EXPERIMENTS ON THE REPORTED FINE STRUCTURE AND THE WAVE-LENGTH SEPARATION OF THE $K\beta$ DOUBLET IN THE MOLYBDENUM X-RAY SPECTRUM

By Samuel K. Allison and John H. Williams
University of California, Berkeley

(Received November 26, 1929)

Abstract

A nomenclature is suggested for describing the possible positions of the double x-ray spectrometer. A position may be defined by (n_A, n_B) where n_A is the order of reflection on crystal A; n_B the order on B. n_A is to be considered always positive. n_B is negative if the position of crystal B for the reflection of a wave-length incident upon it is such that by turning B through an angle of less than 90° the reflecting surface of B can be made parallel to that of A, and the given wave-length be reflected in this parallel position. If this convention be adopted it is shown that general equations for the instrument may be easily set up. Experiments on the separation of the $K\beta_1$ doublet of molybdenum at the position (2, 2) at 43–46 kv and 22 m.a. show that if the line $K\beta'$ reported by Davis and Purks[1] exists, its intensity is less than 1/10 that of β_1 at these voltages. An average of eight determinations of $\Delta\lambda$ for MoK, $\beta_1\,\beta_3$ gives 0.572 ± 0.003 XU.

Summary of Previous Work

THE doublet character of the $K\beta_1$ line in x-ray spectra has been noted by various experimenters.[1] Allison and Armstrong obtained a considerable separation of the doublet for molybdenum in the 5th order of a single crystal ionization spectrometer, and found $\Delta\lambda = 0.563$ XU. The intensity ratio β_1/β_3 was found to be 2/1. Larsson achieved a separation of the doublet photographically and found $\Delta\lambda = 0.565$ XU. Kellström investigated the doublet in the second order and obtained good separations in palladium and silver, and a very good separation was obtained by Enger and photometered, for the case of rhodium. Davis and Purks, using a double spectrometer, obtained a complete separation of the doublet with both crystals reflecting in the second order. They report a new line $K\beta'$, 0.172 XU. (24 seconds of arc at the dispersion used) to the long wave-length side of $K\beta_1$, and of intensity about 1/3 to 1/2 that of β_1. The voltage at which their tube was operated was not stated in their report. The photographs taken

[1] M. de Broglie, Compt. Rend. **170,** 1053 and 1245 (1920); Duane and Patterson, Bull. Nat. Res. Counc. USA Vol. 1, part 6, p. 393 (1920); Crofutt, Phys. Rev. **24,** 9 (1924); Allison and Armstrong, Phys. Rev. **26,** 701 (1925); Leide, Compt. Rend. **180,** 1203 (1925); Thesis, Lund (1925); Ehrenberg and von Susich, Zeits. f. Physik **42,** 823 (1927); Larsson, Phil. Mag. **3,** 1136 (1927); Kellström, Zeits. f. Physik **41,** 516 (1927); Enger, Zeits. f. Physik **46,** 826 (1928); Stenman, Zeits. f. Physik **48,** 349 (1928); Edlén, Zeits. f. Physik **52,** 364 (1928); Davis and Purks, Proc. Nat. Acad. Sci. **14,** 172 (1928); J. Valasek, Phys. Rev. **34,** 1231 (1929). The same author has also reported, in a paper read at the Dec. 1929 meeting of the Amer. Phys. Soc., that attempts to find the fine-structure lines announced by Davis and Purks were unsuccessful.

by Enger in rhodium were obtained at 50–60 kv and no such line is indicated on them. An attempt has been made to study this new line in molybdenum, using a double x-ray spectrometer.

Apparatus

Several standard molybdenum target tubes supplied by the General Electric Co. for crystal analysis work were used in the course of the experiments. These tubes were cooled by a pump circulating kerosene through the hollow target; the kerosene after entering and leaving the target through insulated glass tubes, was cooled by passing through a copper spiral immersed in running water. The target and the cathode of the tube were at potentials above and below ground respectively. The focal spot was at a distance of 53 cm from crystal A, and the radiation used was taken off at an angle of 8° with the target face. A description of the double spectrometer used has been previously published.[2] The horizontal angular width of the beam (angular width in a plane perpendicular to the axes of rotation of the crystals) was determined by the width of the slits of the instrument, which were 35 cm apart. These slits were 1.5 and 1.8 mm wide in various experiments. The voltmeter which measured the voltage across the x-ray tube was connected between the cathode side of the tube and ground, and therefore measured only half the total potential drop across the tube. It was found by trial that the potential of the anode above ground was very nearly equal to that of the cathode below ground so that the indication of the voltmeter needed only to be multiplied by two. The tube current in all experiments was 22 m.a., the voltage in some was 43 kv and in some 46 kv. In the course of the experiments three different sets of calcite crystals were used.

Nomenclature for the Double X-ray Spectrometer

Since two crystals are used in the double x-ray spectrometer, we have found it convenient to specify their positions by giving two numbers n_A and n_B which represent the orders in which crystals A and B are reflecting respectively. The corresponding glancing angles are θ_A and θ_B. The sign of n_A is to be taken as positive in all cases. The sign of n_B is determined as follows. If the position for crystal B for the reflection of a given wave-length incident upon it is such that by turning B through an angle less than 90° the reflecting surface of B can be made parallel to that of A, and the given wave-length reflected in this parallel position, n_B is negative. If an angle greater than 90° must be traversed in order to bring the crystals to this type of parallel position, n_B is positive. According to this convention, so-called "parallel positions" (Ehrenberg and Mark[3] Case I; Schwarzschild[4] Case II) are special cases of a number of positions in which n_B is to be considered negative. Using this convention, we may write for the dispersion D,

[2] Williams and Allison, J.O.S.A. & R.S.I. **18,** 473 (1929).
[3] Ehrenberg and Mark, Zeits. f. Physik **42,** 807 (1927).
[4] Schwarzschild, Phys. Rev. **32,** 162 (1928).

$$D \equiv \frac{d\theta_B}{d\lambda} = \frac{n_A}{2d \cos \theta_A} + \frac{n_B}{2d \cos \theta_B} \tag{1}$$

in which $d\theta_B$ is the angular range on crystal B corresponding to the wave-length range $d\lambda$, and d is the grating space (assumed to be the same on both crystals).

If the absolute value of n_B is greater than that of n_A and n_B is negative, D is negative, and the sense of rotation of crystal B to pass from shorter to longer wave-lengths is the reverse of that for cases in which D is positive. This is the case, for example, in the position $n_A = 1$, $n_B = -2$, which we designate as the $(1, -2)$ position. Here the dispersion is negative, and for molybdenum K radiation its magnitude is only slightly greater than that from a single crystal reflecting in the first order.

Using the conventions suggested here, Schwarzschild's equation[5] for the "geometric breadth" $\delta\theta_B$, in the case in which the two axes of rotation lie in the reflecting faces of the crystals and are parallel, may be written

$$\delta\theta_B = \tfrac{1}{2} D\lambda\phi^2. \tag{2}$$

In the preceding equation, $\delta\theta_B$ is the angular range through which crystal B may be turned while reflecting the wave-length λ. D is the dispersion defined by (1). ϕ is one-half of the maximum angle between any two rays incident on crystal A in a plane parallel to the axis of rotation of A. In other words, if the only restraint upon the divergence of the x-ray beam is that it must pass through two equal rectangular apertures separated by a distance L, whose height, or dimension in a plane parallel to the axis of rotation of the crystal is h, then $\phi = h/L$.

If the geometric width $\delta\theta_B$ has been made small in comparison to the observed width, and can be neglected, the following equation holds for the width observed for any line in the spectrum at any position of the crystals:

$$W = (W_A^2 + W_B^2 + D^2 W_\lambda^2)^{1/2}. \tag{3}$$

In this equation W represents the half width at half maximum in angular measure of the observed "rocking curve," W_A the half width at half maximum in angular measure of the curve (assumed Gaussian error curve) representing the intensity of reflection from crystal A as a function of the deviations from the Bragg angle, W_B is the analogous quantity for crystal B, D is defined in (1) and W_λ is the half width at half maximum of the line in question in linear measure.

Attempt to Find the Line $K\beta'$

Some of the curves we have taken which have the most direct bearing on the intensity of the line $K\beta'$ are shown in Fig. 1. These curves were all

[5] Schwarzschild expressed this equation in the form $\delta\theta_B = 1/2(\tan\theta_1 \pm \tan\theta_2)\phi^2$ in which the negative sign was to be chosen when the crystals are in a position where "the first incident and the last reflected rays are on opposite sides of the first reflected ray." This agrees with our method of designating the sign of n_B.

taken in the (2, 2) position (both crystals in the second order, reflecting faces not parallel).

Curve (*a*). This curve was taken at 43 kilovolts and 22 milliamperes. The rate of deflection of the electrometer observed on a scale 225 cm from the instrument was 0.744 mm per second at the highest point of $K\beta_1$. At the base-line point on the short wave-length side it was 0.163 mm per second. The voltage sensitivity of the electrometer on the scale at this distance was 4.5 meters per volt. The capacity of the insulated system was not accurately known but was of the order of magnitude of 10^2 cm. The width of the lines

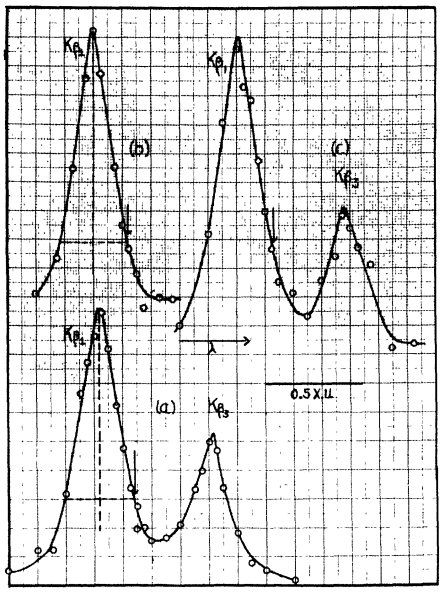

Fig. 1. Typical curves bearing on the intensity of $K\beta'$.

to be expected from geometric sources may be calculated from Eq. (2). The vertical adjustment of the two crystal faces was made by observing the reflection of a beam of light from their faces. This beam as made horizontal by passing through two narrow slits held on a cathetometer and was very nearly perpendicular to the reflecting crystal surfaces. The crystal was then tilted about a horizontal axis until the reflected beam was in the same horizontal plane as the incident beam. This adjustment was accurate to 2 minutes of arc. ϕ was calculated from the height of the focal spot (3 mm) and the height of crystal B (18 mm) and the distance from the target of the tube to crystal B (71 cm). This gives $\phi = 0.0147$, $\delta\theta_B = 9.5$ seconds of arc. The half width at half maximum of the curve for β_1 is approximately 15.5 seconds of arc; the preceding calculation shows that this cannot be explained as due to geometrical causes only. We do not wish to take up the question of the width of x-ray lines here, leaving this for a later publication. The half

width at half maximum of the curve at (1, −1) for these crystals was 3.1 seconds of arc.

Curve (*b*). This curve was taken with the same arrangement as that of curve (a) except that a vertical stop 7.5 mm high was introduced at a distance of 48 cm from the target. This gives $\delta\theta_B = 5.2$ seconds of arc from Eq. (2). The voltage was 43 kv. The rate of deflection of the electrometer (scale and sensitivity as for curve (a)) at the highest point on the peak was 0.398 mm per second; at the lowest point shown on the short wave-length side it was 0.093 mm per second. The half width of the peak at half maximum is about 14 seconds. An accident to the x-ray tube prevented continuing the curve to cover β_3.

Curve (*c*). This curve was taken on a different set of crystals and with a different target from that used in curves (a) and (b). The voltage was 46 kv. The rate of deflection of the electrometer (same arrangement as for (a) and (b)) at the highest point of β_1 was 0.475 mm per second; at the lowest point on the short wave-length it was 0.162 mm per second. The value of ϕ and consequently of $\delta\theta_B$ was the same as that for curve (a). For various unknown reasons the curve (c) is less reliable (as indicated by the scattering of the points) than curves (a) and (b). The half width at half maximum of the curve at (2, −2) for the crystals used was 1.5 seconds of arc.

The vertical arrows in Fig. 1 show the angular positions at which β' should appear (24 seconds of arc to the long wave-length side of β_1) according to the results of Davis and Purks.[1] In curves (a) and (b) the total intensity here is about 1/5 of that at the maximum. In these curves, the vertical dotted line represents the center of the line $K\beta_1$; the horizontal dotted line its width at an angular distance of 24″ from the center. It is evident that within the accuracy of the readings the curve is symmetrical in this region about an ordinate through its maximum. We can therefore obtain no positive evidence for the presence of the line $K\beta'$ at the voltage used.

A rough estimate of the maximum possible intensity in the form of the line $K\beta'$ which could be present in our curves may be obtained by assuming a Gaussian error curve for β' symmetrical about the position indicated, and of the same half width as that for β_1. The distortion of the symmetry of β_1 which would be thus produced can be plotted by adding up the contributions from β_1 and the supposed β' at various abscissae. Proceeding by this method the conclusion was reached that the curves (a) and (b) could not have failed to show evidence of a line in the specified position of intensity 1/10 that of β_1. Our conclusion is therefore that there is no line at this position of intensity greater than 1/10 that of β_1 under the conditions of the experiment.

Determination of the Wave-Length Separation of the Doublet $K\beta_1$, β_3 in Molybdenum

In the course of the investigation many curves have been taken of the doublet in question in various positions of the double spectrometer. Eight of the most reliable of these have been selected for the purpose of obtaining an accurate value of $\Delta\lambda$ for this doublet. The results are shown in Table I.

TABLE I. *Observations on the wave-length separation of* β_1, β_3.

Position n_A	Position n_B	Dispersion from Eq. (1)	$d\theta_B$ obs.	Av. $d\theta_B$	$\Delta\lambda$ calc.	Weight
1	1	68.46″/XU	39.1″	39.1″	0.5711XU	2
1	2	103.8	61.0 61.2 59.5	60.6	.5835	9
1	3	140.7	80.0	80.0	.5687	4
2	2	139.2	78.5 77.0	77.8	.5587	8
2	3	176.0	101.5	101.5	.5766	5

The weights assigned in the last column of Table I are the products of the number of observations for a given position by (n_A+n_B) for that position, since it was supposed that higher dispersion gave more accurate results. The weighted mean of the measurements shown in Table I is

$$\Delta\lambda=0.572\pm0.003\text{XU}$$

in which the probable error has been computed according to the usual methods.[6] This value is slightly higher than the values 0.563 XU observed by Allison and Armstrong[1] and 0.565 XU observed by Larsson.[1] In general the effect of greater resolution of a close doublet should be to increase the estimate of its wave-length separation. The errors in the value quoted must be mainly due to two factors (1) the uncertainty of the electrometer readings, and (2) the fact that a change of temperature of the crystals might have taken place between the time of reading one peak and the time for the next.

[6] For instance, Birge, Phys. Rev. Supp. **1**, 1 (1929), pp. 5–6.