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Shapes and Wavelengths of *K* Series Lines of Elements Ti 22 to Ge 32

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A double crystal spectrometer was used to measure the widths at half-maximum and the indices of asymmetry of the principle *K* series lines of the elements Ti 22 to Ge 32. When sufficient intensity was available, measurements were made in three orders of diffraction, namely, in the $(1-2)$, $(1+1)$ and $(1+2)$ positions. Curves of width *vs.* atomic number and degree of asymmetry *vs.* atomic number are different in the various orders. These differences are discussed. Measurements were also made of the widths of certain satellites and of their intensities and displacements relative to an adjacent line. The diffraction angles of the peaks of the lines were determined with precision in two orders and wavelengths calculated. Comparisons are made with single crystal photographic spectrometer work and the higher degree of accuracy obtained in the present work is pointed out.

INTRODUCTION

MEASUREMENTS of the shapes and wavelengths of certain x-ray lines have been made by previous investigators with both single[1] and double[2] crystal spectrometers. In studies on line shapes with either type of instrument the effect of the crystal diffraction patterns must be considered. However, the limitations imposed on the slit system to utilize fully the resolving power of the crystals are more easily realized with the double crystal than with the single crystal instrument. In addition, it has been shown that the double crystal spectrometer is capable of measuring x-ray wavelengths with a precision equal to or greater than that attained with the single crystal system.

The purpose of the present work was first, to determine accurately the shape and thus the asymmetry of the lines of the *K* series of the elements from Ti 22 to Ge 32, and to study the correlation between the asymmetry of the lines and atomic number; secondly, to measure with high precision the diffraction angles from a calcite crystal in the first and second orders. The wavelengths of these lines have been calculated using the usual assumed grating constant of calcite ($d_\infty = 3.02945$A) in order that the results could be directly compared with previous measurements by other methods.

APPARATUS

The double crystal spectrometer was made by the Societé Genevoise. The first crystal was mounted on a slide midway between the target and the second crystal and perpendicular to a line joining them,[3] providing a rapid and simple means of changing the wavelength setting. The second crystal table was mounted on the precision circle spindle in such a way that it could be rotated relative to the circle in order that any given angle could be measured on different parts of the divided circle. Four carefully calibrated microscopes read the precision circle. Since two lines ten minutes apart were read in each microscope, eight angular readings were obtained for each individual setting of the circle. This arrangement considerably reduced the error due to random variations in the rulings. The circle was calibrated every five degrees to 0.2 second of arc by the four-microscope method. The appropriate correction as obtained from the calibration curve was applied to the measured angle. The accuracy of the divided circle can be judged from the fact that the largest correction applied to any measured angle was only 0.3 second.

Each crystal holder was constructed so that the crystal was supported at three points on its reflecting surface and held in place by pins and springs on the other side of the crystal and directly opposite the supporting points. This type

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* National Research Fellow, Cornell University.

[1] *Shapes:* N. Seljakow, A. Krasnikow and T. Stellezky, Zeits. f. Physik **45**, 548 (1927); A. Larsson, Phil. Mag. **3**, 1136 (1927); J. H. van der Tuuk, Zeits. f. Physik **41**, 326 (1927), (*L* series). *Wavelengths:* Siegbahn, *Spectroscopie der Rontgenstrahlen*, 2nd ed.

[2] *Shapes:* Reference 1, S. K. Allison, Phys. Rev. **44**, 63 (1933); L. G. Parratt, Phys. Rev. **44**, 695 (1933); **45**, 364 (1934); **46**, 749 (1934); F. K. Richtmyer and S. W. Barnes, Rev. Sci. Inst. **5**, 351 (1934); L. G. Parratt, Rev. Sci. Inst. **5**, 395 (1934); J. H. Williams, Phys. Rev. **45**, 71 (1934); Phys. Rev. **37**, 1431 (1931); L. P. Smith, Phys. Rev. **46**, 343 (1934); F. K. Richtmyer and S. W. Barnes, Phys. Rev. **46**, 352 (1934); F. K. Richtmyer, S. W. Barnes and E. Ramberg, Phys. Rev. **46**, 843 (1934). *Wavelengths:* A. H. Compton, Rev. Sci. Inst. **2**, 365 (1931); J. H. Williams, Phys. Rev. **40**, 636 (1932); **40**, 791 (1932); J. A. Bearden, Phys. Rev. **43**, 92 (1933).

[3] P. A. Ross, Phys. Rev. **39**, 550 (1932).

of mounting eliminates the possibility of warping the crystal. That no warp was present was verified by the observation that the $(1-1)$ width was independent of the width of the x-ray beam.

The cone bearing on the spindle of the spectrometer which supported the second crystal was adjusted in the following manner. One of the mirrors of a Michelson interferometer was placed in the second crystal holder parallel to, and on, the axis of rotation.[4] If the spindle were loose, the fringes would not return to their original position when the table was pushed backward or forward and released.

Before the Michelson mirror was removed, a telescope with a Gauss eyepiece was placed perpendicular to the spectrometer axis with the aid of the mirror. The calcite crystal was substituted for the interferometer mirror and adjusted parallel to the axis of rotation by means of the telescope. Thus the reflecting surface of the crystal was on the axis of rotation within 0.01 mm and parallel to it within 15 seconds.

The next adjustment was that of setting the first crystal parallel to the second. This was accomplished by placing the crystals in the $(1-1)$ position and adjusting until a strong x-ray line was reflected onto a fluorescent screen. If the crystals were not parallel, the line came in from the top or bottom and disappeared at the bottom or top as the second crystal was rotated. The first crystal was tilted until the line came in uniformly from the side. A final adjustment was then made by obtaining the minimum width of the $(1-1)$ rocking curve.

Sixty cycle a.c. was supplied by a generator driven by a d.c. motor operated from the campus supply. The speed control described in another paper[5] was used to maintain the primary voltage constant to 0.1 percent. Four oil-immersed kenotrons rectified the high voltage and a 0.5 mfd condenser was used to reduce the voltage ripple. The high voltage was measured by a microammeter in series with a 50 meghom Taylor resistance. The filament of the broad-focus cathode was operated from a transformer.

It is well known that second to variations of supply voltage, the small changes of gas pressure in an x-ray tube are the chief cause of variations of the intensity of the x-rays. Such bursts of gas cause a variation in the flow of thermionic current in the tube. Two methods have been tried in an effort to overcome this difficulty. In the first method the potential drop through a resistance connected in series with the x-ray tube was partially balanced by a battery and the residual voltage applied to the grid of a thyratron tube which paralleled the resistance in the primary of the filament transformer. The intensity could be controlled to one percent when the filament transformer was supplied by 500-cycle current and the 0.5 mfd condenser was employed in the high voltage circuit. The arrangement was not satisfactory when 60-cycle current was used and the condenser was disconnected.

A more convenient and equally effective method is the balanced x-ray filament high voltage circuit. Although this circuit has previously been given in the literature,[6] it has not been widely used and the principle of operation has not been described so far as the authors are aware. Fig. 1 gives the diagram of the circuit.

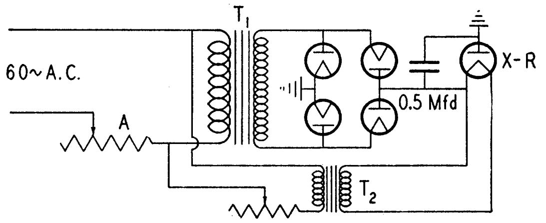

FIG. 1. Balanced x-ray filament-high voltage circuit.

This arrangement is designed to correct for changes of space charge, charges on the walls of the tube and minute changes of gas pressure. If for any of these reasons the current through the x-ray tube increases, the reaction through the high voltage transformer T_1 is such as to increase the current through the primary circuit, thus decreasing the voltage across the filament transformer. The cooling of the filament which results reestablishes the normal current through the x-ray tube. In like manner a decrease of current through the tube produces the reverse reaction. The optimum value of the resistance A depends, of course, upon the reactance of the transformer

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[4] J. A. Bearden, Phys. Rev. **37**, 1210 (1931).

[5] J. A. Bearden and C. H. Shaw, Rev. Sci. Inst. **5**, 292 (1934).

[6] J. A. Bearden, Phys. Rev. **29**, 20 (1927).

T_1 and the impedance of the x-ray tube. For most x-ray circuits a resistance of not less than 4 ohms has been found satisfactory.

The copper target of the x-ray tube was mounted rigidly and permanently in a vertical position. The target was cut at an angle of 12 degrees with the horizontal and the focal spot thus acted as the first height limiting slit for the spectrometer. The glass body of the tube could be lowered over the target and the ground joint between tube and target made tight with picein wax. This arrangement made possible the change of targets without disturbing its alignment with the crystals of the spectrometer. Those metals which could be electroplated, namely Cr, Mn, Fe, Co, Ni and Zn were plated onto the target from solutions of chemically pure salts. The Ti, Va and Ge metals were finely divided either by crushing or filing and a small quantity pounded into the copper face of the target. Thermal contact between the powdered metal and the water-cooled copper was sufficient to prevent melting except in a few small regions. About 70 percent of the target was covered by the metal. Two samples each of Ti and Va were used: One Va sample was a 92 percent commercial alloy containing 2 percent Mo, 2 percent Fe and small amounts of other metals, and the other sample of Va was 99.7 percent pure with traces of Fe and Si (0.1 percent each). The first sample of Ti was of unknown purity and the second was exceptionally pure—spectroscopically free of Fe. Since Ga has a melting point of 30°C and a boiling point of 2000°C, it can be used in an x-ray tube even though it is in the liquid state. A small quantity of Ga metal was rubbed onto the copper target, to which it adhered, although there was no evidence of amalgamation.

For all the work with the first crystal in the first order, the first slit (projection of the focal spot) was 1 mm high, the second was 8 mm and they were separated by 53 cm. For the curves taken in the $(2+2)$ order the second slit was reduced to 3 mm. No slits were used to limit the horizontal divergence of the incident beam.

The ionization chamber was constructed of iron,[7] carefully sandpapered inside and filled with argon. Alpha-particles were recorded about five minutes apart on the average. The ionization current was measured by an FP54 pliotron arranged in the circuit described by DuBridge and Brown.[8] A leakage resistance of 10^{11} ohms was used. In measuring the weakest lines (ionization current of 10^{-14} amp.) a voltage sensitivity of 200,000 mm/volt was employed. Such readings were accurate to two percent.

The ionization current circuit was constructed so that either an electrometer or the vacuum tube could be used to measure the ionization current. For the measurement of strong lines the vacuum tube has two main advantages over the electrometer. First, the direct deflection method is more convenient and permits of greater speed in the making of observations, which greatly reduces the errors due to slow shifts in the apparatus. Second, since the sensitivity may be varied easily, a change from the measurement of a weak line to the measurement of a strong line can be accomplished without altering the operating conditions of the x-ray tube.

For weak lines there is still some question as to which method is more precise. In either the electrometer or the vacuum tube method there are two principle limitations on the accuracy of measurement of an ionization current. The first of these is the statistical variation in the number of ionizing particles produced in the chamber by the entering radiation. For ionization currents of 10^{-14} ampere and for a time of observation of one minute the average deviation from the mean is about 0.5 percent. The second limitation is the random emission of alpha-particles from radioactive contamination on the walls of the chamber. If an electrometer is being used to measure the ionization current, the longer range alpha-particles may be detected; however, the average range particles cannot be detected and will therefore contribute an appreciable error to any given reading. Because of its high sensitivity, the vacuum tube possesses the advantage that even short range alpha-particles may be detected and their effect eliminated from the reading. In the case of the vacuum tube, the period of the galvanometer and the electrical time constant of the grid circuit are usually about fifteen seconds. This would increase the average deviation of readings except for the

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

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

fact that a greater effective time of observation may be obtained by observing the fluctuations of the galvanometer and estimating the average position. This method was found to be satisfactory for times of observation up to two minutes.

In the present experiments it was found that ionization currents of 10^{-14} ampere could be measured about equally well with either the electrometer or the vacuum tube. The convenience of operation of the vacuum tube system, however, made its use preferable for the measurement of both strong and weak lines.

Study of Crystals

Several pairs of calcite crystals were tested before a pair giving the $(1-1)$ width predicted by theory[9] was found. The effect of etching with HCl was also tried and was found to decrease the $(1-1)$ width within about 5 percent of the theoretical value at 1.54A. Table I gives the treatment and $(1-1)$ width in seconds for Cu $K\alpha$ radiation (1.54A) for the several pairs of crystals tested.

TABLE I. *Effect of treatment on (1−1) width at 1.54A for several different pairs of calcite crystals.*

Origin of crystals	Treatment	Width $(1-1)$ (seconds)
Montana I	ground and polished	38
	Wash HCl	11.1
	Repeat	11.1
Montana II	cleaved	11.5
	Wash HCl	10.4
Spain I	cleaved	10.2
Spain II	cleaved	11.0
Iceland	cleaved	10.4
Argentina	cleaved	9.8

The Argentina pair of crystals was used in all the subsequent work in the present paper. No change of $(1-1)$ width could be found over a period of a year. A further test of the Argentina crystals was made by observing the $(1-1)$ width as a function of wavelength from 1.1A to 2.5A. Fig. 2 shows the results. The open circles represent the theoretical width of perfect calcite crystals as calculated by Allison and Parratt.[9] It is apparent that these crystals are as "perfect" as any previously used.

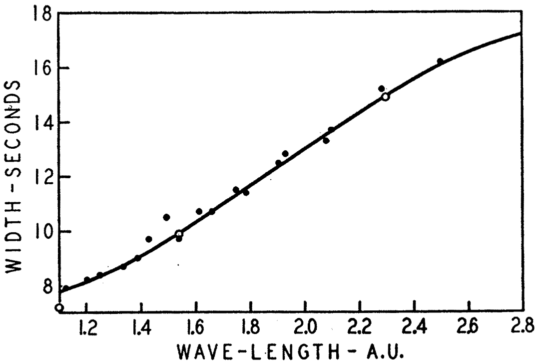

FIG. 2. Rocking curve widths at half-maximum as a function of wavelength for crystals employed in the present work. The open circles are theoretical values.

In order to utilize the full resolving power of the crystals, the slits limiting the vertical divergence should be of such heights that the geometrical resolving power is not less than the resolving power of the crystals themselves. The geometrical resolving power for the double crystal spectrometer is given by[10]

$$\lambda/d\lambda = 4/\varphi_m^2, \tag{1}$$

where φ_m is the maximum vertical divergence in radians from the central ray. In the present apparatus for the $(1\pm n)$ order the geometrical resolving power was 50,000, and was increased to 250,000 in the $(2+2)$ order by narrowing the second vertical slit to 3 mm.

In the $(n+n)$ positions the physical resolving power of the crystals is expressed by[11]

$$\lambda/d\lambda = \lambda D/w, \tag{2}$$

where D = dispersion and w = full width in radians at half maximum of the rocking curve in the $(n-n)$ position. The full width of the $(2-2)$ curve was measured for Cu $K\alpha$ (1.54A) and Ge $K\alpha$ (1.25A) and found to be 2.4″ and 1.7″, respectively. The physical resolving power in the $(1+1)$ position is 11,000 for Cu $K\alpha$ and 10,000 for Ge $K\alpha$, while in the $(2+2)$ order it is 100,000 in both cases. Thus it is seen that the resolving power in all cases is limited by the diffraction patterns of the crystals.

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[9] S. K. Allison, Phys. Rev. **41**, 1 (1932); L. G. Parratt, Phys. Rev. **41**, 561 (1932).

[10] L. G. Parratt, Phys. Rev. **46**, 749 (1934).

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

TABLE II. *Widths at half-maximum of K series lines in seconds.*

LINE	ORDER	Ge	Ga	Zn	Cu	Ni	Co	Fe	Mn	Cr	Va	Ti
$K\alpha_1$	$1-2$	18.3	19.9	22.4	25.3	28.1	37.2	48.7	59.0	61.4	76.0	
	$1+1$	31.8	33.0	36.9	39.9	43.8	55.5	68.4	76.5	75.5	75.6	80.9
	$(1+1)^{12}$					50.5		73.5	80	80	86	94.5
	$(1+1)^{13}$	30		36	41	45	58	72				
	$1+2$	43.6	47.0	51.0	56.5	61.5	81.1	104.2	122.8			
	$1-3$			49.4								
	$1+3$			79.2								
	$2-1$				25.7							
	$2+1$				56.7							
	$2+2$	55.5			72.5							
$K\alpha_2$	$1-2$	18.7	19.9	25.3	32.8	36.8	45.3	56.8	65.9	79.0	104.3	
	$1+1$	33.9	34.6	43.1	51.5	59.0	69.6	80.1	89.8	90.4	99.5	109.7
	$(1+1)^{12}$					64		85	95	103	114	121
	$(1+1)^{13}$	32		41	54	58	67	76				
	$1+2$	45.4	49.0	60.9	77.9	87.4	105.6	123.9	144.4			
	$1-3$			58.5								
	$1+3$			95.5								
$K\beta_{1,3}$	$1-2$	32.0	34.0	38.0	42.5	46.3	50.0	48.2	53.6	58.0	71.5	
	$1+1$	57.2	59.3	63.5	72.5	75.7	77.8	73.2	76.5	77.4	87.4	110.2
	$1+2$	83.6	88.5	94.5	109.6	112.5	113.8	110.3	115.9	119.6		
$K\beta_{2,5}$	$1+1$	37.0	64.3	91.0	——	99.2	115	119	139.3	135.0	141	

RESULTS

Widths of lines

The widths of the $K\alpha_1(K-L_{\text{III}})$, $K\alpha_2(K-L_{\text{II}})$ and $K\beta_{1,3}(K-M_{\text{II, III}})$ lines were measured in the $(1-2)$, $(1+1)$ and $(1+2)$ positions and in general were found to be slightly different in the various orders. The low intensities of the $K\beta_2(K-N_{\text{II, III}})$ and $K\beta_5(K-M_{\text{IV, V}})$ lines allowed them to be measured in the $(1+1)$ order only. Four determinations were made of each line width and in general the maximum variation was not greater than one percent. No attempt was made to resolve the $K\alpha$ lines into components because not enough information on their shapes is available to perform the resolution in an analytical manner.

The widths of the K series lines obtained in the present work are shown in Table II together with measurements made by previous investigators.[12, 13] The only previous results for which accuracy was claimed are those by Allison and Parratt. In both cases the α_1 and α_2 lines only were studied in the $(1+1)$ order. Parratt's results are in every case wider than the present measurements. For Ti $K\alpha_1$ his value is about 14 seconds wider than the present width. This point has been rechecked with the two different samples of Ti mentioned before and has also been measured on our apparatus with Parratt's target and in each case the width was 81.0±0.4 seconds. Some of Allison's values are lower than those obtained in the present work, but the differences lie within the estimated experimental errors.

Fig. 3 shows the variations of the line widths in volts with atomic number. It is apparent that in this atomic number region such curves are not simple functions. The various maxima and minima observed seem without doubt to be real.

On referring to Fig. 4 it will be seen why the curves in Fig. 3 for the $\beta_{1,3}$ line rise for higher atomic numbers. The β_1 and β_3 lines are just beginning to show a separation at Ni 28, and at Ge 32 the dual characteristic is quite apparent. For lower atomic numbers the α lines are somewhat wider than the component lines because here the resolution is not complete.

A correction was made for the effect of the $K\beta_{1,3}$ doublet on the shape of the $K\beta_2$ and $K\beta_5$ lines. The intensity curve was carried to several minutes of arc on either side of the weaker line and the base line drawn in. Subtraction of this base line from the observed curve gave the shape of the line. Because this base line cannot be determined very accurately, the estimated error in the width of $K\beta_{2,5}$ is 5 percent. Since the $K\beta_{2,5}$ line for Cu 29 is an unresolved doublet the width is abnormally large, being 125 seconds. So far as these experiments show, the line $K\beta_2$ is entirely absent from Ti 22 to Ni 28, leaving $K\beta_5$ as the strong line in this region. At Cu 29 the doublet structure indicates the appearance of $K\beta_2$, which is as yet relatively weak. At Zn 30 the intensity of the $K\beta_5$ line has decreased markedly and the intensity of the $K\beta_2$ line in-

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[12] L. G. Parratt, Phys. Rev. **44**, 695 (1933).

[13] S. K. Allison, Phys. Rev. **44**, 63 (1933).

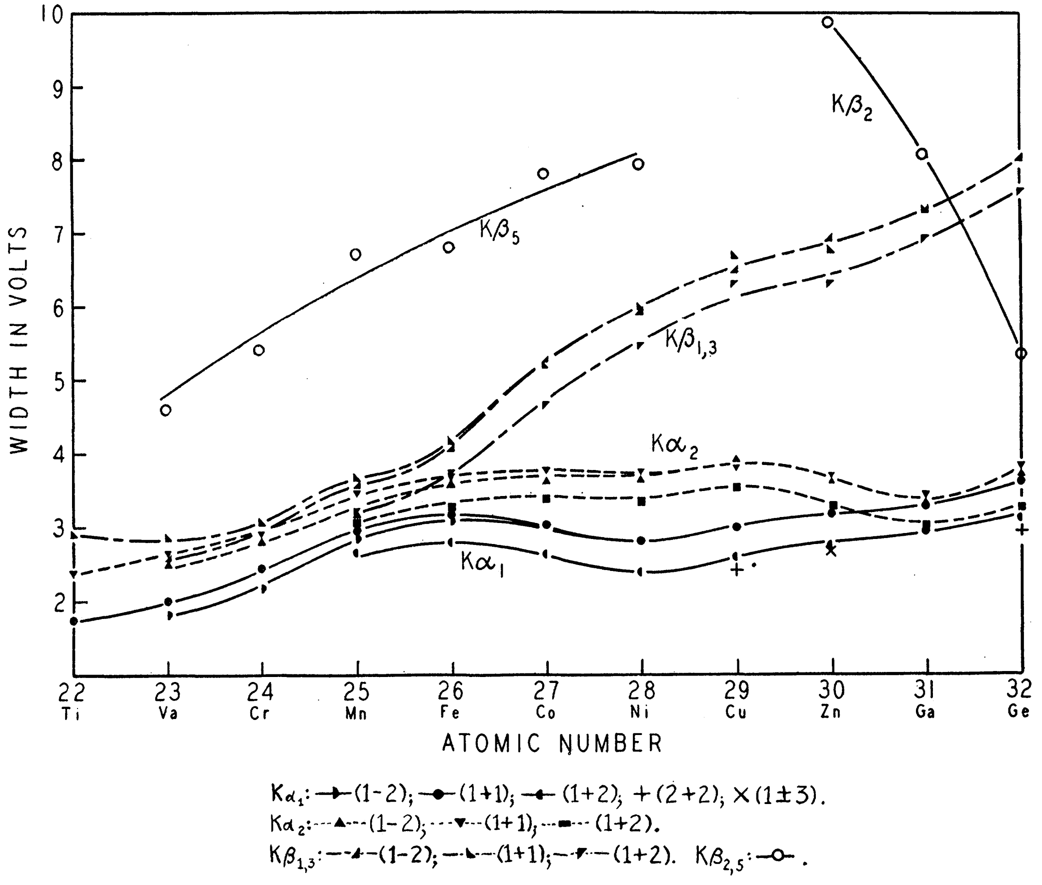

FIG. 3. Widths at half-maximum of lines as a function of atomic number.

creased so that the relative intensities are reversed. Fig. 5 shows these lines for several elements.

It will be observed that for lower atomic numbers the width curve for the $(1-2)$ order lies below that for the $(1+1)$ order, while at higher atomic numbers they coincide. This indicates that the resolving power for lower atomic numbers in the $(1-2)$ order must be greater than that in the $(1+1)$ in spite of the decreased dispersion. The resolving power in the $(1+1)$ and $(1-2)$ for the Cu $K\alpha$ and Ti $K\alpha$ wavelengths may be calculated as follows. Eq. (2) requires the width of the rocking curve in the parallel position. For the calculation of the resolving power in the $(1+1)$ position we use the width in the $(1-1)$ order. In the (1 ± 2) positions, however, the value to use is not obvious, but it lies somewhere between the $(1-1)$ and $(2-2)$ widths. To obtain the width of the single crystal diffraction pattern from the width of the $(n-n)$ curve, it has been assumed that the former is of the Gaussian error shape.[11] On this assumption the width of the single crystal diffraction pattern in the nth order is given by

$$w_a = w_{(n-n)}/\sqrt{2}$$

and the w value (Eq. (2)) in the (1 ± 2) order should be the square root of the sum of the squares of the first and second order single crystal diffraction patterns. For Cu $K\alpha$ radiation this becomes

$$\begin{aligned} w &= [w^2_{(1-1)}/2 + w^2_{(2-2)}/2]^{\frac{1}{2}} \\ &= [(9.8)^2/2 + (2.4)^2/2]^{\frac{1}{2}} = 7.1 \text{ sec.} \end{aligned}$$

The $(1-1)$ width for Ti $K\alpha$ is about 17.4″ (Fig. 2). If we arbitrarily choose 5″ for the $(2-2)$ width, the value of w is about 12.5″. Using these values the resolving powers as calculated are shown in Table III.

Thus the resolving power in the $(1-2)$ and

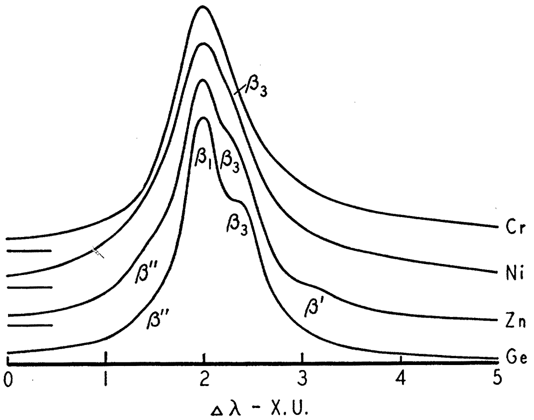

FIG. 4. $K\beta_{1,3}$ doublet. No separation can be seen for atomic numbers less than Ni 28.

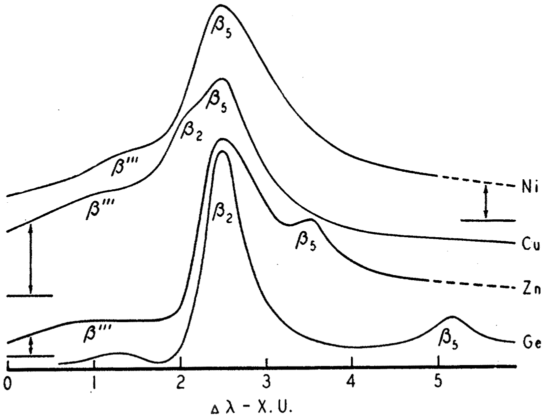

FIG. 5. $K\beta_2$ and $K\beta_5$. $K\beta_2$ was not observed for atomic numbers less than Cu 29.

TABLE III. *Resolving power of crystals employed.*

Order \ λ	1.54A	2.74A
1+1	11,000	12,000
1−2	9,200	26,000
1+2	24,000	42,000

(1+1) are the same for the higher atomic numbers and the curves should be of the same width, while at the lower atomic numbers the resolving power of the (1−2) is considerably greater than that of the (1+1) and the width is correspondingly less. Whether one assumes a Gaussian, classical[14] or other reasonable shape for the single crystal diffraction pattern, probably leaves these general conclusions unaltered.

Asymmetries of lines

The index of asymmetry of an x-ray line has been defined[13] as the ratio of the part of the full width at half-maximum lying to the long wavelength side of the maximum ordinate to that on the short wavelength side. Four independent determinations of each index were made and the average deviation from the values listed in Table IV was usually not greater than 2 percent. Especial care was taken in the measurement of the asymmetry of Fe $K\alpha_1$ in the three orders and the error is thought to be not greater than one percent.

Fig. 6 shows a graph of the variation of the index of asymmetry with atomic number. Here again the curve for the β-line rises sharply for

TABLE IV. *Indices of asymmetry of K series lines.*

Line	Order	Ge	Ga	Zn	Cu	Ni	Co	Fe	Mn	Cr	Va	Ti
$K\alpha_1$	1−2	1.03	1.08	1.08	1.11	1.12	1.28	1.54	1.41	1.32	1.18	
	1+1	1.04	1.05	1.12	1.13	1.22	1.39	1.61	1.52	1.37	1.27	1.24
	(1+1)[12]					1.35		1.65	1.60	1.30		
	(1+1)[13]				1.4	1.1	1.5	1.8				
	1+2	1.06	1.08	1.06	1.15	1.22	1.40	1.66	1.52	1.48		
	1−3			1.04								
	1+3			1.08								
	2−1				1.12							
	2+1				1.12							
	2+2	1.04			1.10							
$K\alpha_2$	1−2	1.08	1.10	1.19	1.20	1.18	1.25	1.22	1.13	1.00	0.87	
	1+1	1.10	1.20	1.33	1.31	1.19	1.30	1.26	1.20	1.03	0.94	0.84
	(1+1)[12]					1.35		1.40	1.35			
	1+2	1.11	1.14	1.34	1.29	1.21	1.30	1.30	1.24			
	1−3			1.30								
	1+3			1.32								
$K\beta_{1,3}$	1−2	2.00	1.79	1.43	1.17	1.23	1.67	1.64	1.36	1.45	1.46	
	1+1	1.96	1.83	1.48	1.09	1.30	1.68	1.75	1.40	1.53	1.54	1.73
	1+2	2.09	1.78	1.67	1.19	1.32	1.78	1.81	1.42	1.57		
$K\beta_{2,5}$	1+1	1.21	2.93	3.02	——	1.75	2.06	2.44	2.34	2.54	2.90	

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

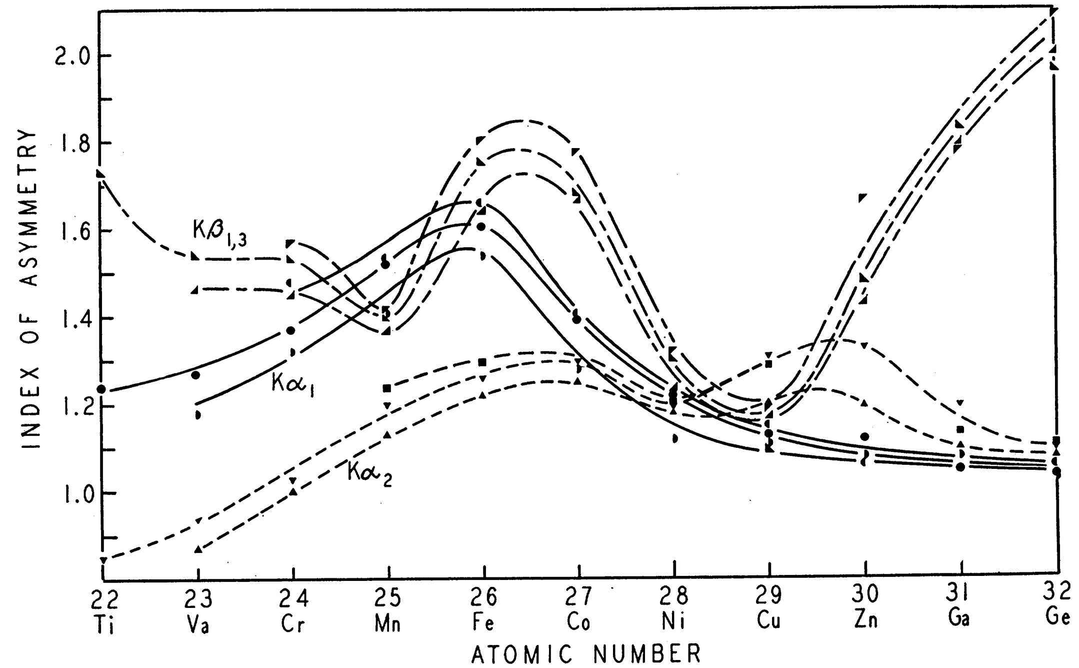

FIG. 6. Indices of asymmetry of lines as a function of atomic number. See Fig. 3 for legend.

high atomic numbers because β_1 and β_3 are not of the same intensity (Fig. 4). The indices for low atomic number are somewhat too high for the α_1-lines and too low for the α_2-lines because the lines are not completely resolved. The variation of asymmetry with order of diffraction increases in the order $(1-2)$, $(1+1)$, $(1+2)$. This is contrary to what one would at first expect since the single crystal diffraction pattern in the second order is certainly much narrower than that in the first order. A possible explanation may be the following: As the crystal is rotated to obtain the intensity curve in any given order the two single crystal patterns slip over one another and give a contribution at any particular point equal to the integral of the product of the two curves. The theoretical single crystal diffraction patterns are not symmetrical[9] and the asymmetry is in the direction to augment the true line asymmetry. In the $(1-1)$ position the theoretical patterns are equal and oppositely superimposed, so that all asymmetry disappears. In the $(1+1)$ order the patterns are superimposed in the same direction and the asymmetry is correspondingly greater. Assuming that the first and second order single crystal diffraction patterns have different degrees of asymmetry we find the situation is somewhat altered in the (1 ± 2) orders. In the $(1-2)$ order the two patterns are superimposed oppositely so that the asymmetry of the one partially nullifies that of the other, and the curve is more nearly symmetrical than that in the $(1+1)$. Bearing in mind the manner in which these curves combine, let us examine the conditions in the $(1+2)$. Although the second order single crystal pattern is narrower than that of the first, a greater degree of asymmetry of the second order pattern may possibly be the determining factor in fixing the crystal contribution to the asymmetry of the measured line. On this interpretation, then, the present data indicate that the second order single crystal diffraction pattern is more asymmetrical than the first. It will be noticed from Table IV that for both Cu 29 and Ge 32 the $(2+2)$ asymmetry is less than the $(1+2)$ value. In this case, apparently, the single crystal patterns are so narrow that the degree of asymmetry no longer plays an important part in determining the line shape. It is interesting to note that the ratio of $(1+1)$ width to $(1-1)$ is 4, while that of the $(2+2)$ to the $(2-2)$ is about 30.

Attention is called to the fact that Ga 31 was used in the liquid state, while the other elements were in the solid state. The curves show no marked irregularity for either width or asymmetry for Ga, indicating that the state has little influence on the widths of the K series lines in this particular region of atomic number. This is probably not true for the lower atomic number elements because the electrons involved in the K transitions are not so well shielded from external influence. It seems reasonable that the same factors would be involved in any observed change of width with state as are involved in the alloy effect.[15] Since no change with state was observed for Ga one would expect that the alloy effect would likewise be negligible. The Ge 32 metal used was of unknown purity, but for these reasons it is thought that the widths and asymmetries are within experimental error of those for pure Ge.

No difference greater than the experimental error was detected for the widths and asymmetries of the $K\alpha$ and $K\beta$ lines of the pure and impure samples of Ti 22 and Va 23.[16] It is possible that the particular kind of impurity present affected the widths of the lines very little, or that the effect produced by one impurity was cancelled by that of another.

The question of the origin of the asymmetry of the lines was raised by Seljakow, Krasnikow and Stellezky.[1] They suggested that there might be some connection with the fact that the M shells are being filled in the region from Sc 21 to Cu 29, where their experiments indicated that the asymmetry disappears. Inspection of Fig. 6 shows that the asymmetry is greater than unity for elements whose M shells are filled, namely, Cu, Zn, Ga and Ge. If the crystals were contributing greatly to the asymmetry in this region one would hardly expect the asymmetry to be changing with wavelength or atomic number to any appreciable extent. Thus it appears that there is little or no connection between the degree to which the inner shells are filled and the asymmetries of the lines. In all probability the answer will be found in asymmetries of the energy levels.

A test of the dependence of the width and asymmetry on the exciting voltage was also made for the Fe $K\alpha_1$ line using the filtered supply. No change greater than the experimental error of one percent was found from 10 kv to 35 kv or greater than the error of 5 percent at 8 kv, which is only 15 percent above the excitation potential.

Satellites

Accompanying the β_1 and β_5-lines were certain satellites, some of whose characteristics could be measured roughly. Table V gives the widths of the satellites at half maximum and the ratios of the areas of the adjacent line to that of the satellite. The strongest and most easily measured of these lines was the β' line on the long wavelength side of $\beta_{1,3}$. In general it was possible to measure this line in two or three orders. No β' satellite was detected in any order for Ti, Va, Cr, Ni or Ge. The next most prominent of the satellites measured, β'', was observed for the elements of higher atomic number only and to the short

TABLE V. *Satellite widths at half-maximum and intensities relative to an adjacent diagram line.*

ELEMENT	ORDER	WIDTH (X.U.)	RATIO AREAS $\beta_{1,3}/\beta'$
		β' LINE	
Mn	$1-2$	1.5	32
	$1+1$	1.5	30
	$1+2$	1.2	73
Fe	$1-2$	1.5	55
	$1+1$	1.4	73
Co	$1-2$	0.83	82
	$1+1$	.77	98
	$1+2$	.75	89
Ni	None		
Cu	$1-2$	.38	100
	$1+1$	.55	73
	$1+2$	.52	75
Zn	$1+1$	.32	220
	$1+2$	.25	200
Ga	$1+1$	.25	400
	$1+2$	.25	400
Ge	None		
		β'' LINE	
			$\beta_{1,3}/\beta''$
Cu	$1+2$	.36	120
Zn	$1+1$	.29	120
	$1+2$	.33	60
Ga	$1+1$	.36	81
	$1+2$	.29	60
Ge	$1-2$	.29	100
	$1+1$	.33	87
	$1+2$	.30	95
		β''' LINE	
			β_5/β'''
Mn		.47	280
Fe		.88	65
Co		.58	100
Ni		.62	70
Cu		1.1	—
			β_2/β'''
Zn		1.1	15
Ga		None	
Ge		.58	17

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[15] L. G. Parratt, Phys. Rev. **45**, 364 (1934).

[16] However, a sample of MnO_2 gave the $K\alpha_1$ width 15 percent higher than that from pure Mn.

wavelength side of the $\beta_{1,\,3}$ doublet. No trace of this satellite was found from Ti 22 to Ni 28. The intensity relative to the $\beta_{1,\,3}$ doublet is substantially constant in this range. The satellites, β''', accompanying the $\beta_{2,\,5}$ lines were very difficult to measure. The maximum ionization current due to the satellite was not much greater than 10^{-15} ampere so it was necessary to measure the region of the satellite several times. The satellites as well as the $\beta_{2,\,5}$ lines themselves could be measured in the $(1+1)$ order only. The intensity for the Ga $K\beta_2$ line was so weak that it was impossible to detect the satellite. However, in the case of Cr 24 the satellite should have shown up if it existed. No indication of its presence was found.

Wavelengths

Glancing angles corresponding to the peaks of the lines were measured in both first and second orders from the second crystal. For those lines showing structure the position of maximum intensity was measured. At the present time line shapes are not known with sufficient accuracy to allow components to be drawn. It is very probable that the components are not symmetrical in any case and in order to locate the peaks of the components one must know something about the degree of asymmetry and either their widths or separation.

In determining a glancing angle the position of the peak was taken alternately in the $(1\pm n)$ order until three independent determinations of the angle had been made. The temperature of the crystals was read to 0.1°C at every determination and usually did not change during a complete observation by more than 0.3°C. The angle between the $(1+n)$ and $(1-n)$ positions with 180° subtracted represented twice the diffraction angle. Three corrections must be applied to the measured angle in order to obtain the Bragg angle θ: (1) The temperature correction for crystal expansion; (2) the correction due to slit height; and, (3) the calibration correction of the divided circle.

The linear coefficient of expansion, 1.02×10^{-5} per °C, computed by C. D. Cooksey and D. Cooksey[17] was used to reduce the measured angle to the angle corresponding to 18°C, as follows,

$$d\theta''=2.10\ (t-18)\tan\theta.$$

The slit correction was made from the expression[18]

$$d\theta''=2\times10^5[(a^2+b^2)/24L^2]\tan\theta,$$

where a and b are the heights of the two slits and L is their distance apart.[19] The circle correction was made from the calibration curve as described above.

The crystals used were taken from the same sample of Argentina calcite that Bearden used to determine the grating space of. calcite.[20] The density was found to be within experimental error of the average $\rho=2.71030$ g/cc at 20°C of several crystals from widely different localities. At 18°C this increases to $\rho=2.71046$ g/cc according to the linear expansion coefficient found by Cooksey.[17] The grating space as computed by Bearden[20] is $d_\infty=3.02810$A at 18°C on the assumption of Millikan's value for $e=4.768\times10^{-10}$ e.s.u.

The determination of the true value of the grating constant of any crystal depends essentially on the value assigned to the electronic charge, which is not accurately known. Since diffraction angles can be measured to 0.001 percent most writers have used for calcite the arbitrarily assumed grating constant $d_\infty=3.02945$A. The ruled grating wavelength measurements of Bearden[4] differ from those obtained with calcite crystals by about 0.22 percent.[21] These values

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[17] C. D. Cooksey and D. Cooksey, Phys. Rev. **36**, 85 (1930).

[18] J. H. Williams, Phys. Rev. **40**, 636 (1932).

[19] See, however, Compton and Allison, *X-Rays in Theory and Experiment*, p. 737, where it is concluded that any correction for slit height is meaningless. Parratt has recently shown (Phys. Rev.) that Williams' correction should be

$$d\theta''=2\times10^5[(a+b)^2/24L^2]\tan\theta.$$

If this correction formula is used instead of the one above the Ge $K\alpha_1$ result in the first order is lowered by one part in 400,000, while the Ti $K\alpha_1$ value in the second order is lowered by one part in 200,000. Compton and Allison point out that a correction should be made for the effect of the asymmetry of the single crystal diffraction pattern on the position of the peak of the measured line. The correction is in such a direction as to *increase* the measured wavelength and is uncertain because these asymmetries are not accurately known.

[20] J. A. Bearden, Phys. Rev. **38**, 2089 (1931).

[21] E. Bäcklin, Nature **135**, 32 (1935). With improved experimental technique he now finds for the Al $K\alpha$ line

$$\frac{\lambda\ \text{grating}-\lambda\ \text{crystal}}{\lambda\ \text{crystal}}=0.218\ \text{percent}$$

instead of the 0.14 percent as previously found. The new value agrees very satisfactorily with the value obtained by Bearden.[4]

have also been confirmed by refraction measurements on quartz[22] and on diamond.[23] The value of the calcite grating constant calculated from the ruled grating measurements is $d_\infty=3.03560$A. This is probably a much more precise value of the grating constant than can be obtained from the usual crystal constants. Since ruled grating experiments are in progress from which a more accurate value of d_∞ may be obtained, it was thought best to retain the Siegbahn arbitrary value for the present computations. Thus all wavelengths in the present paper have been calculated with the following values of the grating constant

$$d_1=3.02904\text{A}, \qquad d_2=3.02934, \qquad d_3=3.02940.$$

Beyond 2.3A the correction for anomalous dispersion becomes appreciable and was made according to Siegbahn.[24] For shorter wavelengths the corrective term for refractive index was taken as $\delta/\lambda^2=3.69\times10^{-}.^{6}$

Tables VI and VII give the wavelengths of the K series lines of the various elements together with previous results from single crystal photographic spectrometer work. Very little seems to have been done on second order measurements and consequently not many comparisons can be made. In the present work the agreement between the results obtained in the first and second orders indicate the high accuracy that has been attained by this method. It will be seen that the single crystal measurements of previous investigators are generally in satisfactory agreement with the new values except for Ti and Va. The previous measurements on Ti and Va for which the highest accuracy was claimed are those of v. Friesen.[25] For the Ti $K\alpha_1$, $K\alpha_2$, $K\beta$ lines his values are, respectively, about 10″, 5″ and 6″ higher than the results in the present experiments. The angular separation of the Ti $K\alpha_1$ and $K\alpha_2$ was carefully measured and found to be 279.0″ in the (1+1) position, whereas v. Friesen obtained a value corresponding to 270″. These disagreements were so great that the measurements were repeated quite carefully. The diffraction angle obtained by v. Friesen for Va $K\beta_5$ is 37″ greater than that from the present work. In view of the repeated measurements and also the fact that our Va $K\beta_5$ value is within experimental error of the $(\nu/R)^{\frac{1}{2}}$ curves, it appears that v. Friesen's measurements are in error.

Attention should also be called to the determinations for Ge 32 and Ga 31. The accuracy for Ge has been considerably increased, as judged by the agreement between first and second orders. The last measurement on the K series of Ga was made in 1917 by Uhler and Cooksey[26] with an estimated accuracy of a few seconds of arc.

The arrangement of apparatus was such that the ionization chamber could not be carried to a large enough angle to observe the (1+2) order of Ti 22 and Va 23, although the (1−2) order could be measured. To measure the second order diffraction angle in these cases the following procedure was used. The angle between the (1−1) and (1−2) positions was measured. The first-order diffraction angle was added to this measured angle, after making the necessary allowance for slit and temperature correction, thus giving the second-order diffraction angle. The appropriate slit and temperature corrections were then applied to this resultant angle.

The $(\nu/R)^{\frac{1}{2}}$ values for the $K\alpha_1$ lines in the present work vary from a smooth curve by an average deviation of 0.001 percent, while the deviation in previous work is about 0.003 percent. This indicates that greater accuracy has been achieved by the double crystal spectrometer than with the photographic spectrometers.

No attempt has been made to correct the diffraction angles for the overlapping of the α_1 and α_2 lines. In the case of the β_1 line the diffraction angles for the elements Ni 28 to Ge 32 are too large, because of the doublet characteristic of the line. The intensity of the $K\beta_5$ line was so low for Ga 31 that it could not be measured. As previously mentioned, the Cu 29 $K\beta_{2,\,5}$ is a doublet and here the longer wavelength component has been assumed to be the β_5 line. In the region from Va 23 to Ni 28 the present values of the wavelengths of $K\beta_5$ are lower than previous measurements have indicated. This may be due to the

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[22] J. A. Bearden and C. H. Shaw, Phys. Rev. **46**, 759 (1934).

[23] J. A. Bearden, Phys. Rev. **47**, 811 (1935).

[24] M. Siegbahn, *Spectroscopie der Röntgenstrahlen*, 2nd ed., p. 45.

[25] S. v. Friesen, Zeits. f. Physik **58**, 781 (1929).

[26] H. S. Uhler and C. D. Cooksey, Phys. Rev. **10**, 645 (1917).

TABLE VI.

		$K\alpha_1$ line—KL_{III}				$K\alpha_2$ line—KL_{II}			
		First order		Second order		First order		Second order	
El.	Obs.	$\theta_{18^\circ\mathrm{C}}$	λ	$\theta_{18^\circ\mathrm{C}}$	λ	$\theta_{18^\circ\mathrm{C}}$	λ	$\theta_{18^\circ\mathrm{C}}$	λ
Ti	I	26°55′15.0″	2.742866A	64°52′54.5″	2.742872A	26°57′34.5″	2.746518A	65° 2′36.8″	2.746491A
	II	26 55 25.0	2.74311			26 57 39.5	2.74665		
Va	I	24 21 23.1	2.498428	55 33 43.4	2.498417	24 23 45.7	2.502243	55 41 23.1	2.502229
	II	24 21 23.1	2.49842			24 23 44.5	2.50221		
Cr	I	22 9 33.3	2.285000	48 57 45.3	2.284974	22 11 56.3	2.288889		
	III	22 9 34.5	2.285033			22 11 57.0	2.288907		
Mn	I	20 15 25.5	2.097507	43 49 12.3	2.097504	20 17 48.3	2.101442	43 55 24.7	2.101446
	III	20 15 25.4	2.097506			20 17 49.8	2.101489		
Fe	I	18 35 52.4	1.932070	39 37 35.0	1.932049	18 38 13.6	1.936000	39 43 22.7	1.935979
	III	18 35 52.6	1.932075			18 38 14.1	1.936013		
	IV	18 35 52.3	1.932067	39 37 34.8	1.932046	18 38 13.2	1.935989		
	V	18 35 52.7	1.932078						
Co	I	17 8 22.3	1.785314	36 6 35.3	1.785295	17 10 39.8	1.789173	36 12 1.1	1.789158
	III	17 8 21.4	1.785287	36 6 33.2	1.785273	17 10 40.3	1.789187	36 12 1.7	1.789169
Ni	I	15 50 57.3	1.654505	33 6 14.9	1.654512	15 53 12.9	1.658336	33 11 25.9	1.658336
	III	15 50 57.2	1.654503	33 6 9.7	1.654450	15 53 13.5	1.658353	33 11 24.0	1.658315
Cu	I	14 42 4.0	1.537400	30 29 51.6	1.537400	14 44 18.5	1.541220	30 34 53.4	1.541218
		(2±1) order		(2±2) order				(2±2) order	
	I	14 42 4.4		30 29 52.1				30 34 52.8	
	VI	14 42 3.9	1.537397	30 29 51.2	1.537397	14 44 19.3	1.541243		
	V	14 42 4.1	1.537402						
	V	14 42 3.9	1.537397						
Zn	I	13 40 30.1	1.432219	28 12 54.2	1.432218	13 42 44.1	1.436042	28 17 50.8	1.436055
				(1±3) order				(1±3) order	
	I			45 9 59.4	1.432217			45 19 14.7	1.436045
	VII, VIII	13 40 28.4	1.432170			13 42 43.7	1.436032		
Ga	I	12 45 11.4	1.337329	26 11 49.8	1.337337	12 47 27.7	1.341233	26 16 45.9	1.341238
	IX	12 45 5	1.337152			12 47 15	1.340869		
Ge	I	11 55 19.2	1.251478	24 24 3.7	1.251483	11 57 36.7	1.255429	24 28 58.6	1.255426
	VIII, X	11 55 13.0	1.25130			11 57 29.1	1.25521		

TABLE VII.

		$K\beta_{1,3}$ line—KM_{III}				$K\beta_5$ line—$KM_{IV,V}$		$K\beta_2$ line—$KN_{II,III}$	
		First order		Second order		First order		First order	
El.	Obs.	$\theta_{18^\circ\mathrm{C}}$	λ	$\theta_{18^\circ\mathrm{C}}$	λ	$\theta_{18^\circ\mathrm{C}}$	λ	$\theta_{18^\circ\mathrm{C}}$	λ
Ti	I	24°27′48.8″	2.508744A						
	II	24 27 54.9	2.50890						
Va	I	22 6 19.6	2.279730	48°48′40.0″	2.279708A	21 57′12.9″	2.26485A		
	II	22 6 22.0	2.27979			21 57 50.0	2.26586		
Cr	I	20 5 12.1	2.080597	43 22 41.8	2.080587	19 56 42.4	2.06653		
	III	20 5 11.7	2.080586			19 56 49.0	2.06671		
Mn	I	18 20 27.4	1.906301	38 59 46.7	1.906274	18 12 36.3	1.89316		
	III	18 20 23.6	1.906195			18 12 40.0	1.89327		
Fe	I	16 49 11.6	1.752991	35 21 25.3	1.752987	16 41 48.7	1.74054		
	III	16 49 12.5	1.753013			16 41 58.0	1.74080		
Co	I	15 29 8.1	1.617483	32 16 18.8	1.617479	15 22 7.6	1.60558		
	III	15 29 6.5	1.617436			15 22 9.0	1.60562		
Ni	I	14 18 26.0	1.497080	29 36 57.2	1.497048	14 11 40.3	1.48553		
	III	14 18 24.8	1.497045			14 11 43.0	1.48561		
Cu	I	13 15 29.7	1.389364	27 17 57.9	1.389378	13 9 2	1.37828		
	VI	13 15 29.2	1.389349			13 9 0.6	1.378236		
Zn	I	12 19 11.6	1.292610	25 15 29.2	1.292609	12 13 8	1.28220	12°12′29.4″	1.281067A
	VII	12 19 9.3	1.292546			12 12 58	1.2819	12 12 29.4	1.281068
Ga	I	11 28 37.4	1.205409	23 26 52.6	1.205422			11 21 45.2	1.19354
	IX	11 28 30	1.20520					11 21 54.0	1.1938
	VIII	11 28 38.0	1.20543						
Ge	I	10 43 3.6	1.126618	21 49 59.4	1.126627	10 37 36	1.1172	10 36 6.0	1.11457
	VIII, X	10 43 6.8	1.12671			10 37 44	1.1174	10 36 8.2	1.11463

Tables VI, VII. I—Present results; II—Sten v. Friesen, Zeits. f. Physik **58**, 781 (1929); III—S. Eriksson, Zeits. f. Physik **48**, 360 (1928); IV—A. Larsson, Zeits. f. Physik **41**, 507 (1927); V—M. Siegbahn, Ark. Mat., Astr. o. Fysik (A) **21**, Nr. 21 (1929); VI—Ina Wennerlöf, Ark. Mat., Astr. o. Fysik (A) **22**, Nr. 8 (1930); VII—B. Edlén, Zeits f. Physik **52**, 364 (1928); VIII—H. Beuthe, Zeits. f. Physik **60**, 603 (1930); IX—H. S. Uhler and C. D. Cooksey, Phys. Rev. **10**, 645 (1917); X—A. Leide, Comptes rendus **180**, 1203 (1925).

TABLE VIII. *Wavelengths of satellites.*

Element	Order		λ
		β' LINE	
		$\lambda\beta' - \lambda\beta_{1,3}$	
Mn	1 − 2	4.0 X.U.	
	1 + 1	4.2	1.9101A
	1 + 2	3.2	
Fe	1 − 2	3.0	1.7560
	1 + 1	3.1	
Co	1 − 2	2.2	
	1 + 1	2.2	1.6197
	1 + 2	2.2	
Ni	None		
Cu	1 − 2	1.4	1.3907
	1 + 1	1.3	
	1 + 2	1.3	
Zn	1 + 1	1.2	1.2938
	1 + 2	1.2	
Ga	1 + 1	1.0	1.2064
	1 + 2	1.0	
		β'' LINE	
		$\lambda\beta_{1,3} - \lambda\beta''$	
Cu	1 + 2	1.0 X.U.	1.3884A
Zn	1 + 1	.62	1.2920
	1 + 2	.59	
Ga	1 + 1	.59	1.2048
	1 + 2	.63	
Ge	1 − 2	.62	1.1260
	1 + 1	.61	
	1 + 2	.59	
		β''' LINE	
		$\lambda\beta_5 - \lambda\beta'''$	
Mn	1 + 1	2.0 X.U.	1.8912A
Fe		1.9	1.7386
Co		1.8	1.6038
Ni		1.2	1.4843
Cu		1.5	1.3768
		$\lambda\beta_2 - \lambda\beta'''$	
Zn		1.6	1.2795
Ga		None	
Ge		1.4	1.1133

fact that these lines are very asymmetrical and hence on a photographic plate the center of gravity may not coincide with the position of maximum intensity. The $K\beta_2$ line disappears abruptly at Cu 29, at least so far as these experiments show. In any event, it would be so close to $K\beta_5$ for atomic numbers less than that of Cu that the two could not be resolved.

Because of the large width and the fact that they are usually superimposed on the side of a stronger line the positions of the various satellites were not determined very accurately. Some check is possible where the satellites were observed in more than one order. Table VIII gives the wavelength data for these satellites in decreasing order of wavelength.

We are indebted to Drs. L. G. Parratt and L. P. Smith for helpful discussions and to Dr. Lewis V. Judson of the Bureau of Standards for valuable aid in the calibration of the divided circle. The Geneva Society spectrometer was a generous donation by Dr. A. L. Loomis of Tuxedo Park. The samples of pure Va and Ti metals were kindly supplied by the Vanadium Corporation of America and the Titanium Alloy Manufacturing Company.

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A Measurement of the Absolute Probability of *K*-Electron Ionization of Silver by Cathode Rays

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The method of Ross's balanced foils was used to separate the $K\alpha$ quanta from the thin silver foil target radiation. The x-ray energy was absorbed in CH_3Br and SO_2 in a standard ionization chamber and the ionization currents measured by means of a Compton electrometer and calibrated ionization system. Stockmeyer's value for the energy per ion pair for these gases was used to compute the number of quanta absorbed in the chamber. The number of Ag *K* ionizations per bombarding electron was then calculated, after the necessary target and absorption corrections. Measurements were made on 10 thin targets of average thickness 0.17 micron, and the *K*-electron ionization cross section for silver for 70.0 kv electrons was determined to be $\Phi(U) = (4.80 \pm 0.43) \times 10^{-23}$ cm². The measurements of relative probabilities of *K* electron ionization for silver by Webster, Hansen and Duveneck are normalized at 70.0 kv, ($U = 2.75$) by the above value of $\Phi(U)$, and these experimental data compared with classical quantum theory and the wave mechanics theories of Massey, Mohr and Burhop, Soden and Wetzel. The theories of Soden and Wetzel compare more favorably with the experimental data than those of Massey, Mohr and Burhop, or indeed with the classical theory.

I. INTRODUCTION

THE problem of determining the probability of *K*-electron ionization by electron impact has been studied both theoretically and experimentally by numerous authors. Theoretical solutions have been given for hydrogen,[1] helium,[1, 2] silver[3, 4] and mercury,[3] and the experimental determinations cover hydrogen,[5] helium[6] and silver.[7] The experimental work on silver by

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[1] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A140**, 613 (1933).

[2] W. W. Wetzel, Phys. Rev. **44**, 25 (1933).

[3] D. Graf Soden, Ann. d. Physik **19**, 409 (1934).

[4] E. H. S. Burhop and W. W. Wetzel have given solutions as yet unpublished, but discussed in the theoretical section of this paper.

[5] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

[6] P. T. Smith, Phys. Rev. **36**, 1293 (1930).

[7] D. L. Webster, W. W. Hansen and F. B. Duveneck, Phys. Rev. **43**, 851 (1933).