FINE STRUCTURE IN THE K-SERIES OF COPPER AND NICKEL AND THE WIDTH OF SPECTRAL LINES

By Harris Purks

Abstract

Width and fine structure of the $K\alpha_1$, $K\alpha_2$ and $K\beta$ lines of Ni, Cu, Mo and Ag.— High resolving power was obtained by means of the double x-ray spectrometer. The minimum width of slits was 1.75 mm. Wide slits made possible the study of the lines after second order reflection from two calcite crystals. Ionization currents were measured with a Compton type electrometer of sensitivity 5000 mm per volt at one meter. At 40 kv and in the first order the widths at half-maximum of the lines (in X.U.) were found to be: Ni $K\alpha_{1,2}$, 0.66; Cu $K\alpha_{1,2}$, 0.63; Mo $K\alpha_{1,2}$, 0.47; Ag $K\alpha_{1,2}$, 0.43; Mo $K\beta_{1,2}$, 0.43; Ag $K\beta_{1,2}$, 0.40. In the second order the estimated width of the components of Ni $K\alpha_{1,2}$ and Cu $K\alpha_{1,2}$ was 0.4 X.U. which was also the estimated width of Ni $K\beta_{1,2}$ and of Cu $K\beta_{1,2}$. Structure to the lines of nickel and copper was clearly indicated by the shapes of the curves. The first order curves of the $K\alpha$ lines of Ni and Cu showed an asymmetry on the long wave-length side which was checked as regards position and intensity by the second order curves. It was found that the lack of symmetry could be explained by the presence of weak lines at displacements 0.42 and 0.35 X.U. from Cu $K\alpha_1$ and Cu $K\alpha_2$, respectively, and 0.45 and 0.38 X.U. from Ni $K\alpha_1$ and Ni $K\alpha_2$, respectively. The $K\beta$ doublets of Mo and Ag were clearly resolved after first order reflection from two crystals. Their separations were, for Ag $K\beta_2-K\beta_1$ 0.63 X.U. and for Mo $K\beta_2-K\beta_1$, 0.58 X.U. These doublets for Ni and Cu were not resolved after second order reflection. However, the shapes of the curves obtained permitted a solution of the problem of intensities and displacements. Their separations were 0.32 X.U. and 0.29 X.U. for Cu $K\beta_2-K\beta_1$ and Ni $K\beta_2-K\beta_1$, respectively. The shapes of the $K\beta$ curves of Ni and Cu showed evidence of the spark line $K\beta'$ and the curve of Cu showed evidence of a line corresponding to the $K\beta''$ line found by Hjalmer for Ca, K, Cl.

Variation with potential of the width of the $K\alpha$ lines of Ni, Cu, Mo and Ag.— Curves showing a variation of width of the $K\alpha$ lines with voltage were obtained. The widths increased with increasing voltage but seemed to approach a limiting value at about 40 kv. The width at the excitation potential was about two-thirds the width at 40 kv. The variation is explained as due to the successive appearance of spark lines.

BY A method proposed by Professor Bergen Davis it has been found possible to gain greater resolving power for x-rays by means of the double x-ray spectrometer. This method has been described in two recent papers by Davis and Purks.[1,2] Simultaneously, Ehrenberg and Mark[3] and Ehrenberg and Susick[4] have used the double x-ray spectrometer for the determination of the natural breadth of the spectral lines. These authors used only first-order reflection and made no use of the possibilities of very wide slits. In the first two papers mentioned[1,2] it has been shown that this method permits the use of wide slits which in turn permits the use of the

[1] B. Davis and H. Purks, Proc. Nat. Acad. Sci., **13,** No. 6, (June, 1927).
[2] B. Davis and H. Purks, Proc. Nat. Acad. Sci., **14,** No. 2, (Feb. 1928).
[3] Ehrenberg and Mark, Zeits. f. Physik. **42,** (May, 1927).

higher orders of reflection with considerable energy. It has been found possible[2] to obtain a rocking curve of Mo$K\alpha_1$ after third-order reflection from both crystals.

Apparatus and Method

Two split calcite crystals were mounted as shown in Fig. 1. The slits were 1.75 mm wide and 6 mm high except in the case of the second order curves of the K-lines of nickel. In this case the width was 2.75 mm. The distance between slits was 50 cm and the distance from the source of the x-rays to the center of the first crystal was about 80 cm. The distance between centers of crystals was about 5 cm. The ionization currents were measured by a Compton type electrometer of a sensitivity of 5000 mm per volt at one meter.

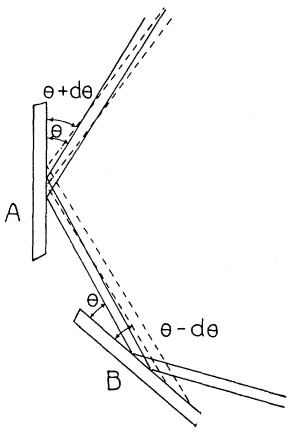

Fig. 1. Crystal arrangement.

In this method the first crystal A played the role of a collimator in that all the rays reflected from it were parallel to within the few seconds of arc given by the tolerance angle of the crystal. The wide slits permitted the reflection of a considerable range of wave lengths. Crystal B acted as an analyzer in that it selected from the number of bundles of parallel rays reflected from A that one which made with B the reflecting angle θ_n. This bundle alone was reflected from B.

From the geometry of the figure and the Bragg reflection law it follows that the angular displacement measured on crystal B between two wavelengths λ and $\lambda+d\lambda$ will be given by:

$$\Delta\theta=\frac{nd\lambda}{2d\cos\theta_n}+\frac{md\lambda}{2d\cos\theta_m}$$

where n and m are the orders of reflection from crystals A and B respectively.

The crystals were carefully adjusted as regards angles about a horizontal axis. The tube was placed so that the source and the center of the crystals formed a horizontal line. It was necessary to adjust the two crystals so that this line and the normals to the two crystals lie in the same plane. It was desirable that this plane be horizontal but small deviations from this condition were of no consequence since there was no collimation of the rays until they had struck the first crystal. The adjustment of the orientation of the crystals was done by finding the orientation of B about a horizontal axis which gave the minimum width to rocking curves. At this position the normals and the horizontal line lie in the same plane.

The width of rocking curves from crystal B are independent of the width of slits. This is obvious if the crystals are assumed perfect. A test was made and it was found that the widths of curves were independent of slit-width

as long as the beam did not strike the rough edges of the crystals. The maximum width which could be used was determined by the dimensions of the crystals and the angle of reflection. The only function of the horizontal width of slits was to confine the beam to the crystal path and to diminish the effects of scattered radiation.

The height of slits however does affect the width of curves. If crystal B is set at an angle $2\theta_n$ to crystal A then a horizontal ray of length λ will strike B at the angle θ_n. It will be reflected. Other rays of the same wave-length but not horizontal will be reflected from A and these rays strike B at an angle $(\theta_n - \epsilon)$. They are reflected from B only after it has been turned through the small angle ϵ. Such rays increase the widths of curves. They are eliminated by decreasing the height of slits. It was found that the widths of curves successively decreased with diminishing height of slits until a height of about 6 mm was reached. After this further diminution of height had no measureable effect upon the width of curves. Calculation shows that at this height the angle ϵ is approximately equal to the tolerance angle of the crystal, i.e., from four to six seconds of arc.

Relative intensities of lines measured by this method will be correct under certain conditions. In general crystal A is not rotated. The slits are made so wide that both lines are reflected at one setting. The curves from crystal A were about 15 minutes wide at half-maximum. These curves were flat to better than one percent over a region of four or five minutes. The intensities of two lines whose separation is not greater than the above interval may be compared by obtaining rocking curves from crystal B since the two lines are reflected in their true ratio of intensities from crystal A, when A is set at any position within the interval containing the flat top of the curve.

RESULTS

The spectral lines closely investigated in the course of this experiment were the K-series of copper and nickel. In addition a few measurements were taken of the K-series of molybdenum and silver.

Ehrenberg and Mark[3] and Ehrenberg and Susick[4] have measured the widths of certain spectral lines by a similar method. Among their results are listed the half-widths of copper K-lines. The observations were made at first-order reflection. They corrected for the effect of the crystal itself upon the width of lines. Their correction formula was:

$$H_\lambda = (H_2^2 - H_1^2)^{1/2} 2d \cos\theta_n / 2n$$

where H_2 and H_1 are one-half the angular widths at half-maximum of rocking curves taken with crystals as in Fig. 1 and with parallel crystals respectively. The half-value is taken because the angular displacement measured on crystal B is twice the Bragg law differential for a single crystal. In addition they have divided again by two so that their results give the half-width at half-maximum.

[4] Ehrenberg and Susick, Zeits. f. Physik, **42**, (May, 1927).

In the course of this experiment it was found that when both crystals were set for first-order reflection of the Cu $K\alpha$ lines the curves were 44 seconds wide at half-maximum. This corresponded to a wave-length interval of 0.63X.U. An attempt was made to reduce the width of the curve by decreasing the height of slits below 6 mm. No decrease resulted. This width of 0.63X.U. for the total width checks well with the half-width of 0.35X.U. found by Ehrenberg and Susick.

The $K\alpha$ lines of nickel were also investigated. A width of 46 seconds was obtained which corresponds to a wave-length interval of 0.66X.U.

The curves obtained were not symmetrical. The slopes on the two sides were equal but in each case there appeared on the long wave-length side a bulge which had the appearance of a weak unresolved line. It was first thought that these bulges were due to crystal imperfections of some kind and an attempt was made to eliminate them by making the beam fall on different crystal reflecting areas. In each case however the same bulge appeared. In order to get an approximation for the position, width, and intensity of a weak line which would explain the asymmetry, the principal line was assumed to be symmetrical and its ordinates subtracted from the experimental curve. Typical curves are shown in Figs. 2 and 3.

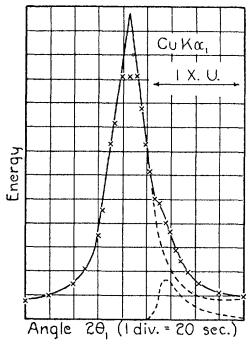

Fig. 2. Rocking curve—Cu $K\alpha_1$—first order.

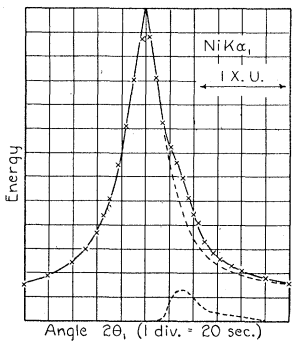

Fig. 3. Rocking curve—Ni $K\alpha_1$—first order.

By the subtraction of ordinates it was found that the bulges could be explained by weak lines at displacements of 0.42X.U. and 0.35X.U. to the long wave-length sides of Cu $K\alpha_1$ and Cu $K\alpha_2$ respectively, and 0.45X.U. and 0.38X.U. to the long wave-length sides of Ni $K\alpha_1$ and Ni $K\alpha_2$ respectively.

The $K\alpha$ lines of molybdenum have been investigated at first order by Davis and Purks.[1] They showed no asymmetry. In the course of this experiment the $K\alpha$ lines of silver were also investigated. At first order these lines showed no asymmetry. The widths of the $K\alpha$ lines of molybdenum and silver measured at first order were 32 seconds and 30 seconds respectively.

It was noticed that at lower voltages the curves of Cu $K\alpha$ were narrower than at high voltages. This led to the investigation of the

width-voltage relations. The results are shown in Fig. 4. The curves at voltages near the excitation voltage were about two-thirds the width at 35 kilovolts. The widths increased with voltage quite rapidly at first and then seemed to approach a limiting value. The widths of all lines investigated above 30 kilovolts could be determined with an accuracy of better than two percent. For voltages below 30 kilovolts the copper and nickel curves could be determined to at least 4 percent. The widths of the molybdenum and silver curves were not so precise near the excitation limit. This was due to the magnitude of the general radiation intensity in comparison to that of the lines and also to the difficulties of shielding for small reflecting angles. The precision of these latter widths near the limit was probably not better than 15 percent. Nevertheless the results did show a definite break in the widths and that this break was sharp in comparison to that for copper and nickel.

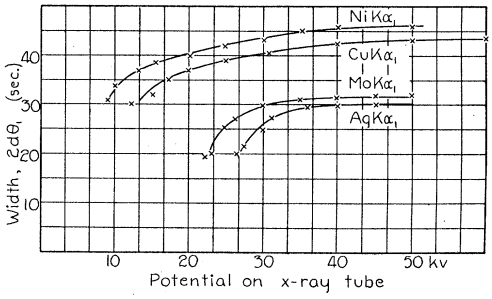

Fig. 4. Increase of width with voltage.

The $K\beta$ lines of the elements mentioned were also investigated at first order. The molybdenum and silver $K\beta$ doublets separated clearly. The separations were 0.58X.U. and 0.63X.U. for molybdenum[1] and silver respectively. The $K\beta$ lines of copper and nickel were not resolved into doublets at first order but the curves showed indications of the presence of the doublet. The widths of the $K\beta$ lines of copper and nickel are not listed here because of their multiple nature. The widths of the $K\beta_1$ and $K\beta_2$ lines were found to be 30 seconds and 28 seconds for molybdenum and silver respectively.

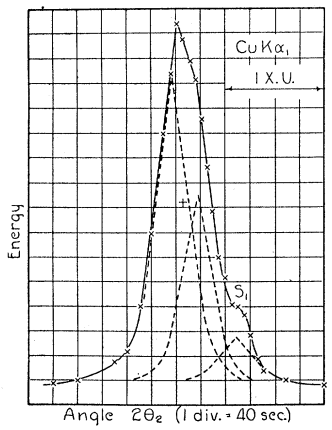

Fig. 5a. Cu $K\alpha_1$—second order.

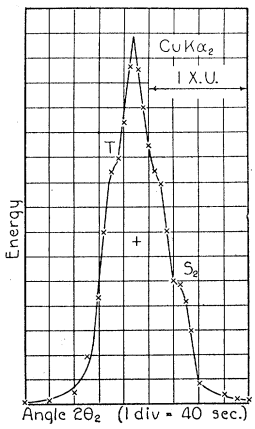

Fig. 5b. Cu $K\alpha_2$—second order.

It had been found[2] that when both crystals were set for second order reflection of Mo $K\alpha_1$ and Mo $K\alpha_2$ the curves were narrower than at first order. This could be explained in part by the smaller reflecting area of the crystals at second order. In an effort to resolve the weak lines indicated by the bulges on the $K\alpha$ lines of copper and nickel these lines were investigated at second-order reflection. Unlike the molybdenum lines these lines were almost twice as wide at second order as at first order. It was inferred that this was due to the natural width of the lines or a structure of some sort which spread out under the increased dispersion. The curves obtained are shown in Figs. 5 and 6. It will be noticed that in each case there is an asymmetry which corresponds in position and intensity to that found at first order. This asymmetry is lettered S on the curves. In addition to this there was noticed other asymmetrical bulges nearer the center of what at first order appeared to be one principal line.

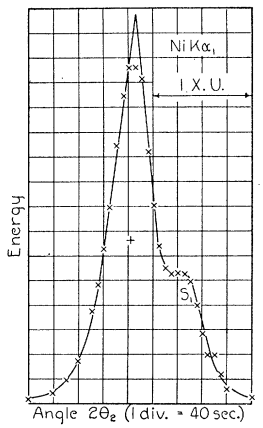

Fig. 6a. Ni $K\alpha_1$—second order.

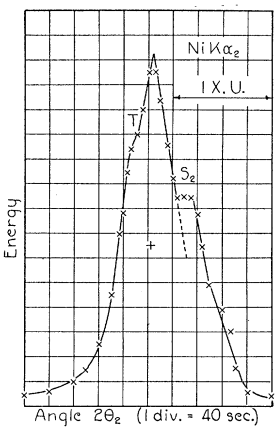

Fig. 6b. Ni $K\alpha_2$—second order.

The $K\beta$ doublets of copper and nickel were also investigated at second order. The resolution of the two components was not perfect but the curves (Figs. 7 and 8) permit quite definite conclusions as to their separation and intensities. Possible solutions to the curves are shown by the dotted lines. The copper doublet was more in evidence than the nickel doublet. The separation was not as great in the case of nickel and also the nickel components may be reasonably expected to be slightly wider. The observed β doublet separations are 0.32X.U. and 0.29X.U. for copper and nickel respectively. In addition to the doublet lines there appeared evidence of the spark lines $K\beta'$ and $K\beta''$ which have been found for some of the elements of lower atomic number. The $K\beta'$ lines on the long wave-length side were fairly definite but the $K\beta''$ lines were merely indicated by the slope of the short wave-length side of the main body of the curves. The $K\beta''$ lines have been found for only three elements Cl, K, Ca.[5]

[5] Hjalmar, Zeits. f. Physik **7**, 341–350 (1921).

Discussion

The second-order curves of the Cu $K\alpha$ and Ni $K\alpha$ lines (Figs. 5 and 6) indicate the existence of structure within the lines. Obviously any attempt to solve the problem of structure will lead to very uncertain conclusions. In the case of two unresolved lines calculations may be made which certainly lead to approximations. But when there are three or more components present many solutions are possible. A possible solution of the structure of Cu $K\alpha_1$ is shown by the dotted lines in Fig. 5(a). There may be present more than three components but if these others are assumed to be of weaker intensity then at least the width of the components given by the dotted lines is reasonable. The width thus found is 60 seconds at half-maximum or a wave-length interval of 0.4X.U.

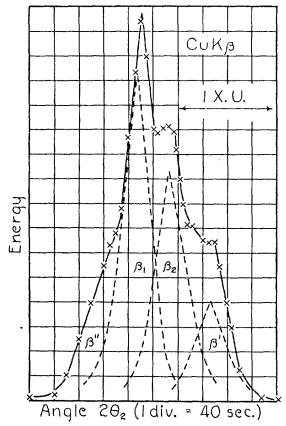

Fig. 7. Cu $K\beta$ doublet.

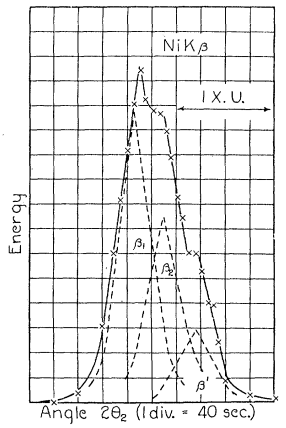

Fig. 8. Ni $K\beta$ doublet.

The significance of the width of the curves at half-maximum is small if as is indicated the lines have structure. For example, the curve of Ni $K\alpha_2$ (Fig. 6b) would have its width reduced from 125 seconds to about 90 seconds if the cause of the asymmetry at S had its intensity reduced by one-sixth of its value. This affords an explanation why the curve of Ni $K\alpha_1$ ($Z=28$) is narrower at half-maximum than that of Cu $K\alpha_1$ ($Z=29$).

The width of the component lines is of great importance. It has been found[6,7] that the natural breadth of a spectral line calculated on the basis of damped oscillations of an electron should be independent of the wave-length and of magnitude 0.12X.U. From the curves it is seen that a reasonable value of the widths of the components of the copper and nickel $K\alpha$ lines is 0.4X.U. It has been found[2] that the $K\alpha$ lines of molybdenum show evidence of components of width slightly less than 0.1X.U., which is less than the predicted value of 0.12X.U. These experiments indicate that the breadths of the components are not constant from element to element and

[6] G. E. M. Jauncey, Phys. Rev. Jan. 1922.

[7] A. H. Compton, X-rays and Electrons, p. 56.

that the breadth of what is called the emission line is dependent upon the number, width, position, and intensity of these components.

The work of Dauvillier, Hjalmar, Siegbahn, Dolejsek and others shows that the K-series of the elements of lower atomic numbers contain many lines not predicted by the regular energy level diagram. These lines have been referred to as spark lines and are explained by Wentzel as due to multiple ionization of the inner levels of the atom. The lines found by these authors appear (with one exception $K\beta'$) on the short wave-length side of the principal lines. The spark lines found by Dauvillier[8] associated with the $K\alpha$ lines were at a displacement corresponding to the order of 100 volts. The lines associated with the $K\beta$ lines had a displacement corresponding to less than 10 volts. Siegbahn and Larsson[9] have found that the $L\alpha$ lines of molybdenum are complex. These lines have associated with them spark lines whose displacement corresponds to about 10 volts.

The lines in the neighborhood of the $K\alpha$ lines of nickel and copper found in the course of this experiment all lie (with the exception of the line indicated by the asymmetry at T, Figs. 5 and 6) on the long wave-length side of the principal lines. The magnitude of their displacements corresponds to about 3 volts. Since the $K\alpha$ lines follow from the transition ($L \rightarrow K$) the suggestion is offered that these spark lines follow from transitions from multiply ionized L-levels to normal K-levels. The energy differences and the directions of displacements are consistant with this suggestion.

The curves of Siegbahn and Larsson show that as the voltage increased there appeared more spark lines in the neighborhood of Mo $L\alpha$. This caused a marked increase in the width of the line. The curves of Fig. 4 indicate that the widths of the $K\alpha$ lines of the elements investigated increased with voltage. These curves are consistent with the theory of successive appearance of spark lines as the voltage increased. An attempt was made to obtain width-voltage curves with both crystals at second order, but at voltages near the excitation limit the available energy was not sufficient to give accurate curves.

A table of the results of this experiment is given below. No attempt has been made completely to solve the problem of structure of the $K\alpha$ lines. However, the components indicated by the bulges found at first order are listed because the results at second order confirm them (see the bulges marked S, Figs. 5 and 6). These displacements of S on the second order curves check very well those found at first order provided the displacements be measured from the middle of the main curve at half-maximum rather than from the peak. These middle points are designated by the crosses (+) on Figs. 5 and 6.

These displacements of S from the center of the principal lines are significant in that they represent an interval in which there is evidence of structure. The maximum interval in which there is structure is larger than this by perhaps fifty percent.

[8] A. Dauvillier, Jour. d. Physique, Serie 6, **3**, (July, 1922).

[9] Siegbahn and Larsson, Ark. o. Physik, **18**, No. 18, (1924).

The widths of lines listed are not corrected for crystal imperfections by the Ehrenberg and Mark formula. This was considered unnecessary since the correction factor $(H_2^2-H_1^2)^{1/2}$ is equal practically to H_2 since

TABLE I. *Values for the widths, and separations of the components, of K series lines of Ni, Cu, Mo and Ag (40 kv.).*

Lines	Total Width Seconds	X. U.	Lines	Displacements Seconds	X. U.
		First Order			
Ni $K\alpha_{1,2}$	46	0.66	Ag $K\beta_2-K\beta_1$		0.63
Cu $K\alpha_{1,2}$	44	.63	Mo $K\beta_2-K\beta_1$		.58
Mo $K\alpha_{1,2}$	32	.47	S_1-Cu $K\alpha_1$		.42
Ag $K\alpha_{1,2}$	30	.43	S_2-Cu $K\alpha_2$		.35
Mo $K\beta_{1,2}$	30	.43	S_1-Ni $K\alpha_1$		.45
Ag $K\beta_{1,2}$	28	.40	S_2-Ni $K\alpha_2$		.38
		Second Order			
Components of			S_1-Cu $K\alpha_1$	80	0.5
Ni $K\alpha_{1,2}$ and			S_2-Cu $K\alpha_2$	65	.4
Cu $K\alpha_{1,2}$	60	0.4	S_1-Ni $K\alpha_1$	80	.5
Ni $K\beta_{1,2}$	60	.4	S_2-Ni $K\alpha_2$	65	.4
Cu $K\beta_{1,2}$	60	.4	Cu $K\beta_2-K\beta_1$	50	.32
			Cu $K\beta'-K\beta_1$	100	.7
			Ni $K\beta_2-K\beta_1$	45	.29
			Ni $K\beta'-K\beta_1$	100	.7

the value of H_1 found in these laboratories was less than two seconds of arc at second order and about three seconds of arc at first order.

In conclusion the author wishes to express thanks to Professor Bergen Davis for many helpful suggestions and for the use of the double x-ray spectrometer devoted to his personal researches.

PHYSICS LABORATORIES,
COLUMBIA UNIVERSITY,
March 12, 1928.