the $L\alpha$ satellites of Ag(47), he noted that in passing from 8.0 to 4.7 kv "an emission band and two satellites vanished." Ag $L\alpha$ satellites should first be excited with small intensity at 3.79 kv ($V_{L_z}=3.79$ kv). If the $L_{\rm I}$ shell is ionized, the radiationless transition $L_{\rm I}\rightarrow L_{\rm III}$ takes place, ionizing the $L_{\rm III}$ and the $M_{\rm IV,V}$ shells, since an $M_{\rm IV,V}$ electron is ejected, leaving the atom in the initial state for the $L\alpha$ satellites. This is the first significant result on excitation potentials.

Backlin[16] deliberately set out to test Wentzel's theory by means of excitation potentials of K satellites of Al(13). According to Wentzel, α_3 is due to KL ionization, while α_4 is due to K^2 ionization. Therefore Backlin deduced that α_3 should have an excitation potential of 1.62 kv, while α_4 should have an excitation potential of 3.1 kv, distinctly different. (The parent lines should be excited at 1.55 kv.) The results were as follows: he determined that the excitation potential of $K\alpha'$ lay between 2.9 and 3.2 ± 0.05; that the excitation potential of $K\alpha_{5,6}$ lay between 3.1 and 4.0 kv; α_4 was still excited at 2.9 kv. Now Ramberg and Kennard[52] have shown that $K\alpha'$, α_3, and α_4 are due to KL ionization, while $K\alpha_{5,6}$ are due to KL^2 ionization. Hence part of Backlin's results are in agreement with Ramberg and Kennard, since Backlin showed that the excitation potential of $K\alpha_{5,6}$ is considerably higher than 2.9 kv, where they are absent. How Backlin excited $K\alpha_{3,4}$ and not $K\alpha'$ remains a mystery. According to Backlin, he found $K\alpha_{5,6}$ present at 3.1 kv and not at 3.2 kv; this, too, is odd. We must conclude that some error in potential measurement must have crept in.

DuMond and Hoyt[31] studied the energy of $K\alpha_3$ of Cu(29) as a function of the applied voltage by means of the two-crystal spectrometer. The result was that they found $K\alpha_3$ differed in excitation potential from $K\alpha_1$ by less than 200 volts. Since the L-excitation potential of Zn(30) is about 1200 volts, they rejected the Wentzel-Druyvesteyn theory[23] and embraced the Richtmyer double-jump theory.[25] Their extrapolation method of determining the energy of $K\alpha_3$ must have been at fault in the light of later results.

Coster and Thijssen[48] did a beautiful piece of photographic work on the $K\alpha_{3,4}$ excitation potential of S(16). They studied Int. $K\alpha_{3,4}$/Int. $K\alpha_1$ as a function of applied voltage, and found an excitation potential of 2700 volts. ($K_z+L_{z+1}=2465+200=2665$ ev.) Hence $K\alpha_{3,4}$ are due to KL ionization as shown by Kennard and Ramberg.[52]

Coster, Kuipers, and Huizinga[59] in 1935 studied the excitation potential of the $L\alpha$ group of Cb(41) photographically with the result that if $V<2700$ volts, very little intensity of the satellites remained. (Cb, $L_{\rm I}=2580$ ev.) They remarked that the intensity remaining might be due to the foot of $L\alpha_{\rm I}$ and that the satellites were due to the radiationless transition $L_{\rm I}\rightarrow L_{\rm III}$ with ejection of an $M_{\rm IV,V}$ electron.

Parratt[61] studied the excitation potential of the $K\alpha_{3,4}$ lines, and carefully discusses the subject. He finds experimentally that the excitation potential of $K\alpha_{3,4}$ of Ti(22) is 5450 ± 100 volts. ($K_z+L_{Z+1}=4950+514=5464$ ev.) This supports the Wentzel-Druyvesteyn theory if we assume the double ionization is performed by a single electron.

Parratt[62] has studied the excitation potential of the $K\alpha''$ satellite of Ca(20), with the two-crystal spectrometer and finds it to be 4020 ± 250 volts. According to Druyvesteyn,[23] it is due to KL ionization, but Parratt finds it is probably due to KM ionization: for Ca, $K_z=4030$ ev, and $(M_{\text{II,III}})_{Z+1}=37$ ev. The sum is 4067 ev and Parratt concludes that either the Wentzel-Druyvesteyn or Richtmyer theory applies in this case.

Dauvillier[14] experimented with fluorescence spectra, attempting to excite the Fe, $K\alpha_{3,4}$ lines by means of Cu, K radiation. It is clear why he should have: according to Kennard and Ramberg[52] $K\alpha_{3,4}$ are due to KL_{II} ionization. ν/R for Fe, K is 523.9; ν/R for $(L_{\text{II}})_{z+1}=58.8$; the two summed are 582.7. ν/R for Cu, $K\alpha_1$ is 592.74 and evidently the energy required is just right to be supplied by Cu, $K\alpha$ radiation. He failed to excite the $K\alpha_{3,4}$ lines, but in three minutes at 800 watts he had intense plates of Fe, $K\alpha_{1,2}$. Previously, Dauvillier had remarked[11] that "satellites should not appear in fluorescence spectra."

Later, Coster and Druyvesteyn[18] succeeded in obtaining Fe, $K\alpha_{3,4}$ in fluorescence excited by Cu, K radiation.

Hirsh and Richtmyer[47] excited Zr(40), Mo(42), Ru(44), Rh(45), Pd(46), and Ag(47) by Ag radiation excited at 20 kv and found a decrease in the $L\alpha$ satellite intensity, relative to the parent line, when L_z+M_{z+1} excitation becomes impossible. They concluded that $L+M$ ionization is the cause of the $L\alpha_1$ satellites.

(C) I_s/I_p vs. Z

The first attempt to determine the energy of x-ray satellites with respect to their parent lines was made by F. K. and R. D. Richtmyer[26] who resolved the satellite spectrum into continuous spectrum and line components. Unfortunately, they used a badly over-exposed plate of Ag, $L\alpha$.

Next, DuMond and Hoyt[31] found the energy of $K\alpha_{3,4}$, of Cu(29), relative to $K\alpha_1$, was 1 : 120 by areas, and 1 : 440 by maximum ordinates on the two-crystal spectrometer.

Richtmyer and Taylor[33] used the two-crystal ionization spectrometer to resolve the $K\alpha_{3,4}$ lines of Cu(29), finding more than two components. They estimated the satellite relative energy at 1 : 400.

Hirsh and Richtmyer[47] using a photographic method, found the energy of the $L\alpha$ satellites, relative to their parent line, to range up to 70 percent in cathode-ray excitation.

Mrs. Pearsall,[51] using the same method, measured the energy of the $L\beta_2$ satellites, relative to their parent line, and found them to range up to 50 percent. She later did some inaccurate work[54] in the K series, which led to erroneous conclusions.

Hirsh[56] published a comparison of the integrated relative energies of the satellites of $L\alpha$ and $L\beta_2$. The curves both have the same high atomic number foot, but the $L\alpha$ satellite energy is apparently greater, because of use of a symmetrical (classical) shaped parent line for the $L\alpha_1$ line which is decidedly asymmetrical as later work has shown.

Hirsh[57] measured the energy of the $L\beta_1$ satellites, relative to their parent line, again using the photographic method, and demonstrated the presence of an Auger satellite intensity maximum which Coster and Kronig[58] had said could not exist.

Valadares[78] made intensity plots of the L satellites of Pb(82) photographically, in good agreement with Richtmyer and Ramberg.[69]

Randall and Parratt[79] repeated the curve of Hirsh[56] which had been done photographically. Using the ionization method, they found exactly the same shape, but reduced the relative energies considerably. The higher relative energies of Hirsh[56] are due entirely to the method of analysis of the $L\alpha$ line complex: in which a symmetrical (classical) parent line on a line actually asymmetrical, and broader on the short wave-length side, adds to the apparent satellite energy. This error was made on low resolving power.

Pincherle[82] has studied the $L\alpha$ satellites from $Z=37$ to $Z=56$. Using the Hartree self-consistent field, Pincherle has calculated the electrostatic integrals for $Z=37$ and $Z=56$, interpolating between them linearly to obtain the intermediate values. His initial and final states are those of Coster and Kronig.[58] He calculates satellite relative intensities and separations from the parent line, finding profiles which agree quite well with the results of Randall and Parratt.[79] He also calculates profiles for $L\beta_1$ for Pd(46) and $L\beta_2$ for Cs(55). One important result is that he shows that the separation of a satellite from its parent line (energy units) is a linear function of atomic number, in exact agreement with Coster.[9] He attributes the changing aspect of the $L\alpha$ satellites to the progressive decrease in $\Delta\nu$ for the $L\alpha_2$ satellites which through the given range of atomic numbers then move through the $L\alpha_1$ group. This paper is a most careful and excellent theoretical treatment of the problem.

(D) Line Widths

Cooper[83] has studied the widths of L levels, showing that the L_{I} level width increases rapidly where the probability for the transition $L_{I} \rightarrow L_{III}M_{IV\ V}$ increases rapidly. The L_{II} and L_{III} levels show no such change, however, according to Cooper's results. Since the radiationless (Auger) transition, due to its high probability, robs the radiation transitions involving L_{I} as initial state, they should become weak relative to those transitions involving L_{II} and L_{III} as initial state. Cooper also shows this to be true experimentally. Cooper also presents some data on the $L\alpha$ satellites including intensities at high atomic numbers by Shrader, previously unpublished, which confirm the Coster-Kronig theory[58] most beautifully, showing super-imposed Auger satellite intensity maxima due to the high resolution of the M_{IV} and M_{V} levels.

Munier, Bearden, and Shaw[80] have studied the widths and wave-lengths of the $M\alpha_1$ and $M\beta$ satellites of W(74) with the two-crystal ionization spectrometer. By estimating the background, they obtain the total satellite structure which they analyze into symmetrical components. Incidentally, casual scrutiny will reveal that their components will not add up to the original structure: this error is especially bad in the case of the $M\alpha_1$ line. They also present the satellite structure of $M\zeta_1$ and $M\zeta_2$.

IV. CONCLUSION

While the Wentzel-Druyvesteyn theory[23] gave correct frequency separations for satellites and parent line, it failed in the correct prediction of excitation potentials in the L and M series where the Auger effect is important. However, it is known to be correct in the case of the K satellites. The failure of predicting correct excitation potentials, led to the occasion for the prominence of the "double-jump" theory. The real answer to the problem of L and M satellite origin lies in the Coster-Kronig theory[58] which, beyond all doubt, is correct for all L- and M-series satellites.

Any interest the writer may have shown in the field of x-ray satellites is largely due to the inspiration of his late teacher and friend, F. K. Richtmyer, who was the first to set in motion a systematic attack on the problem of satellite origin in the Cornell X-Ray Laboratory.

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Note added in proof: Since the article has gone to press, I have become aware of the omission of a reference (D. Coster and W. J. DeLangen, Physica **3** (1936)), which is placed here to avoid much expensive resetting of type and renumbering of references.