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The Relative Intensities of Certain *L*-Series X-Ray Satellites in Cathode-Ray and in Fluorescence Excitation

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Using a specially designed x-ray tube, the authors have measured the relative intensity of satellites and their parent $L\alpha_1$ line, for both cathode-ray and fluorescence excitation for the elements Zr(40), Mo(42), Ru(44), Rh(45), Pd(46) and Ag(47). Cathode-ray excitation was by 20 kv electrons. Fluorescence excitation was caused by the radiation from a target of Ag(47) bombarded by 20 kv electrons. A photographic method is used; in which spectrograms, Moll microphotometric records and density plots are made, from which it is possible to obtain the relative intensity of the satellites and their parent $L\alpha_1$ line. The results for fluorescence excitation suggest that LM ionization is the most probable origin of the $L\alpha$ satellites. On the other hand, the rapid variation in relative intensity of the satellites with atomic number for cathode-ray excitation, seems to indicate that the peripheral electron structure of the atom plays a fundamental rôle in the production of satellites. The magnitude of the integrated intensity of the group of satellites accompanying $L\alpha$ varies from 10 percent to 70 percent of the intensity of the parent line, depending on the element and the method of excitation.

INTRODUCTION

D. COSTER,[1] in 1922, stated that if x-ray non-diagram (or satellite) lines are of true spark origin, they should not appear in fluorescence spectra; whereas they are present in spectra obtained by cathode-ray excitation. Agreeing with this conclusion is the statement of M. A. Dauvillier,[2] who also remarked that the "supplementary" K lines (K satellites) should not appear in fluorescence. Dauvillier's researches[3] apparently confirmed this opinion, for he failed to observe the satellite doublet $K\alpha_{3,4}$ in the fluorescent spectrum of Fe(26). D. Coster and M. J. Druyvesteyn[4] repeated Dauvillier's experiment, using a specially designed x-ray tube, and succeeded in exciting the so-called "spark lines" of the K-series of Fe(26). They noted that, relative to the parent line, the fluorescent non-diagram lines of Fe K were about 1/6 as intense in fluorescence as in cathode-ray excitation.

The study of x-ray satellites produced by fluorescence offers a suggestive line of approach to the puzzling question of the origin of these lines. There is need of additional quantitative data on the relative intensities of fluorescent, as compared with cathode-ray excited satellites. Further, in determining excitation potentials, there are certain advantages in the use of the definite quanta $h\nu$ of line spectra as exciting sources, as compared with the rather indefinite energies of the electrons in the cathode stream. The latter lose energy rapidly as they penetrate the target; whereas monochromatic radiation,

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[1] D. Coster, Phil. Mag. **43**, 1106 (1922).

[2] M. A. Dauvillier, Comptes Rendus **174**, 445 (1922).

[3] M. A. Dauvillier, Comptes Rendus **177**, 167 (1923).

[4] D. Coster and M. J. Druyvesteyn, Zeits. f. Physik **40**, 765 (1927).

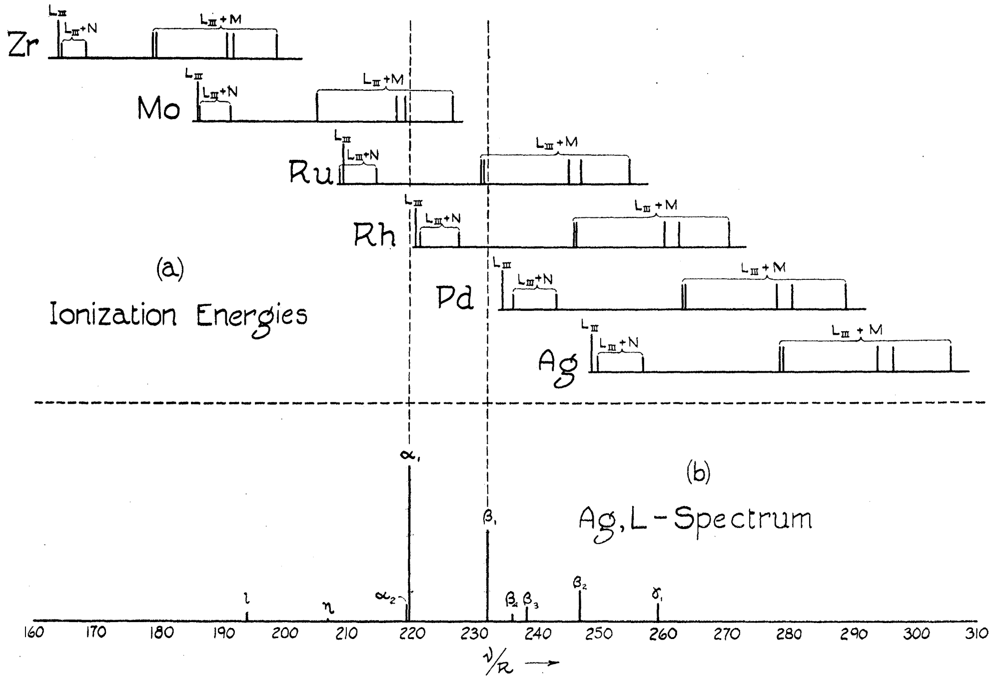

FIG. 1. (a) Plots of various single and double ionization energies. (b) The L-spectrum of Ag(47) showing approximate relative intensities.

as it penetrates the fluorescing substance, although suffering *reduction in intensity*, maintains the same $h\nu$ value, and therefore, when photoelectrically absorbed, gives to each atom exactly the same quantum of energy. Also, from the laws of absorption of x-rays, it is clear that the smaller the amount by which the frequency of the exciting radiation exceeds the absorption limit, the more intense is the fluorescence radiation; with cathode-ray excitation the reverse is the case.

In the present investigation the relative intensities of the satellites of the $L\alpha$ line of Zr (40), Mo(42), Ru(44), Rh(45), Pd(46) and Ag(47), produced by fluorescence excitation, have been obtained and compared with similar results for cathode-ray excitation. The fluorescence excitation was produced by the radiation from an Ag(47) target bombarded by 20 kv electrons. The cathode-ray excitation was by 20 kv electrons.

In Fig. 1b is shown the L-spectrum of Ag(47), plotted to a frequency (ν/R) scale. The heights of the lines represent approximate relative intensities. In Fig. 1a there are shown to the same frequency scale, the L_{III} absorption limits of Zr(40), Mo(42), Ru(44), Rh(45), Pd(46) and Ag(47). It is to be noticed from Fig. 1 that the quantum energy of Ag $L\alpha_1$, the most intense L-series line, is sufficient to ionize the L_{III} shells of Zr(40), Mo(42) and Ru(44) and *possibly* also their accompanying satellites. The L_{III} series of Rh(45), Pd(46) and Ag(47) will not be excited by Ag $L\alpha_1$. Similarly Ag $L\beta_1$, the other strong L-series line, will excite the L_{III} series of Zr(40), Mo(42), Ru(44) and Rh(45); but not the L_{III} series of Pd(46) and Ag(47).

It is generally agreed that satellites arise from some form of double ionization, which, for the satellites of $L\alpha_1$, should be $(L_{III}+M)$ or $(L_{III}+N)$ ionization. For an atom of atomic number Z the energy required for this double ionization will be[5] either $(L_{III})_Z+(M)_{Z+1}$ or $(L_{III})_Z+(N)_{Z+1}$. Plots of the energy, in ν/R units, for L_{III}, $(L_{III}+M)$ and $(L_{III}+N)$ ionization are shown in part (a) of Fig. 1 for the six elements used as fluorescers in this research. If the satellites of $L\alpha_1$ originate in $(L_{III}+N)$

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[5] Approximately, since the screening effect of an L electron on the M or N shell is a little less than one.

ionization, their relative intensities in Ru(44) should presumably be similar to the intensities for Zr(40) and Mo(42), since both $L\alpha_1$ and $L\beta_1$ of Ag(47) can excite $(L_{\text{III}}+N)$ ionization in all three of these elements. If, however, the satellites originate in $(L_{\text{III}}+M)$ ionization, there should be an abrupt change in satellite intensity between Mo(42) and Ru(44), since, except for $M_{\text{IV, V}}$, $(L_{\text{III}}+M)$ ionization cannot be excited in Ru(44) by $L\alpha_1$ and $L\beta_1$ of Ag(47). For elements above Ru(44), such $(\text{L}_{\text{III}}+M)$ ionization as is produced arises mainly from the continuous spectrum of the Ag(47) target run at 20 kv. Since the mean ν/R value of this continuous spectrum is around 1100, its effect in producing either single or double ionization should be nearly equal in all these elements.

Apparatus and Technique

Since at best, fluorescent x-ray spectra are very weak, it is necessary that the exciting radiation should be as intense as possible. This requires: (1) that the anticathode, which is the source of the exciting radiation, should be close to the fluorescing material and (2) that the physical properties of the anticathode material should be such as to make it possible to put a relatively large amount of power into the x-ray tube. Thus the K radiation from a Cu(29) target can be most effectively used to excite the K fluorescence radiation of Ni(28), Co(27), Fe(26) and Cr(24). Similarly the L radiation from a Ag(47) target may be used to excite the L_{III} series of lines in Rh(45), Ru(44), Mo(42) and Zr(40); or with a Au(79) target we may excite the M-series of Ir(77), Os(76), W(74) and Ta(73).

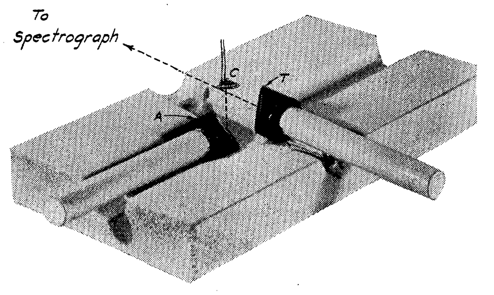


FIG. 2a. Schematic model of x-ray tube, showing relation of cathode, C, to x-ray anticathode, A, and fluorescent target, T.

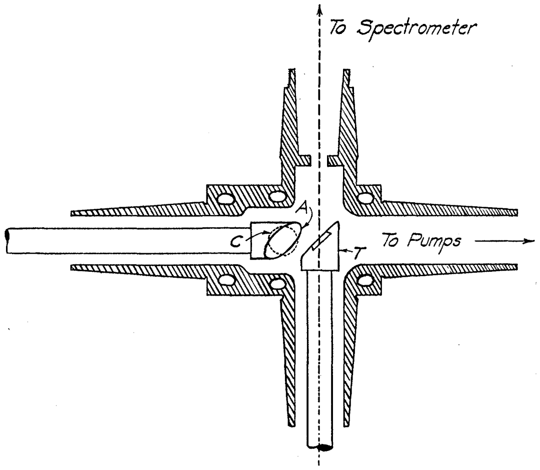


FIG. 2b. Central section of fluorescent x-ray tube.

A special x-ray tube, designed for use with a Siegbahn vacuum-spectrograph, is shown schematically in Fig. 2a and in cross section in Fig. 2b. The hot cathode, C, is centered over the primary x-ray anticathode, A. This anticathode and the fluorescent target, T, are centered in the x-ray tube by the usual glass insulating sleeves. The end of the cylindrical pure-silver head of the anticathode is bevelled off at 45°. The plane face thus formed is tilted (see Fig. 2a) in such a manner that none of the primary (exciting) x-rays from it may enter the spectrograph directly. The primary anticathode, A, is maintained at a high positive potential during operation of the tube; is adequately water-cooled; and faces the fluorescent target, T, which is also water-cooled. Both fluorescent target, T, and cathode, C, are grounded; so that no scattered electrons can reach the target with energy sufficient to excite x-rays. The x-ray tube was run at 20 kv d.c. and 30 m.a. The excitation potential for the L_{III} series of Ag(47) is 3.79 kv.

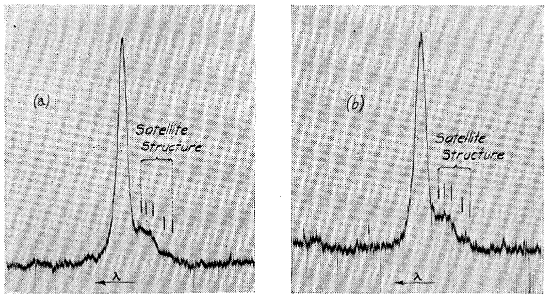
A preliminary investigation showed that it was essential to clean both the anticathode and the fluorescent target after every hour of operation. Without this precaution, the tungsten layer formed by evaporation from the hot tungsten cathode would actually prevent the emission of the easily absorbed secondary radiation from the fluorescent target, T, and would also prevent much of the silver L radiation from leaving the anticathode.

The most suitable thin window for use between the x-ray tube and spectrograph was found to be a thin film of collodion covered with aluminum leaf to exclude light. The collodion film when freshly made may be subjected to considerable abuse without breaking. Collodion carefully dropped on the surface of clean water immediately spreads into a transparent film. This, if carefully removed, dried and covered with very thin aluminum leaf, serves admirably as a thin window, transmitting about 80 percent of the energy of the Ru $L\alpha_1$ line, ($\lambda = 4.836$A).

The slit of the Siegbahn spectrograph was used at a width of 0.5 mm. This width was found necessary in order to secure sufficient intensity of the fluorescence radiation but was narrow enough to resolve the $L\alpha_{1,\,2}$ lines and satellites of the elements used as fluorescers (see Fig. 3).

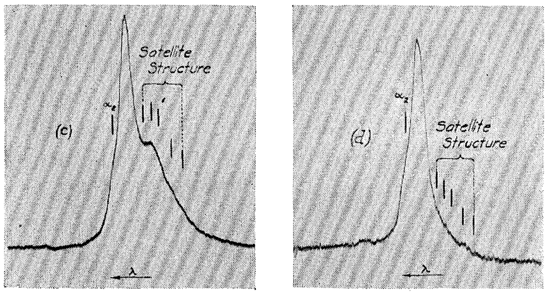
Analysis of Spectrograms

Spectrograms of the $L\alpha$ doublet and satellites of Zr(40), Mo(42), Ru(44), Rh(45), Pd(46) and Ag(47) were obtained by both fluorescence and cathode-ray excitation. Microphotometric records of these spectrograms were made, by using a Moll microphotometer with a device for reducing grain effects as described by Richtmyer and Hirsh.[6] Fig. 3a and b show the microphotometric records of spectrograms of the $L\alpha$ lines of Zr(40) in cathode-ray and in fluorescence excitation, respectively. Similar records for Rh(45) are shown in Fig. 3, c and d.



Cathode Ray Excitation Fluorescence Excitation

Zr (40)



Cathode Ray Excitation Fluorescence Excitation

Rh (45)

FIG. 3. Microphotometer records of the $L\alpha$ line of Zr(40), (a and b), and of Rh(45), (c and d), produced by cathode-ray and by fluorescence excitation, respectively. Short vertical lines designate positions of satellites and of $L\alpha_2$ as measured by comparator.

It has been shown[7] that the density of a

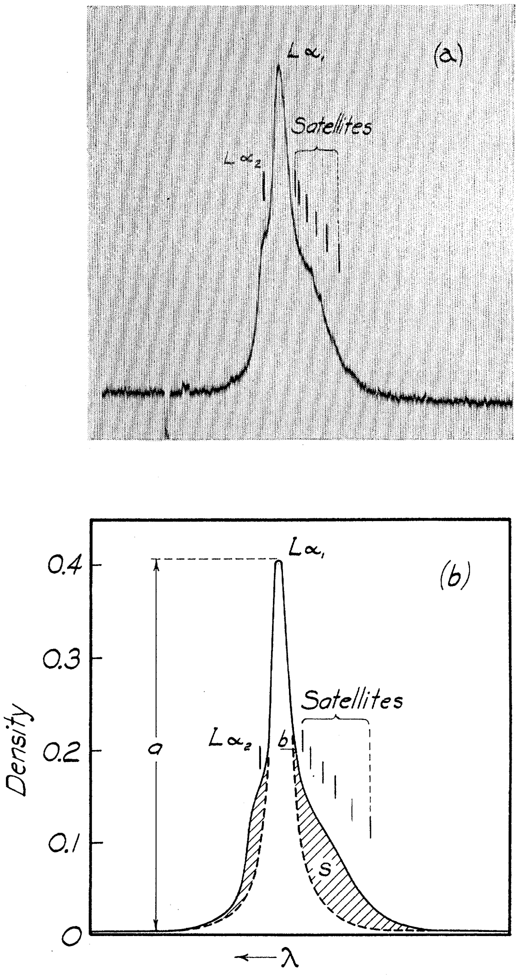


FIG. 4. (a) Microphotometer record of the $L\alpha$ doublet of Ag(47). (b) Density plot derived from microphotometer record. Dotted lines show the foot of $L\alpha_1$ as computed by the Hoyt equation.

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[6] F. K. Richtmyer and F. R. Hirsh, Jr., R. S. I. 4, 353 (1933).

[7] Unpublished work by Professor C. C. Murdock.

photographic plate resulting from exposure to x-rays, is very nearly proportional to exposure[8] for densities up to 0.5. Accordingly, density plots of the microphotometric records were made to show the true energy distribution through the line.[9] Fig. 4a shows the microphotometric record of Ag $L\alpha$ (excitation by 20 kv cathode rays); and Fig. 4b shows the corresponding density plot.

To separate the satellite structure from the parent line, these density plots were analyzed as follows: the location of the background of the parent line was carefully estimated, and its maximum ordinate, a, and half width at half maximum, b, were determined. By using the Hoyt equation[10] $y=a/(1+(x/b)^2)$ the shape of the lower part of the parent line was computed. (See dotted part of Fig. 4b.) The (shaded) area S representing the satellite structure, and the area P of the parent line were then determined. The ratio S/P is then a measure of the relative energy sought.

RESULTS

The relative energies of the satellites and their parent lines, secured by the method described in the preceding section, are given in Table I.

TABLE I.

Element	Relative Energies Cathode-ray excit.	Fluorescence excit.
Zr(40)	0.19	0.19
Mo(42)	0.30	0.20
Ru(44)	0.54	0.11
Rh(45)	0.72	0.07
Pd(46)	0.40	0.10
Ag(47)	0.33	0.08

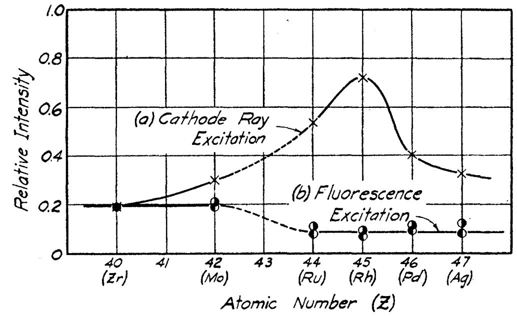

FIG. 5. Relative (integrated) intensities of satellites of $L\alpha_1$ for (a) cathode-ray excitation, and (b) fluorescence excitation

The data of Table I are plotted as Fig. 5. The relative energies for cathode-ray and for fluorescence excitation, respectively, are seen to be equal (see also Fig. 3, a and b), for Zr(40). From there, towards increasing atomic numbers, the cathode ray curve (Fig. 5a) rises to a maximum at Rh(45) where the disparity between cathode-ray and fluorescence excitation is the greatest (see also Fig. 3, c and d). From there on, the relative intensity by cathode-ray excitation decreases to the last element studied.

The relative intensities for fluorescence excitation[11] (see Fig. 5b) exhibit a different behavior. For Zr(40) and Mo(42) the satellites' relative intensities are nearly the same; however, at Ru(44) and on through Ag(47) *the relative intensity is about half of the value for Zr(40) and Mo(42).*

The Wentzel-Druyvesteyn hypothesis[12] of satellite origin suggests a reason for this decrease. According to this hypothesis, the $L\alpha$ satellites occur as a result of the simultaneous ionization of the L_{III} electron shell and some of the M-shells, with a single electron transition. H. C. Wolfe[13] has recently considered the possible merits of the Wentzel-Druyvesteyn hypothesis with encouraging results in the calculation of the frequency separations of the K-satellites and their parent $K\alpha_1$ line for K(19). Very recently, an article by Coster and Thijssen[14] reports that the excitation potential for the satellites $K\alpha_{3,\,4}$ of S(16) is 2700±25 volts, whereas 2675 is the theoretical value for S(16) KL ionization.

The decrease in the relative intensity for the fluorescent satellites in passing from Mo(42) to Ru(44),[15] (Fig. 5, curve b), suggests $(L+M)$

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[8] G. W. Brindley (Phil. Mag. **16**, 686 (1933)), finds that for the Mo $K\alpha$ doublet, $(\lambda\sim 0.7\mathrm{A})$, density is proportional to intensity for values of the density up to 1.4.

[9] The reciprocity law of photographic exposure is assumed to hold for x-rays. See F. C. Blake, Rev. Mod. Phys. **5**, 193 (1933).

[10] A. Hoyt, Phys. Rev. **40**, 477 (1932).

[11] In Fig. 5b independent data from two sets of plates are recorded.

[12] M. J. Druyvesteyn, *Dissertation*, Groningen (1928).

[13] H. C. Wolfe, Phys. Rev. **43**, 221 (1933).

[14] D. Coster and W. J. Thijssen, Zeits. f. Physik **84**, 689 (1933).

[15] It is to be regretted that Ma(43) is not available in sufficient quantity for study.

ionization as the origin of some, at least, of the satellites of $L\alpha_1$, as explained in the introduction.

However, curve *a* of Fig. 5 shows that the relative intensity of satellites for cathode-ray excitation varies rapidly as we pass through the atomic number range studied. Since, in this small range of atomic numbers, the only changes in electron configuration which take place are in N and O shells,[16] we must conclude that, in cathode-ray excitation at least, the electron population of N and O shells exerts a profound influence on the production of the satellites of $L\alpha$. It is not at all clear how this influence could be exerted if these satellites originate in $L+M$ ionization.

Attention should be called to the magnitude of the intensity of the satellites. Frequently, satellites are spoken of as weak lines; and, indeed, many of them are. But the present data show that the integrated intensity of the group of lines which make up the satellites of $L\alpha_1$ may be as high (in the case of Rh(45)) as 72 percent of the intensity of the parent line. No theory of double ionization yet advanced accounts for intensities as great as this.

ACKNOWLEDGMENTS

The senior author (F. K. R.) wishes to acknowledge his indebtedness to the Heckscher Research Council of Cornell University, for grants which made possible the purchase of certain apparatus used in this study.

The junior author wishes to express his sincere appreciation of the action of the Physics Department of Cornell University in placing research facilities at his disposal.

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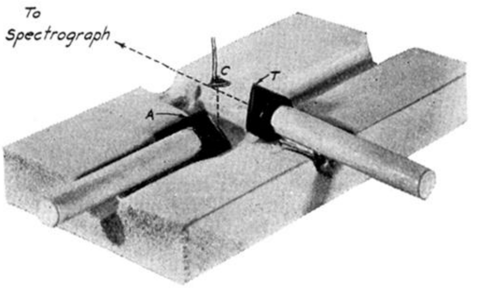
[16] See, for example, the *Structure of Line Spectra* by Pauling and Goudsmit for a table of the electron configuration of the elements.



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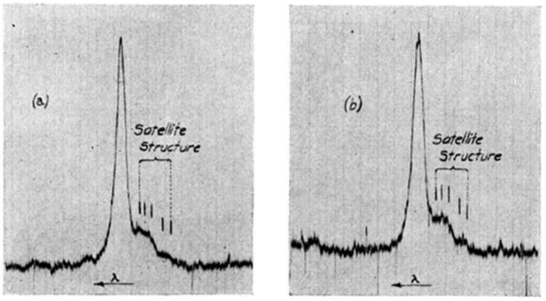
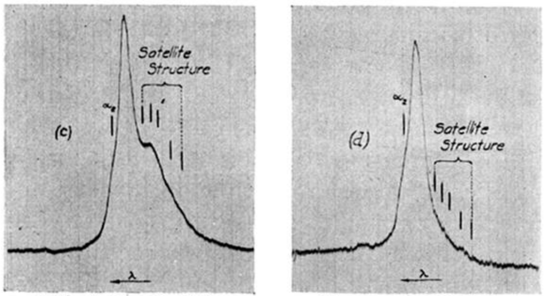


Cathode Ray Excitation Fluorescence Excitation

Zr (40)



Cathode Ray Excitation Fluorescence Excitation

Rh (45)

FIG. 3. Microphotometer records of the $L\alpha$ line of Zr(40), (a and b), and of Rh(45), (c and d), produced by cathode-ray and by fluorescence excitation, respectively. Short vertical lines designate positions of satellites and of $L\alpha_2$ as measured by comparator.

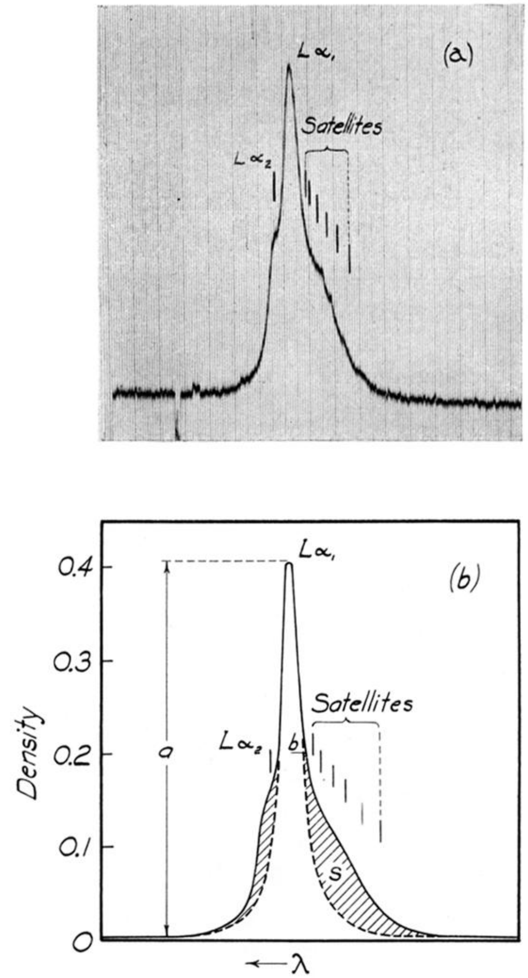


FIG. 4. (a) Microphotometer record of the $L\alpha$ doublet of Ag(47). (b) Density plot derived from microphotometer record. Dotted lines show the foot of $L\alpha_1$ as computed by the Hoyt equation.