

experiments a total of 180 have been measured. These showed a peak near $H\rho=1500$ and, by inspection, an upper limit at $H\rho=7500$ (1.8 MEV). Since the source holder covered only one-fourth of the circumference of the chamber wall, it does not seem likely that more than 45, or four percent of the "disintegration" tracks were spurious, and when the fourth root of the number of tracks is plotted, this would mean only a one percent change in a point on the K. U. plot.

In the case of manganese and arsenic the active sources were deposited chemically on filter paper. The amount of deposit was small so that the straggling of the beta-particles was presumably negligible. That this assumption was approximately correct is borne out by the fact that several sources, prepared from KMnO_4 and NaMnO_4 , in which the amount of deposit varied, gave the same results to within ten percent. Furthermore, since the active sources were placed directly in the chamber, no corrections had to be made for the passage of the particles through metallic foils.

The two beta-ray components observed in manganese and arsenic may be connected with the emission of a gamma-ray. It is, of course, possible that the K. U. theory may not be correct and that a plot of $(N/f)^{1/2}$ against $(1+\eta^2)^{1/2}$ should

not give a straight line. The theory, however, appears to fit existing data on other radioactive elements. The difference in results obtained in the present paper and those obtained by Gaerttner, Turin and Crane may be accounted for by the fact that they used thick emitters. This is somewhat borne out by the fact that the endpoint obtained by us for indium, using a thick emitter, is in substantial agreement with theirs. It should be pointed out that the procedure adopted by them, namely plotting $(N/f)^{1/2}$ for $Z=0$ is not correct for elements of atomic number as high as manganese (25) and may lead to erroneous results. We have replotted their results for indium and find that, while the shape of the curve is considerably changed when the correct value of Z is used, the extrapolated endpoint is not seriously effected.

The authors are indebted to Dr. D. P. Mitchell and Mr. G. A. Fink of Columbia University for preparing for us one of the sources of radio-manganese. We are indebted to Dr. C. B. Braestrup of the Department of Hospitals of the City of New York for many favors, and also to the American Association for the Advancement of Science for a grant to one of us (A. C. G. M.) with the help of which apparatus has been purchased.

OCTOBER 1, 1936

PHYSICAL REVIEW

VOLUME 50

On X-Ray Satellites, Relative Intensities and Line Widths

LYMAN G. PARRATT,* *Cornell University, Ithaca, New York*

(Received July 13, 1936)

Preliminary data are reported on the $L\alpha_{1, 2, 3, 4, 5, 6, 7}$ lines for Ag(47) and on the $M\alpha, \beta$ lines for Au(79) recorded with a two-crystal spectrometer. But the primary purpose of this note is to indicate some of the difficulties in interpreting these and similar data. The disagreement between the present and earlier interpretations and results is large: a factor of about 2.5 in widths of M series lines, a factor of about 2 in α_2/α_1 relative intensities, and a factor of about 4 in the satellite relative intensities. These discrepancies are due to differences in (1) the effective resolving power of the instruments used and in (2) the assumed shapes of the component lines comprising an unresolved complex structure.

RADIATIONLESS transitions, or Auger effects, are assuming a major role in explaining and correlating several perplexing x-ray

phenomena: the observed widths of x-ray emission lines and absorption limits,¹ and the relative

* The author is indebted to the Carnegie Foundation for a grant-in-aid (made to Professor F. K. Richtmyer) of this research.

¹ G. Wentzel, *Handbuch der Physik*, Vol. 24, Part 1 (1933), 768; F. K. Richtmyer, S. W. Barnes and E. G. Ramberg, *Phys. Rev.* **46**, 843 (1934); E. G. Ramberg and F. K. Richtmyer, *Phys. Rev.* **47**, 805A (1935); L. G. Parratt, *Phys. Rev.* **50**, 1 (1936); and others.

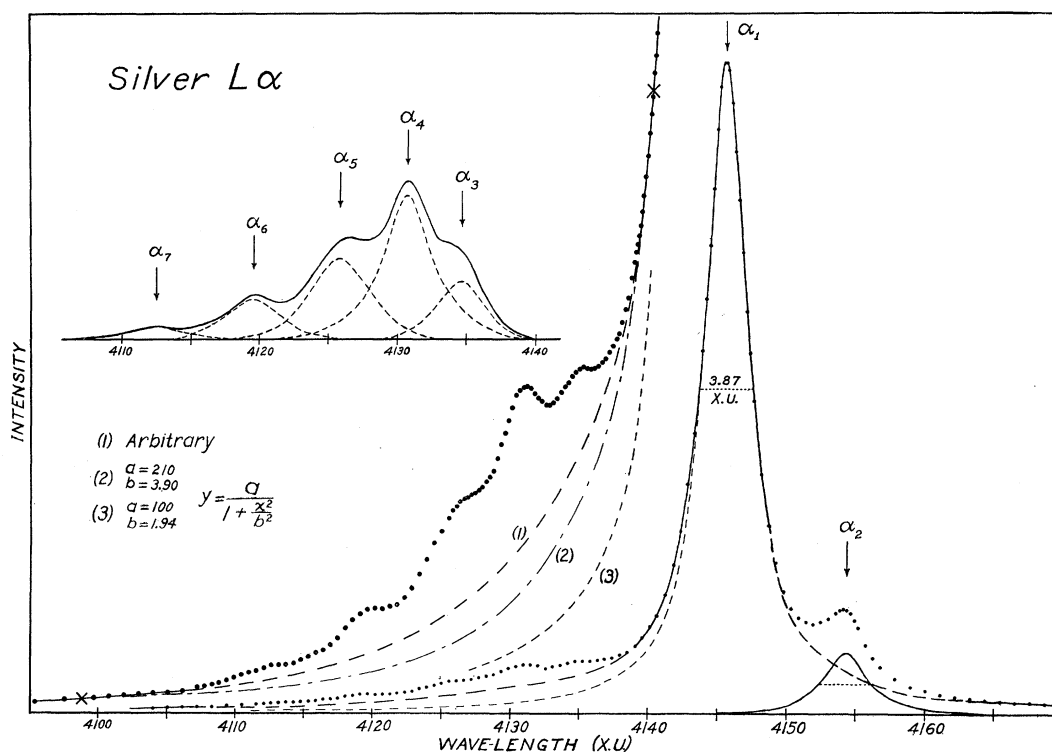


FIG. 1. Ionization curve of the Ag $L\alpha$ region recorded with a two-crystal vacuum spectrometer. The upper satellite region, on the short wave-length side of the α_1 peak, is replotted with an intensity scale increased 6.3 times. The uncertainty of the background of this satellite region is illustrated by the three possible backgrounds sketched in, each defined as indicated in the figure and discussed in the text. The satellite contour and component structure in the upper left part of the figure is determined with background (1).

intensities of x-ray lines, especially of the so-called satellite lines.² This development has brought about a rejuvenation of interest in these phenomena and promises to increase considerably our knowledge of subatomic dynamic structure.

To keep pace with this development the experimentalist is hard-pressed to refine his techniques in obtaining quantitative data. Creditable progress has been made by means of the photographic method but the well-known uncertainties inherent in this method make it a treacherous one when quantitative results, involving an accurate intensity scale, are sought. More reliable information has been obtained with the ionization method. The two-crystal spectrometer seems best adapted to this work because of the comparative ease with which a satisfactory compromise between intensity and

resolving power can be attained. The present note presents some preliminary data on the $L\alpha_{1, 2, 3, 4, 5, 6, 7}$ lines for Ag(47) and on the $M\alpha, \beta$ lines for Au(79), but the primary purpose of this note is to indicate some of the difficulties in interpreting quantitatively these and similar data.

Figs. 1 and 2 are reproductions of ionization curves of the Ag $L\alpha$ and Au $M\alpha$ regions.³ We are interested in obtaining from such curves (1) widths at half-maximum intensity (and possibly shapes) of *all* the component lines, (2) intensities of the lines relative to one another, and eventually, (3) the wave-length position of the maximum ordinate of each component line.

Firstly, to obtain these data, we must record the curves with an instrument of as high resolving power as is practical, and we should have a

² D. Coster and R. de L. Kronig, *Physica* **2**, 13 (1935); D. Coster and K. W. de Langen, *Physica* **3**, 282 (1936); F. R. Hirsh, Jr., *Phys. Rev.* **50**, 191 (1936); and others.

³ The two-crystal vacuum spectrometer, calcite crystals A_4B_4 , and accessory equipment used in recording these curves have been discussed elsewhere. See *Phys. Rev.* **50**, 1 (1936).

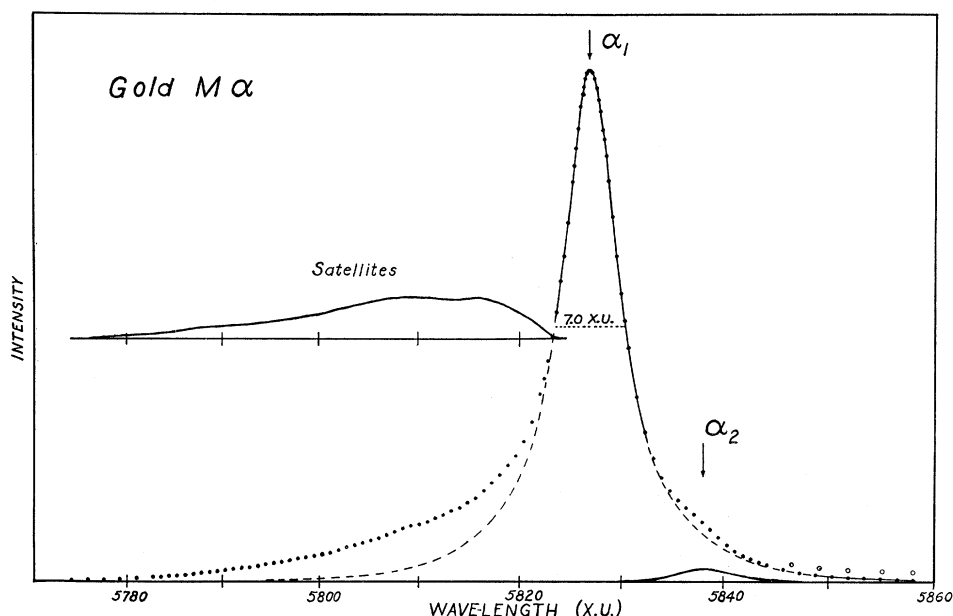


FIG. 2. Ionization curve of the Au $M\alpha$ region. The open circles at the extreme lower right part of the curve are calculated from the dispersion expression matched at the maximum and half-maximum ordinates of the α_1 line. The satellite background in this curve is determined from the assumptions that the α_1 line is symmetrical, that the shape (and width) of the α_2 line is about the same as of the α_1 line, and that the α_2 intensity is about 2.5 percent of the α_1 intensity.

good notion as to the magnitude of the effective resolving power. The "practical" choice of resolving power is a compromise between two factors: (1) the emergent intensity, or, rather, the accuracy and ease with which the intensity readings are to be made, and (2) the accuracy desired in the final results. (The concepts of resolving power and dispersion must not be confused.) Numerically, the resolving power used in recording the curves of Figs. 1 and 2 is of the order of 11,000; the $d\lambda$ interval (full width at half-maximum intensity of the diffraction pattern) is about 1/10 of the full width of the Ag $L\alpha_1$ line and about 1/14 of the full width of the Au $M\alpha_1$ line. We may assume that the resolving power is infinite but if we do we introduce thereby a first error in our interpretation and in our final results.⁴ Actually, for some measurements, the correction for a resolving power as high as 11,000 is negligible (compared with a subsequent uncertainty soon to be discussed) but it is to be emphasized that this correction is *not* negligible when the effective $d\lambda$ interval is a much larger

fraction of the true widths of the lines being studied. By way of illustration we may refer to the excellent pioneer work of Molin⁵ on M series lines. This work, with an ionization single-crystal spectrometer, deals primarily with relative intensities but for the purpose of illustrating resolving power we shall consider certain line width measurements only. Molin's observed full widths of the Au $M\alpha_1$ and $M\beta_1$ lines are 19.7 and 18.6 X.U., respectively; the present full widths of the same lines are 7.0 and 6.5 X.U. In obtaining true component structure, the need for high resolving power is obvious. This need is increasingly greater for L and K series lines because the intrinsic widths of these lines are correspondingly less, being approximately 2/3 and 1/3 as wide as the M series lines for the same wave-length.

Assuming for the present that we have infinite resolving power, we meet an insurmountable difficulty when we attempt to draw in *uniquely* the component structure. We know very little

⁴ See L. G. Parratt, Rev. Sci. Inst. **6**, 387 (1935) and Phys. Rev. **50**, 1 (1936).

⁵ K. Molin, Inaugural-Dissertation, Upsala, 1927, and M. Siegbahn, *Spektroskopie der Röntgenstrahlen*, second edition (1931), pages 362-368.

about the true shapes of these x-ray lines. Many lines are unquestionably *not* symmetrical (about their maximum ordinates). Furthermore, we cannot with impunity assume that the width or shape of one component line is the same as the width or shape of an adjacent component line in an unresolved structure.

In drawing in component structure, many investigators have gained help, at least for the sake of reproducibility, from the assumption that the shape of the component line (or lines) is given by the Gaussian error curve, $y = ke^{-ax^2}$, or, more recently by the classical dispersion curve, $y = a/(1+x^2/b^2)$. There is good theoretical support (as far as the theory has been developed⁶) for this use of the latter curve and, in fact, the shapes of many x-ray lines have been found experimentally to agree with the dispersion shape.⁶ But this assumption, of definite help in some cases, is not a panacea. In Fig. 1 three attempts are made to draw in the short wave-length side of the α_1 line, or what amounts to the satellite background. Background (3) is a sketch of part of the dispersion curve when the constants a and b are chosen to match the α_1 line at the maximum and half-maximum ordinates on the short wave-length side of the α_1 peak. (The α_1 line is not symmetrical at half-maximum intensity, excess energy being found on the *long* wave-length side of the α_1 peak.) This background is obviously inadequate unless one is willing to define as satellites *everything* above such a background *and also* be content either with rather peculiar component shapes or with a large number of components, satellites perhaps, almost approaching a continuum.⁷ Background (2)

is another attempt to use the above expression, this time the constants a and b are determined by matching the curves on either side of, and adjacent to, an arbitrary but more "reasonable" satellite region. (The curves are matched at the two points indicated by crosses in the figure.) The values of the constants used in cases (3) and (2) are indicated in the figure. Background (1) is entirely arbitrary. The writer believes that a "reasonable" background must lie between (1) and (2).

The satellite contour and structure in the upper left part of Fig. 1 is determined with background (1). It may be in point to say that the shapes of the satellite component lines are in better agreement with Gaussian error curves than with dispersion curves. Although considerable latitude is present in the component shapes the author believes that it is not possible to draw in component lines, each having the dispersion shape, whose sum is equal to the observed unresolved satellite contour without introducing additional components for which there are no specific irregularities in the observed ionization curve. This statement holds when either background (1) or (2) is used.

The total $L\alpha$ satellite intensity (area) relative to the intensity (area) of the α_1 line is 0.16, 0.09 and 0.06 for the three backgrounds, respectively. *As a consequence of the background uncertainty, the satellite relative intensity is uncertain by some 35 percent.*⁸

Because the observed $M\alpha_1$ and $M\beta_1$ lines for Au(79) are each practically symmetrical at half-maximum intensity they may be *arbitrarily* assumed to be entirely symmetrical. Both observed curves approach the base line more quickly than does the expression $y = a/(1+x^2/b^2)$, and more slowly than does the Gaussian error curve. The α_2 background may be arbitrarily determined and, then, the short wave-length side of α_1 may be drawn in with the above assumption of symmetry. With such a dividing line between satellites and parent line the ratios of intensities are 0.19 for the total satellite struc-

⁶ See references given in L. G. Parratt, Phys. Rev. **50**, 1 (1936).

⁷ A judiciously over-exposed photographic plate may be remarkably sensitive to the number of satellite lines, and, if the effective resolving power is not too low, permits fairly accurate measurements of their wave-length positions. Compare, for example, Fig. 1 with Fig. 1 of a paper by F. K. Richtmyer and R. D. Richtmyer, Phys. Rev. **34**, 574 (1929). (The continuous spectrum on the short wave-length side of the satellites reported by Richtmyer and Richtmyer for the Ag $L\alpha$ region is not found in the present work, but this negative result is conclusive only in setting an upper limit of the total intensity, about 2 percent of the α_1 line, which is about the present experimental error due to the uncertainty of the base line intensity. Because of the difficulties in transposing the ordinate scale of the Richtmyers' densitometer curve to a scale which is linearly proportional to intensity, one cannot say what one might expect for the relative intensity of this continuous spectrum.)

⁸ This estimate of the uncertainty in relative intensities varies, of course, with line and with element. For the $K\alpha$ satellite lines this uncertainty is about 5 percent for S(16) and increases with atomic number to perhaps more than 50 percent for Pd(46). See reference 6 and C. H. Shaw and L. G. Parratt, Phys. Rev. to be published.

ture to the α_1 line and 0.21 for the total satellite structure to the β_1 line. In appearance the satellite contours of Au $M\alpha_1$ and $M\beta_1$ are very similar. As yet, neither contour (from these curves) has been satisfactorily resolved into satellite components.⁹

The background of the α_2 line can be drawn with somewhat more assurance than the satellite background because of the smaller extent of the uncertain part of the α_1 line. As the present backgrounds are drawn, the ratio of intensities of the α_2 to α_1 lines are 0.065 and 0.025 for Ag $L\alpha$ and Au $M\alpha$, respectively. *It is to be noted that these values are considerably less than those predicted by the Burger-Dorgelo sum rules, 0.11 and 0.05, respectively.* The writer recognizes that he may be criticized for his particular choice of backgrounds which result in such low relative intensities for the α_2 lines. In fact previous investigators have chosen to draw in the α_1 line in such a manner that much better agreement is found with the sum rules.¹⁰ While these rules have been found valid for many multiplets for some atomic number ranges, the writer is convinced that they do not apply in this simple manner in the present cases.

As stated above,⁷ a good notion of wavelength positions of relatively weak lines which are closely adjacent to an intense line can be obtained from photographic plates. The lack of

adequate effective resolving power, however, is apt to introduce considerable uncertainty. As an example we may refer to measurements of the Au $M\alpha_{1,2}$ separation. Lindberg¹¹ measures 14 X.U.; Hirsh,⁹ 10.2 X.U.; the separation obtained from the curve of Fig. 2 is 11.1 X.U. Furthermore, from Fig. 2, it is obvious that the α_2 background may be drawn in, with increasing α_2/α_1 relative intensity, so that the $\alpha_{1,2}$ wavelength separation may be either slightly increased or decreased, depending upon the α_1 shape one wishes to assume.

*The disagreement between the present and earlier interpretations and results is large: a factor of about 2.5 in widths of M series lines, a factor of about 2 in α_2/α_1 relative intensities, and a factor of about 4 in the satellite relative intensities.*¹²

The ultimate accuracy of proposed quantitative measurements on component lines, resolved from contours as illustrated in Figs. 1 and 2, is limited essentially by the large *true* line widths, unknown line shapes, and the particular line groupings. It appears that ultimately we must resort to the observer's judgment as to the "reasonableness" of the component line shapes. But *nevertheless* a great deal of uncertainty and ambiguity can be eliminated by recording the line contours with high resolving power, with an accurate intensity scale (and, of course, intensity readings), and also, possibly in some respects, by comparing measurements on as many similar regions of adjacent elements as possible. As stated above, the data of this note are preliminary, and more measurements are now in progress.

⁹ See F. R. Hirsh, Jr., Phys. Rev. **38**, 914 (1931), and references. That distinct satellite lines are observed on carefully exposed (over-exposed) photographic plates is due to the physiological or psychological effect of the eye in seeing contrast.

¹⁰ For example, see A. Jönsson, Zeits. f. Physik **46**, 383 (1928); R. C. Spencer, Phys. Rev. **38**, 630 (1931); F. R. Hirsh, Jr., Phys. Rev. **48**, 722 (1935); M. Siegbahn, reference 5, page 366 and pages 356-362; A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (1936), pages 646 to 654; and references.

¹¹ E. Lindberg, Nova Acta Reg. Soc. Sci. Upsaliensis, Ser. IV, Vol. 7, No. 7, 1931.

¹² F. R. Hirsh, Jr., Phys. Rev. **48**, 722 (1935).