A similar series of reflection pictures was taken with the same crystal by using the third harmonic of the same mode of vibration. For the third harmonic there was even less distinction between the expected nodal and antinodal regions than existed for the fundamental. Indeed, a "disturbed" area seemed to occupy the major portion of the reflecting surface of the crystal. On the basis of a large number of pictures, the effect was greater for the nodal than for the antinodal regions.

The microphotogram in Fig. 2E shows that no increase of intensity was present in the reflection pictures taken from the end of this long crystal, while it was vibrating at the fundamental of its low frequency mode of vibration. This result was expected since for this mode of vibration the planes parallel to the end of the crystal are in a configuration similar to that of the planes parallel to the face of the crystal for the mode of vibration determined by the thickness of the crystal.

An extensive study was made of a number of Rochelle salt crystals. The increases of intensity were small and could not be consistently repeated. This may be attributed to the difficulty of maintaining the equivalent of an etched surface for the reflection pictures; and for the Laue pictures, to the fact that most of the modes of vibration used were similar to those of quartz which showed little effect in their Laue pattern. Fox and Fraser[6] report an effect for Rochelle salt, but much smaller than for quartz.

The writer wishes to acknowledge his appreciation to Professor J. M. Cork of this department for suggesting the problem and for aid in interpreting the results. He is especially indebted to Professor N. H. Williams also of this department for the loans of equipment from his laboratory, and for valuable criticism and encouragement during this investigation.

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Excitation Potential of $K\alpha_{3,4}$ Satellite Lines

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With a two-crystal vacuum spectrometer the curve of the intensity of $K\alpha$ satellite lines *vs.* voltage of the x-ray tube has been determined for the $K\alpha_{3,4}$ lines of titanium. For voltages greater than 11 kv the satellite intensity (total area of the $K\alpha_{3,4}$ satellite structure) relative to the intensity of the Ti $K\alpha_1$ lines is 2.21 percent; the ratio of peak intensities α_4/α_1 is 0.69 percent. The measured excitation potential of the Ti $K\alpha_{3,4}$ lines is 5450 ± 100 volts, 500 volts in excess of the excitation potential of the $K\alpha_{1,2}$ lines. Assuming 0.85 as the screening constant of a missing K electron on an L electron, one calculates that the voltage required to produce a state of KL_{III} ionization in the titanium atom is 5455 volts. This value is in excellent agreement with the measured excitation potential and the conclusions of the experiments are in support of the Wentzel-Druyvesteyn theory of the origin of the $K\alpha_{3,4}$ satellite lines.

I. Introduction

The phenomena associated with nondiagram or satellite lines represent an enigma of many years standing in x-ray spectroscopic theory. For some time we have been able to account satisfactorily for the essential features of the production of diagram lines as either dipole or quadrupole radiations, but, perhaps because of a paucity of accurate, unambiguous experimental information, we are confronted with various contradictory theories which attempt to "explain" satellite lines. The voltage required for the production of satellites is of crucial importance in testing the validity of these various theories and in the present paper we shall be concerned with a determination of this excitation voltage.

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In 1921 Wentzel[1] proposed that satellites originate in multiply-ionized atoms. For example, the $K\alpha_4$ line was supposed to arise from a $KK \rightarrow KL$ transition where KK refers to an atomic state in which two K electrons are missing. The probability of two (or more) electrons being ejected from an atom by successive impacts of the cathode-rays is much too low[2, 3] to account for the observed satellite intensities—the multiple-ionization process would have to take place by a single impact. Then, the x-ray tube voltage necessary to excite the $K\alpha_4$ satellite line in accord with Wentzel's proposal is somewhat more than twice the voltage required to excite the $K\alpha_{1,2}$ lines, for which the initial state of the atom is simply K ionization.

Early qualitative determinations[3–7] of the excitation voltage of satellites gave values considerably less than twice that of the parent diagram lines, although in these experiments the satellite excitation voltage seemed consistently to be the higher. Druyvesteyn[3] accordingly[8] modified Wentzel's scheme by proposing that the initial state of the atom giving rise to satellite lines is one in which the double-ionization never refers to the same electronic shell.[8a] In the Wentzel-Druyvesteyn theory the $K\alpha_4$ line is the radiated result of a $KL \rightarrow LL$ transition, and the excitation potential is approximately equivalent to the total energy required to remove the K electron of atom Z plus the energy required to remove an L electron of atom $Z+1$.

So great were the technical difficulties in experimentally measuring the satellite excitation potentials that the early experiments did not clearly defend the Wentzel-Druyvesteyn theory. Except for the work of Jönsson[6] and that of DuMond and Hoyt,[9] all of these experiments employed the photographic method of measuring the x-ray intensities. The photographic method is especially treacherous in these studies because of the great difference in intensity between the satellites and the parent lines. The parent line[10] is, of necessity overexposed in order to bring out the faint satellite lines on the photographic plate. The satellites are found on a rapidly changing background, on the side of the overexposed parent line, and we do not know the form of the photographic density curve of the parent line in the satellite neighborhood. The effective resolving power of the spectrograph is not only low but, in part because of the overexposure, is also unknown so far as concerns a possible correction in the relative intensity measurements. DuMond and Hoyt in attempting to eliminate the uncertainties inherent in the photographic method adapted the two-crystal ionization spectrometer to the determination of the excitation potential of the $K\alpha_{3,4}$ satellite lines of copper. This measurement, with the ionization method, gave a value for the excitation potential which is *less* than that required for KL ionization. This value was based, however, on a questionable extrapolation.

DuMond and Hoyt's measurement was in agreement with another theory of satellite origin which had been proposed by Richtmyer.[11] This theory, the "double-jump" theory, based on semi-Moseley graphs of the wave-length separations of the satellites and the parent lines, ascribes the satellite lines to two simultaneous electron transitions in the atom, one transition being that which alone would give rise to the parent line and the second transition being one between two outer or semi-optical levels. In the case of $K\alpha$ satellites this outer transition involves two M levels. The excitation potential of the $K\alpha$ satellite lines according to Richtmyer's hypothesis

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[1] G. Wentzel, Ann. d. Physik **66**, 437 (1921); **73**, 647 (1924); Zeits. f. Physik **31**, 445 (1925).

[2] D. Coster, Phil. Mag. **44**, 546 (1922); S. Rosseland, Phil. Mag. **45**, 65 (1923).

[3] M. J. Druyvesteyn, Zeits. f. Physik **43**, 707 (1927); Dissertation, Groningen, 1928.

[4] E. Bäcklin, Zeits. f. Physik **27**, 30 (1924).

[5] M. Siegbahn and A. Larsson, Arkiv f. Matematik, Astronomy och Fysik **18**, 1 (1924).

[6] Axel Jönsson, Zeits. f. Physik **43**, 845 (1927).

[7] S. W. Barnes, Dissertation, Cornell University, 1930, and S. W. Barnes and F. K. Richtmyer, Phys. Rev. **35**, 661A (1930).

[8] Also important in this modification are considerations of the wave-length separations of the satellites and the associated diagram lines.

[8a] To account for certain satellite lines, for example, the $K\alpha_{5,6}$ lines, an initial state of triple-ionization was proposed in which two of the three missing electrons may be from the same electronic shell.

[9] J. W. M. DuMond and A. Hoyt, Phys. Rev. **36**, 799 (1930).

[10] The term "parent line" refers in the present discussion to the nearest intense diagram line. Evidence has been presented (O. R. Ford, Phys. Rev. **41**, 577 (1932), F. K. Richtmyer, Phil. Mag. **6**, 64 (1928), *et al.*) to show that the true parent line may be more distant in wave-length. For example, the $K\alpha_2$ rather than the $K\alpha_1$ line may be the parent line of the $K\alpha_{3,4}$ satellites.

[11] F. K. Richtmyer, J. Frank. Inst. **208**, 325 (1929); see also F. Bloch, Phys. Rev. **48**, 187 (1935).

is in excess of the ionization energy of the K shell of atom Z by approximately the ionization energy of the M shell of atom $Z+1$.

Recently Coster and Thijssen[12] reported a determination, using the photographic method, of the excitation potential of the $K\alpha_{3,4}$ satellites of sulphur, obtaining a value in agreement with KL ionization. More recently, Coster, Kuipers and Huizinga[13] have measured photographically the excitation potential of the $L\alpha$ satellites of niobium. This value also agrees with LM ionization (which in the Wentzel-Druyvesteyn theory corresponds to KL ionization with K series satellites), and also gives supporting evidence for the Coster-Kronig theory[14] for the augmented intensities in the range of certain atomic numbers of L and M series satellite lines. (The Coster-Kronig theory, based on radiationless transitions as increasing the probability of an atom finding itself in the initial state for satellite emission, does not apply to K series satellites, although it depends for its meaning upon the Wentzel-Druyvesteyn theory.)

It was felt that the status of the problem as described above demanded a new evaluation of the satellite excitation potential using the ionization method of recording the intensities, which method is free from the objections to the photographic method, and using a two-crystal spectrometer which has a much higher resolving power. The excitation potential of the $K\alpha_{3,4}$ satellite lines of titanium has been determined and the value obtained is in agreement with the energy required to produce KL ionization, in support of the Wentzel-Druyvesteyn theory.

II. Experimental Part

The vacuum spectrometer and accessory equipment used in this work have been described in previous papers.[15] Mounted on the instrument were calcite crystals, etched cleavage-surfaces, crystals A_4B_4 of previous reports.[16, 17] These crystals had been found to be "spectrometrically perfect."[18]

The size of the focal-spot of the target of the x-ray tube was adjusted to be about 2 mm in diameter. This diameter matched the height of each of two slits which limited the maximum vertical divergence of the x-ray beam (with respect to the central ray) to 6×10^{-3} radian. The horizontal divergence of the beam was limited by the collimating action of the first crystal and by the effective size of the focal-spot. As mentioned in another paper,[16] this arrangement causes the x-ray beam to shift along the surfaces of both crystals as the angle of the second crystal is altered. The crystals, however, had been previously tested and found to have uniform reflectivity over their surfaces. The advantages of this aperture-arrangement are (1) in utilizing at all times all the intensity generated in the x-ray tube, (2) in obviating the problems of nonuniform intensity distribution in the focal-spot, and (3) in reducing the number of adjustments in going from one point to another on a curve.

The ionization currents were recorded with the constant deflection method by means of an FP-54 amplifying tube in the DuBridge-Brown circuit.[15, 19] Either of two high resistances, 3.4×10^{11} and 6×10^{9} ohms, could be placed in the circuit by a simple switching device. With the alternate use of these two resistances the assumption of linearity of the amplifying system over the large range of a factor of 1000 was not necessary, although by test, applying known voltages with a potentiometer, the circuit and galvanometer (type HS Leeds and Northrup) were linear over a range of more than 100.

Several important features served to increase the accuracy with which the feeble ionization currents were measured. (1) The Pliotron tube was in a vacuum, inside the massive steel tank. (2) This tank, because of its large heat capacity,

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[12] D. Coster and W. J. Thijssen, Zeits. f. Physik **84**, 686 (1933).

[13] D. Coster, H. H. Kuipers and W. J. Huizinga, Physica **2**, 870 (1935).

[14] D. Coster and R. de L. Kronig, Physica **2**, 13 (1935).

[15] L. G. Parratt, Phys. Rev. **41**, 553 (1932); Rev.. Sci. Inst. **5**, 395 (1934).

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

[17] L. G. Parratt and F. Miller, Jr., Phys. Rev. in press (1936).

[18] "Spectrometrically perfect" crystals are defined as "perfect" crystals of "Class I." "Perfect" crystals are defined as crystals whose reflectivities (usually taken as merely the widths of the (1, −1) rocking curves) measured in the parallel positions agree with the theoretical reflectivities. "Class I" crystals are crystals whose (1, +1) curve width of the $K\alpha_1$ line of Mo, Cu or Ti is narrow (a minimum) for the corresponding (1, −1) width. See reference 16.

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

served to maintain constant temperature conditions. (3) The ionization chamber, filled with one atmosphere of argon, was small,[20] 2.4 cubic inches, and constructed of steel to reduce[21] the number of extraneously produced ions. (4) The effect of an alpha-particle was a rather violent "kick" and since these kicks were rare, a maximum range alpha-particle (causing a scale deflection of about 12 cm) being observed about one per hour, the x-ray intensity readings could be taken between them or their effects visually discounted. (5) And, finally, the wave-lengths studied are relatively long with correspondingly small disturbances due to the statistical variations in the number of quanta entering the ion chamber to produce a given ionization current.

From the observed variations in the scale position of the light-beam of the galvanometer an ionization current of 10^{-16} ampere could be measured with an estimated accuracy of ± 15 percent. Assuming an energy of 35 electron volts per ion pair,[22] one calculates that a current of 10^{-16} ampere is produced by less than 5 quanta ($\lambda = 2.75\text{A}$) completely absorbed per second. The time constant of the measuring system (given by $T = RC$ of the ion chamber-Pliotron circuit rather than by the period of the galvanometer) is approximately 6 seconds. In 6 seconds, then, 30 quanta are absorbed and the standard deviation in measuring 10^{-16} ampere is given by

$$\sqrt{n}/n = \sqrt{30}/30 = 18 \text{ percent.}$$

The ballastic type of recordings, in which the charge is accumulated for several minutes would, statistically, increase the sensitivity without sacrificing accuracy but, when one considers the observer's opportunity with the constant deflection method to discount the alpha-particle kicks and to further smooth out the fluctuations by watching the scale position of the light-beam for a period of time longer than 6 seconds, one is justified in concluding that in measuring the ionization currents produced by x-rays the present techniques have practically reached the theoretical limits. In the actual recordings, except with the tube voltages of 5.75 and 6 kv, the ionization currents observed at the peak of the $K\alpha_4$ line were greater than 10^{-15} ampere: At 20 kv and 20 ma the deflection at the α_4 peak was 100 cm corresponding to an ionization current of 3×10^{-14} ampere.

Many considerations are important in choosing an element for the target of the x-ray tube in this work. (1) The target must be capable of dissipating as much power as possible with constant x-ray emission. (2) The wave-length must not be so long that absorption difficulties become great. (3) The $K\alpha_{3,\,4}$ satellite intensity relative to that of the parent line should be high. (4) The excitation potential of the parent line should be such (high) that the already small difference between the exciting potential of the parent line and of the satellites be large to allow a relatively more accurate measurement. (5) The satellites should be far removed from the parent line and the width of the parent line should be small so that the uncertainty of the sloping satellite background, actually the side of the α_1 line, may be a minimum. (6) The total internal component structure of the satellites should be narrow to allow the sloping background to be drawn in as accurately as possible. Before the target-element was decided upon, preliminary ionization curves were taken of the satellites from S(16) to Ge(32), and Ti(22) was chosen as being most satisfactory.

A good thermal contact to titanium must be established before it will serve as a satisfactory target. This contact was made with the use of evaporated films.[23] The preparation of the target, discussed elsewhere,[24] was briefly as follows: On a freshly cleaned surface of a Ti disk, about 1/2 inch in diameter and 1/16 inch thick, was condensed in vacuum a layer of chromium and then a layer of copper. The disk was removed from the evaporating jar and more copper electroplated onto the condensed copper until a sufficiently thick deposit allowed the disk to be soldered to the target carriage. This target would

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[20] Radiation of 2.75A wave-length is about 95 percent absorbed in a 3 cm path (one atmosphere of argon) in the ionization chamber. With such sudden absorption it is important that there be no "dead pockets" in the electric field in the ion chamber near the entrance window. Accordingly, in the present experiments a cellophane window was used on the inner side of which had been placed a thin but electrically conducting layer of aluminum. The argon path in the chamber was 6 centimeters and in this distance the radiation was completely absorbed.

[21] J. A. Bearden, Rev. Sci. Inst. **4**, 271 (1933).

[22] O. Gaertner, Ann. d. Physik **3**, 325 (1929); **10**, 825 (1931).

[23] The author is indebted to Dr. John E. Ruedy of the Evaporated Films Company for his generous advice and assistance in the preparation of this target.

[24] L. G. Parratt, Rev. Sci. Inst. **6**, 372 (1935).

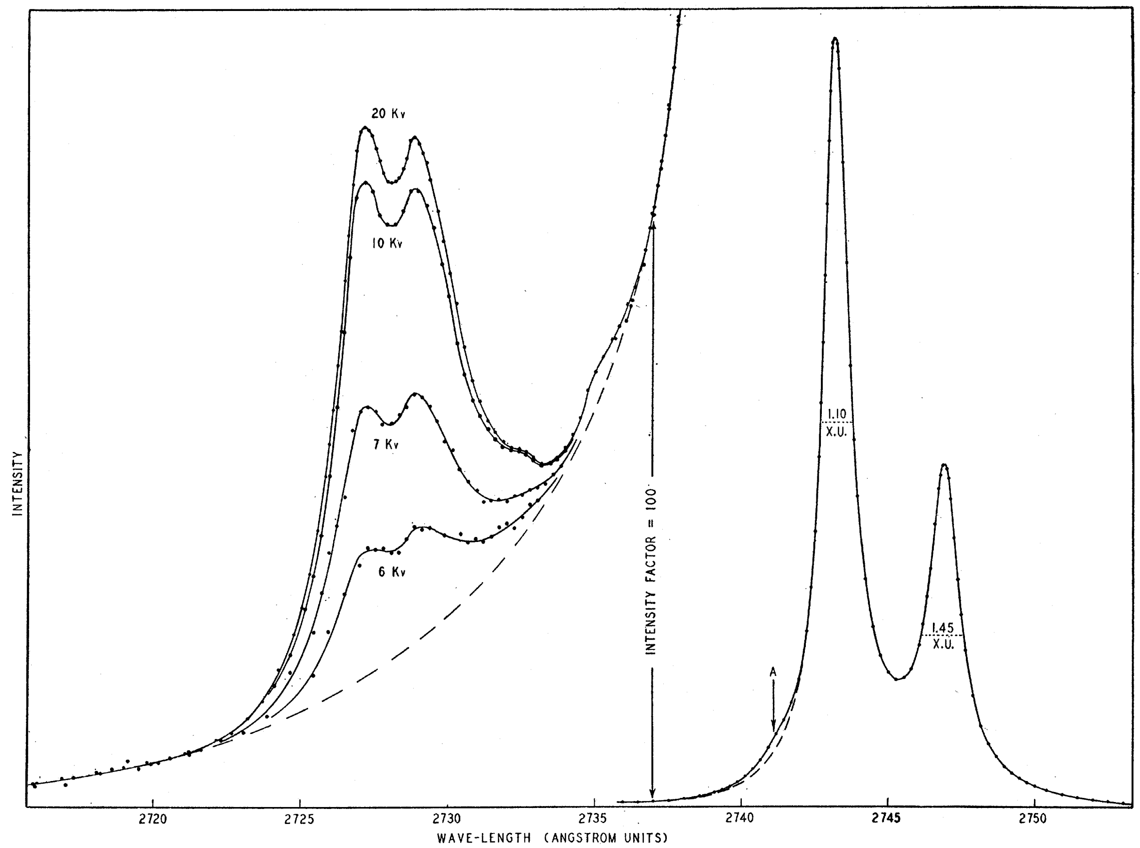

FIG. 1. Ionization curves of the $K\alpha_{3,\,4}$ region of titanium recorded with various voltages across the x-ray tube. (This particular $\alpha_{1,\,2}$ curve was recorded at 20 kilovolts.) The four curves are matched for the intensity of the $\alpha_{1,\,2}$ lines. The satellite lines are plotted to an intensity scale 100 times the scale used in plotting the diagram lines. On the short wave-length side of the $K\alpha_1$ line, at the position of the arrow A, is a new faint component line. See text.

dissipate about 750 watts with a focal-spot about 2 mm in diameter.

Needless to say a good vacuum must be maintained in the x-ray tube to eliminate the intolerable tungsten deposit (from the filament) which would otherwise accumulate on the target surface and on the window of the tube. Because of the x-ray absorption in tungsten a good vacuum becomes rapidly more important as the wave-length is increased. When the vacuum was maintained, and the tube voltage (the primary voltage of the high-tension transformer was supplied by a motor-generator) was held constant by manually adjusting the filament current, the emitted intensity was constant within 2 percent over a period of several hours.

The voltage across the x-ray tube was measured with an accurate milliammeter in series with a three megohm wire-wound resistance. The calibration of this voltmeter was checked by a measurement of the known excitation potential of the Ti $K\alpha_{1,\,2}$ lines. The ripple in the high voltage was smoothed out by a filter circuit: At 6 kv and 80 ma the ripple was 48 volts as measured with an oscillograph,[25] and about the same as calculated from the constants of the filter circuit.

III. DISCUSSION OF RESULTS

In Fig. 1 are plotted several ionization curves of the Ti $K\alpha_{3,\,4}$ region as recorded with various voltages across the x-ray tube. The particular curve of $\alpha_{1,\,2}$ shown in the figure was recorded at 20 kilovolts. The observed points on these curves

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[25] The author is indebted to Mr. T. T. Goldsmith of this laboratory for assisting in this measurement.

illustrate the accuracy with which the intensity measurements were made.

With the tube operating at 30 kv and 9.7 ma the total background radiation, due to the continuous spectrum and to scattering of the x-rays, was less than 1/10 of the peak of the α_4 line or less than 1/1100 of the peak of the α_1 line. This fractional background was less at lower voltages.

Shown in the curves are at least two satellite components, α' and α_3'' (a new component), in addition to the $\alpha_{3,4}$ lines. The α_3' line, which has been observed by Bäcklin and by Ford on photographic plates with elements Si(14) to Cl(17), appears to be changing its wave-length position relative to the $\alpha_{3,4}$ lines, moving from the long wave-length side of α_4 at S(16) to the short wave-length side as the atomic number is increased. In the case of Ti(22) α_3' is about coincident in wave-length with α_4. With this element, Ti, the intensity of the α_3' line is roughly 29 percent of that of α_4. A subsequent paper is being prepared in which is discussed the structure and intensities of the satellites in the $K\alpha_{1,2,3,4}$ region with elements S(16) to Ge(32), and our interest in the present paper will be confined to the satellite intensity as a function of the x-ray tube voltage and current. The above brief mention of the α_3' line is pertinent in the present discussion in view of the possibility that the origin of this satellite is not the same as the origin of the other satellites in the $\alpha_{3,4}$ group. If the origins are different one might expect a different intensity-voltage function for the two types of satellites. Experimentally no change in the Ti $K\alpha_{3,4}$ satellite structure was observed as the tube voltage was varied; but this check was not sufficiently sensitive below 7 or 8 kv to have much significance and it is probably in the low voltage range that the check is most important.

On the short wave-length side of the $K\alpha_1$ line, at the position of the arrow designated by "A" in Fig. 1, there appears a little "bump," evidence of another component satellite line.[25a] This line has been observed in the present work with elements V, Ti, Sc, Ca, K, Cl and S (elements of lower atomic number than that of S(16) have not yet been studied) and will be discussed in more detail in a subsequent paper. The area under this line has not been considered as part of the intensity of the $K\alpha_{3,4}$ satellite group. Rather, it seems possible that this new line is another group of satellites for which the initial atomic state is one of KM ionization.

The definition of the relative intensities of two x-ray lines refers to the ratio of the areas contained under the lines when the spectral analysis is complete, that is, when the lines are observed with an instrument of infinite resolving power. If the instrument used in the analysis is of low resolving power a more fitting definition of relative intensities is simply the ratio of the observed maximum ordinates of the two lines, although (except with extremely low resolving power) unless the x-ray lines in question have identical "true" widths and "true" shapes, the ratio of maximum ordinates does not give the relative intensities.

It is well known that the resolving power of the two-crystal spectrometer is considerably greater[16, 26] than that of the single-crystal instrument, especially when, as is usually the case, the latter is operated with the confining slits so arranged that they, rather than the diffraction pattern of the crystal, are effective in limiting the resolving power. Even with the two-crystal instrument with "spectrometrically perfect" calcite crystals the $d\lambda$ interval due to the finite resolving power of the crystals is about 1/4 of the true width of the Ti $K\alpha_1$ line.[16] As seen from Fig. 1 the observed width at half-maximum intensity of the Ti $K\alpha_{3,4}$ satellite region is much greater than, a factor of about 4.3, the observed width of the sharp $K\alpha_1$ line. The effect of the instrument is (1) to depress the peak of the $K\alpha_1$ line a greater fraction than the depression of the satellite peaks, and (2) to increase the area of the $K\alpha_1$ line a greater fraction than the increase in the satellite area.

An x-ray line having a true shape $L(\theta)$ is transformed, in two successive acts, by the two single-crystal diffraction patterns $F_A(\theta)$ and $F_B(\theta)$ into the line shape $L_B(\theta)$ which is observed after reflection from crystal B. These functions are related[27] by

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[25a] This "bump" appears to be the same as the "emission band" reported by Dolejsek, Comptes rendus **174**, 441 (1922), on the short wave-length side of the $K\alpha_1$ line of Sc, Ca, K and Cl.

[26] S. K. Allison, Phys. Rev. **38**, 203 (1931).

[27] For a more accurate discussion of these functions see Compton and Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Co., 1935), pp. 709–750. See also L. P. Smith, Phys. Rev. **46**, 343 (1934).

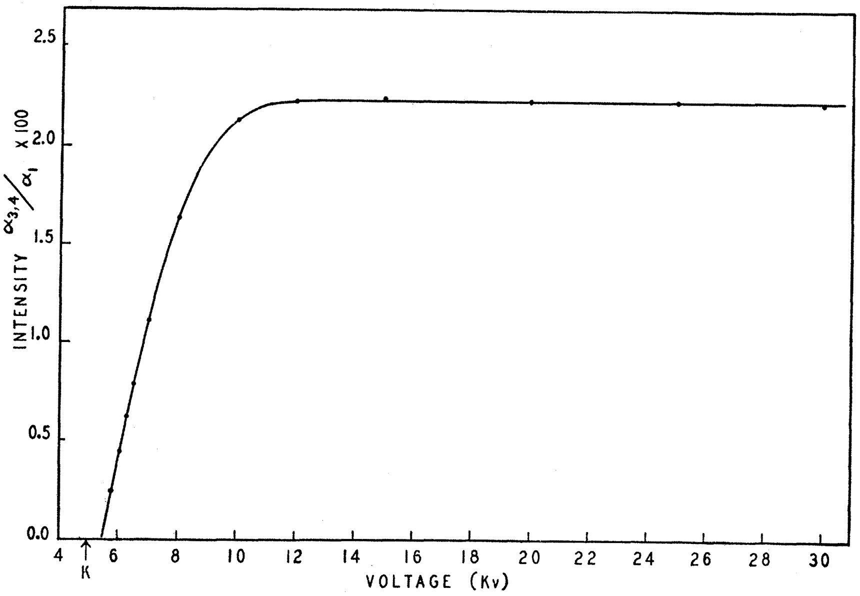

FIG. 2. Intensity of the Ti $K\alpha_{3,\,4}$ satellite lines relative to the intensity of the $K\alpha_1$ line as a function of tube voltage. The abscissae value at which the intensity ratio $\alpha_{3,\,4}/\alpha_1$ falls to zero is the excitation potential of the satellite lines. The voltage indicated by K is the excitation potential of the $K\alpha_{1,\,2}$ diagram lines.

$$L_A(\theta)=\int_{-\infty}^{+\infty}L(\theta-\beta_A)F_A(\beta_A)d\beta_A$$

and

$$L_B(\theta)=\int_{-\infty}^{+\infty}L_A(\theta-\beta_B)F_B(\beta_B)d\beta_B,$$

in which $L_B(\theta)$ is the only shape that is experimentally known. The order of magnitude of the width at half-maximum of the crystal functions F_A and F_B can be inferred from the width of the observed (1, −1) curve. The shape of the theoretical diffraction pattern $F(\theta)$ is not symmetrical. We know also that the width of $L_B(\theta)$ at half-maximum intensity is about 25 percent greater than the width of $L(\theta)$. From this incomplete information we are interested in obtaining $L(\theta)$.

For the present purposes we will be content with an approximate solution, one which gives the maximum ordinate and the area of $L(\theta)$ within about ±3 percent. A graphical solution has been discussed by Spencer[28] in which each of several types of $F(\theta)$ are considered. None of Spencer's $F(\theta)$ types is applicable. If the full width of $F(\theta)$ be taken arbitrarily as the (1, −1) width (0.22 X. U. in the present case) divided by $\sqrt{2}$, the $F(\theta)$ contour may be adjusted by trial and error to give, following Spencer's double inverse graphical method, an $L(\theta)$ whose width agrees with the true width as previously ascertained.[16] In this manner approximate correction factors were evaluated for the Ti $K\alpha$ lines of Fig. 1: The ratio of the observed peak intensities $\alpha_{3,\,4}/\alpha_1$ are to be multiplied by 0.93 and the ratio of observed areas $\alpha_{3,\,4}/\alpha_1$ by the factor 1.05. The corrections are of no importance in the value of the excitation potential but they are greater than the estimated maximum error in the relative intensity measurements.

Measurements of the relative intensities of the satellite lines to the α_1 line as recorded at various tube voltages are listed in Table I and given graphically in Fig. 2. These values, the averages of many trials, have an estimated maximum observational error of ±4 percent, except with the voltages of 5.75, 6.0 and 6.25 kv where the error may be as large as ±15 percent. No satisfactory analytical method of drawing in the satellite background, the side of the asymmetrical α_1 line, has been developed and the uncertainty of the arbitrary way in which this background was determined (drawn in free-hand) introduces the greatest error in the relative intensity measurements. The area under the α_1 line was taken as 2/3 the area under the $(\alpha_1+\alpha_2)$ contour.

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[28] R. C. Spencer, Phys. Rev. **38**, 618 (1931).

TABLE I. *Intensity of the Ti $K\alpha_{3,4}$ x-ray satellite lines, relative to the intensity of the Ti $K\alpha_1$ diagram line, with various x-ray tube voltages.* (Area of satellites, designated $\alpha_{3,4}$, refers to the area of the total satellite structure which may include component satellite lines in addition to the α_3 and α_4 lines.)

Corrections:
(1) The subtraction of the intensity of the overlapping α_1 line from the observed intensity at the peak of the α_4 line.
(2) For the finite resolving power of the spectrometer (see text).

TUBE VOLTAGE (kv)	TUBE CURRENT (ma)	RATIO OF OBS. PEAKS α_4/α_1 (percent)	RATIO OF PEAKS α_4/α_1 (percent) CORRECTED (1) (2)	RATIO OF OBS. AREAS $\alpha_{3,4}/\alpha_1$ (percent)	RATIO OF AREAS $\alpha_{3,4}/\alpha_1$ (percent) CORRECTED (2)
5.75	80.0	0.26	0.079	0.237	0.249
6.00	80.7	0.326	0.140	0.423	0.444
6.25	80.6	0.39	0.200	0.603	0.633
6.50	80.5	0.44	0.247	0.749	0.785
7.00	78.5	0.55	0.345	1.05	1.10
8.00	66.0	0.72	0.505	1.54	1.62
10.00	54.6	0.89	0.664	2.07	2.17
12.00	32.3	0.92	0.690	2.11	2.21
15.00	22.2	0.93	0.700	2.12	2.22
20.00	21.4	0.92	0.690	2.11	2.21
25.00	20.0	0.92	0.690	2.11	2.21
30.00	9.7	0.91	0.690	2.10	2.20

Matching the various satellite curves for the same α_1 peak intensity affords a much more sensitive test than has ever before been made of the shape of the α_1 line with different tube voltages and currents. The side of the α_1 line adjacent to the satellite region in all of the matched curves agrees within the experimental error—the ratio of the intensity at this remote part of the α_1 line to the intensity at the peak of the line does not vary with voltage or current within the experimental error of about five percent of one percent. The voltage range used is admirably suited to this test.

For voltages less than twice the excitation potential the intensity of the $K\alpha_{3,4}$ satellite lines is not the same function of voltage that applies in the case of the diagram lines; for voltages greater than twice the excitation potential the functions are the same. The ratio of satellite intensity to that of the α_1 line was found to be linear with the x-ray tube current over a factor range of 4. Since the intensity of the α_1 line is known to be linear with tube current it follows that the same relation holds for the satellite intensity.[29]

An extrapolation of the curve of Fig. 2 to zero satellite intensity gives the excitation potential. This potential, 5450 volts, is 500 volts in excess of the ionization energy of the K shell of electrons. Great care was taken in determining the relative intensities at the low voltages and if these experimental values are assumed to be accurate without any observational error the uncertainty in the extrapolation is less than ±40 volts. This assumption may seem warranted from the internal consistency of the data but it is not justified. The estimated maximum observational error is about 100 volts.

Of course, it is not certain that the extrapolation in Fig. 2 is the correct one: A point of inflection below 5.75 kv would bring the satellite excitation potential more nearly in agreement with that of the parent line. Such an inflection point is, however, unlikely.

IV. CONCLUSIONS

The ionization energy[30] of a K electron of atom $Z=22$ (titanium) is 4950 volts. The ionization energy of an L_{III} electron of atom $Z+1=23$ (vanadium) is 514 volts; the L_{III} energy of an hypothetical atom[31] $Z+0.85$ is 505 volts. The sum of the two energies, approximately the energy required to produce a state of KL ionization in the Ti atom, is 5455 volts, taking the screening constant as 0.85 instead of unity. This energy is in excellent agreement with the measured excitation potential of the Ti $K\alpha_{3,4}$ satellites, 5450±100 volts, and the conclusions of the experiments are in support of the Wentzel-Druyvesteyn theory of the origin of the $K\alpha_{3,4}$ satellite lines.

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[29] The possibility of the double ionization process being one of successive cathode-ray impacts, tandem style, has been ruled out as being too improbable to account for the observed satellite intensities. The fact that the satellite intensity is linear with tube current rules out on a second score the tandem process which requires the intensity to be proportional to the square of the current.

[30] The ionization energies are calculated from the ν/R values given in Siegbahn, *Spectroscopie der Röntgenstrahlen* (Julius Springer, 1931), p. 348.

[31] J. C. Slater, Phys. Rev. **36**, 57 (1930) gives 0.85 as the approximate screening constant of a missing K electron on an L electron.