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Experimental Study of the Widths and Shapes of the $K\alpha$ X-Ray Doublet from Ca (20) to Ni (28)

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The rocking curves of the $K\alpha$ x-ray doublet of elements Ca (20) to Ni (28) have been recorded with a vacuum double-crystal spectrometer, and measurements of the full widths at half maximum intensity, relative intensities, asymmetry and degree of resolution have been made. Resolution of the observed overlapping curves into the two component lines α_1 and α_2 has been attempted. The relative intensity of the doublet lines α_1 to α_2, if defined in terms of the double-crystal spectrometer as the ratio of areas under the component curves, is 2 to 1 for all elements studied within an estimated error of ± 2 percent. The asymmetry of the lines is found to increase from Ca to Fe, then to decrease with increasing atomic number. The values of the full widths, uncorrected for divergence and for the finite resolving power of the crystals, of the component lines, in X.U., follow:

	Ca	Ti	Va	Cr	Mn	Fe	Ni
$K\alpha_1$	1.60	1.22	1.15	1.08	1.10	1.02	0.72
$K\alpha_2$	1.54	1.43	1.35	1.30	1.22	1.12	0.88

The ratio of peak intensities is observed to vary from element to element in such a way as to compensate for the variations in line widths so that the ratio of component areas remains constant.

INTRODUCTION

THIS paper is a report of measurements of the contour of the $K\alpha$ x-ray doublet of elements Ca (20) to Ni (28) with a vacuum double-crystal spectrometer. Since the pioneer work of Ehrenberg and Mark and of Davis and Purks in the application of the high resolving power and dispersion of the two-crystal spectrometer, many investigators have reported experiments similar to these on x-ray lines of wave-lengths suitable to work with an open air instrument. Allison[1] of this laboratory very recently reported an experimental study of widths of the $K\alpha$ doublet from Fe (26) to Ag (47), and the present work with the vacuum spectrometer was undertaken to extend this series of measurements in the long wave-length region.

The calcite crystals employed in this research have been previously studied[2] in the parallel position (zero dispersion) throughout a wide range of wave-lengths, 1.54 to 5A, and have been found to present no evidence of mosaic structure in the crystal lattice. With these crystals, practically perfect, the rocking curves obtained in the (1, +1) position should yield valuable information about the natural shapes or the intrinsic inhomogeneity of wave-length contained in the x-ray "lines." Especially is this true in the study of K lines from elements of low atomic number because (1) the lines are broader in this region (in angular units but narrower in energy units) allowing greater relative accuracy in their measurement, and (2) rudimentary ideas as to what factors determine line widths and shapes

[1] Allison, Phys. Rev. **44**, 63 (1933).

[2] Parratt, Phys. Rev. **41**, 561 (1932).

seem to indicate that the region of low atomic number is more fertile for this type of research.[3]

Discussion of Apparatus

Details of the design and construction of the vacuum double-crystal spectrometer with which these rocking curves were observed have been presented in an earlier paper by the author.[4] No alterations have been made in the instrument, with one minor exception: The window of the ionization chamber has been increased in width from 3 mm to 5 mm to eliminate any chance that it would not be sufficiently wide to accommodate the full x-ray beam. A lead shield placed between the crystals reduces the base line to 1.7 percent for Ca and to 3 percent for Fe, of the maximum ordinate of the α_1 line. All curves were taken with the x-ray tube operating at 15 kilovolts and from 3 to 10 milliamperes. The maximum horizontal and vertical divergences of any ray, with respect to the central ray, in the beam before reaching the first crystal are approximately 8.7×10^{-3} and 1×10^{-2} radians respectively.

Distortions in Observed Rocking Curves

(1) Due to divergence

Allison discusses[1] the effect of slit width and height on the (1, +1) rocking curves and arrives at the conclusion that, if the spectral range covered by the rocking curve is not too wide, the divergence of the beam incident on the first crystal has negligible effect on the rocking curve observed from the second crystal. Just how wide this range may safely be is not exactly known and the divergence with the relatively large spectral ranges covered in recording the present lines of long wave-length may have a slight effect on the observed curves.

(2) Due to moving second crystal only

Other possible perturbations on wide rocking curves due to the fact that measurements are taken by moving the second crystal only, leaving the slits and first crystal fixed in position, have been discussed by DuMond and Hoyt.[5] First, the portion of the beam being reflected into the ionization chamber progressively moves across the face of the crystals in the process of recording a rocking curve and it is known that the reflecting properties of a crystal are not uniform over its face. Second, the portion of the beam whose intensity is being observed is emitted from but a fraction, a vertical section (due to the action of the slits), of the focal spot, and this section gradually changes in position, sweeping slightly across the focal spot, in the course of a rocking curve. This introduces difficulties because the intensity emitted from the focal spot is not uniform over its area. However, Allison[1] eliminated the question of the effect of these two perturbations on the curves for cobalt by rotating both crystals simultaneously, after the manner of DuMond and Hoyt.[5] The spectral width at half maximum intensity of Co $K\alpha_2$ is 0.95 X.U. and for this range the perturbations seem to have no appreciable effect. The maximum line width covered in the present report is that of Ca $K\alpha_1$, 1.68 X.U. Several rocking curves were taken of Ca $K\alpha_1$ with the focal spot, slits and first crystal set at various positions, at the peak of α_1, then at 300 seconds of arc (3.67 X.U.) on either side of the peak. The differences in the observed widths of α_1 were approximately twice as large as the experimental error, which is estimated as about 2 percent. However, measurements on all the curves except those of calcium are felt to be free (within the experimental error in recording electrometer readings) of disturbances of the type mentioned above.

(3) Due to finite size of focal spot

In measuring wide lines by rotating the second crystal only it is imperative that the focal spot be rather broad and as uniform in emission as possible. The face of the target was cut at 45° to the long axis to aid in attaining this objective. Then the shape of the focussing cup and filament-target distance were varied until a broad, fairly uniform focal spot was obtained. The x-ray tube is constructed with a sylphon and screw arrange-

[3] From the results of work now in progress (Parratt, Bull. Am. Phys. Soc. **8**, 26 (1933) Abs. No. 74) on the differences in the shape of the doublet lines as obtained from pure and alloy targets, there seems to be evidence to believe that the valence or outer electrons are in a large part responsible for the shape of the x-ray curve. If this be true, the region of long wave-lengths should prove especially rich for contour work due to the stronger couplings between the inner and outer electrons.

[4] Parratt, Phys. Rev. **41**, 553 (1932).

[5] DuMond and Hoyt, Phys. Rev. **36**, 1702 (1930).

ment in the target end[4] which allows slow horizontal motion of the target with respect to the rest of the tube and slits while the tube is in operation. The breadth and uniformity of the spot is conveniently measured as follows: With the slits and crystals set on the peak of an α_1 line, the intensity of the beam reaching the ionization chamber is observed as a function of the position of the target. If this curve is wide and flat the focal spot is broad and uniform. When the width of each slit is 2 mm, the widths used in all the work reported here, this curve of intensity *vs.* position of target is quite flat-topped over an angular range[6] of about 600 seconds of arc (more than twice the separation between α_1 and α_2) with an approximately 3 percent decrease at a distance of 800 seconds of arc from the optimum position of the target. Of course, moving the target alters the characteristics of the focal spot also, so that this method does not allow a true picture of the emitted intensity, but the relatively slight variations of $\frac{1}{4}$ to $\frac{1}{2}$ mm in the distance of 15 mm should not be very serious.

Because of the overlapping of the rocking curves of the two α-lines, curves of both lines were taken in a single "run." A preliminary curve of the type described in the previous paragraph, with the slits and crystals set on the angle midway between the peaks of the doublet, afforded an accurate determination of the optimum position for the focal spot, midway in the spectral range to be covered. The target was so placed prior to the recording of each rocking curve.

Base line readings were taken at distances of 500 and 600 seconds of arc removed from the peaks and a 3 percent correction due to the finite size and characteristics of the focal spot has been made on these readings. Errors in electrometer readings are of this order of magnitude and this 3 percent correction is probably superfluous.

(4) Due to the crystals

Distortions, of a type asymmetrical as well as symmetrical, due to the action of the two crystals as diffraction gratings may be present in the observed rocking curves. But for this distortion, though perhaps small, inherent in all two-crystal instruments, no satisfactory method of correction has been developed, and for this reason interpretations of the particular line contours reported in this paper and in similar research cannot be completely divorced from the type of instrument with which they are observed.

In order to make certain that the reflecting properties of the crystals had not changed and that the spectrometer had remained in proper adjustment, curves of calcium and titanium, the first to be studied, were repeated, and were the last to be recorded. Agreement was within the experimental error.

Preparation of Targets

The targets were of pure elements and made up in individual buttons of more or less uniform size that could be soft-soldered to the water-cooled target-carriage of the tube. The calcium button was made as follows: In a $\frac{1}{2}$ inch nickel rod, a flat-bottomed hole was drilled $\frac{5}{16}$ inch in diameter to a depth of about $1\frac{1}{4}$ inches. Bits of pure Ca, having a minimum amount of oxide on their surfaces, were pressed in the hole and hermetically sealed with melted borax to prevent further oxidation. The unit was then heated with an oxygen flame to a temperature slightly above the melting point of calcium. The liquid Ca fused with the sides and bottom of the nickel cup which, when cooled, was turned down to the desired size on the lathe and soldered to the target-carriage. The melting points of titanium and vanadium are sufficiently high that good thermal contact to the copper base of the target is not necessary. A piece of pure Ti was placed in a pool of liquid silver-solder to supply mechanical

[6] As previously mentioned, the portion of the beam whose intensity is being observed in the course of recording a rocking curve is emitted from but a fraction, a vertical section, of the focal spot and this effective section gradually sweeps across the focal spot as the second crystal is turned. The importance of the size and uniformity of the focal spot is that the intensity emitted throughout the spectral range including the α-lines be constant so that rocking curves of these lines will not be distorted by irregularities in the focal spot. Consequently, it is convenient to express in angular measure the linear distance that the focal spot can be moved without appreciably disturbing the intensity of the beam passing through the slits. This angular range, in radians, is obtained by dividing the linear distance of the target-motion by the distance from the focal spot to the first crystal.

TABLE I. *Measurements of rocking curves of the Kα x-ray doublet.*

Obs. = Observed curve (without corrections for overlapping).
Comp. = Component curve (corrected for overlapping).

Element	Ratio of peak intensities α_1/α_2 Obs.	Comp.	Ratio of areas under comp. curves α_1/α_2	Overlapping factor	Index to asymmetry Comp. α_1	α_2	Separation $\alpha_1 \rightarrow \alpha_2$ Obs. $\Delta\theta$	X.U.	Seigbahn X.U.
20 Ca	1.83	1.93	2.00	0.50	1.15	1.13	266″	3.26	3.26
22 Ti	2.19	2.31	1.98	0.34	1.15	1.10	281″	3.68	3.64
23 Va	2.22	2.35	1.99	0.32	1.25	1.15	287″	3.84	3.78
24 Cr	2.26	2.38	2.00	0.27	1.30	1.25	285″	3.88	3.88
25 Mn	2.15	2.24	2.00	0.22	1.60	1.35	288″	3.97	3.98
26 Fe	2.07	2.16	1.97	0.18	1.65	1.40	286″	3.98	3.95
28 Ni	2.30	2.35	1.92	0.09	1.35	1.35	278″	3.93	3.85

support when cooled and a free surface of Ti was obtained by grinding on an emery wheel. Va was treated in the same manner as Ti. Pure manganese is wet by low-melting-point silver-solder with borax as a flux, and, if care is taken to prevent sudden and uneven cooling, the Mn will not fracture. The samples of Ti, Va, Cr, Mn and Fe were prepared by an alumino-thermic reduction from their oxides, thus assuring a purity within a few tenths of one percent.

RESULTS

Fig. 1 is a reproduction of six of the rocking curves. The curves are drawn through the experimental points and no points deviated from the curve by more than the width of the lines drawn. The dotted line in each case is an attempt to resolve the observed contour into the two components α_1 and α_2. This resolution will be discussed later. Measurements of these curves are given in Tables I and II. The data listed in these tables are the averages of at least three individual curves, usually more than five. In all of these curves the second crystal only was rotated and from long to shorter wave-lengths. After the completion of each curve the peak intensity of α_2 was checked and the curve discarded if the intensity had changed more than 4 percent. Most of them checked within 2 percent. An insufficient number of trials was taken to give a probable error, but an index to the degree of experimental consistency may be obtained from the following: The maximum deviation from the average of the width measurements is about 2 percent, and of the ratio of peak intensities about 4 percent, considering all the curves, except those for Ni, not discarded on the basis of the above criterion. The nickel curves were taken when the temperature in laboratory was just 100°F and the vacuum grease between the bearings[4] of axis B was suspected of gradually changing in thickness. This may have caused slight lateral distortions in the angular readings but would not disturb the peak intensities. Consequently the width measurements on the Ni curves may be less reliable than the other data.

ASYMMETRY AND RESOLUTION

From Fig. 1 it is observed that both α_1 and α_2 are asymmetrical about a line drawn through the maximum ordinate. To serve as an index of the asymmetry Allison has introduced[1] the ratio of that part of the full width at half maximum on the long wave-length side of the maximum ordinate to that part of the width on the short wave-length side. Values of these indices from the resolved component lines α_1 and α_2 are given in Table I. Both the Ca and Ti lines are but slightly asymmetrical, the asymmetry increasing to Fe then decreasing. For $K\alpha$ lines from elements of atomic number greater than Cu (29) the index of asymmetry rapidly decreases to unity.[1]

The fact that these curves are asymmetrical may lead one to suspect the existence of unresolved component lines[7] in addition to the α_1 and α_2 lines. However, considering the relatively large widths and the fact that the curves are quite smooth as observed with an instrument of very high resolving power, a preferable inter-

[7] Bearden and Shaw, Bull. Am. Phys. Soc. **8**, 15 (1933) Abs. No. 50.

pretation is that these asymmetrical curves actually represent the true experimental contour of the two α-lines.[8]

The method of resolving the observed curve into components is one of trial and error. Several attempts on each curve are made and the one giving the "most reasonable" component curves is decided upon. There is really not a very large difference between any "reasonable" components that can be drawn, and these differences except for calcium are close to the experimental error in recording the observed curve.

In Table I are listed values of the "overlapping factor," a term which is introduced by Allison[1] to indicate the reciprocal of the degree of resolution of the two overlapping lines. This term is defined as the ratio of the minimum ordinate between the peaks of the rocking curve of α_1 and α_2 to the maximum ordinate of α_1, all multiplied by the ratio of intensity of α_1 to α_2, which, for these K lines, is taken as 2 to 1.

Relative Intensities

The term relative intensity of two x-ray lines has been defined experimentally as the ratio of the peaks or maximum intensities of the two lines as measured with a single-crystal spectrometer. Some confusion has arisen as to the meaning of the term when applied to rocking curves obtained with a double-crystal spectrometer. In Table I is listed the ratio of peak intensities of α_1 to α_2. These values for the component lines vary with atomic number from 1.93 for Ca to 2.38 for Cr. The ratio of the areas under the component curves is also given (Table I) and is seen to be constant, 2 to 1, within experimental error. The Burger-Dorgelo "summation rules" predict the relative intensity of α_1 to α_2 as 2 to 1, constant for all elements, which also agrees with experimental work on the $K\alpha$ doublet with the single-crystal spectrometer.[9] The present work can be interpreted in either of two ways: (1) as determining the meaning of the term relative intensity as referring to the area under the component curves measured with a double-crystal spectrometer, or (2) on the assumption that the area ratio should be 2 to 1, as justifying the particular resolution into components employed in the analysis for the above data and as giving evidence for the accuracy of the data.

Widths

Fig. 2 presents graphically the data given in the last column of Table II. The points for Cu, Zn and Ge are taken from Allison's data.[1] It should be pointed out that the peculiar variations in width shown by this graph are well outside of the experimental error. The widths of both α_1 and α_2 vary, but also the ratio of peak intensities changes in such a compensating manner that the ratio of areas, as mentioned above, remains constant.

The series of elements here reported overlap the series studied by Allison.[1] The values of the widths of Fe $K\alpha_1$ and α_2 observed by Allison are 1.00 and 1.06 X.U., respectively with an estimated error of ± 10 percent, and the widths in Table II of this paper are 1.02 and 1.18 X.U. with an estimated error of ± 2 percent. Allison's values of the widths of the Ni lines are 0.64 and 0.82 X.U. with an error estimated as ± 5 per cent, and the present measurements give 0.72 and 0.91 X.U. for $K\alpha_1$ and α_2, respectively with an error of perhaps ± 5 percent.

This disagreement may possibly be explained as experimental. However, it should be investigated further. Three different types of targets were used in the present experiments: First,

[8] The rocking curve to be expected from the theory of x-ray reflection from a single calcite crystal is not symmetrical (reference 2, page 565), and if two such crystals are used in any anti-parallel position the rocking curve of the doubly-reflected monochromatic radiation would also be asymmetrical (reference 1). Of course, the theoretical rocking curve is derived on the assumption of monochromatic radiation incident on the first crystal and the width of this curve is rather narrow compared with the width of the observed curve. At any rate, it should follow that even though the x-ray line be symmetrical in its inhomogeneity of wave-length as emitted from the target, the rocking curve as observed with the double-crystal spectrometer would be expected to be somewhat asymmetrical. However, considering that symmetrical rocking curves are observed for $K\alpha$ radiation from elements of higher atomic numbers, say Mo (42) or Ag (47), in which the widths of the (1, -1) curves are a greater fraction of the (1, $+1$) curves, one might conclude that the effect of the crystals in producing asymmetry is small, and that the asymmetry of the $K\alpha$ lines reported in this paper are to a large extent characteristic of the radiation as it emerges from the target.

[9] Williams, Phys. Rev. **44**, 146 (1933).

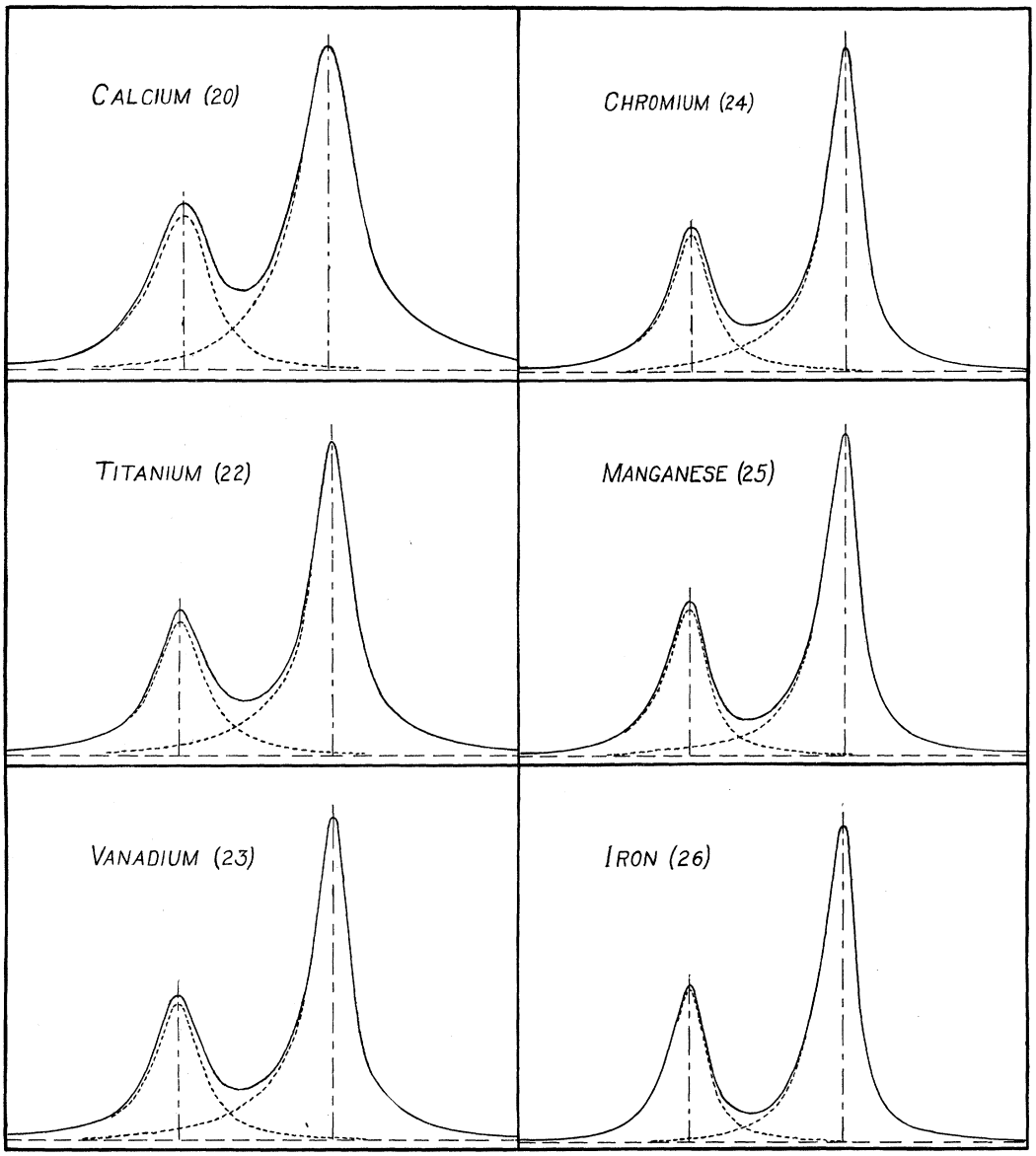

FIG. 1. Rocking curves of the $K\alpha$ x-ray doublet.

cold-rolled steel, second, pure Fe produced alumino-thermically and quickly chilled in water so that the crystal size would be microscopic, and, third, a single crystal of Fe produced by maintaining the temperature just a few degrees below the melting point of Fe for a period of 1000 hours, then cooling very slowly. The first two types of targets gave identical rocking curves but the single crystal of Fe gave widths of 1.06 and 1.23 X.U. for $K\alpha_1$ and α_2, respectively. This difference in the rocking curves, apparently due to the different heat treatments of the targets, is felt to be greater than experimental error, but warrants further study.[10] The samples of both Fe and Ni used in the present measure-

[10] The values of the widths of the Fe $K\alpha$ lines given in Table II and included in Fig. 2 are taken from the rocking curves with the first and second types of Fe targets. Perhaps the widths measured from the single-crystal of Fe should be taken as those characteristic of pure iron.

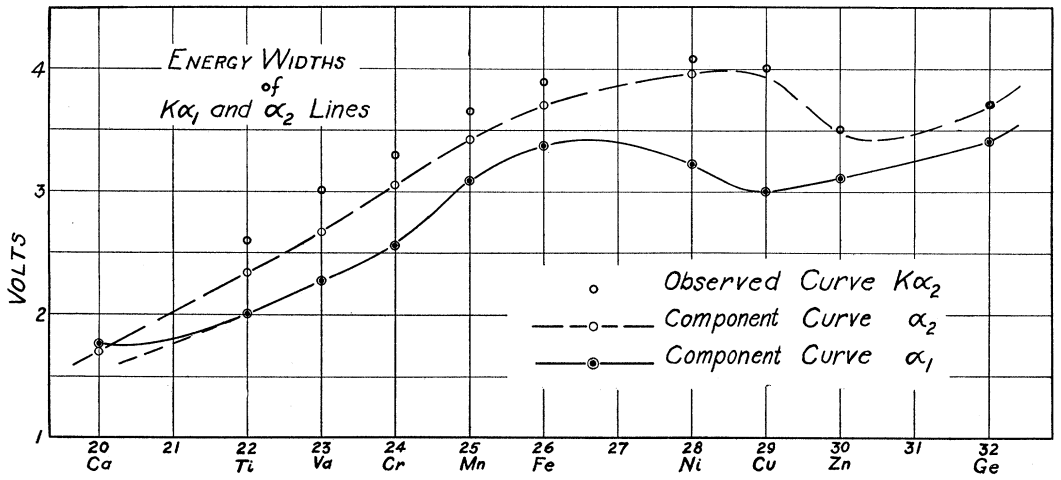

FIG. 2. Full widths (in volts) at half maximum intensity of the $K\alpha_1$ and $K\alpha_2$ x-ray lines. The values for Cu, Zn and Ge are taken from Allison's data (reference 1).

TABLE II. *Full widths at half maximum intensity of $K\alpha_1$ and $K\alpha_2$ x-ray lines.*

Obs. = Observed curve (without corrections for overlapping).
Comp. = Component curve (corrected for overlapping).

Line	Wave-length Angstroms	Widths					
		Seconds of arc		X. Units		$\Delta\nu/R$	Δv volts
		Obs.	Comp.	Obs.	Comp.	Comp.	Comp.
20 Ca $K\alpha_1$	3.352	137	131	1.68	1.60	0.130	1.76
$K\alpha_2$		—	126	—	1.54	0.125	1.69
22 Ti $K\alpha_1$	2.743	94.5	93.5	1.24	1.22	0.148	2.00
$K\alpha_2$		121	109	1.58	1.43	0.172	2.33
23 Va $K\alpha_1$	2.498	86	85.5	1.15	1.15	0.167	2.26
$K\alpha_2$		114	101	1.53	1.35	0.197	2.67
24 Cr $K\alpha_1$	2.285	80	79.5	1.09	1.08	0.188	2.55
$K\alpha_2$		103	95	1.40	1.30	0.225	3.05
25 Mn $K\alpha_1$	2.098	80	80	1.10	1.10	0.228	3.09
$K\alpha_2$		95	89	1.31	1.22	0.253	3.43
26 Fe $K\alpha_1$	1.932	73.5	73.5	1.02	1.02	0.249	3.37
$K\alpha_2$		85	80.5	1.18	1.12	0.273	3.70
28 Ni $K\alpha_1$	1.655	50.5	50.5	0.72	0.72	0.238	3.23
$K\alpha_2$		64	62	0.91	0.88	0.293	3.96

ments were different from those in Allison's experiments.

In Table I is included the observed separation in X.U. of the maximum ordinates of α_1 and α_2, and, for comparison, the values given by Siegbahn. In general the agreement is very good. This may be considered as a check on the regularity of motion of the second crystal and the calibration of the drum from which the differences in angular positions are read.

To convert the observed line width into terms of the natural or intrinsic width of the x-ray line as it emerges from the target, two corrections, in addition to the overlapping, are to be considered. First is the effect of the divergence of the beam incident on the first crystal which effect has been assumed to be of little importance. Second is the correction for the contributions to the width due to the finite resolving power of the crystals. This correction

depends in some way on the width of the rocking curve in the $(1, -1)$ position of the spectrometer. For wave-lengths 2.4 to 3.2A the width of the $(1, -1)$ curve is almost constant,[2] 18.2 seconds of arc, which is but 1/5 of the width of the $(1, +1)$ curve for the same wave-length.

It is interesting to note that the region of elements in which occur these curious variations in widths, asymmetry and peak intensity ratios is the one in which the incompleted subshell of electrons, the $3d$ electrons of the M level, is being filled. Every element studied has just two N electrons, of the $4s$ type, except Cr, which has but one. Of course these atomic configurations are derived from the optical spectra of the elements in the gaseous form, and the explanation of the effects reported here may very likely be in terms of the distortions of the atom as it exists in the solid form—distortions of the symmetry of the electric and magnetic fields surrounding the atom which may cause subdivision of the energy levels of the atomic states in question.

The author is at present studying the rocking curves of the $K\alpha$ doublet from an element in various alloy targets. The results so far seem to indicate that the calcium data given here are not correct for pure Ca but rather apply to calcium plus a surface layer of oxide. Calcium oxidizes rather readily and in spite of the fact that the surface of the target was filed clean of oxide just previous to the recording of each rocking curve, some oxide had certainly formed before the tube could be pumped out. Such a layer of oxide on a manganese target has been found to increase the width of the $K\alpha_1$ line of Mn 5 to 15 percent depending upon the relative amount of oxide present; the corresponding increase in the width of $K\alpha_2$ is somewhat less than for that of α_1. In all cases except calcium the data here reported apply to pure elements.

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