a nucleus, the latter allowing the conservation laws to be satisfied. More work is being done to clear up this matter.

Upon consideration of these results, it seems to us that this method of measuring the energy and relative intensity of gamma-radiation is fairly satisfactory in the energy range from 0.5 to 3 Mev. As far as radiation emitted from the lighter elements is concerned, it appears to be the most reliable method so far used to obtain these quantities.

The authors are very grateful to Professor E. O. Lawrence and to Professor J. R. Oppenheimer for many discussions of this work. We are also indebted to the Chemical Foundation and the Research Corporation and the Josiah Macy, Jr., Foundation for grants making the experimental work possible.

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$K\alpha$ Satellite Lines for Elements Zn(30) to Pd(46)

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With a two-crystal spectrometer, ionization curves of the $K\alpha_{3,4}$ group of x-ray satellite lines have been recorded for elements Zn(30) to Pd(46). In this satellite group are found four component lines for elements $30 \leq Z \leq 33$, three components for $34 \leq Z \leq 40$ and two components, α_3' and α_4, for $41 \leq Z \leq 46$. The wave-length position, relative intensity, and line width at half-maximum intensity of each component has been measured. A sharp and anomalous decrease (with increasing Z) in the total satellite intensity relative to the α_1 intensity is found in the region of $Y(39)$. Curious and anomalous intensity relations are also found among the individual satellite components.

I. INTRODUCTION

EXPERIMENTAL knowledge of x-ray satellite lines has recently been advanced very considerably by the application of the two-crystal ionization spectrometer. Feeble ionization currents can now be measured with an accuracy which is limited chiefly by the statistical variation in the number of quanta entering the ion chamber,[1] and the ratio of two x-ray intensities differing by a factor of 10,000 can be measured with an uncertainty of but a few percent. Measurements with such precision combined with high resolving power are indispensable in obtaining quantitative information, especially of intensity relationships, about the extremely faint x-ray satellite lines accompanying the intense $K\alpha_1$ lines.

Wave-length positions, relative intensities and line widths are reported in the present paper for the component lines α_3, α_3' and α_4 for elements Zn(30) to Pd(46). This report extends a previous study[2] of the $K\alpha$ satellite lines and, with the previous study, provides systematic and relatively precise information about these lines for the wide atomic number range S(16) to Pd(46).

II. EXPERIMENTAL PART

The two-crystal spectrometer used in these measurements has been described elsewhere.[3]

Crystals

The calcite crystals were ground, polished and etched several times in an effort to make of them "perfect" crystals of Class I.[4] As these crystals were used, their degree of perfection was good though somewhat indefinite. No attempt was made in the present work to study *accurately* (i.e., to 1%) line widths and shapes, and our knowledge of the diffraction patterns of these crystals was considered adequate for the satellite study. As an index to the effective resolving power, the observed $K\alpha_1$ widths are given in a subsequent table of data.

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* National Research Fellow.

† Indebted to the Carnegie Foundation for a grant-in-aid (made to Professor F. K. Richtmyer) of this research.

[1] L. G. Parratt, Phys. Rev. **49**, 132 (1936), and others.

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

[3] F. K. Richtmyer and S. W. Barnes, Rev. Sci. Inst. **5**, 351 (1934), and F. K. Richtmyer, S. W. Barnes and E. G. Ramberg, Phys. Rev. **46**, 843 (1934).

[4] L. G. Parratt, Rev. Sci. Inst. **6**, 387 (1935).

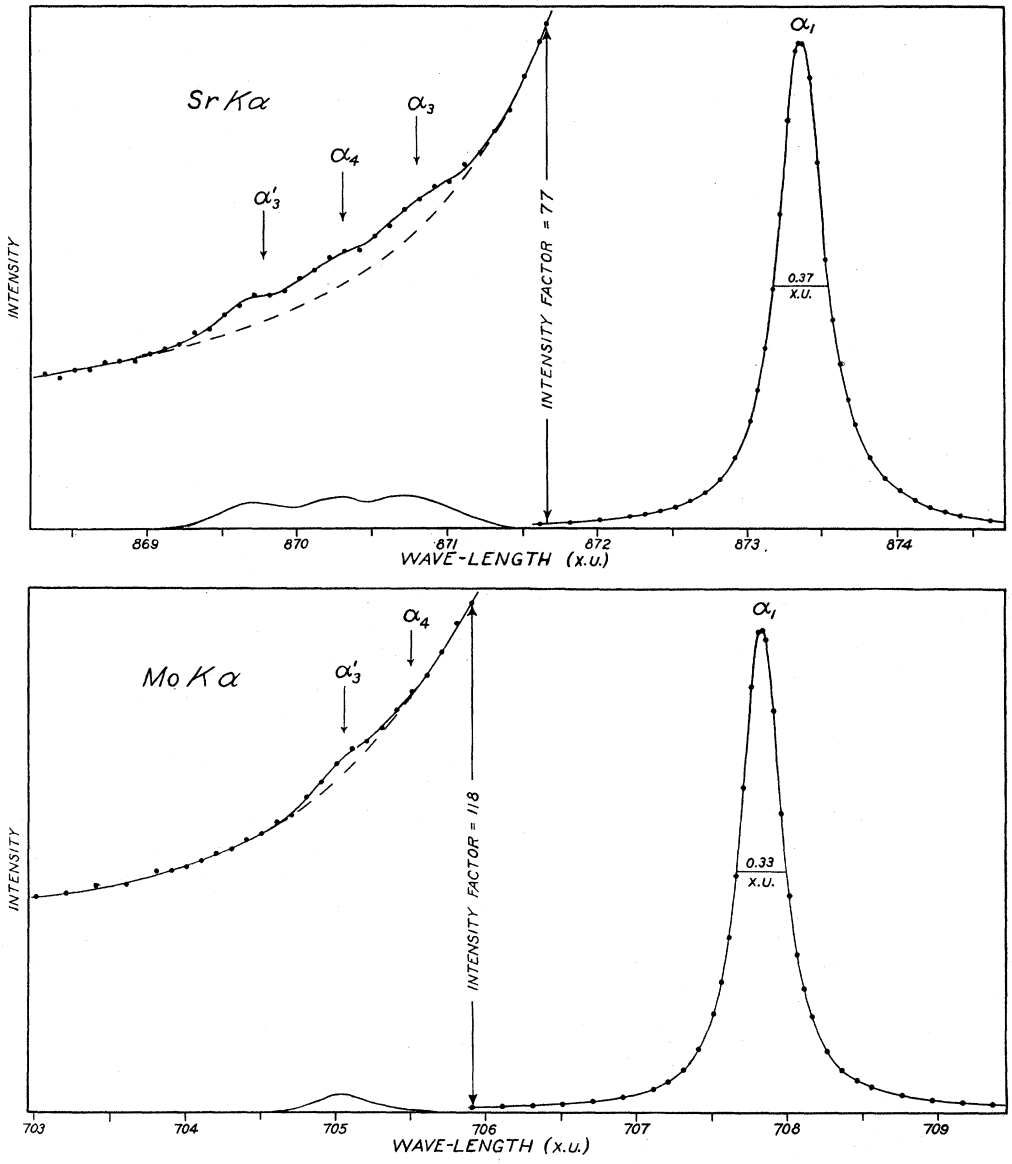

FIG. 1. Ionization curves of the $K\alpha_1$ region for Sr(38) and for Mo(42). The $\alpha_{3,4}$ group of satellites in each case is plotted to an intensity scale magnified, relative to the scale of the α_1 line, by the intensity factor indicated. The satellite background (the side of the α_1 line) is sketched in and the reduced satellite contour is drawn. As the atomic number increases, the satellite intensity relative to the α_1 line decreases, the satellites are found "higher up" on the side of the α_1 line, and the continuous spectrum, comprising part of the satellite background, is relatively more intense. (Spuriously scattered radiation, although reduced to a minimum, is, of course, also present in the background.)

Ionization currents

A steel ionization chamber, two inches in diameter and ten inches long, was filled with argon at three atmospheres pressure. The ionization currents were amplified with an FP-54 electrometer tube in a modified DuBridge-Brown circuit[5] having a sensitivity of about 100,000 mm/volt, and the amplified currents were recorded with a L. and N. type R galvanometer. Any one of four high resistors, 10^8, 10^9, 10^{10} or 10^{11} ohms, could be placed in the control-grid

[5] L. A. DuBridge and H. Brown, Rev. Sci. Inst. **4**, 532 (1933).

circuit by a simple switching device. These resistances, whose ratios were known, allowed the measurement of the ratio of widely differing ionization currents with a much smaller corresponding change in the control-grid voltage. Furthermore, the control-grid voltage was maintained roughly constant by an applied e.m.f. obtained from an auxiliary battery with a L. and N. type K potentiometer in the control-grid circuit. In this manner the electrometer tube and circuit were used as a null instrument, assuring beyond question the linearity of the system for recording *ionization currents*. As an experimental check on the linearity for *x-ray intensities*, to make sure of saturation in the ion current, etc., the absorption coefficient of silver was determined for Mo $K\alpha_1$ radiation for two silver foils. One of these foils reduced the ionization current from about 10^{-11} amperes to about 5×10^{-12}; the other to about 10^{-14} amperes, one-thousandth of the I_0 current. The two absorption coefficients so determined differed by about 3 percent and were within the experimental error of the accepted value.

Targets

The targets of the various elements were prepared as follows: Zinc was electroplated onto copper. Small bits of metallic arsenic were pressed with a hydraulic press into a sheet of silver which was then soft-soldered to the water-cooled target carriage. Metallic selenium was melted on a silver sheet, forming a thin layer of Ag_2Se which adhered tenaciously to the silver. The copper target carriage was dipped into bromine gas until a very *thin* layer of $CuBr_2$ had formed. Metallic strontium was pressed into a $\frac{1}{2}$-inch hole drilled in a copper rod, sealed with borax to prevent oxidation, and heated with an oxygen flame to a temperature slightly above the strontium melting point. The strontium fused with the copper on the flat bottom and around the walls of the cup. When cooled, the unit was turned on a lathe to the desired shape of a disk about $\frac{1}{8}$ of an inch thick, about half of which was copper, and $\frac{5}{8}$ of an inch in diameter. After soft-soldering the disk to the target carriage, a fresh surface of strontium, obtained by a few strokes of a file, was preserved by a coating of napthalene which coating soon evaporated when the pumps were applied to the x-ray tube. Metallic zirconium, columbium and molybdenum sheets were each spot-welded to a nickel sheet. Metallic palladium was soft-soldered directly to the target carriage.

X-ray tube power

It has been noted previously[1, 6] that the intensities of $K\alpha$ satellite lines relative to the

[6] D. Coster and W. J. Thijssen, Zeits. f. Physik **84**, 686 (1933). See also D. Coster, H. H. Kuipers and W. J. Huizinga, Physica **2**, 870 (1935); and L. G. Parratt, Phys. Rev. **49**, 502 (1936).

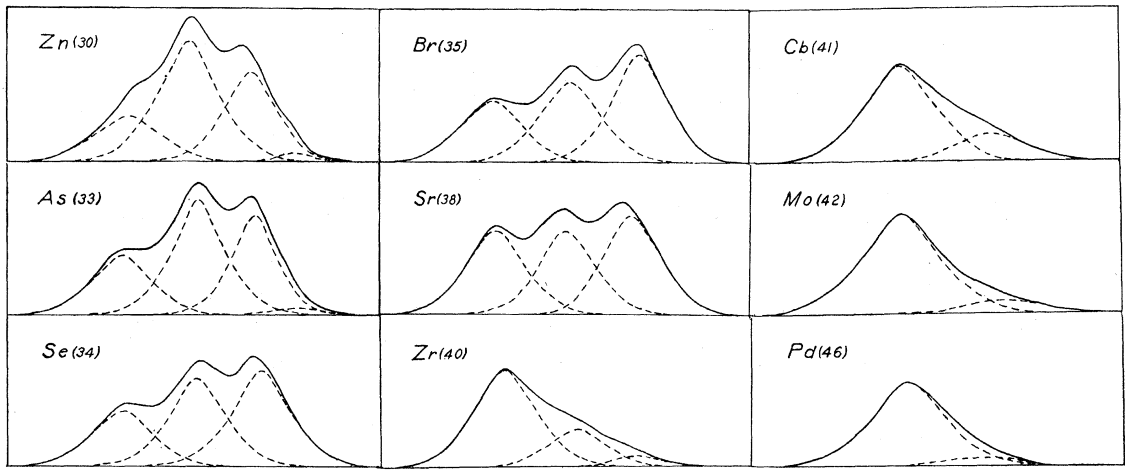

FIG. 2. Contours of the $K\alpha_{3,4}$ satellite group, reduced to a uniform background, for elements Zn(30) to Pd(46). Arbitrary abscissae and ordinate scales are used for each element. The reduced contours are resolved into the structural component lines as discussed in the text. From left to right the components are α_3', α_4, α_3 and α'. All four satellite components are found for elements $30\leq Z\leq 33$, three components for $34\leq Z\leq 40$, and two components, α_3' and α_4, for $41\leq Z\leq 46$.

intensity of the $K\alpha_1$ line is constant for x-ray tube voltages greater than about twice the excitation potential. In the present work this condition for maximum satellite relative intensity was maintained for each element. The x-ray tube was operated as follows: For $30 \leq Z \leq 35$ the voltage was 35 kv and the current about 15 ma; for $38 \leq Z \leq 42$, 40 kv and 15 ma; and for $Z = 46$, 50 kv and 16 ma.

The largest observed α_1 peak intensity was for As(33), an equivalent scale deflection at maximum sensitivity of 48,000 cm produced by an ionization current of 1.2×10^{-11} amperes; the minimum α_1 peak equivalent deflection was 9000 cm for Br(35).

Ionization curves

In Fig. 1 are reproduced the ionization curves for Sr(38) and Mo(42) as representative of the present $K\alpha$ regions. The satellites α_3, α_3' and α_4 are plotted in each of these curves to an intensity scale 77 and 118 times the scale used in plotting the $K\alpha_1$ lines.

Reproduced in reference 2 for elements of lower atomic number are ionization curves similar to those in Fig. 1.

III. Resolution Into Components

As seen in Fig. 1, the satellite lines appear as small irregularities on the side of the α_1 line. We are interested in analyzing as far as possible these observed irregularities in terms of the component line structure. Firstly, we are obliged to draw in the side of the α_1 line under the satellite region. Partly because of the unknown shape of the α_1 line (and of the unknown relative intensity of the continuous spectrum and of the spuriously scattered radiation), and partly because of the observational errors in the intensity readings, this satellite background is necessarily arbitrary: the attending relative uncertainty in the satellite contours is large, with an increasing relative uncertainty as the satellite intensity decreases. With the writers' opinion of a "reasonable" background, the satellite contour for each of the present elements is illustrated in Fig. 2. These contours have been analyzed into component structure, as indicated in Fig. 2, in a manner similar to that discussed in reference 2. It is, of course, not possible to arrive at a unique component structure and the present analysis is but the writers' "reasonable" guess. The essential features of the structure, however, are unambiguous.

The α' component

The α' line appears consistently for Zn(30) and As(33) although the external evidence for this line is about equal to the estimated observational errors. It would be possible to include α' in the resolved structures for Se(34), Br(35) and perhaps also Sr(38) but this has not been done since for these elements the line is certainly within the errors.

The α_3 component

The α_3 line is in strong evidence through Sr(38) and is questionably present for Zr(40). For elements above Zr(40) α_3 is certainly within the errors. The greatest factor in the errors, especially for elements of atomic number above Sr(38), is the uncertainty of the background intensity. One might draw in a background for each of the elements $40 \leq Z \leq 46$ which would leave considerable intensity for the α_3 component, say $\frac{1}{3}$ the intensity of α_3'. Such backgrounds would also (1) approximately double the total satellite intensity relative to the α_1 line, (2) result in markedly asymmetrical shapes of the component satellite lines and considerably increase the component line widths, (3) slightly alter the wave-length positions, and (4) finally, and most important, require a greater observational error in the intensity recordings than the writers are willing to grant. On the other

Table I. *Wave-lengths in X.U. of $K\alpha$ satellite lines.* These measurements for each element are referred to the wave-length of the $K\alpha_1$ line.*

Target	Element	α_1	α'	α_3	α_4	α_3'
Electroplated	Zn(30)	1432.22	1427.7	1427.00	1426.12	1425.28
metal	As(33)	1173.44	1170.1	1169.59	1168.94	1168.09
Ag_2Se	Se(34)	1102.48	—	1098.92	1098.28	1097.52
$CuBr_2$	Br(35)	1037.59	—	1034.28	1033.65	1032.93
metal	Sr(38)	873.45	—	870.87	870.35	869.80
metal	Zr(40)	784.30	—	782.0	781.6	781.16
metal	Cb(41)	744.65	—	—	742.1	741.69
metal	Mo(42)	707.83	—	—	705.5	705.06
metal	Pd(46)	584.27	—	—	582.5	582.14

* The wave-length for the $K\alpha_1$ line for Zn(30) is taken from Bearden and Shaw, Phys. Rev. **48**, 18 (1935); for all other elements the $K\alpha_1$ wave-lengths are taken from Siegbahn, *Spektroskopie der Röntgenstrahlen* (1931).

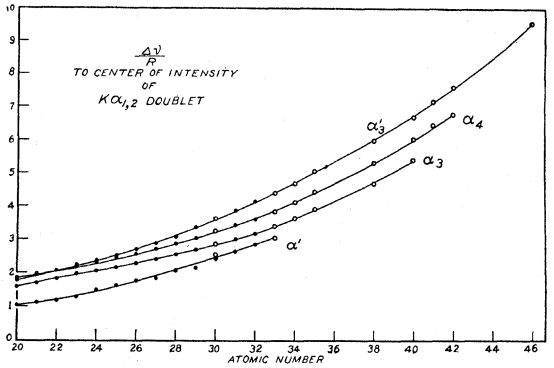

FIG. 3. Wave-length separations, in $\Delta\nu/R$ units, of the satellite components from the center of intensity of the $K\alpha_{1,2}$ doublet lines. The open circles represent the present data; the solid circles are measurements taken from Parratt, reference 2.

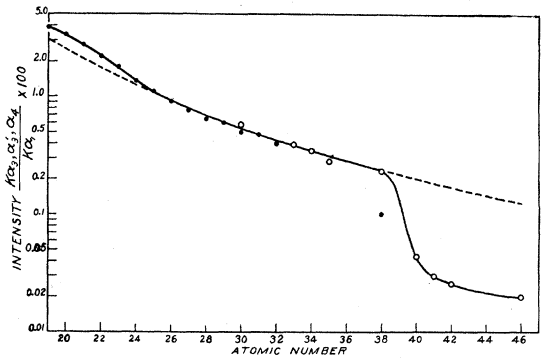

FIG. 4. Intensity of the $K\alpha_{3,4}$ group of satellites relative to the intensity of the $K\alpha_1$ line for elements K(19) to Pd(46). The open circles are the present data; the solid circles are measurements[8] by Parratt, reference 2. The dashed curve represents Richtmyer's theoretical predictions: The sudden drop (to about $\frac{1}{8}$) in the experimental curve near Y(39) is quite unexpected.

hand, there could be permitted, within the observational errors, a background for each element $40 \leq Z \leq 46$ which would exclude the presence of all components except α_3'. Such backgrounds are not drawn because of the belief that the width of the α_3' component is at least as great as the width of the α_1 line.

The α_3' and α_4 components

No question can be raised as to the presence of the α_3' line for any of the elements studied. The α_4 line is strongly evidenced through Sr(38) and is included in the component structure for higher atomic numbers because of the arbitrary criterion of symmetry for the α_3' line and for the reasons mentioned in the previous paragraph.

Hulubei has recently reported[7] photographic measurements of the α_3, α_3' and α_4 lines for elements Cu(29), Zn(30) and As(33), of α_3' and α_4 for elements Se(34) to Y(39), and of α_4 for Rh(45). Attention has been called previously[2] to the interchange of Hulubei's notation for the α_3' and α_4 components. That Hulubei detected these extremely faint satellites by the photographic method speaks well of his care in examining the plates and of his effective resolving power.

TABLE II. *Separation in $\Delta\nu/R$ units of the $K\alpha$ satellite lines referred to the center of intensity of the $K\alpha_{1,2}$ doublet lines.* (The type of target used for each element is given in Table I.)

Element	α_1	α'	α_3	α_4	α_3'
Zn(30)	0.567	2.58	2.89	3.29	3.66
As(33)	0.879	3.09	3.44	3.87	4.44
Se(34)	1.009	—	3.69	4.17	4.74
Br(35)	1.144	—	3.95	4.49	5.11
Sr(38)	1.654	—	4.74	5.37	6.03
Zr(40)	2.075	—	5.49	6.09	6.74
Cb(41)	2.318	—	—	6.52	7.20
Mo(42)	2.586	—	—	6.84	7.65
Pd(46)	3.869	—	—	8.61	9.58

IV. MEASUREMENTS

Wave-lengths

The wave-lengths of the peaks of the resolved satellite components are listed in Table I. These

TABLE III. *Intensities of $K\alpha$ satellite lines.* For each element the intensity of the $K\alpha_1$ line is taken as 100. No correction for the finite resolving power of the crystals has been made. (The type of target used for each element is given in Table I.)

Element	α_1	$\alpha_{3,4}$ Group	α'	α_3	α_4	α_3'
Zn(30)	100	0.59	0.008	0.18	0.28	0.12
As(33)	100	0.39	0.004	0.13	0.16	0.09
Se(34)	100	0.35	—	0.14	0.13	0.08
Br(35)	100	0.28	—	0.11	0.09	0.075
Sr(38)	100	0.23	—	0.08	0.07	0.08
Zr(40)	100	0.044	—	0.003	0.011	0.030
Cb(41)	100	0.030	—	—	0.007	0.023
Mo(42)	100	0.026	—	—	0.003	0.023
Pd(46)	100	0.020	—	—	0.002	0.018

[7] M. H. Hulubei, Comptes rendus **201**, 544 (1935). Studying the $K\alpha_{1,2}$ lines for Kr(36), E. Wilhelmy, Zeits. f. Physik **97**, 312 (1935), detected a faint new line on the short wave-length side of the α_1 line. Wilhelmy estimates (in a private communication to the authors) that the intensity of this line is 1 to 2 percent of the α_1 intensity. This new line, which is much closer to the α_1 line (0.6 X.U. separation) than is any of the present lines of the $\alpha_{3,4}$ group, is not found for any of the elements in the present study.

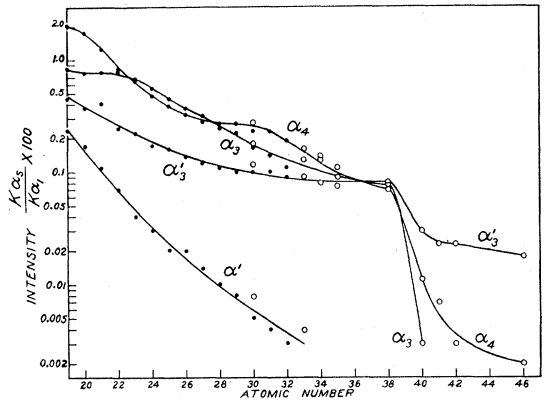

FIG. 5. Intensity of each satellite component relative to the intensity of the $K\alpha_1$ line. The open circles are the present data; the solid circles are measurements by Parratt, reference 2.

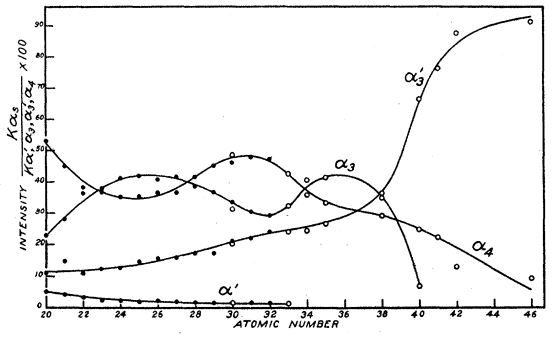

FIG. 6. Several curious intensity reversals are found among the satellite components as shown by this graph of the percent intensity of each component relative to the total group. The open circles are the present data; the solid circles are measurements taken from reference 2.

wave-lengths for each element are referred to the position of the α_1 line, the wave-length of which is taken from other investigators and is included in the table.

The separations in $\Delta\nu/R$ units of the satellite components referred to the center of intensity of the $\alpha_{1,2}$ doublet are listed in Table II and shown graphically in Fig. 3 as a function of atomic number. The graphs of Fig. 3 are not linear; they serve at the present time primarily to identify the component lines.

Relative intensities

The sensitivity of the satellite intensities to the particular background is obvious from the above discussion. Especially is this so for the total satellite intensity relative to the α_1 intensity and for certain components relative to the intensity of the total structure. With the backgrounds that the writers have chosen, the satellite intensities are as listed in Table III. The ratio of the total intensity[8] of the satellite group to the intensity of the α_1 line is plotted as a function of atomic number in Fig. 4. The sudden drop in the curve at about Y(39) is quite outside of the uncertainties due to backgrounds. As yet no theoretical explanation of such a drop is in sight: The recent theoretical intensity predictions of Richtmyer[9] agree with experiment surprisingly well for elements of atomic numbers $Z<39$ but disagree by a factor of about five to eight for $Z>39$. In the writers' opinion a factor of no more than two is possible by readjusting the backgrounds.

The intensities of the individual components relative to the α_1 line are plotted in Fig. 5 and relative to the satellite group as a whole in Fig. 6. None of these several intensity reversals has been explained by theory;[2, 10] nor was it to be expected that the α_3 and α_4 components would decrease in intensity, leaving the α_3' component to dominate the group for the higher atomic numbers.

Widths and shapes of satellites

The widths at half-maximum intensity of the component satellite lines resolved as in Fig. 2 are listed in Table IV. For easy comparison the

TABLE IV. *Full widths, in X. U., at half-maximum intensity of Kα lines.* These widths refer to the component lines as resolved in Fig. 2. No correction for the finite resolving power of the crystals has been made. (The type of target used for each element is given in Table I.)

Element	α_1	α_3	α_4	α_3'
Zn(30)	0.52	0.90	0.98	1.10
As(33)	0.43	0.61	0.68	0.78
Se(34)	0.41	0.61	0.66	0.70
Br(35)	0.40	0.60	0.64	0.67
Sr(38)	0.37	0.51	0.53	0.55
Zr(40)	0.34	—	0.43	0.45
Cb(41)	0.34	—	0.40	0.41
Mo(42)	0.33	—	—	0.37
Pd(46)	0.31	—	—	0.34

[8] The relative intensity measurements given in reference 2 for the satellite group and for each component contain a correction for the finite resolving power of the crystals. This correction, a reduction of 5 percent in $\alpha_{3,4}$ group intensities from the observed values, accounts for part of the difference between the relative intensity measurements as plotted in Figs. 4, 5 and 6.

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

[10] E. H. Kennard and E. G. Ramberg, Phys. Rev. **46**, 1040 (1934).

observed widths of the α_1 lines[11] are included in the table. For some components the uncertainty in the satellite widths is rather large, perhaps 50 percent. As the widths are listed, the ratio of satellite widths to the α_1 width decreases with increasing atomic number.

As in the previous study,[2] very little can be said about the shapes of the individual components. The component lines were assumed to be roughly symmetrical. As these lines are drawn in Figs. 2 of the present and previous studies, the shapes approximate more nearly Gaussian error curves, $y=pe^{-\alpha x^2}$, than they do classical dispersion curves, $y=a(1+x^2/b^2)^{-1}$. While the satellite contours are not known in these studies with sufficient accuracy to determine the component shapes, it might be in point to say that attempts to apply the dispersion curve to the satellite components of the $K\alpha_{3,4}$ group for Ti(22) and Zn(30) and of the $L\alpha_{3-7}$ group[12] for Ag(47) lead to the necessity of assuming additional components, components for which there are no specific irregularities in the ionization curves, to account for the observed contours. The writers do not believe that the present evidence for any particular line shape can serve to justify such a method of component analysis.

[11] In most cases just one ionization curve of the α_1 line was recorded and no especial care was taken in measuring accurately (within, say, 6 or 7 percent) the α_1 line widths. The case of Mo is an exception: The Mo $K\alpha_1$ line width was measured many times with considerable care in a study of the effective resolving power of the crystals. Except for this excessively wide Mo $K\alpha_1$ line (with an estimated observational error of ± 2 percent) one might conclude from the (1, +1) widths of the α_1 lines in Table IV that the present crystals were "perfect" crystals of Class I.[4]

[12] L. G. Parratt, Phys. Rev. **50**, 598 (1936).

V. Effects of Chemical Combination

No direct tests of the effects of chemical combination have been made in this study. In view of previous tests of these effects, one would not expect them to be very large in the present range of elements. But, in view of the present work, Figs. 4 and 5, the sharp and anomalous drop in satellite intensities near Sr(38) warrants further examination. The abruptness of this intensity drop depends on the measurements for Sr(38). (See Figs. 4 and 5.) In the previous measurements,[2] the satellites for Sr(38), with a *strontium-oxide* target, were observed to have considerably less intensity (Fig. 4) than is indicated by the present data with a *metallic* strontium target. Unfortunately, there is a large uncertainty in the previous Sr(38) curves and no definite conclusions can be drawn. However, it appears that here, if anywhere, the effects of chemical combination in x-ray satellite lines may be profitably studied.

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Atomic Wave Functions for Two Stages of Ionization of Silicon*

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Normalized one-electron wave functions and the corresponding fields, accurate to four decimal places, have been calculated by the self-consistent field method for the ions Si^{+2} and Si^{+3}. The values of the energy parameter associated with the various self-consistent field calculations have been compared with experimental values of the energy levels ν/R. The extent to which the core wave functions for silicon are perturbed by the addition of an extra $3s$ electron is noted.

Introduction

THE purpose of this paper is to tabulate atomic wave functions which were obtained by the "self-consistent" field method for the ionized silicon states, Si^{+2} and Si^{+3}. Wave functions for the core, Si^{+4}, have already been computed by McDougall.[1] With results for the core available, it seemed interesting to examine the extent to which the core wave functions for this atom are perturbed by the addition of the outer groups of electrons. Also, silicon is in the middle

* Part of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

† Now at RCA Manufacturing Company, Camden, New Jersey.

[1] J. McDougall, Proc. Roy. Soc. **A138**, 550 (1932).