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$K\alpha$ Satellite Lines

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With a two-crystal vacuum spectrometer, ionization curves of the $K\alpha_{3,4}$ group of x-ray satellite lines have been recorded for elements S(16) to Ge(32). In the $K\alpha_{3,4}$ satellite group are found five component lines for $16 \leq Z \leq 28$ and four components for $29 \leq Z \leq 32$. The wave-length position, relative intensity, and line width at half-maximum intensity of each satellite component has been measured. The widths and shapes of the $K\alpha_{1,2}$ lines were determined and a brief discussion of these data is given.

I. INTRODUCTION

SO-CALLED satellite lines are known to accompany many of the intense diagram lines in x-ray spectra. $K\alpha$ satellites¹⁻⁴ have been observed for elements Na(11) to Rh(45); $K\beta$ satellites¹⁻⁶ for elements Na(11) to Sn(50); satellites of certain L series lines^{1, 7} for elements Ni(28) to U(92); and of M series lines^{1, 8, 9} for elements Sm(62) to U(92). As many as twelve $K\alpha$ and seven $K\beta$ satellites have been reported. Although satellites comprise a large fraction of the total number of characteristic x-ray emission lines we do not yet have a generally acceptable

explanation of the atomic phenomena involved in their production.

The term "nondiagram lines," in common use in referring to satellites, signifies that the atomic (or ionic) energy states involved in the emission of these lines are not included in the ordinary energy diagrams. A complete system of diagrams *must* include the levels involved in the satellite transitions: These transitions are apparently between energy states of multiply rather than singly-ionized atoms. As our understanding of these levels increases, the term "nondiagram lines" should become a misnomer as is the case for the term "forbidden lines" in x-ray spectra. Then, x-ray satellites may be known properly as second and higher order diagram lines. (The term "satellites" is purely descriptive and is non-committal as to the origin of the lines.)

Several significant theoretical advances^{10, 11}

* The author is indebted to the Carnegie Foundation for a grant-in-aid of this research.

¹ M. Siegbahn, *Spektroskopie der Röntgenstrahlen* (Julius Springer, 1931), and references.

² A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Co., Inc., 1935), and references.

³ O. R. Ford, *Phys. Rev.* **41**, 577 (1932).

⁴ M. H. Hulubei, *Comptes rendus* **201**, 544 (1935).

⁵ H. Karlsson and M. Siegbahn, *Zeits. f. Physik* **88**, 76 (1934).

⁶ E. C. Ingelstam, *Zeits. f. Physik* **87**, 283 (1934), and references.

⁷ S. Kaufman, *Phys. Rev.* **45**, 385, 613 (1934).

⁸ E. Lindberg, *Nova Acta Reg. Soc. Sci. Upsaliensis Ser. (IV)* **7**, No. 7, (1931).

⁹ F. R. Hirsh, Jr., *Phys. Rev.* **38**, 914 (1931).

¹⁰ M. J. Druyvesteyn, *Zeits. f. Physik* **43**, 707 (1927); B. B. Ray, *Phil. Mag.* **8**, 772 (1929); R. M. Langer, *Phys. Rev.* **37**, 457 (1931); M. Sawada, *Kyoto Coll. Sci. Mem.* **15**, 43 (1932); H. C. Wolfe, *Phys. Rev.* **43**, 221 (1933) and others. See also R. D. Richtmyer, *Phys. Rev.* **49**, 1 (1936). For the double jump theory see F. K. Richtmyer, J. Frank. Inst. **208**, 325 (1929), and F. Bloch, *Phys. Rev.* **48**, 187 (1935).

¹¹ E. H. Kennard and E. G. Ramberg, *Phys. Rev.* **46**, 1040 (1934).

in the construction of higher order diagrams for x-rays have been made but the compromising assumptions and the difficulty of the calculations have hindered this development. However, the lack of unambiguous experimental descriptions of these lines has been perhaps the most important factor in allowing the enigmatic status of satellites to persist.¹²

Practically all of our information to date about satellites has been obtained from analyses of photographic plates. In supplying such information the photographic method is subject to two serious limitations: (1) The uncertain intensity calibrations, and (2) the low and indefinite effective resolving power. These limitations, especially serious in studying the faint satellite lines which appear on the side of an intense, overexposed diagram line, have restricted quantitative measurements, for the most part, to determinations of wave-length positions. Even in these measurements, because of the low resolving power and the uncertain satellite backgrounds, the accuracy leaves something to be desired.

Recently several important contributions¹³⁻¹⁵ to our empirical knowledge of these lines have been made utilizing the high resolving power of the double spectrometer and the ionization method of recording intensities. In the present paper are reported experiments in which the two-crystal spectrometer was used in determinations of the relative intensities, wave-lengths, and widths and shapes of the various components of the $K\alpha_{3,4}$ group of satellites for elements S(16) to Ge(32). A measurement of the excitation potential of these lines has been reported in a previous paper.¹⁴ Another $K\alpha$ satellite, α'' , not of the $\alpha_{3,4}$ group, has also been studied and the results previously reported.¹⁵

¹² The analogy between optical spectra and x-ray satellite spectra deserves further comment. From the point of view of theory there is a comparable degree of complexity between the two types of spectra. From the point of view of experiment the situations are somewhat different. This difference is due principally to the enormously greater relative widths of the x-ray lines. Because of the great line widths, wave-length positions cannot be determined with a comparable degree of precision and they do not have the practical physical meaning that obtains in the optical region. This circumstance has contributed materially to the relatively retarded progress in explaining x-ray satellites.

¹³ For example, see F. K. Richtmyer and L. S. Taylor, *Phys. Rev.* **36**, 1044 (1930); J. W. M. DuMond and A. Hoyt, *Phys. Rev.* **36**, 799 (1930); and F. Wisshak, *Physik. Zeits.* **35**, 301 (1934).

¹⁴ L. G. Parratt, *Phys. Rev.* **49**, 132 (1936).

¹⁵ L. G. Parratt, *Phys. Rev.* **49**, 502 (1936).

Measurements of the widths and shapes of the $K\alpha_{1,2}$ lines for elements S(16) to Mo(42) and a brief discussion of these measurements in terms of the recent developments in the effects of radiationless transitions are also included in this study.

II. EXPERIMENTAL PART

Spectrometer

The two-crystal vacuum spectrometer and the accessory equipment employed in these experiments have been previously described.^{16,17} The experimental set-up was identical with that discussed in an earlier report¹⁴ except in one regard: In studying radiations of wave-lengths less than 1.5A, methyl-bromide, at a pressure of one atmosphere, was placed in the ionization chamber instead of argon which was used with wave-lengths greater than 1.5A.

The accuracy with which the x-ray intensities, or the ionization currents, were measured has been previously discussed.¹⁴

In regard to the measurements of the line widths and shapes and of the relative intensities it is important that we have as much information as possible about the resolving power of the spectrometer. It is well known that the resolving power of the double spectrometer (with slits properly arranged) is limited by the diffraction patterns of the crystals. The calcite crystals used in the present work were specimens A_4B_4 which have been previously studied^{17,18} and found to be "spectrometrically perfect," that is, with diffraction pattern widths and shapes that yield a maximum effective resolving power.¹⁹

¹⁶ L. G. Parratt, *Phys. Rev.* **41**, 553 (1932) and *Rev. Sci. Inst.* **5**, 395 (1934).

¹⁷ L. G. Parratt, *Rev. Sci. Inst.* **6**, 387 (1935).

¹⁸ L. G. Parratt and F. Miller, Jr., *Phys. Rev.* **49**, 280 (1936).

¹⁹ Greater resolving power than was used in the present experiments is possible, e.g., with the (11·0) planes of quartz crystals or, for wave-lengths less than 3A, with calcite crystals in second order reflection. However, in double-crystal as in single-crystal spectrometry, we are now obliged to accept a compromise between intensity and resolving power. The present calcite crystals, A_4B_4 , in first order reflection, represent a satisfactory compromise in studying the faint satellite lines; higher resolving power would have been advantageous in studying the *complete shapes* of the intense diagram lines. In the latter study, as far as it is pursued in the present paper, it is hoped that our knowledge of the effects of the calcite crystals A_4B_4 is sufficient to permit adequate corrections for the crystals in the measurements of line *widths* at half-maximum intensity.

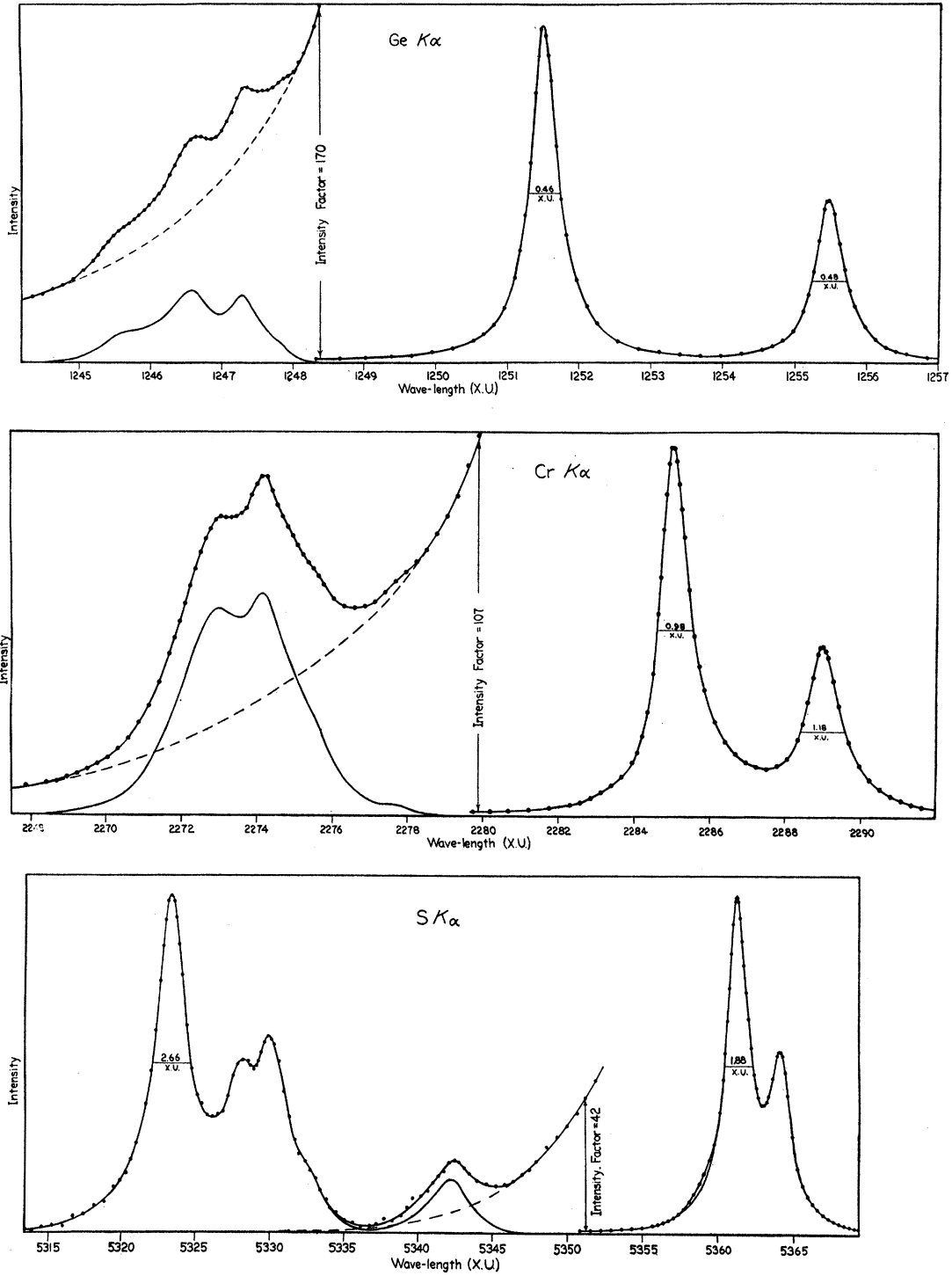


FIG. 1. Ionization curves of the $K\alpha$ region for Ge(32), Cr(24) and S(16). The $\alpha_{3,4}$ group of satellites is plotted in each case to an intensity scale magnified, relative to the scale of the $\alpha_{1,2}$ lines, by the intensity factor indicated. For each element the satellite background (the side of the α_1 line) is sketched in and the reduced satellite contour is drawn.

Targets

The preparation of a satisfactory target of a nonmetallic element is more difficult than of a metallic element. For the recording of an ionization curve of the relatively wide $K\alpha_{1, 2, 3, 4}$ spectral region the emitted x-ray intensity must remain constant within the observational error for a period of several hours. And for recording curves of the weak satellite lines the power which must be dissipated by the target is relatively great: In the present experiments, with the focal spot approximately 2 mm in diameter, this power was of the order of 500 to 1200 watts. In photographic work these target problems are not so pertinent: Constant intensity is usually not necessary and long periods of exposure compensate for low power.

The targets of elements S(16) to V(23) used in the present experiments have been previously described.¹⁵ Cr(24) and Mn(25) were electroplated onto copper. Elements Fe(26) to Ge(32) were used in the chemically pure metallic form and, except Ga(31), were soldered to the target carriage. Ga(31), a metallic liquid, rubbed and pressed with the finger onto a roughened copper surface, made a very satisfactory target: An ionization current of 3×10^{-12} amperes or an equivalent scale deflection, at maximum sensitivity, of more than 10,000 cm was observed for the peak of the Ga $K\alpha_1$ line. Targets of Br(35) and of Sr(38) were prepared by pressing powdered crystals of KBr and SrO into a roughened, pinpricked copper surface. Zr(40) and Mo(42), in metallic form, were spotwelded to nickel.

Ionization curves

Representative of the observed $K\alpha_{3, 4}$ regions, ionization curves for S(16), Cr(24) and Ge(32) are reproduced in Fig. 1. In these curves the $K\alpha_{3, 4}$ group of satellite lines is plotted to an intensity scale 42, 107 and 170, respectively, times the scale used in plotting the $K\alpha_{1, 2}$ lines. The accuracy with which the curves were recorded is indicated by the consistency of the observed points. In these figures the side of the α_1 line has been sketched in and the satellite contours have been reduced to a uniform background by a subtraction of the α_1 ordinates.

Curves similar to those of Fig. 1 are reproduced for Ti(22) in reference 14 and for Ca(20) in reference 15.

Resolution into components

The ionization curve of the $K\alpha_{3, 4}$ group of satellites for each element from S(16) to Ge(32) has been reduced to a uniform background in the arbitrary manner indicated in Fig. 1. Special care was taken in recording the intensities on either side of the satellite group to minimize this background uncertainty, but, since no analytic function could be found to approximate satisfactorily the shape²⁰ of this region of the α_1 line for a series of elements, the consequent arbitrariness introduces an uncertainty in the reduced satellite contours which, for elements of atomic numbers above K(19), is greater than the random observational errors in the intensity readings.

The reduced satellite contour for each element is presented in Fig. 2. Each contour is plotted to arbitrary abscissae and ordinate scales. The two principal "humps" are the $\alpha_{3, 4}$ lines, α_4 being on the left, the short wave-length side, of α_3 . An inspection of the suggestive irregularities in the contours indicates five components for S(16). These components are, from right to left, with decreasing wave-length, α' , α_3'' (a new component), α_3 , α_3' and α_4 . Each of the relatively intense $\alpha_{3, 4}$ lines can be traced easily throughout the present range of elements. The α' line is likewise probably present for all the elements—"probably" because for many elements the contour irregularity indicating this component is close to, and in some cases within, the observational error. The intensity of the line α_3'' apparently decreases to zero near Ni(28). The external evidence for the reality of this line, α_3'' , for elements Cr(24) to Ni(28) is meager.

The component α_3' appears conspicuously between α_3 and α_4 for S(16) and moves progressively as the atomic number increases. This progressive movement is inferred from the absence of the

²⁰ As mentioned later, the classical dispersion (Hoyt) shape, $I = p/1 + (\Delta\lambda/w)^2$, matches fairly well the symmetrical part of the observed α_1 line when the constant w , half-width at half-maximum intensity, is adjusted. This fit, however, is not good enough (even when the constant p , as well as constant w , is adjusted to match more nearly the limited α_1 region adjacent to the satellites) to be of service in determining the satellite background.

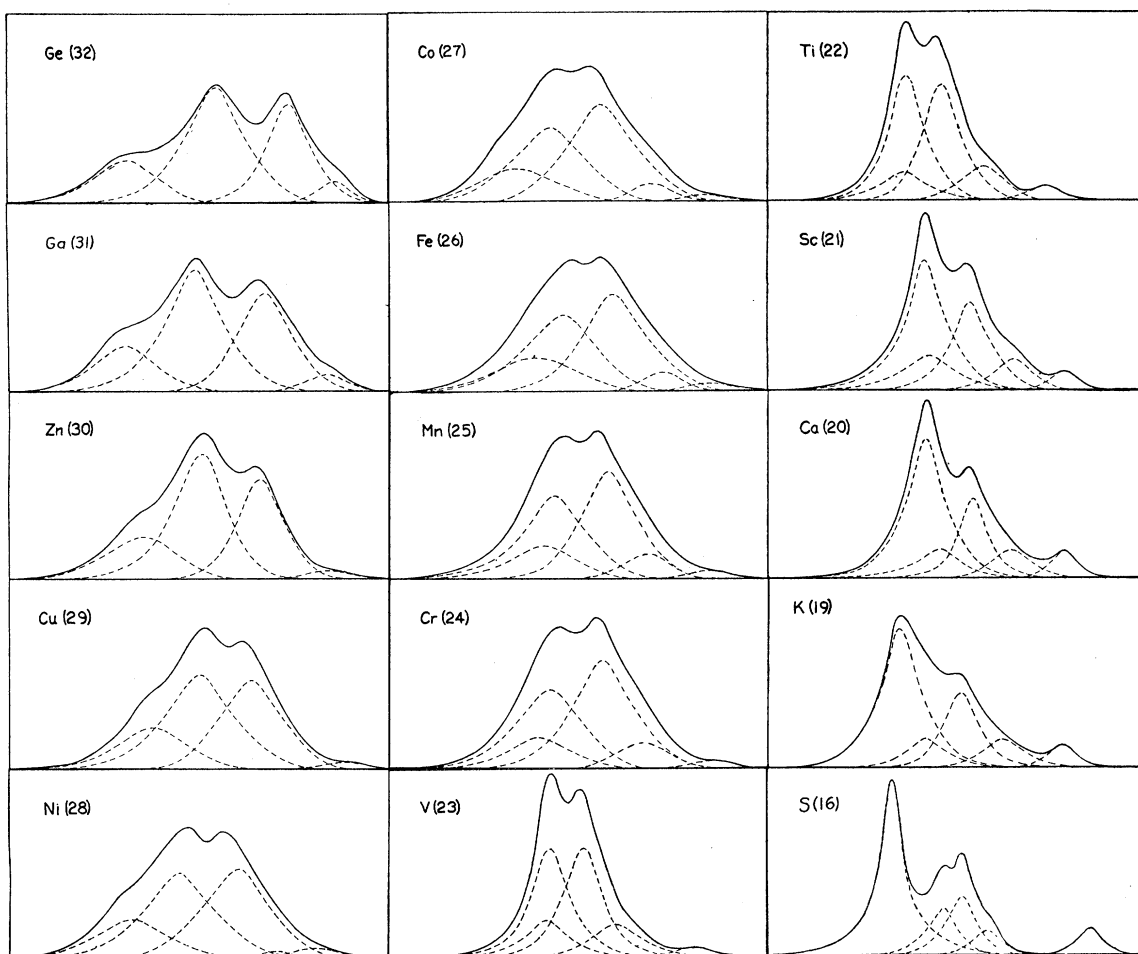


FIG. 2. Contours of the $K\alpha_{3,4}$ satellite group, reduced to a uniform background, for elements S(16) to Ge(32). Arbitrary abscissae and ordinate scales are used for each element. The reduced contours are resolved into the structural component lines as discussed in the text.

minimum between α_3 and α_4 for K(19), the slight trace of a component on the α_4 side of the minimum for Ca(20), the relatively sharp and narrow contours for Ti(22) and V(23), and the gradual appearance of a component on the short wave-length side of α_4 as the atomic number increases above V(23). For Ti(22) the α_3' and α_4 lines are approximately coincident in wave-length; for atomic numbers greater than 22, α_3' is on the short wave-length side of α_4 .

From such an inspection of the ensemble the number of constituent components for each element was decided upon and the contours resolved as illustrated in Fig. 2. In this resolution the following criteria were used: The number of components was fixed, the component shapes

were assumed to be roughly symmetrical, and the sum of the component intensities at any wave-length must add up to the intensity of the contour. For the region of elements Ca(20) to Cr(24), in which no specific irregularity in the contours was observed for the α_3' component, the intensity of α_3' , relative to the intensity of the entire $\alpha_{3,4}$ group, was assumed to be about the same as for the adjacent elements. No other assumption as to relative intensities was made. A qualitative check on the resolution is afforded by the resultant consistency from element to element in the shapes of each component: No shape comes out to be what may be called "unreasonable."

The α'' component

For elements S(16) to V(23) inclusive another satellite component, the $K\alpha''$ line, not one of the $\alpha_{3,4}$ group, was observed close to and on the short wave-length side of the $K\alpha_1$ line. This component was first reported in 1922 by Dolejšek but, as far as the writer is aware, was not again detected until the present measurements were made. For S(16) the α'' line is indicated in Fig. 1. An earlier report¹⁵ discusses this satellite line in more detail.

III. MEASUREMENTS

Relative intensities

The relative intensity of two x-ray lines is defined as the ratio of areas under the line contours (the contours being plots of intensity *vs.* frequency) when the spectral analysis is complete, that is, when the contours are observed with an instrument of infinite resolving power. Although the two-crystal spectrometer has the greatest effective resolving power of all present x-ray instruments the $d\lambda$ interval cannot be neglected in case the two lines whose relative intensities are to be measured are of different widths and shapes. With calcite crystals A_4B_4 mounted on the instrument the $d\lambda$ interval²¹ in first order reflection is about one-fourth the width of each of the $K\alpha_{1,2}$ lines at half-maximum intensity and is about one-twentieth the width of the $K\alpha_{3,4}$ group.

The perturbations due to the finite resolving power are present in the observed contours, and the appropriate corrections should be applied to the observed curves rather than to the resolved components. The observed curves for the present range of elements vary considerably in shape and, strictly speaking, different corrections should be applied to each contour. The corrections to be made in the wide satellite contours are within the experimental errors; the corrections for the $K\alpha_{1,2}$ lines are greater than the errors. For Ti(22) the correction to the ratio of the intensity of the entire $K\alpha_{3,4}$ group relative

to the intensity of the $K\alpha_1$ line has been determined¹⁴ as a factor of 1.05. This factor has been applied to the observed intensities relative to the $K\alpha_1$ intensities in the present work for each satellite component as well as for the $\alpha_{3,4}$ group for all the elements studied. The uncertainty of this correction is within the observational errors. In fact, for elements of atomic numbers greater than 29 the $\alpha_{3,4}$ group intensity relative to the α_1 intensity is uncertain by some 8 percent because of the indefiniteness of the satellite background.

It has been shown previously^{14, 15, 22} that the intensity of $K\alpha$ satellite lines relative to the intensity of the $K\alpha_1$ line is constant for a given element when the x-ray tube voltage is greater than about twice the excitation potential. In the present work the voltage was maintained at two to five times the satellite excitation potential.

In Table I are listed the measured relative intensities, corrected for the resolving power of the crystals. In Fig. 3 the intensity of the $\alpha_{3,4}$ group relative to the intensity of the α_1 line is plotted for the range of elements Na(11) to Sr(38). A logarithmic ordinate scale in Fig. 3 provides a conveniently open scale for the low values.

TABLE I. *Intensities of $K\alpha$ satellite lines.* For each element the intensity of the $K\alpha_1$ line is taken as 100. Except in the cases of Na(11) and Si(14), recorded photographically, the correction for the finite resolving power has been applied to the $\alpha_{3,4}/\alpha_1$ ratio; the intensities of the component lines have been determined relative to the corrected intensity of the $\alpha_{3,4}$ group.

TARGET	ELEMENT	α_1	$\alpha_{3,4}$ GROUP (Cor- rected)	α'	α_3''	α_3	α_4	α_3'	α''
SrO	Sr(38)	100	0.08						
metal	Ge(32)	100	0.40	0.003		0.11	0.19	0.09	
liquid	Ga(31)	100	0.48	0.004		0.14	0.23	0.10	
metal	Zn(30)	100	0.50	0.005		0.16	0.23	0.10	
metal	Cu(29)	100	0.60	0.008		0.22	0.27	0.10	
metal	Ni(28)	100	0.65	0.01	0.01	0.25	0.27	0.11	
metal	Co(27)	100	0.77	0.014	0.03	0.32	0.28	0.12	
metal	Fe(26)	100	0.91	0.02	0.05	0.37	0.33	0.14	
electro- plated	Mn(25)	100	1.10	0.02	0.08	0.45	0.39	0.16	
electro- plated	Cr(24)	100	1.37	0.03	0.13	0.56	0.48	0.17	
metal	V(23)	100	1.80	0.04	0.20	0.68	0.66	0.22	0.30
metal	Ti(22)	100	2.20	0.07	0.23	0.80	0.84	0.24	0.90
Sc ₂ O ₃	Sc(21)	100	2.78	0.11	0.24	0.78	1.25	0.41	1.40
CaO	Ca(20)	100	3.36	0.17	0.27	0.77	1.78	0.37	2.25
K ₃ PO ₄	K(19)	100	3.90	0.23	0.31	0.84	2.07	0.45	2.10
CaCl ₂	Cl(17)	100							1.40
FeS	S(16)	100	7.25	0.58	0.51	1.30	3.84	1.02	1.00
metal	Si(14)	100	17.						
NaCl	Na(11)	100	33.						

²¹ The width of the $d\lambda$ interval is given roughly by the width of the curve observed with the crystals in positions of zero dispersion, the parallel positions. The reader is referred to previous papers, references 14 and 17, for discussions of the crystal-perturbations which distort the true x-ray line contours into the observed curves.

²² 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).

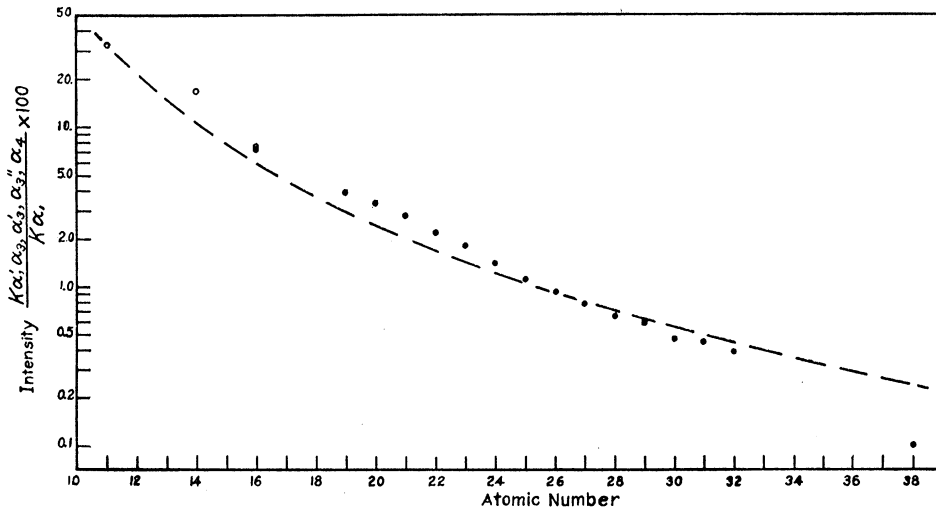


FIG. 3. Intensity of the $K\alpha_{3,4}$ group of satellites relative to the intensity of the $K\alpha_1$ line for elements Na(11) to Sr(38). The dashed curve represents Richtmyer's theoretical predictions. The open circles for Na(11), Si(14) and S(16) are values obtained photographically.

The photographic method, with a single gypsum crystal mounted on a Siegbahn type vacuum spectrograph, was used in measuring the satellite intensities for elements of atomic numbers lower than S(16), wave-lengths beyond the reach of the calcite crystals of the ionization double spectrometer. The experimental errors in the photographic data are much greater than in the ionization data although the average of several carefully exposed plates²³ for S(16) gave a relative intensity measurement in excellent agreement with that obtained with the double spectrometer. These measurements for the low atomic numbers were made so as to check the possible relative intensity maximum reported by Mrs. Pearsall.²⁴ No evidence for such a maximum was found.

Accurate satellite data for elements above Ge(32) were not obtained in the present study, but a preliminary measurement of the ratio of the intensity of the $K\alpha_{3,4}$ group to the intensity of $K\alpha_1$ for Sr(38) gave a value of less than 0.10 percent. More work on the satellites for elements $Z > 32$ is now in progress.

In Fig. 4 is plotted, for the elements S(16) to Ge(32), the intensity of each component relative to the intensity of the entire $\alpha_{3,4}$ group. For the intensity plot of α'' see reference 15.

²³ The author is indebted to Dr. F. R. Hirsh for his generous assistance with the photographic plates.

²⁴ A. W. Pearsall, Phys. Rev. **48**, 133 (1935).

R. D. Richtmyer¹⁰ has recently calculated the intensity of the $\alpha_{3,4}$ group as a whole relative to the intensity of the α_1 line, basing his calculations on the Wentzel-Druyvesteyn theory of satellite origin. Richtmyer's theoretical intensities are indicated by the dashed line in Fig. 3. The agreement between theory and experiment is remarkably good.²⁵

Kennard and Ramberg¹¹ have calculated, on the basis of an extension of the Wentzel-Druyvesteyn theory, the relative intensities of α' , α_3 and α_4 as being approximately²⁶ 1, 9 and 5,

²⁵ The relative intensity given by Richtmyer is, as a function of atomic number Z ,

$$I_s/I_{\alpha_1} = C(Z - \sigma)^{-3}$$

where σ , an internal screening constant, is taken for all elements as 4.5 and $C=91$ as determined from the computation for K(19).

²⁶ Kennard and Ramberg suggest the following coordinations:

$$\begin{array}{l} K\alpha' \dots\dots\dots \left\{ \begin{array}{l} 1s2p^5 \ ^1P \rightarrow 2p^4 \ ^1S \\ 1s2s \ ^1S \rightarrow 2s2p^5 \ ^1P \end{array} \right. \\ K\alpha_3 \dots\dots\dots 1s2p^5 \ ^3P \rightarrow 2p^4 \ ^3P \\ K\alpha_3' \dots\dots\dots 1s2s \ ^3S \rightarrow 2s2p^5 \ ^3P \\ K\alpha_4 \dots\dots\dots 1s2p^5 \ ^1P \rightarrow 2p^4 \ ^1D \end{array}$$

There is some difficulty in interpreting the relative intensity predictions from these coordinations. Two different types of transitions, $1s2p \rightarrow 2p^4$ and $1s2s \rightarrow 2s2p^5$, are considered by Kennard and Ramberg and the probability of one type of transition is *not* related in their work to the probability of the other type. Coordinated with the experimental α' line are transitions of both types, with $\alpha_{3,4}$ just one type, and with α_3' the other type alone. If we may relate the two transition probabilities by comparing the observed intensity of α_3' with the intensity of α_3 or of α_4 we obtain a probability of about 2 to 1 for the types of transitions $1s2p \rightarrow 2p^4$ and $1s2s \rightarrow 2s2p^5$, respectively. This

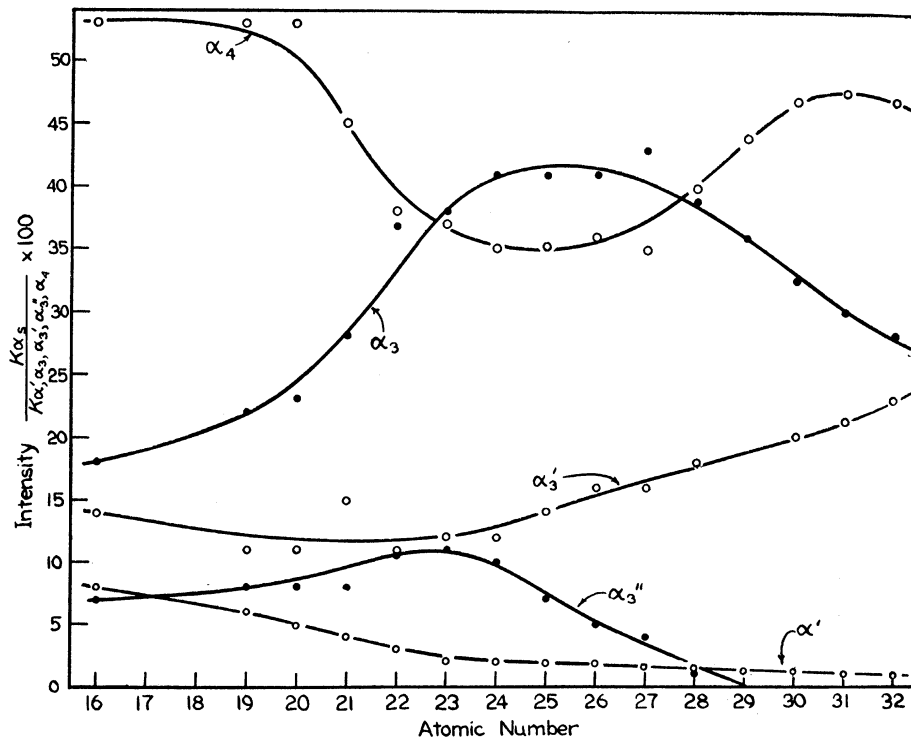


FIG. 4. Intensity of each component of the $K\alpha_{3,4}$ group of satellites relative to the intensity of the $K\alpha_{3,4}$ group as a whole for elements S(16) to Ge(32).

respectively, for Na(11) to 1, 3.75 and 5, respectively, for higher atomic numbers. The reversal in the relative intensities of α_3 to α_4 between P(15) and S(16) reported by Ford³ may possibly be explained as suggested by Kennard and Ramberg¹¹ by the method of coordinating unresolved components with the α_3 line.²⁷ However, in view of the structures of the ensemble of Fig. 2, the two relative intensity reversals of α_3 and α_4 illustrated in Fig. 4 cannot be explained in this manner.

Hulubei⁴ has recently detected and measured the wave-lengths of $K\alpha$ satellites for elements Cu(29) to Rh(45). For Rh(45) just the α_3' line was reported²⁸ indicating that, as the atomic

rough relation of 2 to 1 is in fair agreement with the ratio, 2.5 to 1, given (estimated) by Richtmyer, reference 10. However, the observed variations in the intensity ratios α_3' to α_3 and α_3' to α_4 , Fig. 4, reduces this probability relation to a questionable status.

²⁷ In this intensity reversal observed by Ford, the α_3' and α_3 lines are experimentally coordinated unresolved components whose combined intensities are considered as the intensity of α_3 . See footnote 12 of reference 15.

²⁸ The writer has previously called attention, reference

number increases, the α_3' component becomes the most intense of the group. Conforming with this indication, an extrapolation of the curves of Fig. 4 gives at least two additional intensity reversals for higher atomic numbers.

Wave-lengths

The wave-length positions of the peaks of the resolved satellite components are listed in Table II. The writer's spectrometer does not have a precision circle so only relative wave-lengths can be determined; in the present work the peak of the $K\alpha_1$ line is taken as the reference wave-length. The estimated uncertainty of the satellite wave-lengths in Table II is of the order of 10^{-3} percent.

The excellent agreement between the present $\alpha_1 \rightarrow \alpha_2$ separations and those of Bearden and Shaw²⁹ checks the calibration of the spectrometer. Bearden and Shaw's measurements do

15, to the migratory nature of the α_3' component and that Hulubei's notation for α_3' and α_4 should be interchanged.

²⁹ J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).

TABLE II. *Wave-lengths in X, U, of K α satellite lines.* These measurements for each element are referred to the wave-length of the K α_1 line.* The type of target used for each element is given in Table I.

ELEMENT	α_2	α_1	α''	α'	α_3''	α_3	α_4	α_3'
Ge(32)	1255.43	1251.48		1247.82		1247.31	1246.55	1245.60
Ga(31)	1341.24	1337.33		1333.40		1332.66	1331.83	1331.00
Zn(30)	1436.05	1432.22		1427.98		1426.98	1426.13	1425.28
Cu(29)	1541.22	1537.40		1533.01		1531.57	1530.70	1529.87
Ni(28)	1658.34	1654.51		1649.49	1648.80	1648.04	1647.04	1646.42
Co(27)	1789.17	1785.31		1780.10	1779.05	1778.10	1777.02	1776.40
Fe(26)	1936.00	1932.06		1926.05	1924.92	1923.94	1922.76	1922.16
Mn(25)	2101.44	2097.51		2090.92	2089.33	2088.32	2086.92	2086.55
Cr(24)	2288.89	2285.00		2277.70	2275.64	2274.43	2272.90	2272.58
V(23)	2502.24	2498.42	2496.5	2490.85	2487.74	2486.09	2484.45	2484.19
Ti(22)	2746.52	2742.87	2740.9	2734.40	2731.20	2726.91	2724.90	2724.90
Sc(21)	3028.35	3025.03	3022.8	3014.87	3011.65	3009.10	3006.31	3006.61
Ca(20)	3354.93	3351.69	3349.1	3340.10	3336.30	3333.44	3330.10	3330.97
K(19)	3736.82	3733.68	3730.9	3720.60	3716.20	3713.14	3709.01	3710.51
Cl(17)	4721.17	4718.2	4714.8					
S(16)	5364.12	5361.28	5359.4	5342.50	5333.10	5330.00	5323.45	5328.10

* The wave-lengths of the K α_1 line for elements Ge(32) to Ti(22) are taken from Bearden and Shaw, Phys. Rev. **48**, 18 (1935); for elements Sc(21) to Cl(17) from Siegbahn, *Spektroskopie der Röntgenstrahlen*, 1931; and for S(16) from Valasek, Phys. Rev. **43**, 612 (1933).

not include elements of atomic numbers less than Ti(22) and the present $\alpha_1 \rightarrow \alpha_2$ separations for $15 < Z < 22$ are probably more reliable than the values given in Siegbahn's book.¹

No simple relation is observed between the atomic number and the satellite separations from the K $\alpha_{1,2}$ lines. The evidence which has been presented in the literature in favor of the α_1 or of the α_2 line as being the "parent" line of a given satellite is to be understood in terms of empirical convenience only in classifying satellites. The present results do not yield the convenient linear relation.³⁰ The $\alpha_1 \rightarrow \alpha_2$ is a spin-doublet separation; the satellite \rightarrow "parent" line interval is a complex screening separation which also includes part of the $\alpha_1 \rightarrow \alpha_2$ separation. Without further evidence the center of intensity of the doublet seems as reasonable a reference wave-length as any other. In Fig. 5 are plotted the $\Delta\nu/R$ values for the satellite separations from this center of intensity reference; the values are listed in Table III.

It is interesting to compare the observed multiplet structure of the contours of Fig. 2 with the calculated structures of Fig. 1 of Kennard and Ramberg's paper.¹¹ The progressive shift of the α_3' component relative to the α_4 line is apparently qualitatively accounted for.

³⁰ The semi-Moseley graph $(\Delta\nu/R)^{1/2}$ vs. Z is closer to linearity when $\Delta\nu$ is referred to α_2 than when referred to α_1 . Two factors are present: (1) The $\Delta\nu$ intervals are greater when referred to the α_2 lines and the relative deviations from linearity are less, and (2) a peculiar variation in the $\alpha_1 \rightarrow \alpha_2$ separation is present in the atomic number range Sc(21) to Cu(29), see Fig. 203 of Siegbahn, reference 1.

Widths and shapes of satellites

As mentioned above,¹² the fact that x-ray lines are so broad detracts from the definiteness of the wave-length positions, especially in cases of overlapping lines, and reduces the effectiveness of wave-lengths as a tool for comparing theory with experiment. However, compensation lies in the fact that the lines are so broad that their widths (and shapes if they do not seriously overlap with one another) can be measured with a fair degree of precision, and the property of widths (and shapes) may be of help in ascertaining the atomic processes involved in their production. In view of the recent rapid progress³¹ in accounting for the widths of diagram lines by considering the Auger or radiationless transitions,

TABLE III. *Separation in $\Delta\nu/R$ units of the K α 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_2	α_1	α''	α'	α_3''	α_3	α_4	α_3'
Ge(32)	1.532	0.76		2.90		3.21	3.65	4.19
Ga(31)	1.330	0.66		2.68		3.06	3.48	3.91
Zn(30)	1.135	0.57		2.46		2.90	3.28	3.66
Cu(29)	0.983	0.49		2.19		2.74	3.08	3.40
Ni(28)	0.853	0.43		2.10	2.33	2.59	2.92	3.13
Co(27)	0.732	0.37		1.87	2.17	2.44	2.75	2.92
Fe(26)	0.640	0.32		1.79	2.07	2.31	2.60	2.74
Mn(25)	0.542	0.27		1.64	1.97	2.18	2.47	2.55
Cr(24)	0.450	0.23		1.51	1.87	2.08	2.35	2.41
V(23)	0.373	0.19	0.47	1.30	1.75	1.99	2.23	2.27
Ti(22)	0.294	0.15	0.39	1.19	1.57	1.85	2.10	2.10
Sc(21)	0.222	0.111	0.33	1.13	1.46	1.71	1.99	1.98
Ca(20)	0.172	0.088	0.30	1.04	1.35	1.58	1.85	1.76
K(19)	0.138	0.069	0.25	0.93	1.22	1.42	1.69	1.59
Cl(17)	0.0813	0.041	0.18					
S(16)	0.0604	0.030	0.09	0.63	0.93	1.03	1.24	1.09

³¹ See J. A. Prins, Physica **2**, 231 (1935), and references.

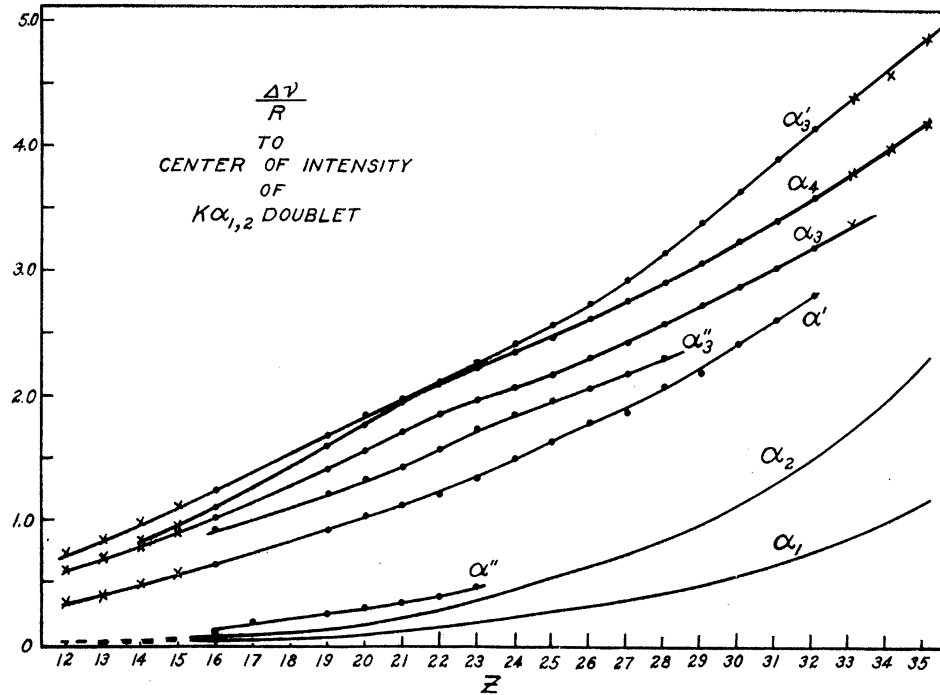


FIG. 5. Wave-length separations, $\Delta\nu/R$ units, of the satellite components from the center of intensity of the $K\alpha_{1,2}$ line doublet lines. The solid circles represent the present measurements, the crosses are values taken from Ford, reference 3, for the low atomic numbers, and from Hulubei, reference 4, for the high atomic numbers.

an experimental knowledge of the widths of satellite lines is very desirable.

The widths at half-maximum intensity of the component satellite lines, resolved in the manner discussed above, are listed in Table IV and shown graphically in Fig. 6. These widths can

TABLE IV. Full widths, in X.U., at half-maximum intensity of $K\alpha$ satellite lines. These widths refer to the resolved component lines of the reduced contours of the observed ionization curves. 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''	α'	α_3''	α_3	α_4	α_3'
Ge(32)		0.48		0.65	0.73	0.79
Ga(31)		0.58		0.74	0.81	0.88
Zn(30)		0.62		0.84	0.96	1.07
Cu(29)		0.76		1.08	1.21	1.25
Ni(28)		0.87	0.97	1.26	1.39	1.43
Co(27)		0.90	1.18	1.35	1.63	1.69
Fe(26)		1.06	1.30	1.58	1.77	1.90
Mn(25)		1.24	1.58	1.71	1.89	1.95
Cr(24)		1.40	1.81	1.92	2.04	2.10
V(23)		1.63	2.16	2.16	2.21	2.30
Ti(22)		1.10	1.89	2.45	2.36	2.50
Sc(21)		1.16	1.98	2.68	2.60	2.74
Ca(20)		1.30	2.25	2.81	2.76	2.95
K(19)		1.38	2.41	3.01	2.92	3.09
Cl(17)		1.98				
S(16)	1.88	2.65	3.05	2.85	2.62	3.30

have no more quantitative value than the reader is willing to grant for the particular resolution in which the writer has indulged in Fig. 2. In some instances, as in the case of $SK\alpha_4$, the accuracy may be as high as 6 percent; in other instances, as in the cases of the weak α' and α_3'' components for $Z > 22$, the uncertainty may be 50 percent. Another attempt in resolving the contours into components could give greater widths of the α' and α_3'' lines for $Z > 22$ but the uncertainty is so large that such an attempt is not worth while. The consistent trends in the relative intensities, Fig. 4, and in the widths, Fig. 6. speak well of the somewhat blind resolution and, perhaps, add meaning to the measured values.

It may be significant that the variation in the widths of the satellite α_3 , α_4 and α_3' follow more closely the variation in the widths of the α_2 line than of the α_1 line.

Very little can be said of the possible asymmetries of these satellite lines. One of the criteria used in the resolution is that the components be

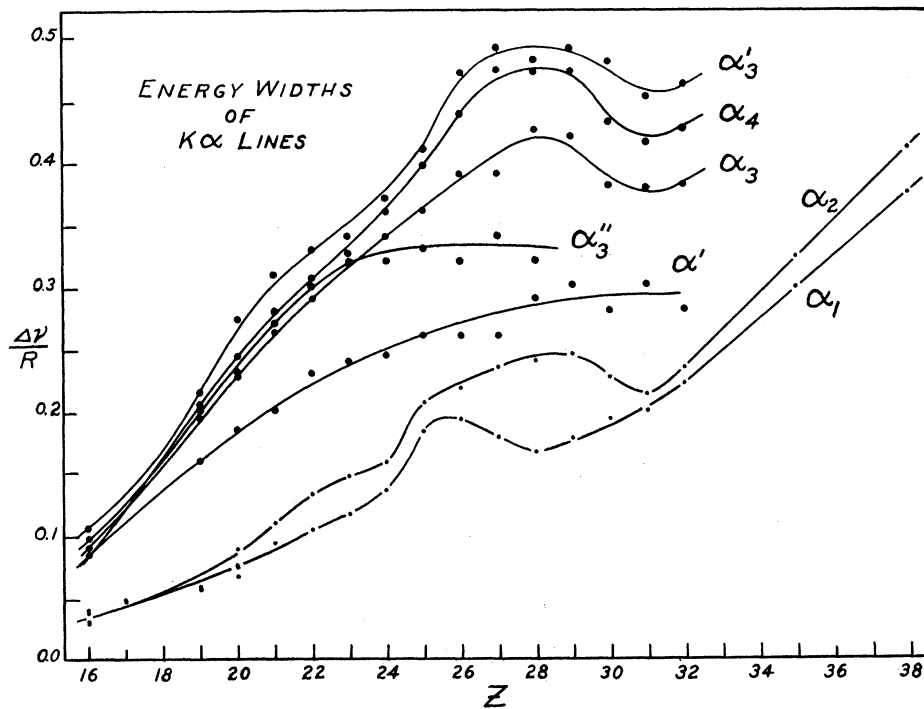


FIG. 6. Full widths, $\Delta\nu/R$ units, at half-maximum intensity of the $K\alpha$ lines. The widths of the α_1 and α_2 component lines are corrected for the crystals as discussed in the text. Effects of chemical binding in the $\alpha_{1,2}$ widths are indicated for Ca(20) and S(16). It is to be noted that the values of the satellite widths are very sensitive to the particular resolution affected; the values given in this figure are characteristic of the resolution illustrated in Fig. 2.

roughly symmetrical and, in every case, the components are so drawn. The greatest accuracy is present for S $K\alpha_4$ and the index of asymmetry at half-maximum intensity for this line is 1 ± 0.10 .

IV. THE $K\alpha_{1,2}$ LINES

Ionization curves of the $K\alpha_{1,2}$ lines were of course recorded for each element in the present study. The observed contours for these overlapping doublet lines have been resolved into the α_1 and α_2 components. The arbitrariness of this resolution is zero at the high atomic numbers and increases as the atomic number decreases (see Fig. 1). The widths and asymmetries of the resolved doublet lines are given in Table V.

The author has previously reported³² on the $K\alpha_{1,2}$ line widths for elements Ca(20) to Ni(28). The crystals employed in these early measurements were unfortunately poor specimens as judged from our present standards,¹⁷ and, conse-

quently, the previously reported widths are excessively large and now serve merely as con-

TABLE V. Full widths, indices of asymmetry and overlapping factors of the $K\alpha_{1,2}$ doublet lines. The type of target used for each element is given in Table I or discussed in the text. Obs. = observed contour of the overlapping doublet lines. Cor. = corrected for overlapping of the two lines. True = corrected for overlapping and also corrected for the finite resolving power of the spectrometer.

ELEMENT	WIDTHS (X.U.)				ASYMMETRY INDEX				OVER-LAPPING FACTOR
	Obs.	α_1 True	Obs.	α_2 True	Obs.	α_1 Cor.	Obs.	α_2 Cor.	
Mo(42)	0.306	0.268	0.317	0.280	1.00	1.00	1.03	1.03	0.00
Zr(40)	0.340	0.300	0.360	0.320	1.02	1.02	1.04	1.04	0.010
Sr(38)	0.360	0.313	0.390	0.343	1.03	1.03	1.04	1.04	0.014
Br(35)	0.410	0.353	0.440	0.382	1.03	1.03	1.06	1.06	0.020
Ge(32)	0.457	0.379	0.482	0.404	1.04	1.04	1.11	1.11	0.030
Ga(31)	0.475	0.389	0.501	0.415	1.04	1.04	1.19	1.19	0.036
Zn(30)	0.530	0.434	0.606	0.510	1.11	1.11	1.33	1.33	0.037
Cu(29)	0.565	0.460	0.740	0.635	1.15	1.15	1.28	1.28	0.057
Ni(28)	0.622	0.504	0.85	0.72	1.22	1.22	1.23	1.25	0.093
Co(27)	0.760	0.63	0.97	0.82	1.44	1.44	1.27	1.30	0.116
Fe(26)	0.946	0.79	1.10	0.90	1.61	1.60	1.30	1.35	0.174
Mn(25)	1.06	0.89	1.24	1.00	1.45	1.43	1.19	1.27	0.23
Cr(24)	0.98	0.78	1.20	0.91	1.35	1.33	1.04	1.14	0.25
V(23)	1.02	0.81	1.34	1.02	1.26	1.23	0.96	1.09	0.29
Ti(22)	1.10	0.87	1.45	1.10	1.22	1.17	0.88	1.04	0.32
Sc(21)	1.16	0.95	1.46	1.12	1.01	0.97	0.89	1.01	0.31
Ca(20)	1.24	0.92	1.29	0.83	0.85	0.81	0.79	0.92	0.35
K(19)	1.38	0.90	1.62	0.88	0.99	0.96	0.78	1.05	0.45
Cl(17)	1.98	1.19		1.16	1.00	0.92		0.94	0.75
S(16)	1.88	0.99		0.94	1.15	1.00		1.00	0.77

³² L. G. Parratt, Phys. Rev. **44**, 695 (1933).

vincing evidence of the importance of a knowledge of crystalline diffraction patterns and of their behavior in the antiparallel positions of the double spectrometer.

Bearden and Shaw²⁹ have recently made exacting measurements of the widths and shapes of the $K\alpha_{1,2}$ lines for elements Ti(22) to Ge(32). For these elements the present work adds nothing to the conclusions of Bearden and Shaw except that in comparing the measurements one finds differences which are slightly greater than the sum of the estimated errors. These differences are greatest in the case of Cr(24) where the present widths are about 4 percent less than those of Bearden and Shaw and in the case of Ti(22) where the present widths are about 4 percent greater. It is not likely that these differences can be explained in terms of different diffraction pattern shapes of the crystals employed. No explanation is offered except the suggestion of the possibility of the effects of an oxide film on the surfaces of the targets.

To obtain the true line widths from the observed widths one must apply a correction for the finite resolving power of the crystals. An empirical correction for crystals has recently been proposed:¹⁷

$$W_T = W_0 - 2.9W_C^{1.7} \quad (1)$$

where W_T is the true width in X.U., W_0 the width in X.U. of the curve observed in the ($n, +n$) position of calcite crystals of Class I type of perfection whose ($n, -n$) width is W_C X.U. The W_C values of the present crystals A_4B_4 are obtained by interpolating the data given in reference 18.

Eq. (1) has been applied to all the component $K\alpha_{1,2}$ lines of the present study and the true widths so obtained are included in Table V and in Fig. 6. Eq. (1) probably overcorrects the α_2 component widths for elements of low atomic numbers because of the difference in shape of the resolved component and the observed contour. In fact, Eq. (1) was derived explicitly for contours of the shape of the $K\alpha_{1,2}$ lines of Ti, Cu and Mo, and the application of the formula to contours of the shape of $S K\alpha_{1,2}$, for example, is not entirely justified. For this reason, together with the uncertainties in the reduced contours and in the resolution, the formula has not been

applied to the satellite widths, although the true width of the $S K\alpha_1$ line is probably close to the value which would be obtained from Eq. (1).

The overlapping factors of the observed doublet contours and the indices of asymmetry of the observed curves and of the resolved components are also listed in Table V.

It is to be noticed that for elements $Z < 21$ the true width of the α_2 lines are less than of the α_1 lines; also, in most cases, the indices of asymmetry are *less* than unity. The α_2 line has also been found³³ narrower than the α_1 line by Allison and by Wilhelmy for several elements in the atomic number range 36 to 45.

The effect of the $K\alpha''$ component on the observed asymmetries of the $K\alpha_1$ lines was suggested in the previous report.¹⁵ At first glance one may suspect a multiplet structure in α'' sufficient to influence materially and be an uncorrected factor in the observed α_1 asymmetries. The α_1 asymmetry is a maximum at Fe(26) whereas the α'' , with atomic numbers increasing above Ca(20), is losing in relative intensity and also is becoming farther removed from the α_1 peak. However, for the lower atomic numbers, S(16) and Cl(17), part of the shape of α_1 may, it must be recognized, be due to a possible multiplet structure of α'' . That α'' is really a satellite line and not an unresolved component in the α_1 line is shown by the α''/α_1 intensity *vs.* voltage relation of Fig. 5 of reference 15.

The rather close correlation in the variations in line widths and in the indices of asymmetry, Table V, indicates that the two properties, widths and asymmetries, for the elements of the present atomic number range, may be considered together. The factors responsible for the width of an x-ray line may be listed as (1) radiation damping, of the order of 0.12 X.U. but varying with line and element,³¹ (2) radiationless transitions or Auger effects, (3) linkage with neighboring atoms, i.e., the chemical and/or the alloy effect, (4) the presence of unresolved component lines, and (5) the external screening effects due to the various degrees of ionization (outer electrons) of the radiating atoms. Some of these factors may well be associated together but convenience indicates a need for the separate categories. In

³³ S. K. Allison, Phys. Rev. **44**, 63 (1933); E. Wilhelmy Zeits. f. Physik **97**, 312 (1935).

TABLE VI. Effects of chemical binding on contour shapes of $K\alpha_{1,2}$ doublet lines for Ca(20), Cl(17) and S(16).*

TARGET	ELEMENT	WIDTHS (X.U.)				ASYMMETRY INDEX				OVERLAPPING FACTOR
		α_1		α_2		α_1		α_2		
		Obs.	True	Obs.	True	Obs.	Cor.	Obs.	Cor.	
metal	Ca(20)	1.40	1.07	1.44	0.92	1.00	0.97	0.82	0.95	0.41
	CaO	1.24	0.92	1.29	0.83	0.85	0.81	0.79	0.92	0.35
	CaCl ₂	1.44	1.11	1.48	0.95	0.94	0.91	0.80	0.93	0.42
	CaCl ₂	Cl(17)	1.98	1.19		1.16	1.00	0.92	0.94	0.75
	CuCl ₂	Cl(17)	1.90	1.14		1.11	1.00	0.92	0.94	0.75
	KCl	Cl(17)	1.95	1.18		1.16	1.00	0.92	0.94	0.75
	SrCl ₂	Cl(17)	1.98	1.19		1.16	1.00	0.92	0.94	0.75
	FeS	S(16)	1.88	0.99		0.94	1.15	1.00	1.00	0.77
	BaSO ₄	S(16)	2.24	1.21		1.30	1.40	1.00	0.97	0.92

* The "true" widths of S $K\alpha_1$ are listed incorrectly in Phys. Rev. 49, 14 (1936).

magnitude, in the case of $K\alpha$ lines for elements of atomic numbers less than 36, the Auger effect dominates,³⁴ and the radiation damping is theoretically of next importance. Of these several factors the first and second contribute to the line width symmetrically on either side of the maximum ordinate—the line shape due to these factors is the classical dispersion (or Hoyt) shape. The third factor is forced upon us experimentally and the asymmetry of the broadened or narrowed line, so far as the available data³⁵ indicate (Table VI), is usually not greatly altered. The data are insufficient to warrant generalizations as to the symmetry or asymmetry of the width contribution of factor three; however, irrespective of the shape of the contribution from each atom, one might expect some displacement of the maximum ordinate from some fraction of the emitting atoms relative to the maximum ordinate from other emitting atoms due to different types of atomic neighborhoods in the crystal lattice.³⁶ This sort of difference might produce in the observed line width an effective contribution of almost any shape and yet be, perhaps, of the classical dispersion shape so far as the individual atoms are concerned. In accounting for the observed asymmetries we have left, then, factor three and factors four and five. The width contributions of the last two

³⁴ G. Wentzel, Zeits. f. Physik 43, 524 (1927).

³⁵ For data in addition to those of Table VI see L. G. Parratt, Phys. Rev. 45, 364 (1934), E. Wilhelmy, Zeits. f. Physik 97, 312 (1935), L. G. Parratt, Phys. Rev. 49, 14 (1936), and H. H. Roseberry and J. A. Bearden, Phys. Rev. 49, 884A (1936).

³⁶ This argument is most apt in the case of alloy mixtures. As data accumulate we may distinguish between the width effect with metallic alloys and with chemical compounds of definite stoichiometric proportions.

factors may be expected to be asymmetrical and have maximum ordinates displaced relative to the maximum ordinate of the contributions of the first two factors alone.

In regard to the unresolved component lines, factor four, the possible momenta couplings between the inner $2p$ electrons with the outer $3d$ and $4s$ electrons in incompleting shells may cause splitting of the L_{II} , L_{III} doublet levels into single and triplet levels or into levels of greater multiplicity. The energy separations due to this splitting are small in any case and for closed outer shells, as for Zn(30), Ca(20) and A(18), there can be no such couplings. The disturbances in the outer shells for elements, especially metals, in the solid state probably invalidate the quantitative conclusions derived from the electronic configurations of the elements in the gaseous state. Nevertheless, it may be significant that the observed $K\alpha_{1,2}$ lines, corrected for overlapping, are practically symmetrical for S(16), Cl(17), K(19), Ca(20) (metal) and for Sc(21); are markedly asymmetrical for elements 22 to 30, the greatest asymmetry being observed for Fe(26); and are again practically symmetrical for elements of atomic numbers greater than Zn(30).

Another significant fact is in regard to the line shapes. Each of the asymmetrical α_1 and α_2 components may be analyzed into the constituent symmetrical and asymmetrical parts. The asym-

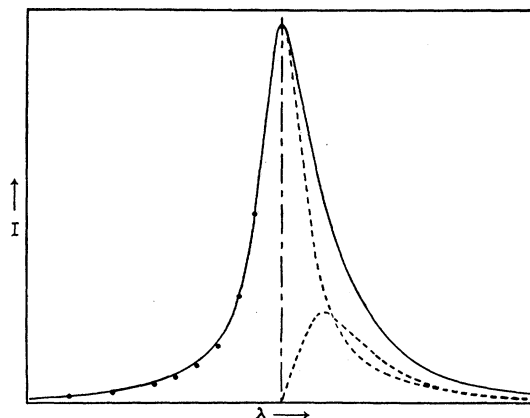


FIG. 7. The solid curve is the Fe $K\alpha_1$ component line from the (1, +1) contour of the $\alpha_{1,2}$ doublet. The dashed curves are the symmetrical and asymmetrical constituent parts of the solid curve. The circles represent the position of the classical dispersion curve matched with the symmetrical part of the α_1 component at the maximum and half-maximum ordinates.

metrical part, itself very asymmetrical, as illustrated for Fe(26) in Fig. 7, lies on the long wave-length side of the maximum α_1 ordinate for all cases in which the index of asymmetry, Table V, is greater than unity. Then, the symmetrical part of the $K\alpha_{1,2}$ lines for a wide range of atomic numbers³⁷ approximates fairly closely³⁸ the classical dispersion shape as predicted by factors one and two of the above list, and, consequently, the anomalous width variations, Fig. 6, may be accounted for roughly in terms of the line asymmetries by the remaining asymmetrical width factors.³⁹

If the line shape due to the chemical and/or alloy effect is symmetrical and agrees with the classical dispersion shape, whether or not the maximum ordinate coincides in wave-length with the maximum ordinate of the line due to the other factors, this shape may possibly be found in the Auger effect—as yet the predictions on the basis of Auger transitions have been made for gaseous atoms only. If this is true one might expect to find a chemical or alloy effect in experimental Auger coefficients (fluorescence yields) with compounds or alloys which give a pronounced effect in line widths. As an alternative, if the chemical width is asymmetrical, or not of the classical dispersion shape, it may possibly be contained in factors four and/or five.

³⁷ F. K. Richtmyer and S. W. Barnes, *Phys. Rev.* **46**, 352 (1934), have observed that the K series lines for W(74) are of the classical dispersion shape.

³⁸ An even better fit is obtained when the shape of the component line is corrected for the perturbations introduced by the finite resolving power of the crystals. This correction can be obviated effectively by observing the line contour with the crystals in second-order reflection. To a first approximation, contours observed in first-order reflection may be corrected roughly by Spencer's double inverse graphical method, see reference 14.

³⁹ It may be pointed out that the long wave-length side of the α_1 or α_2 component line, the side which, for the present lines, contains the asymmetrical part, also matches fairly well the classical dispersion shape. The symmetrical part, or the short wave-length side, of the line is discussed in the text because of the fact that the anomalies in the width plot of Fig. 6 involve excess widths and asymmetry indices greater than unity. Discussion of the other side, the long wave-length side, of the line may be pertinent for such cases as calcium oxide—the asymmetrical width contribution may be on the short wave-length side of the maximum ordinate. It is not inconceivable that in some cases the width "contribution" may be negative.

It should also be pointed out that an asymmetrical contribution which decreases abruptly to zero intensity at the position of the maximum ordinate, as drawn in Fig. 7, probably has little meaning. At the present time it is felt that the complexity of the superimposition of the line-shape factors, combined with the diffraction pattern uncertainties, make further analysis futile.

Indeed, if each of the several factors contributing to line widths can be evaluated, it seems possible that, with more data, a more or less complete interchecking system of Auger coefficients and widths of x-ray lines and limits can be developed somewhat analogous to and somewhat more elaborate than the system of wave-lengths of lines and limits.

V. EFFECTS OF CHEMICAL BINDING

Since satisfactory targets of nonmetallic elements in the free state could not be prepared and, for these elements, resort to chemical compounds was necessary, a test of the effect of chemical binding on the satellite structure was attempted. For calcium targets of metallic calcium, calcium oxide and of calcium chloride no differences in the Ca $K\alpha_{3,4}$ satellite structure or in the wave-length separations were observed greater than the experimental errors. It is to be noticed also that no marked change in the satellite contour is observed for liquid gallium when compared with the solids adjacent in atomic number. This small effect of chemical binding or of the physical state of the target element is not surprising from the point of view of the Wentzel-Druyvesteyn theory of satellite origin, although in the satellite widths an effect of the same order of magnitude may be expected to be present as the effect observed in the $\alpha_{1,2}$ widths. The calcium oxide $\alpha_{1,2}$ lines are some 14 percent narrower than the lines for metallic calcium or for calcium chloride; an equivalent difference in the satellite widths may be present: The accuracy with which the widths of the Ca $K\alpha$ satellite components were measured is not better than ± 15 to 20 percent.

The greatest effects due to chemical binding are perhaps to be expected in cases of radical changes in valency, for example, sulphur in a sulphide as compared with a sulphate. Unfortunately no sulphate target could be made to serve satisfactorily in recording the satellite contours.

Bearden and Shaw²⁹ and Wilhelmy³⁵ have previously remarked on the small effect of the physical state of the target element in the contours of the $K\alpha_{1,2}$ lines for liquid gallium and for gaseous krypton as compared with the line contours for adjacent solids. This indicates that

in some cases at least the line width contribution due to linkage with neighboring atoms is very small.⁴⁰

The narrow $K\alpha_{1,2}$ lines for calcium oxide as compared with the widths for metallic calcium

⁴⁰ An analysis of the widths of the $K\alpha_{1,2}$ lines for Kr(36) measured by Wilhelmy is instructive. The observed widths are 0.37 and 0.33 X.U. for α_1 and α_2 , respectively. Corrected for the crystals by Eq. (1) these widths become 0.31 and 0.27 X.U. Less the radiation damping width, 0.13 X.U. from Table I of Prins, reference 31, the respective widths are 0.18 and 0.14 X.U. Wentzel, *Zeits. f. Physik* **43**, 524 (1927), finds that the Auger width is about equal to the radiative width for Kr(36) so that there are left the small residual widths of 0.05 and 0.01 X.U. (about equal to the observational errors as estimated by Wilhelmy) to be accounted for by the width factors four and five as listed above. This is evidence that factors four and five (and also factor three in the cases of adjacent solid elements when the Kr $K\alpha_{1,2}$ widths are compared with the line widths for these adjacent elements) are of small importance in these lines for $Z=36$. The Kr $K\alpha_{1,2}$ lines are symmetrical and agree with the classical dispersion shape within the errors of observation.

leads one to question the significance of the smoothness of the curves drawn in Fig. 6. The widths for scandium oxide may also be low compared with the widths one might measure for free scandium, but, on the other hand, the oxide of manganese gives wider lines than does pure manganese.⁴¹

VI. ACKNOWLEDGMENTS

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⁴¹ L. G. Parratt, *Phys. Rev.* **45**, 364 (1934); J. A. Bearden and C. H. Shaw, reference 29, footnote 16; and H. H. Roseberry and J. A. Bearden, *Phys. Rev.* **49**, 884A (1936).

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A Precision World Survey of Sea-Level Cosmic-Ray Intensities¹

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With sensitive, vibration-free, self-recording electroscopes sent to many parts of the globe on twelve different voyages a precision survey has now been completed of the variation of cosmic-ray intensities both with latitude and longitude, so that the earth as a whole can now be covered with sea-level, equal intensity, cosmic-ray lines. In going along the longitude line 75° W., which runs from the far north through Washington, D. C., and along the west coast of South America, there is no appreciable change until the magnetic latitude of about 41° is reached. The equatorial dip then begins to set in and shows a maximum decline of 8 percent off Peru and returns again to its normal value off Cape Horn. In going along longitude line 80° E. through southern India the maximum dip is 12 percent. In going south from Alaska in longitude 165° W. to New Zealand the maximum dip is 10 percent. In going south from Liverpool through the Atlantic Ocean—longitude 30° W.—and around Cape Horn the maximum dip

is 8.5 percent. In the region most accurately studied—the west coast of the United States—the intensity remains exceedingly constant until the latitude of Pasadena—41° magnetic—is reached, and then drops remarkably suddenly. In the Atlantic Ocean the drop sets in at about the same magnetic latitude with equal suddenness. It appears also to take place quite suddenly at about magnetic latitude 41° in the southern hemisphere. Nevertheless, the existence of a longitude effect shows that in strictness there is no such thing as magnetic latitude. In other words, the earth's magnetic field, even at the remote distances of thousands of miles at which these deflections occur, is strikingly dissymmetrical with respect to any line passing through the earth's center. This method of study opens up the possibility of determining these dissymmetries at large distances from the earth. The observed magnetic effects are to be expected quite independently of whether cosmic rays are in their origin photonic or corpuscular.

THE first element in the high altitude survey of cosmic-ray intensities as a function of latitude organized in the fall of 1931² was the development of what the first of the authors has

designated as “the Neher vibration free, cosmic-ray electroscope.” It has been with its aid that this sea-level survey has been made.

§1. THE ELECTROSCOPE

This instrument was a modification of the cosmic-ray electroscope which Millikan and Cameron had developed in 1927 and had used in

¹ A condensed report of this work was published in *Science* **82**, 574 (1935).

² I. S. Bowen, R. A. Millikan and H. V. Neher, *Phys. Rev.* **44**, 246 (1933). See also International Conference on Nuclear Physics (Cambridge Univ. Press, 1934), p. 210.