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The Multiple Ionization of Inner Electron Shells of Atoms*

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THERE are, among others, two rather direct and converging lines of attack on the problem of multiple ionization in x-ray levels: the first is through studies of the so-called x-ray satellites; the second, through measurements of the widths of x-ray spectrum lines.

It was a happy coincidence that Bohr's theory of the origin of atomic spectra, based on the Rutherford-Bohr atom model, was announced shortly before Moseley, using the newly developed Bragg x-ray spectrometer, made those now famous pioneer measurements on the x-ray spectra of the elements. For, Bohr's theory made possible an immediate interpretation of Moseley's observations. That is to say, the x-ray spectral lines which he observed were due to transitions between energy levels arising from the absence of an electron from one or another of the inner electron shells. In stepwise sequence, new lines were discovered; new energy levels were predicted therefrom; the distribution of electrons in shells was determined. And in a surprisingly short time x-ray spectroscopists were able to construct the now well-known x-ray energy level diagram. In accordance with Moseley's hypothesis the energy levels of this diagram arise from *singly* ionized atoms.

X-RAY SATELLITES

It was perhaps fortunate that the spectral apparatus available to Moseley and the early workers did not have the sensitivity and the resolving power of present-day spectrometers. The lines which they observed were the more intense and the more easily resolved lines of x-ray spectra. It is these lines which are represented on the conventional energy level diagram. With improvements in technique, many other lines were subsequently discovered which did not fit this diagram. The majority of these lines were rather faint; were usually found close to, and on the short wave-length side of, the more prominent of the "diagram" lines, and were given the obvious name "nondiagram lines." This term, however, implied too much. For, though these new lines did not fit the energy level diagram based on the concept of *single* ionization, it was evident that they must result from transitions between energy levels of some kind, not included, however, in the single ionization scheme. Hence the noncommittal term "satellites" was ultimately adopted.

With increasing perfection of spectral apparatus has come a corresponding increase in factual information about these lines.

First, they are very numerous. The number of satellites now known exceeds the total number of diagram lines; and it is probable that with the increased sensitivity and resolving power of modern apparatus many more satellites will be discovered when the whole spectrum is carefully studied. Fig. 1 shows the well-known Cu $K\alpha$ doublet, much over-exposed, to bring out what appears to be a faint companion line. This is the satellite "structure" accompanying the $K\alpha$ doublet of Cu(29). An analysis of this whole

* Adapted from presidential address before The American Physical Society, Atlantic City Meeting.

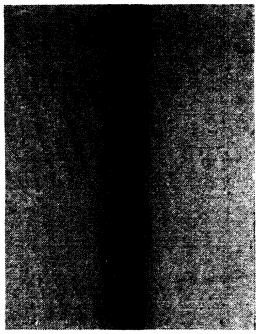

FIG. 1.

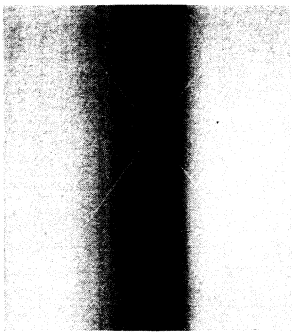

FIG. 3a.

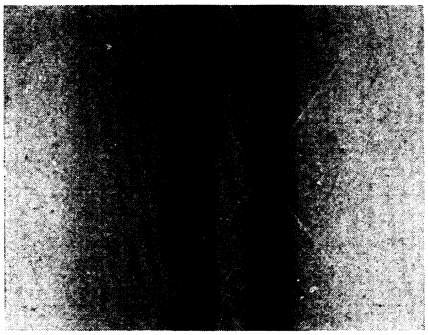

FIG. 4.

FIG. 1. The $K\alpha$ doublet of Cu(29) much over-exposed, showing the faint satellite on the left (high frequency) side.

FIG. 3(a). The $L\alpha$ doublet of Ag(47) much over-exposed to bring out the satellites shown in the left (high frequency) side. Five satellites are clearly visible on the original plate. Enlarged about 5×.

FIG. 4. The $L\beta_2$ line of Ag(47) much over-exposed. The satellite structure appears on the left (high frequency) side, well separated from $L\beta_2$.

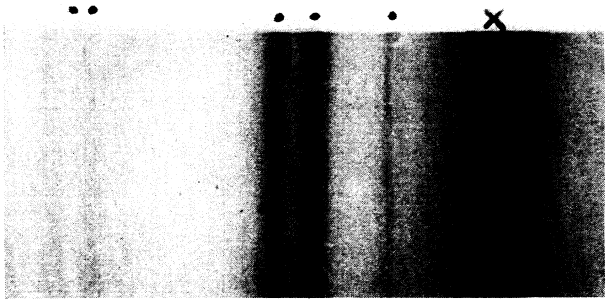

FIG. 5a.

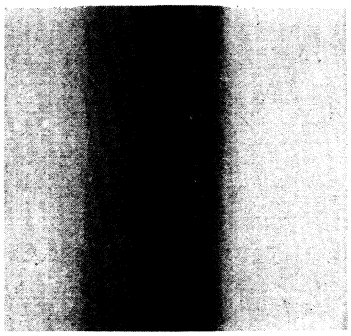

FIG. 8a.

FIG. 5(a). The $K\alpha$ doublet of S(16) indicated by "x." The satellites are designated by dots.

FIG. 8(a). The $L\alpha$ doublet of Sn(50) showing the satellite structure on the left as a wide band, instead of as separate lines observed for Ag(47). See Fig. 3(a) for comparison.

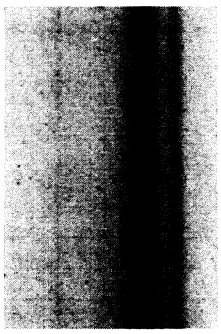

FIG. 8b.

FIG. 9a.

FIG. 9b.

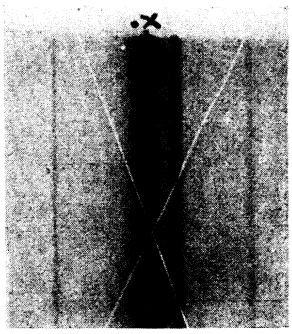

FIG. 9c.

FIG. 8(b). The $L\alpha$ doublet of Ba(56). No satellite structure is observed.

FIG. 9(a) (b) (c). The $L\alpha$ doublet of Ta(73), Os(76) and Ir(77) each indicated by a cross (×). No satellites are observed with Ta. Faint satellites, indicated by a dot, are seen with Os(76) and Ir(77).

structure by Dr. Parratt,[1] using the two-crystal (ionization) spectrometer, is shown in Fig. 2. It is seen that there appear to be at least four components in the satellite group. Fig. 3(a) and (b) show the $L\alpha$ doublet and associated satellites of Ag(47): (a) is from a spectrum plate made by the author; and (b) shows ionization chamber measurements by Dr. Parratt.

Second, the satellite structure associated with the several diagram lines, varies greatly from line to line, both as to the number and the relative intensity of the satellite components. Fig. 4 shows the satellites of the $L\beta_2$ line of Ag(47). The satellites are well separated from the diagram, or "parent," line; at least four components are easily observable on the spectrum plate—there are really many more; and the relative intensities of the components vary greatly from that observed with $L\alpha$ (Fig. 3).

Third, satellites have some characteristics which differentiate them sharply from the respective diagram lines with which they are associated. A given satellite group has a higher excitation potential than its parent lines. How much higher, is not definitely known, except possibly in one or two cases; for, on account of the relatively low intensity of these lines, measurements of their excitation potentials is difficult. Nor have we definite experimental knowledge of possible differences in excitation potentials among the components of a satellite group.

A very striking point of difference between satellites and "parent" lines is the rapid variation with atomic number of intensity of satellite groups relative to that of parent lines. Although our quantitative information on this point is at present hardly more than fragmentary, it is sufficient to provide the most important clue to an understanding of the atomic processes which give rise to these lines; and thereby to contribute materially to the problems of double ionization.

Figure 5(a) shows the $K\alpha$ doublet of S(16) over-exposed to bring out the satellites, five of which are designated by dots. The two on the extreme left are very faint. These two are, however, more prominent for elements of lower atomic number—Al(13); Si(14)—but are not observed above Cl(17). The group of three

[1] Lyman G. Parratt, Phys. Rev. **50**, 1 (1936).

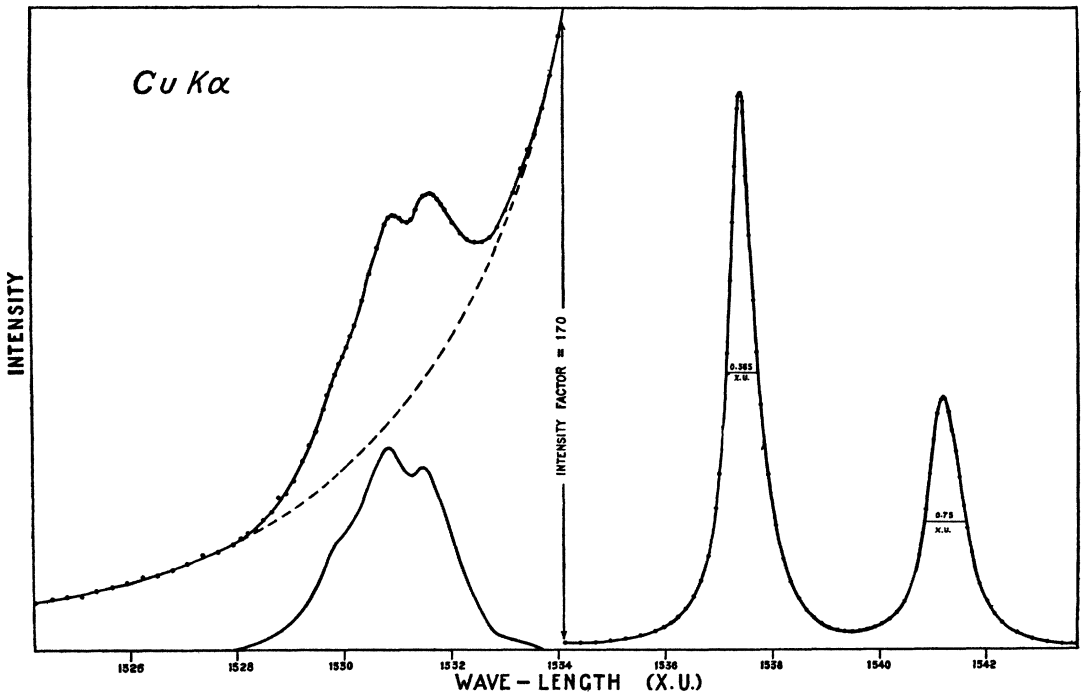

FIG. 2. The $K\alpha$ doublet of Cu(29), with accompanying satellite as measured by Dr. L. G. Parratt with a two-crystal spectrometer.

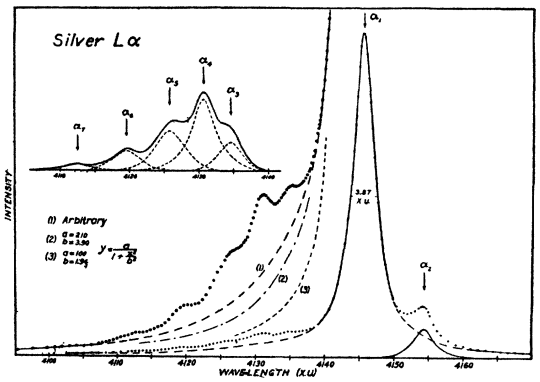

FIG. 3(b). The $L\alpha$ doublet of Ag(47) with accompanying satellite structure. By subtracting the "foot" of $L\alpha_1$ the satellite contour shown in the upper left is obtained. This is shown resolved into components $\alpha_3\alpha_4$, etc.

satellites nearest the parent line may be traced, with constantly, even rapidly, decreasing intensity, up to about Rh(45), above which they disappear completely.

Figure 5(b) shows these "three" satellites as observed by Dr. Parratt with a two-crystal spectrometer. Instead of three, there are at least five components. The energy in the group is about 7 percent of that of $K\alpha_1$.

Figure 6(a), (b) and (c) show the satellites accompanying $K\alpha$ of Ca(20), Ge(32) and Mo(42), respectively, as measured by Parratt. For Ca(20) the structure appears similar to that for S(16), but the intensity has dropped to some 3 percent of $K\alpha_1$. At Ge(32) satellites are still easily observable, but their intensity has dropped by a factor of about 10, i.e., to some 0.3 percent. While at Mo(42) only the most careful measurement shows any satellite structure; and the intensity has dropped by about another factor of 10—i.e. to 0.03 percent.

Figure 7, a composite of observations made by Dr. L. G. Parratt and Dr. C. H. Shaw[2] shows (the solid line) the variation in intensity of this group of satellites over the atomic number range $19<Z<46$. How is this variation of intensity to be explained?

As mentioned previously, there is no place for satellites in the system of energy levels arising from singly ionized atoms. Therefore it is a more or less obvious conclusion that satellites are due to transitions between energy states arising from doubly (or more generally, multiply) ionized atoms. This suggestion was first made by Gregor Wentzel some years ago.

Two primary factors determine the intensity of a given (say x-ray) spectral line: (1) the number of atoms in the target which are in the initial ionized state; and (2) the probability of transition from the initial to the final state. Neglecting the second factor, for the moment, and assuming that the initial state for the production of these $K\alpha$ satellites is a doubly ionized state, the ratio of the intensity of the satellite group to that of the parent lines ($K\alpha$)

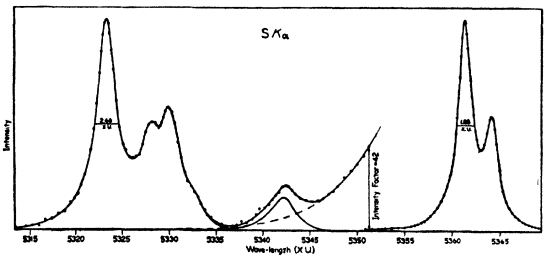

FIG. 5(b). The $K\alpha$ doublet of S(16) as measured by Dr. Parratt, showing the region covered by the first three satellites on left of $K\alpha$ in Fig. 5(a). These are at least 5 components instead of 3 as shown in the spectrum plate.

gives the ratio of the number of doubly ionized atoms present in the target to the number of singly (i.e., K) ionized atoms. Experimental observations, by Dr. Parratt and others, are in accord with theoretical calculations in ascribing the $K\alpha$ satellite group to transitions from KL_1 ionization (or $1s2s$ in spectroscopic notation) to LL ionization (or $2p2s$). Since it has been shown to be reasonable to assume that the probability of the transition ($K\rightarrow L_{11, 111}$), which produces the parent line $K\alpha$, is about the same as the probability of the transition ($KL\rightarrow LL$) which produces the satellites, the data on relative intensities of satellites shown in Fig. 7 give the relative probability of double ionization (KL) to single ionization (K). That is to say, in Ca(20), for example, the number of doubly ionized atoms (KL) is some 3 percent of the number of singly (K) ionized atoms; while for Mo(42) the ratio is only one one-hundredth of this, namely 0.03 percent. Except for the "break" in the curve above Kr(36) the decrease with increasing atomic number is more or less regular.

[2] L. G. Parratt and C. H. Shaw, Phys. Rev. **50**, 1006 (1936).

We then come to the next question: How are these doubly ionized atoms produced in the target of the x-ray tube? A more or less obvious guess is that they are produced by the same type of process as that responsible for producing single ionization, namely by collision between the atom and a cathode-ray electron possessing sufficient energy.

Assuming, thus, that a cathode-ray electron can, by a "direct hit," or "single act" as it is sometimes called, cause the simultaneous expulsion of two electrons (K and L), R. D. Richtmyer[3] has carried out wave mechanical calculations, based on the Born approximation for collision theory, for the relative probabilities of double (KL) to single (K) ionization. His results, using no adjustable constants, are given by the dotted line in Fig. 7. The almost exact agreement between theory and observation over a substantial part of the atomic number range is perhaps fortuitous, partly because of some small uncertainty in the observational determination of intensities; and partly because of the approximations and the uncertainty of some of the fundamental assumptions that must be made in the calculations. Nevertheless, the agreement is sufficiently good to warrant the conclusion that the $K\alpha$ satellites arise from the production of KL ionized atoms by direct impact of a cathode-ray electron. The noticeable variation from regularity beginning just above Kr(36) may be due to the completion of the electron shell at that element.

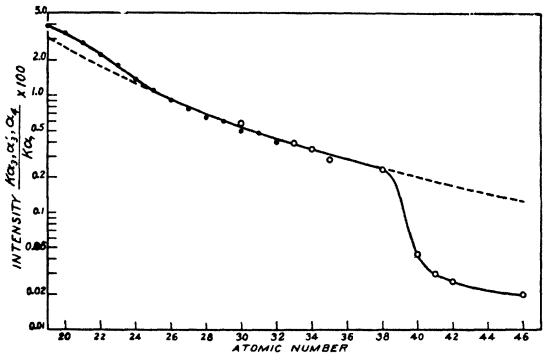

FIG. 7. Ratio of the satellite structure (shown in Figs. 6) to that of $K\alpha_1$ as function of atomic number in the range $19<Z<46$.

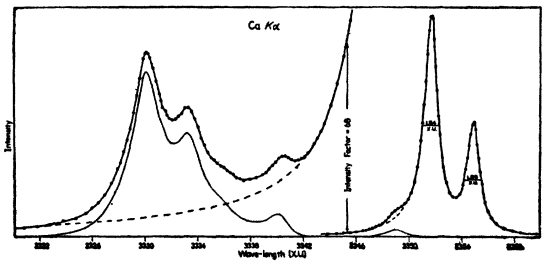

FIG. 6a.

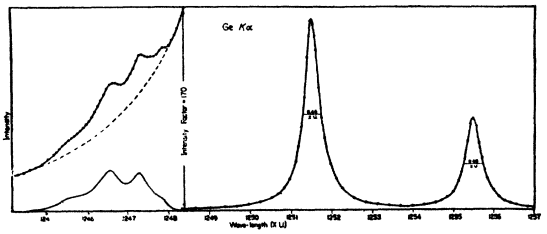

Fig. 6b.

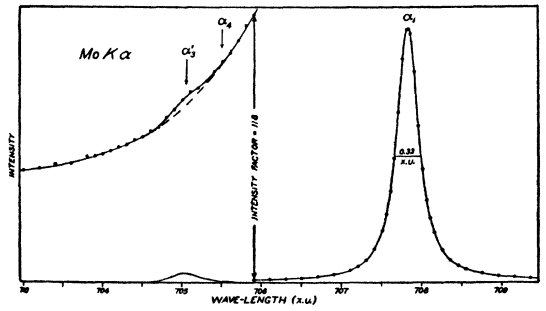

FIG. 6c.

FIG. 6(a) (b) (c). The satellite structures accompanying $K\alpha$ of Ca(20), Ge(32) and Mo(42), showing the rapid decrease in satellite intensity with increasing atomic number.

However, measurements of the intensities of satellites accompanying some of the L x-ray lines show that this theory of the origin of double ionization (i.e., simultaneous expulsion of two electrons by a direct "hit") is inadequate to explain the observed facts.

Figure 3(a) shows the satellite structure accompanying the $L\alpha$ doublet of Ag(47). Five lines are readily seen on the original plate. Fig. 8(a) shows the corresponding structure for Sn(50), three atomic numbers higher. The five well-defined lines have become a band occupying approximately the same frequency range. Fig. 8(b) shows the $L\alpha$ doublet of Ba(56). The satellite structure has entirely disappeared, at least so far as photographic methods show. Through the rare earths, and up to Ta(73) no

[3] R. D. Richtmyer, Phys. Rev. **49**, 1 (1936).

satellites are found; as is seen from Fig. 9(a). Figs. 9(b) and (c) show[4] the $L\alpha$ doublet of Os(76) and of Ir(77), each of which is accompanied by a faint satellite. This structure continues up to U(92). That it is complex, instead of being made up of a single line, is shown by ionization chamber measurements made by Dr. S. W. Barnes[5] and shown in Fig. 10, of the $L\alpha$ doublet of Au(79). The structure is somewhat similar to that accompanying the $L\alpha$ of Ag(47)—see Fig. 3(b).

With the exception of the $L\alpha$ satellites of three or four elements, our knowledge of the intensities of L satellites comes from the rather inexact methods of spectrum photography.[6] However, the photographic measurements, even though only roughly quantitative, are sufficient to bring out the salient features of the variation of intensity with atomic number.

The measurements of Dr. F. R. Hirsh[7] on the intensities of $L\alpha$ satellites in the atomic number range 40 to 52 are shown in Fig. 11. The intensity (relative to that of $L\alpha$) rises rapidly from Zr(40) to a maximum of 70 percent[8] at Rh(45); and drops as rapidly to vanishingly small intensities at Te(52).

Similar measurements for the $L\beta_2$ satellites have been made by Mrs. Pearsall[9] and are shown in Fig. 12.

Diagrammatically—for the data are only fragmentary—the variation of intensity of the satellites of $L\alpha$ over the atomic number range 30 to 92 is shown in Fig. 13.

A significant conclusion may at once be drawn. The probability of the initial doubly ionized state—whatever it is—responsible for the satellites of $L\alpha$ is far greater for Rh(45) than for a near-by element Sn(50). This probability is vanishingly small for the elements from $Z=52$ to about $Z=74$ when, more or less suddenly, it increases again. These facts seem to be inconsistent with the above mentioned theory of the double ionization found adequate to account for the $K\alpha$ satellites. This theory

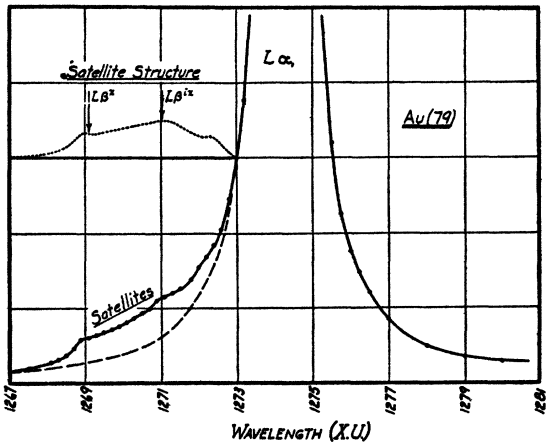

FIG. 10. The "foot" of $L\alpha_1$ of Au(79) showing the satellite structure. From observations by Dr. S. W. Barnes using a two-crystal spectrometer.

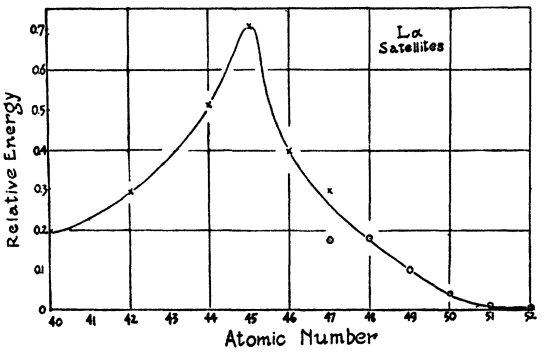

FIG. 11. Intensity of satellites of $L\alpha$ in the range $40<Z<52$, from measurements by Dr. F. R. Hirsh.

assumes that the $K\alpha$ satellites originate in phenomena associated with the K and L, that is, the inner, electron shells. Similarly, one may assume that the $L\alpha$ satellites originate in phenomena associated with the L and M shells. But these shells are completely filled for all the elements included in Fig. 13. That is to say, the interior structures of these atoms are identical. One might expect to find that the probabilities of LM double ionization by direct impact decrease regularly in going from, say, atomic number 40 up, as was found to be the case with KL ionization for elements above $Z=20$. But the data show otherwise. What is it that makes

[4] Figures 9 are from spectrum plates made by Dr. S. W. Kaufman.

[5] See F. K. Richtmyer, S. W. Barnes and E. Ramberg, Phys. Rev. **46**, 843 (1934), Fig. 7.

[6] Dr. Parratt is now using the two-crystal vacuum spectrometer, used by him in the work on $K\alpha$ satellites, (Phys. Rev. **50**, 1 (1936)), to obtain data on L satellites.

[7] F. R. Hirsh and F. K. Richtmyer, Phys. Rev. **44**, 955 (1933); F. R. Hirsh, Phys. Rev. **48**, 722 (1935).

[8] Ionization measurements on Ag(47) by Dr. Parratt indicate that these intensities are too high by perhaps a factor of two or three. But their relative values seem to be approximately correct.

[9] Mrs. A. W. Pearsall, Phys. Rev. **46**, 695 (1934).

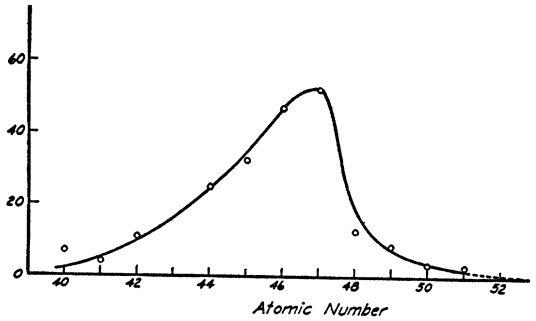

FIG. 12. Intensity of satellites of $L\beta_2$ in the range $40 < Z < 52$, from measurements by Mrs. Anna W. Pearsall.

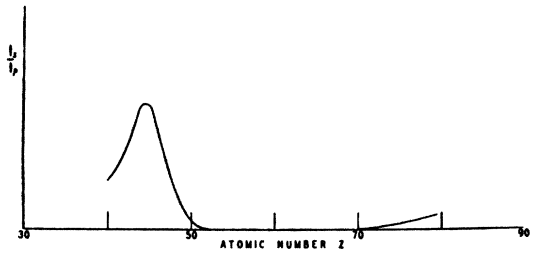

FIG. 13. Schematic representation of the intensity of satellites of $L\alpha$, as a function of atomic number, according to measurements to date.

the probability of double ionization decrease rapidly from Rh(45) on; only to increase again suddenly at about W(74)? The answer to this puzzling question was found a year or two ago by Coster and Kronig—two physicists at Groningen, Holland.

They suggested[10] that the double ionization essential for satellite production may arise from a kind of internal photoelectric effect—a phenomenon long known to take place when gamma-rays from the nucleus pass out through the extra nuclear structure of the atom; and recognized by Auger for radiations originating in the inner electron structure of the atom—the so-called Auger effect.[11]

THE AUGER EFFECT

In a Wilson cloud chamber ionized by x-rays, Auger observed short, fat tracks, the lengths of which were independent of the frequency of the x-rays; but were dependent on the kind of atoms in the chamber. Auger explained these tracks

[10] D. Coster and R. de L. Kronig, Physica **2**, 13 (1935).
[11] P. Auger, Comptes rendus **180**, 65 (1925); **182**, 773 (1926).

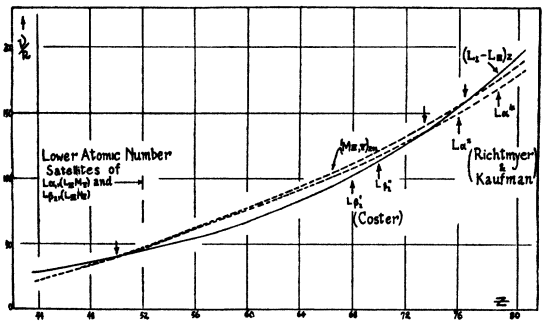

FIG. 14. Coster-Kronig diagram.

as follows. In the ordinary process by which an atom radiates, an electron "falls" from, say, the M_V subshell into a vacancy in, say, the L_{III} shell, and a quantum, in this case $L\alpha_1$, is emitted.

But suppose that initially an L_1 electron is missing. Then let an L_{III} electron, say, drop into the vacant place, thereby freeing energy $(E_{L_I}-E_{L_{III}})$. And let this quantum of energy "on its way out"—adopting a naive picture of atomic processes—be photoelectrically absorbed in, for example, the M_{IV} subshell causing the emission of an M_{IV} electron. The atom will be left doubly ionized $(L_{III}+M_{IV})$; and will be in the initial condition requisite to produce an $L\alpha$ satellite, if either an M_{IV} or M_V electron drops into the vacant L_{III} shell.

However, an M_{IV} or M_V electron will be expelled *only if the energy released*—$(E_{L_I}-E_{L_{III}})$—*is sufficient to expel that electron.* Coster and Kronig showed that herein lies the difference among atoms as regards their inner electron structures. This difference is shown in Fig. 14 (kindly prepared by Dr. F. R. Hirsh).

The full line represents the energy freed from each of the several atoms by the transition of an electron from the L_{III} subshell to the L_I subshell. The dotted lines represent—the upper for M_{IV} and the lower for M_V—the energy necessary to expel an M_{IV} or M_V electron from an atom of next higher atomic number. (The absence of an L_{III} electron increases the effective atomic number by nearly one.) It is seen that in the atomic number range from (about) Sn(50) to (about) W(74) the released energy is insufficient to expel either an M_{IV} or an M_V electron. Both below and above this range double ionization by the Auger process is possible. It is most signifi-

TABLE I. *Widths of certain x-ray lines of Au(79).*

LINE	WAVE-LENGTH IN X.U.	QUANTUM ENERGY IN EV	CLASSICAL RADIATION WIDTH		QUANTUM RADIATION WIDTH[12]		OBSERVED WIDTH[13]	
			X.U.	ev	X.U.	ev	X.U.	ev
$K\alpha_1$	180	68520	0.12	45.7	0.18	68.2	0.15	57.5
$K\gamma_1$	925	13340	0.12	1.7	0.20	2.9	0.75	10.8
$L\alpha_1$	1274	9680	0.12	0.9	0.25	1.9	1.06	8.1
$M\alpha_1$	5828	2116	0.12	0.04	0.19	0.07	6.8	2.5

cant that within this range satellites of $L\alpha$ are not observed; above and below it they are observed.

Double ionization, requisite to the production of satellites, may then be produced by either or both of two ways: (1) by the direct action of an impinging cathode-ray electron; or (2) by the so-called "internal photoelectric effect." The probability of a given type of double ionization by the former decreases, presumably quite rapidly, with increasing atomic number. The corresponding probability by the latter process depends on the relative binding energies of the internal electrons concerned. The sum of the two probabilities determines the number of atoms doubly ionized in a given way and, therefore, the intensity of the associated satellite group. A large amount of data and theoretical calculations are needed completely to check this hypothesis. But it is in qualitative agreement with the facts so far as known.

THE WIDTH OF X-RAY SPECTRUM LINES

Before discussing the agreement between experiment and theory for the one case where comparison has been made, I wish to turn briefly to another approach to the problem of double ionization of inner shells, namely the width of x-ray spectrum lines.

Classical theory, based on the emission of radiation by a vibrating electron, shows that on account of radiation damping, the emitted spectral line should not be mathematically monochromatic; but should be a very narrow band, the width of which at half-maximum should be 0.12 X.U.—the same width for all lines irrespective of frequency.

The quantum theory of the origin of spectrum lines similarly predicts finite widths and definite contours; but by a seemingly very different line of argument. The quantum theory supposes a quantum of radiation $h\nu$ to be emitted when an atom "drops" from a state of potential energy E_1 to one of lower energy E_2. At a given instant let there be, for example, in the target of an x-ray tube, N_1 atoms in the ionized state i_1. Just as radioactive atoms decay at a definite rate, so these ionized atoms "decay," i.e., they leave the state i_1 and "jump" to states of lower energy. And, again just as in radioactivity, we can define the mean life τ_1 of atoms in the state i_1 as the time required for the N_1 atoms initially in that state to be reduced to $1/e$ of N_1, where e is the Naperian base.

Mean life τ in the quantum theory has a close analog in classical theory. In the classical theory of radiation, a single vibrating electron radiates energy at such a rate that in a time τ its energy has been reduced to $1/e$ of its initial value. In quantum theory, a *group* of ionized atoms radiates at such a rate that in time τ the energy of the *group* has been reduced to $1/e$ of its initial value. Just as the classical theory ascribes a finite width to a spectrum line, so quantum theory ascribes a somewhat similar finite width to an energy state; and, as in classical theory, this width is the greater the greater the rate of decay; i.e., the shorter the mean life. Although it does some violence to the theory, we can say, for purposes of visualizing the meaning at least, that a given energy level E_i on the conventional energy level diagram is not sharp, but is a sort of "smear"; the energies of the several N_i atoms ionized in state i are not identical but are distributed about a mean. The transitions, in a large number of such atoms, from state i_1 to some other state i_2 will therefore involve slightly differing amounts of energy; and this gives a finite width to the emitted spectral line as observed.

In Table I are shown the "radiation" widths of certain representative x-ray lines as computed by both classical and quantum-mechanical theories. It is observed (column 6) that the quantum-mechanical widths in X.U. are somewhat greater, but not much, than the 0.12 X.U. predicted by classical theory.

Direct measurements to check these theories are extremely difficult, if not impossible, in the visible spectrum on account of the masking effects of the far greater widths arising from

collisions between atoms and from the Doppler effect. In the x-ray region however, these two disturbances are relatively insignificant and with the high resolution available in the two-crystal spectrometer, direct measurements of x-ray line contours and widths are now possible—though subject to disturbing instrumental corrections if one wishes high accuracy.

It is found that with the exception of the K series lines, x-ray lines are many times—in some cases 40 to 50 times—wider than either classical or quantum theory of radiation predicts. This is shown in Table I, column 8. The width of the $K\alpha_1$ line is about that predicted by either theory; but that of the $M\alpha_1$ line is many times greater.

In Table II are shown the widths of several representative L series lines in the x-ray spectrum of Au(79)—all much wider than either classical or quantum theory predicts; and varying in a seemingly erratic manner from line to line. How are these excess widths to be explained? The Auger effect provides an answer to this question.

We have seen, in discussing the satellite problem, that an atom may drop from an ionized state to one of lower energy by either of two processes: (1) by the emission of the released energy of a quantum—a "radiation transition;" or (2) by the emission of an electron as a result of photoelectric internal conversion of the released energy. The mean life of atoms in a given ionized state, and therefore the "width" of the state, will be determined by the sum of the probabilities of these two processes. Indirect measurements indicate that for many ionized states the probability of the second process—i.e., an Auger transition—is much greater than that of the first, and is therefore responsible for the comparatively great width observed in x-ray lines.

TABLE II. *Observed widths of certain L lines of Au(79).*

Line	Wave-length in X.U.	Observed Width[12]	
		X.U.	ev
γ_4	865.10	1.13	18.6
γ_3	895.81	1.00	15.2
γ_6	901.00	0.53	8.05
γ_2	902.20	1.14	17.2
γ_1	924.61	0.75	10.8
β_{10}	1026.0	1.12	13.1
β_5	1038.0	0.67	7.6
β_3	1065.8	1.93	20.8
β_1	1081.3	0.73	7.7
α_1	1273.8	1.06	8.1
l	1456.9	3.40	19.8

My former colleague, Dr. Edward Ramberg, now with the Radio Corporation of America, has carried out a long and difficult, but highly important, series of calculations[12] to determine the probabilities of these two processes for the x-ray energy states of Au(79); and therefrom the widths of the states and of the resulting lines for comparison with the data of Table II. I would not presume to try to explain the details of the methods of calculation used by Dr. Ramberg. Most of us experimental physicists are quite content, perhaps perforce (!), to accept thankfully and without question, the theories and the calculations of these undulatory mechanicians. May I therefore proceed at once to present Dr. Ramberg's results.

To recapitulate, the width of an x-ray line is made up of two major parts: (1) one part due to radiation transitions; the other to radiationless, or Auger, transitions.

Table III shows the computed contributions of radiation transitions to the widths of the K_1, the L_1 and the N_1 levels—chosen arbitrarily for illustration. These widths are reduced, for convenience, to electron volts, which are proportional to the width in frequency units. An atom may leave the K state by any one of several *radiation* transitions and "drop" to any one of the states, L_{II}, L_{III}, M_{II}, M_{IV} etc. The second column gives the contributions to the total width of the K state of each of these general transitions. It is noted that the probability of the transition K to L_{III} is about twice as great (36.00 *vs.* 16.63) as that for the transition K to L_{II}—in good agreement with the experimental observation that the ratio of intensities of $K\alpha_1$ to that of $K\alpha_2$ is about 2 : 1. The sum of the contributions for these several transitions is the total width of the K state *due to radiation.* This is 66.38 electron volts—as compared with an observed width of the K level (i.e., the width of the K absorption limit) of 54 electron volts.[13] Considering the approximations in the calculations and the uncertainty of the measurements, the agreement

[12] E. Ramberg and F. K. Richtmyer, Phys. Rev. **51**, 913 (1937).

[13] F. K. Richtmyer, S. W. Barnes and E. Ramberg, Phys. Rev. **46**, 843 (1934).

TABLE III. *Contributions of radiation transitions to level widths in electron volts.*

TRANSITION	Δ WIDTH[12]	LINE	TRANSITION	Δ WIDTH[12]	LINE	TRANSITION	Δ WIDTH[12]
K to L_{II}	16.63	$K\alpha_2$	L_I to L_{II}	0.0003	—	N_I to N_{II}	0.0001
L_{III}	36.00	$K\alpha_1$	L_{III}	0.0014	—	N_{III}	0.0008
M_{II}	3.44	$K\beta_2$	M_{II}	0.41	$L\beta_4$	O_{II}	0.0006
M_{III}	6.98	$K\beta_1$	M_{III}	0.92	$L\beta_3$	O_{III}	0.0011
M_{IV}	0.11	—	M_{IV}	0.02	—		
M_V	0.17	—	M_V	0.03	—		
N_{II}	0.83	$K\gamma_2$	N_{II}	0.11	$L\gamma_2$		
N_{III}	1.66	$K\gamma_1$	N_{III}	0.22	$L\gamma_3$		
N_{IV}	0.03	—					
N_V	0.04	—					
O_{II}	0.16	$K\delta_2$	O_{II}	0.02	$L\gamma_4$		
O_{III}	0.32	$K\delta_1$	O_{III}	0.04			
$\Sigma = 66.38$			$\Sigma = 1.78$			$\Sigma = 0.0026$	
Observed[13] width 54			8.7			11.7	

is satisfactory. That is to say: the width of the K state is due, in very large part at least, to radiation transitions.

However, of the observed width 8.7 ev of the L_1 state, only about one-fifth, 1.78 ev, can be ascribed to radiation transitions. For the N_1 state the discrepancy is still greater, the ratio of observed width to computed *radiation* width being of the order of 5000. Table IV shows this same comparison for several of the x-ray levels of Au(79).

Turning now to the widths to be expected from Auger transitions, we see in Table V a sample of Dr. Ramberg's results. This table may need a bit of explanation. Given a K ionized atom—of Au(79); let an L_I electron drop into the K shell; and the energy thus freed be used to expel the other L_I electron. The atom is then left doubly ionized (L_IL_I). This process has a low probability and contributes only 0.055 ev to the width of the K state. Similarly, the process which leaves the atom with L_I and either an L_{II} or L_{III} electron missing contributes 0.193 ev; and with two electrons from the $L_{II}L_{III}$ shells missing, 0.524 ev. The total contribution to the width of the K level arising from Auger transitions which leave the L shell doubly ionized is 0.772 ev. (The probability of double ionization in other shells is negligible.) The computed radiation width for the K shell is 66.38 ev (Table III). Adding to this the width 0.77 ev due to the Auger transition we have for the K state a total width of 67.15 ev as compared with the observed value of 54 ev.

With the L_1 level, however, the situation is very different. The Auger transition from the initial state L_I to a doubly ionized state in which an L_{III} and either an M_{IV} or M_V are electron missing has, relatively, a high probability, and

TABLE IV. *Comparison of (calculated) radiation widths with observed widths of levels for Au(79).*

LEVEL	RAD. WIDTH[12]	OBS. WIDTH[13]
K	66.4 ev	54 ev
L_L	1.78	8.7
L_{II}	2.91	3.7
L_{III}	1.80	4.4
M_I	0.078	15.5
M_{II}	0.090	10.7
M_{III}	0.054	12.1
M_{IV}	0.072	4.2
M_V	0.065	3.5
N_I	0.0026	11.7

TABLE V. *Contributions of Auger transitions to level widths,*[12] *in electron volts, for Au(79).*

INITIAL	FINAL	Δ WIDTH	INITIAL	FINAL	Δ WIDTH
K	L_IL_I	0.055	L_I	$L_{III}M_{IV,\,V}$	8.60
	$L_IL_{II,\,III}$	0.193		$L_{III}N_I$	0.15
	$L_{II,\,III}L_{II,\,III}$	0.524		$L_{II}N_{II,\,III}$	0.23
Auger width	$\Sigma = 0.772$*			$L_{II}O_I$	0.05
Radiation width	66.38			$L_{II}O_{IV,\,V}$	0.026
Total calculated w.	67.15			etc.	etc.
Observed width	54.00		Auger width	$\Sigma = 11.9$	
			Radiation width	1.8	
			Total calculated w.	13.7	
			Observed width	8.7	

* Other contributions negligible.

contributes 8.60 ev to the L_1 width. Other transitions are not so probable, but the total Auger width of the state is 11.9 ev. Adding the previously mentioned radiation width of 1.8 ev makes the total computed width of the L_1 state 13.7 ev—as compared with an observed width of 8.7 ev. The agreement is probably within the limits of error of the calculations and the observations.

Table VI shows the comparison between the total computed width and the observed width for several states. In the case of the N_I level, previously mentioned, the Auger width is practically the entire width.

The comparatively great width of x-ray spectrum lines and levels is thus accounted for, qualitatively at least.

TABLE VI. *Total calculated widths (radiation and Auger) compared with observed widths.*

LEVEL	RAD. W.	AUGER W.	TOTAL[12]	OBSERVED[13]
K	66.38	0.77	67.15	54
L_I	1.78	11.91	13.69	8.7
M_I	0.08	10.23	10.31	15.5
M_{II}	0.09	11.49	11.58	10.7
M_{III}	0.05	4.45	4.50	12.1
N_I	0.003	13.60	13.60	11.7

SATELLITES OF THE $L\alpha$ DOUBLET OF AU(79): COMPARISON BETWEEN THEORY AND OBSERVATION

We now return, briefly, to the satellite problem. The above calculations, supported by confirming data on line and level widths, show that the probability of certain types of double ionization by the Auger process is relatively high. Since satellites originate in doubly ionized atoms, it is to be expected that their intensities will be determined in large part by the probability of Auger transitions. It is thus possible to predict satellite intensities. The initial state for the satellites of $L\alpha$ is $L_{III}+(M_{IV}$ or $M_V)$ double ionization, the satellites being produced when one of the M electrons drops into the L_{III} shell. The different permitted orientations of the orbital and spin vectors for both the initial and the final state predict a rather complicated fine structure

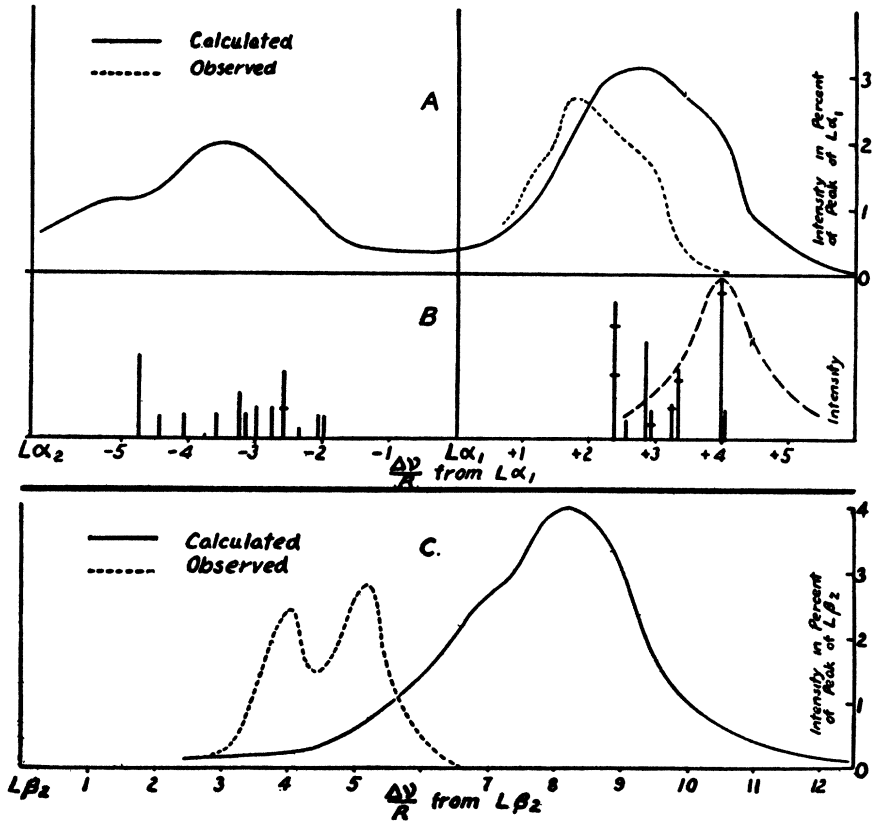

FIG. 15. B. The satellite components accompanying $L\alpha$ of Au(79), as computed by Dr. E. Ramberg. Several of the predicted components overlap so that they cannot be shown separate on the diagram. In such cases the satellites are drawn superimposed, separated by the short horizontal bar. A. The computed and the observed contour of the satellite structure of the $L\alpha$ doublet of Au(79). C. Same for the satellite structure of the $L\beta_2$ line of Au(79).

for this transition. Using Slater's theory of complex spectra for computing the components of the satellite group, and Bartlett's formulae for the relative intensities of super-multiplets, Dr. Ramberg has computed[14] the satellite structure to be expected to accompany the $L\alpha$ doublet of Au(79).

The components of this predicted structure are shown in Fig. 15B. The heights of the several lines[15] are proportional to the computed intensities. Between $L\alpha_1$ and $L\alpha_2$ there are 12 predicted components. These have not as yet been observed, perhaps because they are masked by the "valley" between $L\alpha_1$ and $L\alpha_2$. There are 15 components on the high frequency side of $L\alpha_1$. The width of these lines is not known, but it is at least of the order of magnitude of that shown by the dotted line for the strongest component; from which it is at once obvious that the components cannot be separated spectrometrically. Assuming that each of the lines has the approximate shape and width indicated, the envelope of the group can be computed, and compared with experiment. The full line of Fig. 15A shows the precicted contour; the dotted line gives the observed contour. The agreement is good enough to suggest that it needs only further refinement of the theory, and perhaps better experimental data, to bring theory and experiment into closer accord.

Figure 15C shows the comparison between theory and experiment for the satellites accompanying $L\beta_2$ of Au(79).

Suggestive as are these data and the theories herein outlined, it is obvious that only a small beginning has been made on the problem of the multiple ionization of the inner electron shells of atoms and the accompanying spectra. And our data on the associated problem of line widths are very meager. Much work, both theoretical and experimental, needs to be done before we shall have even an approximation to a complete understanding of this whole subject. To illustrate the ground that must be covered it is necessary only to point out that an atom which has a sufficient number of electron shells to be capable of single ionization in 16 different ways (K to N shells inclusive) can be doubly ionized in 120 different ways. Even with the operation of selection rules, the spectral lines arising from transitions among these 120 different levels are very numerous compared to first-order spectra.

A considerable portion of the material upon which this paper is based is the work of students and other colleagues with whom it has been my privilege to be associated in the x-ray work at Cornell University. In presenting this discussion I am in large part acting as their spokesman. They have devised many of the methods of research, both theoretical and experimental, and have contributed much to the interpretation of the data. To them should go the major part of the credit. I have had opportunity in this paper to mention by name only a few of them. But to all of them I express my appreciation for their respective contributions to this program of research.

[14] F. K. Richtmyer and E. Ramberg, Phys. Rev. **51**, 925 (1937).

[15] Several of the components are too close together to show separately on the plot. They are superimposed and are separated by short horizontal bars.

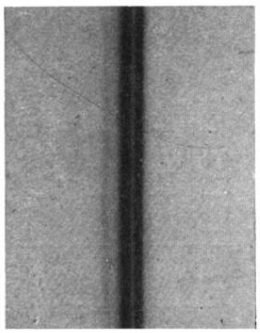

FIG. 1.

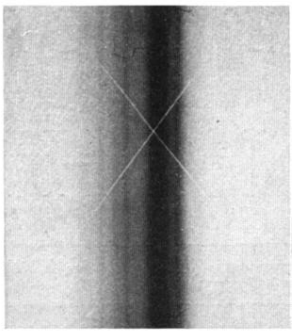

FIG. 3a.

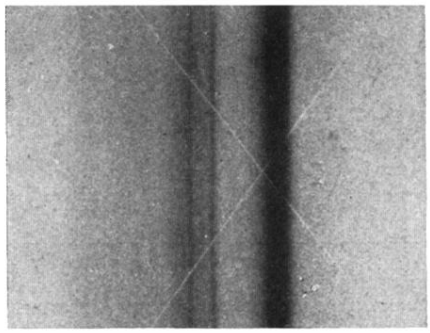

FIG. 4.

FIG. 1. The $K\alpha$ doublet of Cu(29) much over-exposed, showing the faint satellite on the left (high frequency) side.

FIG. 3(a). The $L\alpha$ doublet of Ag(47) much over-exposed to bring out the satellites shown in the left (high frequency) side. Five satellites are clearly visible on the original plate. Enlarged about 5×.

FIG. 4. The $L\beta_2$ line of Ag(47) much over-exposed. The satellite structure appears on the left (high frequency) side, well separated from $L\beta_2$.

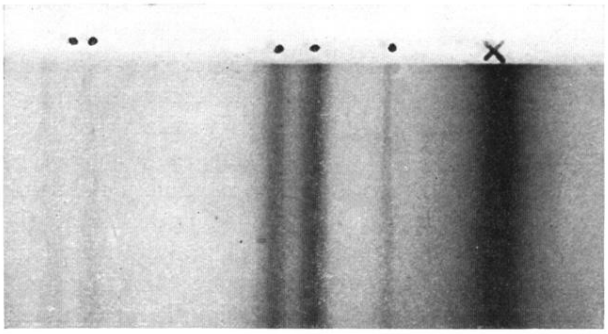

FIG. 5a.

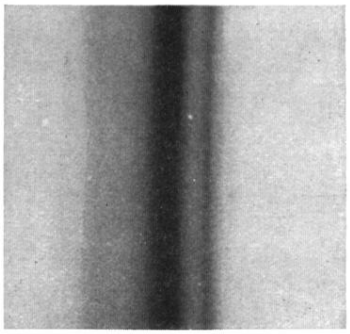

FIG. 8a.

FIG. 5(a). The $K\alpha$ doublet of S(16) indicated by "x." The satellites are designated by dots.
FIG. 8(a). The $L\alpha$ doublet of Sn(50) showing the satellite structure on the left as a wide band, instead of as separate lines observed for Ag(47). See Fig. 3(a) for comparison.

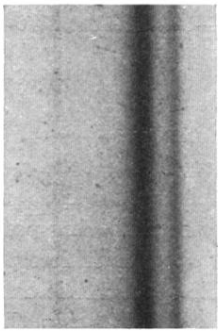

FIG. 8b.

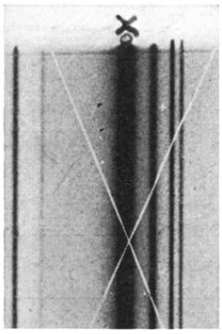

FIG. 9a.

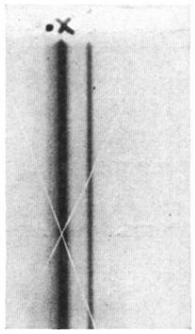

FIG. 9b.

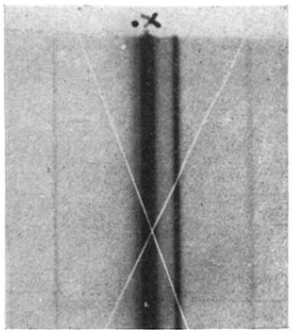

FIG. 9c.

FIG. 8(b). The $L\alpha$ doublet of Ba(56). No satellite structure is observed.
FIG. 9(a) (b) (c). The $L\alpha$ doublet of Ta(73), Os(76) and Ir(77) each indicated by a cross ($\times$). No satellites are observed with Ta. Faint satellites, indicated by a dot, are seen with Os(76) and Ir(77).