THE RESOLVING POWER OF CALCITE FOR X-RAYS AND THE NATURAL WIDTHS OF THE MOLYBDENUM $K\alpha$ DOUBLET

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

(Received May 14, 1930)

Abstract

The half widths at half maximum of the rocking curves in parallel positions of the double x-ray spectrometer have been observed for the first five orders of reflection of Mo$K\alpha_1$ from calcite. The calculated half widths for a single crystal have been compared with the theoretical results of Darwin and Ewald. The observed values are of the same order of magnitude as the theoretical, but slightly larger (1.4 times as large in the first order).

The rocking curve widths in 8 anti-parallel positions for Mo$K\alpha_1$ at 50 k.v. have been observed. Geometric corrections arising from the vertical spread of the beam have been applied. The half width at half maximum of Mo$K\alpha_1$ has been found to be 0.147 X.U. corresponding to an energy width of 3.6 volts. The variation of this width with voltage from 25 to 50 k.v. has been studied, and no significant variation found. The half width at half maximum of Mo$K\alpha_2$ at 50 k.v. was observed in 2 positions and found to be 0.161 X.U., the corresponding energy width being 3.9 volts. The observed difference between α_1 and α_2 is close to the experimental error and may not be real. The observed values are 2.5 times as great as the width to be expected from a classical electronic oscillator damped by its electromagnetic radiation.

The computed life of the excited K state of molybdenum is 1.8×10^{-16} seconds. No evidence of fine structure of Mo$K\alpha_1$ or α_2 was obtained.

THIS paper is a report of experiments performed with the double x-ray spectrometer recently constructed in this laboratory. Experiments analogous to those described here have been carried out by Davis and Stempel,[1] Wagner and Kuhlenkampff,[2] Ehrenberg and Mark,[3] Ehrenberg and von Susich,[4] Davis and Purks,[5] and Allison.[6] These experiments will be discussed later in connection with various topics in this report.

Apparatus

The double spectrometer with which these results were obtained has been described elsewhere.[7] Constants of the spectrometer, some of which were

[1] Davis and Stempel, Phys. Rev. **17,** 608 (1921), **19,** 504 (1922).

[2] Wagner and Kuhlenkampff, Ann. d. Physik **68,** 369 (1922).

[3] Ehrenberg and Mark, Zeits. f. Physik **42,** 807 (1927).

[4] Ehrenberg and von Susich, Zeits. f. Physik **42,** 823 (1927).

[5] Davis and Purks, Proc. Nat. Acad. Sci. **13,** 419 (1927), **14,** 172 (1928), Phys. Rev. **34,** 181 (1929).

[6] S. K. Allison, Phys. Rev. **34,** 176 (1929).

[7] Williams and Allison J.O.S.A. and R.S.I. **18,** 473 (1929). Opportunity is taken here to point out some errors in this paper. The equation on page 474 is only approximately true, the correct expression being Eq. (1) of the present paper. On page 475 the tube holding the slits is stated to be 35 cm long whereas it actually is 30 cm. It is also stated that "the horizontal width of the slits can be adjusted to give the maximum resolving power" whereas the resolving power of the double spectrometer is independent of the slits mentioned.

not previously given, are as follows: distance from the focal spot of the x-ray tube to the first crystal (crystal *A*), 53 cm; distance between the axes of crystals *A* and *B*, 19 cm; distance from the axis of crystal *B* to the ionization chamber window, 4.5 cm; length of the ionization chamber, 40 cm; diameter of the chamber, 4.3 cm. The ionization chamber was filled with a mixture of ethyl bromide and argon at partial pressures of 17 cm and 59 cm respectively. The slit for admitting x-rays into the ionization chamber was 3 mm wide.

Two slit systems were used simultaneously which will be referred to as the horizontal and vertical slits respectively. The vertical slits limited the spread of the beam in a horizontal plane (more generally, a plane perpendicular to the axes of rotation of crystals *A* and *B*). The horizontal slits limited the spread of the beam in a vertical plane (one including the axes of rotation). The vertical slits were 30 cm apart and each 1.5 mm in width. The horizontal slits were 30.95 cm apart. The widths used for them will be given later.

Molybdenum target tubes supplied by the General Electric Company for crystal analysis work were used. In these tubes the face of the target is normal to the impinging electron beam which lies in the long axis of the tube. The radiation used in the spectrometer was taken at a glancing angle of 8° from the target face. It will be shown later that this is not the most desirable arrangement for the double spectrometer. The tubes were cooled by pumping kerosene through the targets.

The high potential for operating the tubes was supplied by a 550 cycle transformer-kenetron-capacity set in which the calculated voltage fluctuations at 50 k.v. and 20 milliamperes tube current were 1.8 percent. The voltages were read on a high voltage electrostatic voltmeter which had been calibrated by measuring the short wave-length limit of the continuous spectrum.

The electrometer has been described in a previous paper.[7]

The calcite crystals used were freshly cleaved from an optically clear parallelopiped whose surfaces were cleavage planes, by placing a razor blade as accurately as possible parallel to the cleavage direction and tapping it sharply with a light hammer. The faces from which the x-rays were reflected were the fresh faces from a single fracture and were rhombs whose sides were 1.9 cm long. These faces were not by any means optically flat. Close inspection showed that the fracture had not been all in one plane but that there were very thin "steps" on the crystal face. The holders for the crystals could be slipped out of the dove-tailed guides[8] and replaced in them without changing the orientation of the crystals more than about 10 seconds of arc about a vertical axis. The crystals were removed in this manner after each set of readings and placed in a dessicator over dehydrated calcium chloride and a few sticks of sodium hydroxide. This was done to safeguard the fresh surfaces from attack by acid fumes which might be in the

[8] See reference 7, Fig. 2 p. 476. The springs *K* were unhooked, and *E* and its superstructure slid out of *F*.

air. There was no evidence of deterioration of the surfaces during the period of observation.

A thermometer which could be read to a few hundredths of a degree centrigrade was placed over the spectrometer and read at frequent intervals while working in anti-parallel positions.

Adjustments

It is convenient to speak of a "central ray" which may be defined as a ray passing through the geometric centers of the slit apertures. The adjustment of the instrument must insure the following conditions.

(1) The central ray must pass through the center of the focal spot of the x-ray tube.

(2) The central ray must intersect the reflecting surface of crystal A near its geometric center.

(3) The axis of rotation of crystal A must intersect the central ray at the point where the ray intersects A's surface.

(4) The axis of rotation of crystal A must lie in its reflecting surface.

(5) The central ray, after reflection from crystal A, must intersect the reflecting face of crystal B near its geometric center.

(6) The axis of rotation of crystal B must intersect the central ray at the point where the ray intersects B's surface.

(7) The axis of rotation of crystal B must be parallel to that of A.

(8) The axis of rotation of crystal B must lie in its reflecting surface.

(9) The central ray after reflection from crystal B, must enter the ionization chamber through the center of its slit and pass down the long axis of the chamber.

A necessary condition for the fulfillment of these requirements is that the central ray, the focal spot of the tube, the geometrical centers of the reflecting faces of the crystals and the axis of the ionization chamber lie in the same (horizontal) plane. This is accomplished partly in the original construction of the instrument and partly in the judicious placing of the crystals on their holders.

The spectrometer was levelled by means of levelling screws. The reflecting face of A was made vertical as follows. A cathetometer carrying a horizontal slit system was set up about 150 cm from the axis of A. The cathetometer was used merely as a rigid support for the slit system. The horizontal slit system of the cathetometer could be rotated about a horizontal axis until its central ray was horizontal to within 30 seconds of arc. This was accomplished by means of a sensitive spirit level. A parallel beam of light from an arc-lens combination was sent through the slits carried by the cathetometer and reflected from crystal A. The cathetometer was set in such a position that the reflected beam from the surface of A almost coincided with the incident beam. By means of a set screw in the crystal holder,[9] A was tilted about a horizontal axis until the beam reflected from it was in the same horizontal plane as the

[9] See reference 7, Fig. 2 476. R is the set screw referred to here.

incident beam. Due partially to the step-like structure of the cleavage surfaces previously mentioned, the reflected beam was not perfectly defined and this allowed an error of perhaps 2 minutes of arc to remain in the verticality of A.

The vertical slit system of the spectrometer was then made vertical by a plumb line or by setting an accurate right angle on the upper flat surface of the spectrometer and sighting past its vertical arm through the slits. The mechanism for closing the jaws of the vertical slits was such that they necessarily opened symmetrically about the central ray. The slits were then made about 0.05 cm wide and a beam of light from an arc sent into the spectrometer. This beam was observed on a ground glass or other translucent material after it had passed the axis of crystal A. Crystal A was then translated horizontally and rotated about its vertical axis until the ground glass showed that its face, when parallel to the light beam, extended just halfway into it. The crystal was then rotated through 180°. In this new position it did not, in general, again bisect the beam. Half of the adjustment necessary was taken up by rotation of the slit system about a vertical axis and half by translation of A horizontally and rotation about its vertical axis. A was then rotated through 180° again and the process repeated. By this method requirements (2), (3), and (4) of the preceding list could be satisfied.

In the adjustment of crystal B it was assumed that in the construction of the instrument requirement (7) has been met. It will be seen that this uncertainty may be a cause of error in the curves obtained in parallel positions. Crystal A was removed from the spectrometer. Crystal B was made vertical by the cathetometer method, and the arm carrying B's axis of rotation (this arm revolved about the axis of A) was set so that the beam of light from the spectrometer slits passed approximately over B's axis. The accurate adjustment was made similarly to that of A by repeated rotations of B through 180°. In this case the arm carrying the axis of B and the horizontal translation of B were adjusted until the surface of B was half-way across the beam at positions 180° apart. In this way requirements (5), (6), (7), and (8) were satisfied. In subsequent settings of the instrument the arm carrying the axis of B was rotated through twice the angle that the crystal A was turned around its axis.

The ionization chamber was set by noting where the beam of light entered its window. Later the position corresponding to requirement (9) was more accurately found by moving the ionization chamber across the reflected beam of x-rays from crystal B and setting it at the center of the angular range through which radiation entered its window.

When the adjustments of crystals A and B and the preliminary adjustment of the ionization chamber had been made the x-ray tube and horizontal slits were put in place. By means of a fluorescence screen it was ascertained that the x-ray beam (which in the actual experiments had a rectangular cross section about 0.15×0.1 cm at crystal A) was horizontal. The vertical slits were then further narrowed and the instrument used as a single crystal spectrometer with only crystal A in use. An emission line of the target was

found and the x-ray tube shifted horizontally until the maximum intensity was obtained. This made certain that the central ray passed through the most intense part of the focal spot of the tube.

Purpose of the Experiments

The purpose of the experiments can best be understood by a brief outline of the theory of the instrument. A notation for the double spectrometer has been suggested by the authors in a previous paper.[10] This notation has been of the greatest service in guiding the course of the experiments and will be retained. A fundmental expression for the instrument is that the dispersion D may be written as follows:

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

in which the meaning of the symbols and the convention as to sign of n_B have been previously given.[10] n_A is to be considered always positive. n_B is negative when the first incident and last reflected rays are on opposite sides of the first reflected ray,[11] otherwise it is also positive. A setting of the instrument is described by giving the values of n_A and n_B in the form (n_A, n_B) and of the wave-length reflected. Eq. (1) is derived by differentiation of the Bragg law and addition of the dispersions of the cystals.

The second equation for the double spectrometer that we shall consider here gives the observed width of the rocking curve for any line in the spectrum at any setting of the instrument. We will temporarily assume that geometric widths due to slit heights and deviations of the crystals from verticality have been made negligibly small. We then have[12]

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

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. In the derivation of (2) it is assumed that the line has a Gaussian error curve distribution of intensity.

From Eqs. (1) and (2) it is seen that the positions of the double spectrometer naturally fall into two classes, so-called parallel and anti-parallel positions. Parallel positions are distinguished by having $D = 0$, or $n_B = -n_A$. If $D = 0$ in Eq. (2) we see that the observed width is due to the angular range through which a crystal may be turned and reflect a single wave-length, in

[10] Allison and Williams, Phys. Rev. **35**, 149 (1930). The interpretation of negative values of D from Eq. (1) is also found here.

[11] Schwarzschild, Phys. Rev. **32**, 162 (1928).

[12] Schwarzschild, reference 11. This equation may be obtained by combining Eqs. (43) and (45) of his paper. Important special cases of this equation had been previously developed by Ehrenberg and Mark, reference 3.

other words, the widths in such positions are closely related to the limit of resolution of the instrument. Anti-parallel positions have $D \neq 0$ and are all positions for which $n_A \neq -n_B$. From Eq. (2) it is seen that the rocking curves in such positions include, in addition to the factors giving the widths in parallel positions, contributions from the widths of the spectrum lines themselves.

Results in Parallel Positions

If $D = 0$ in Eq. (2), it becomes

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

If we now assume that $W_A = W_B = W_c$ we may write this

$$W = 2^{1/2} W_c \tag{4}$$

where W is the observed width and W_c the interference pattern width from a single crystal.

We have investigated the values of W for the reflection of Mo$K\alpha_1$ in the first five orders from the cleavage face of calcite. If the adjustments previously described were not perfect, there would be an appreciable width to the rocking curve in these positions due to geometric causes, that is, there would be a width even if the width of the interference pattern of the crystals were zero. It has been shown by Schwarzschild[13] that this width would be

$$\delta\theta_B' = \frac{2\phi(\delta_A + \delta_B)}{\cos\theta} \tag{5}$$

where $\delta\theta'_B$ is the angular range in parallel positions through which crystal B may be turned and yet reflect some of the radiation sent to it by A. δ_A and δ_B are the angular deviations of the reflecting faces of crystals A and B from verticality, θ is the glancing angle, (the same for both crystals) and ϕ is one half of the maximum angle between any two rays in a plane parallel to the axes of rotation of the crystals. Eq. (5) is derived on the assumption that the axes of rotation of crystals A and B are parallel.

In our experiments it was found that the widths of the rocking curves in parallel positions were very sensitive to deviations from verticality of the crystals. The method of setting for verticality previously described was not sufficiently accurate in general to produce the narrowest curves. The following procedure was adopted. The face of crystal A was set vertical within the limits of accuracy of the cathetometer method. (The reflected light beam was somewhat sharper from A than from B). Crystal B was then set vertical within the limits of error and a rocking curve taken. B was then rotated in small steps[14] around a horizontal axis (a minute of arc at a time) and rocking curves taken for each position until a minimum width was found. If at this position δ_A and δ_B are zero, then from Eq. (4) the width observed should be

[13] Schwarzschild, reference 11. see Eq. (24) of his paper in which $R = 2(\delta_\alpha + \delta_\beta)/\cos\theta$ and $\phi = s/L$

[14] See the figure mentioned in reference 9. The screw R is used.

independent of ϕ. Several experiments were made to test this by changing the value of ϕ after the position of minimum width had been found. ϕ was varied by varying the width of the horizontal slits. The maximum value of ϕ was limited by the height of crystal B and was about 0.015.

TABLE I. *Minimum half width at half maximum in parallel positions as a function of* ϕ. $MoK\alpha_1$.

Position	ϕ	Observed W seconds
(1, −1)	.015	3.0
(1, −1)	.012	3.0
(2, −2)	.015	1.0
(2, −2)	.0072	1.1
(2, −2)	.0054	.90

Table I shows that from a value of ϕ of 0.0054 to a value of 0.015 the changes in the width of the rocking curve observed were within the limit of error to which a given experiment could be duplicated. The low intensity of reflections such as (4, −4) and (5, −5) made the use of the larger value of ϕ very desirable and Table I seems to justify this procedure.

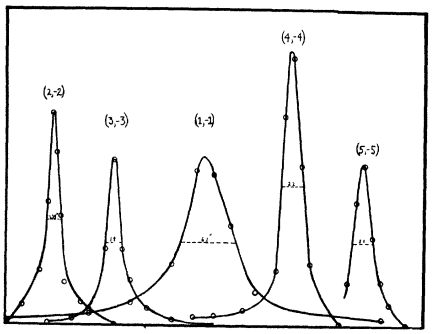

Fig. 1. Observed rocking curves in parallel positions. Ordinates are proportional to ionization currents, abscissae to angular settings of crystal B. The vertical scale is not the same for all the curves.

Fig. 1 shows some of the rocking curves obtained, and in Table II the half widths at half maximum, together with the values of W_c calculated from Eq. (4) are listed.

TABLE II. *Minimum half widths at half maximum in parallel positions.* $MoK\alpha_1$

Position	W(seconds)	W_c(seconds)
(1, −1)	3.0	2.1
(2, −2)	.90	.64
(3, −3)	.95	.67
(4, −4)	1.1	.78
(5, −5)	1.2	.88

Discussion of Results in Parallel Positions

Sources of error. Probably the most important source of error in the values of Table II arises from a possible lack of parallelism of the vertical axes around which A and B were rotated. Unfortunately the apparatus was designed in such a manner that these axes were rigid with respect to each other and no adjustment could be made. Other sources of error are (1) irregularities in the slow motion screw moving B; (2), temperature differences between crystals A and B. No evidence of irregular motion of B was obtained; rotation in regular steps of one-half second of arc seemed possible. Although variations in the temperature of the room of a few tenths of a degree centigrade sometimes occurred while a curve was being taken, the possibility of significant temperature difference between the two crystals (19 cm apart) seems excluded.

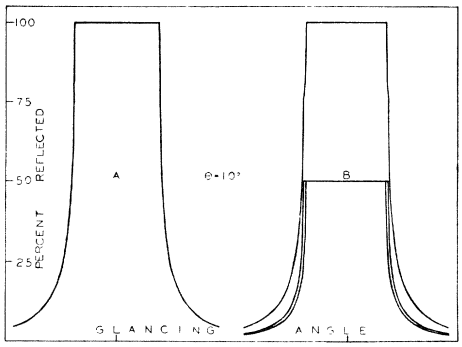

Fig. 2. A. Theoretical reflection curve from a perfect crystal for polarized x-rays (Eq. (6) and (7) and (8), or Eq. (9) and (7) and (8)). B. Theoretical reflection curve for unpolarized rays. The innermost curve represents the reflection of the component whose electric vector lies in the plane of incidence. The intermediate curve represents reflection of radiation polarized so that its electric vector lies perpendicular to the plane of incidence. The outermost curve is the sum of these components.

Comparison with theory of a perfect crystal. The reflection of plane waves from a so-called perfect or ideal crystal in which there is no warping or mosaic structure has been theoretically studied by Darwin[15] and Ewald.[16]

Plane, monochromatic waves fall on an idealised crystal made up of electrons lying on planes separated by a constant distance. The radiation is polarized in such a plane that the electric vector lies perpendicular to the plane of incidence. Fig. 2a shows the intensity of reflection to be expected as a function of glancing angle. The curve is symmetrical about a glancing angle which may be obtained from that calculated by Bragg's law by correcting for the index of refraction. The extent of the region of 100 percent reflection is given by

$$\Delta\theta = 4\delta \operatorname{cosec} 2\theta \tag{6}$$

[15] Darwin, Phil. Mag. **27,** 325 and 675, (1914).
[16] Ewald Phys. Zeits. **26,** 29 (1925).

where $\Delta\theta$ is the range of glancing angle θ; δ is the deviation of the index of refraction from unity. Outside the region of perfect reflection, the intensity falls off rapidly. The equation of the curve in these regions is given by

$$I_{\theta'-\theta} = I_0\left(\frac{\Delta\theta}{2(\theta'-\theta)+(4(\theta'-\theta)^2-\overline{\Delta\theta}^2)^{1/2}}\right)^2, \quad \theta'-\theta > \frac{1}{2}\Delta\theta \tag{7}$$

$$I_{\theta'-\theta} = I_0\left(\frac{\Delta\theta}{2(\theta'-\theta)-(4(\theta'-\theta)^2-\overline{\Delta\theta}^2)^{1/2}}\right)^2, \quad \theta'-\theta < -\frac{1}{2}\Delta\theta \tag{8}$$

where $I_{\theta'-\theta}$ is the intensity at a glancing angle θ', I_0 is the incident intensity, and $\Delta\theta$ is defined by Eq. (6). If $I_{\theta'-\theta}/I_0$ is set equal to $\frac{1}{2}$ in Eq. (7), and the half width at half maximum calculated it is found to lie at a value of $\theta'-\theta$ equal to $1.06\,\Delta\theta/2$.

If the incident radiation is plane polarized in such a manner that the electric vector lies in the plane of incidence, the analogous equation to Eq. (6) is

$$\Delta\theta = 4\delta \cot 2\theta. \tag{9}$$

The radiation used in these experiments was a characteristic emission line of the target, known to be unpolarised. We may consider the unpolarised incident light resolved into two components, with electric vectors parallel and perpendicular to the plane of incidence. The intensity of each one of these components will be half the incident intensity. The reflection curve for unpolarised incident rays will then be the sum of two curves given by Eqs. (6) and (9) and the Eqs. (7) and (8) appropriate to each. Such a curve is shown in Fig. 2b.

The half width at half maximum for the unpolarised curve will be slightly greater than 2δ cosec 2θ by a factor which approaches 1.06 as the glancing angle is decreased and falls off to unity at larger glancing angles. As will be seen later this correction is less than the uncertainty in the structure factors involved and will therefore be disregarded.

For a real crystal, the electrons are of course not situated on equidistant planes but are distributed throughout the structure. In this case the formula for the half width at half maximum for unpolarised radiation becomes

$$2F\delta \operatorname{cosec} 2\theta/Z \tag{10}$$

where

$$F = \sum_i F_i e^{2\pi n i(hx_i+ky_i+lz_i)}. \tag{11}$$

In the preceding equations, F is the structure factor, or equivalent reflecting power of the Z electrons in the unit cell of the crystal, F_i is the ionic structure factor, n is the order of reflection, h, k, l are the Miller indices of the plane, and x_i, y_i, z_i are the coordinates of the atom i in the unit cell.[17] The unit cell of

[17] Our thanks are due Professor Linus Pauling for his aid in calculating the structure factors given here.

calcite contains two molecules of $CaCO_3$. Its sides are not parallel to those of a natural cleavage parallelopiped, so that the Miller indices of a plane in the true unit and the cleavage unit are not the same. The cleavage plane, which has indices (100) in the cleavage unit, has indices (211) in the true unit,[18] and these are the values to use in Eq. (11) for *hkl*. The ionic structure factors for calcium and oxygen were taken from Bragg and West.[19] The ionic structure factor for carbon was assumed to be one-fourth of that for oxygen. The calculation of the structure factors used is indicated in Table III.

TABLE III. *Structure factors for* (100) *planes of calcite for* $MoK\alpha_1$.

Order	$(\sin\theta)/\lambda$	F_{Ca}	F_C	F_O	F
1	0.165	15.1	1.8	6.6	$2(F_{Ca}+F_C+F_O)=47.0$
2	.330	10.5	.9	3.3	$2(F_{Ca}+F_C)-2F_O=16.2$
3	.495	7.6	.4	1.7	$2(F_{Ca}+F_C+F_O)=19.4$
4	.660	5.9	.2	.9	$2(F_{Ca}+F_C)+6F_O=17.6$
5	.825	4.5	.1	.5	$2(F_{Ca}+F_C+F_O)=10.2$

The theoretical half widths at half maximum for the unpolarised $MoK\alpha_1$ radiation from calcite may now be found by inserting the values of F from Table III in Eq. (10), using $Z=100$. The value of δ taken from A. H. Compton[20] is 1.84×10^{-6}. In this way the theoretical values of Table IV were obtained, in which experimental values due to Davis and Purks[21] are included.

TABLE IV. *Comparison of theoretical and observed values of* W_c (*Eqs.* (10) *and* (4). $MoK\alpha_1$

Order	W_c Theory Eq. (10)	W_c Exp. Eq. (4)	W_c Davis and Purks
1	1.5 sec.	2.1 sec.	1.6 sec.
2	.28	.64	.45
3	.22	.67	
4	.16	.78	
5	.08	.88	

The values of Table IV are shown graphically in Fig. 3. It is seen that the crystal reported by Davis and Purks has very nearly the predicted half width for a perfect calcite crystal, while those used in this investigation were less perfect on this criterion. It is interesting to note that the theory gives results which agree well with experiment for the widths of the curves, although it is known that the intensity predictions are not verified.

[18] Strukturbericht of the Zeits. für Krystallographie, pp. 292–295.

[19] Bragg and West, Zeits. f. Krystallographie **69**, 118 (1928).

[20] A. H. Compton, X-rays and Electrons, p. 218 Table VII–2.

[21] Davis and Purks Phys. Rev. **34**, 181 (1929). These investigators state that their observed widths are less than those predicted for a perfect crystal. They used a theoretical formula, however, in which an effective width had been calcualted for the purpose of expressing the reflected energy as the product of the incident intensity by this effective region of 100% reflection.

Results in Anti-Parallel Positions

In the nomenclature which we have adopted for the instrument, D is finite in anti-parallel positions. The total geometrical width in anti-parallel positions is given by the formula

$$\delta\theta_B = \tfrac{1}{2}D\lambda\phi^2 \tag{12}$$

in which $\delta\theta_B$ is the *total* angular range through which crystal B can be turned while reflecting the wave-length λ.[22] Since what we have measured is the half width at half maximum, the correction for geometric width should not be the entire amount of Eq. (12). The purely geometric rocking curve corresponding to Eq. (12) is not symmetrical about its maximum.[23] Its shape depends on the

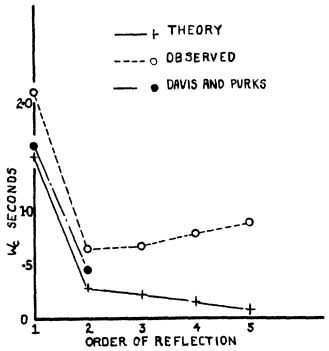

Fig. 3. Comparison of observed and calculated values of the half width at half maximum of the reflection curve from calcite.

intensity of the bundle of parallel rays passing through the slits and making an angle α with the central ray in a vertical plane relative to that of the bundle of rays proceeding parallel to the central ray. This will be referred to as the variation of intensity with vertical divergence of the beam. If the widths of the horizontal slits are h_1 and h_2, $(h_2 \geqq h_1)$, and the distance between them is L,

$$\phi = (h_1 + h_2)/2L. \tag{13}$$

ϕ calculated from Eq. (13) gives the upper limit of α. If we neglect variations of intensity in the focal spot itself, we may assume that the intensity of a parallel bundle of rays is proportional to its cross-section area. This gives

$$I_\alpha = I_0 \text{ for } 0 < \alpha < (h_2 - h_1)/2L \tag{14}$$

$$I_\alpha = I_0(h_1 + h_2)(1 - \alpha/\phi)/2h_1 \text{ for } h_2 - h_1/2L < \alpha < \phi. \tag{15}$$

[22] Eq. (12) occurs in Schwarzschild's paper as $\frac{1}{2}(\tan\theta_1 \pm \tan\theta_2)\phi^2$. It does not, of course, express the entire geometric width if the crystal faces and axes are not vertical. The percentage contribution to the geometric width from lack of verticality is much less in anti-parallel than in parallel positions due to the preponderating influence of the natural line breadths. In our experiments it was found by trial that using the cathetometer and horizontal slits we could set the crystals so nearly vertical that the minimum width was obtained at once in anti-parallel positions, although, as has been previously stated, this was not true in parallel positions. For this reason we do not include a term involving verticality corrections in Eq. (12)

[23] See Schwarzschild, reference 11, p. 166, Fig. 3b curve D. This curve corresponds to a function $I_\alpha = I_0(\phi - \alpha)$, or to horizontal slits of equal width.

In the preceding equations, I_α is the intensity of a bundle of parallel rays having a vertical angular divergence α; I_0 is the intensity of the bundle of rays parallel to the central ray. Due to geometric causes alone, as crystal B is rotated from the position in which the central ray makes the angle of best reflection for a certain wave-length, other vertically divergent rays also can make this glancing angle and be reflected. If ξ is the angular deviation of crystal B from the position of reflection for the central ray, and α the vertical divergence of the bundle of rays making the correct angle for reflection at ξ,

$$\xi = \tfrac{1}{2}D\lambda\alpha^2 \tag{16}$$

We wish to find the value of ξ at which this geometric rocking curve comes to half maximum. If we set $I\alpha/I_0 = \frac{1}{2}$ in Eq. (16) and solve for $\alpha_{\frac{1}{2}}$ we find

$$\alpha_{1/2} = h_2\phi/(h_1 + h_2) \tag{17}$$

and substitution in Eq. (16) gives

$$\xi_{1/2} = \frac{1}{2}D\lambda\phi^2\left\{\frac{h_2}{h_2 + h_1}\right\}^2. \tag{18}$$

In correcting our results for geometric width in anti-parallel positions we have substracted the values of $\xi_{\frac{1}{2}}$ calculated from Eq. (18) from our observed full widths at half maximum.

The temperature correction. In their paper on the natural widths of x-ray lines Ehrenberg and von Susich noted effects on the widths of the rocking curves in anti-parallel positions which they ascribed to a change in temperature of the crystals while the readings were being taken. It is easily shown that

$$d\theta_B/dT = -a\lambda D \tag{19}$$

where $d\theta_B$ is the angular range on crystal B corresponding to a temperature change dT. The negative sign has the same interpretation as that previously given.[10] a is the linear expansion coefficient of calcite in a direction perpendicular to the cleavage planes,[24] which is 1.04×10^{-5}. For the reflection of Mo$K\alpha_1$ in the (1, 1) position Eq. (19) gives $d\theta_B/dT = -0.51$ seconds of arc

TABLE V. *Half widths at half maximum for Mo$K\alpha_1$ at 50 kv.*

Position (n_A, n_B)	λ=707.768 *X.U.* |D| ″/*X.U.*	h_1 cm	h_2 cm	$\xi_{\frac{1}{2}}$	W	W_A	W_B	d=3.02904 Å. no. averaged	W_λ
(1,−2)	35.748	.23	.43	.63″	6.4″	2.1″	.64″	1	.154 *X.U.*
(1,−2)	35.748	.10	.23	.17	6.0	2.1	.64	3	.154 *X.U.*
(2,−1)	35.748	.10	.23	.17	6.5	.64	2.1	1	.168
(1,1)	68.572	.10	.23	.34	11.2	2.1	2.1	4	.155
(1,−3)	74.777	.10	.23	.36	11.4	2.1	.67	2	.148
(1,2)	104.32	.10	.23	.51	15.0	2.1	.64	5	.139
(2,1)	104.32	.10	.23	.51	14.8	.64	2.1	1	.138
(2,2)	140.07	.23	.30	1.2	19.7	.64	.64	3	.136
(1,3)	143.34	.10	.23	.70	19.8	2.1	.67	2	.135
	Weighted average of $W\lambda$=0.147 *X.U.* Corresponding energy width 3.63 volts.								

[24] Siegbahn, Phil. Mag. **37**, 601, (1919).

per degree centigrade. During the readings in the anti-parallel positions, the thermometer was frequently read. The change of temperature during the observations was never over 0.5°C. Accordingly we have made no temperature corrections to our results.

We have investigated the half widths at half maximum of the rocking curves for Mo$K\alpha_1$ for as many positions of the instrument as were conveniently possible with the intensity available. The results are shown in Table V.

The values of W_λ in column 10 of Table V are in general averages of several trials, the number of trials being given in column 9. In taking the averages we have weighted our results according to our estimate of their reliability. Some of the curves taken are shown in Fig. 4.

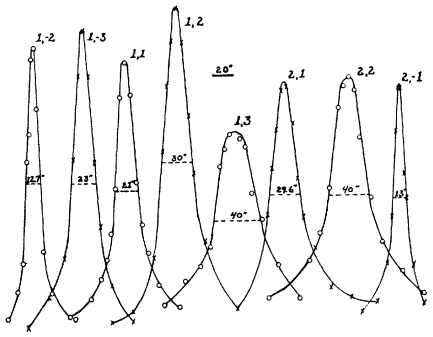

Fig. 4. Observed rocking curves in anti-parallel positions for Mo$K\alpha_1$ at 50 k.v. Ordinates are proportional to ionization currents, abscissae to angular settings of crystal B. The vertical scale is not the same for all the curves.

We have investigated the half width at half maximum of Mo$K\alpha_1$ as a function of voltage from the excitation voltage up to 50 k.v. If part of the observed width is due to satellites arising from multiply ionized states of the atom the width should depend on the voltage. The results are given in Table VI. The details given in Table V are omitted, although all corrections were made.

TABLE VI. *Variation of width of Mo$K\alpha_1$ with voltage. All observations in* (1,1) *position.*

Voltage	W_λ
25.0 kv	0.143 *X.U.*
37.0	.162
46.2	.150
50.0	.155

We have also investigated the width of the line Mo$K\alpha_2$ in the (1, 1 and (1, 2) positions as shown in Table VII. It was assumed that the crystal widths W_a and W_b were the same as had been measured for Mo$K\alpha_1$.

TABLE VII. *Half widths at half maximum for MoKα_2 at 50 k. v.*

Position (n_A,n_B)	λ=712.078 X. U. D ″/X.U.	h_1 cm	h_2 cm	$\xi_{\frac{1}{2}}$	W	d=3.02904 Å. W_A	W_B	no. of observations	W_λ
(1,1)	68.572	0.10	0.23	0.34″	12.2″	2.1″	2.1″	5	0.169X.U.
(1,2)	104.36	.10	.23	.52	16.2	2.1	.64	5	.151

Weighted average of W_λ=0.161 *X.U.*
Corresponding energy width 3.92 volts.

DISCUSSION OF RESULTS IN ANTI-PARALLEL POSITIONS

We shall first discuss the results given in Table V. It is seen that in positions in which D varies from 35.748 to 143.34 seconds per X. U. the half width at half maximum W_λ varies from 0.155 X. U. (if we disregard the single observation at (2, -1)) to 0.135 X. U. or a variation of about 13 percent. This variation is not random, however; there is a distinct trend toward lower values of W_λ with higher values of D. A systematic error is therefore indicated. We are not certain where this systematic error lies, but offer the following hypotheses (1). The actual shape of the lines differs from the Gaussian error curve shape sufficiently to make Eq. (2) inapplicable; (2) The effect is due to the finite size of the focal spot.

It is possible to calculate the size of focal spot which would explain the effect. Due to the fact that during the measurement of a line, crystal A is left stationary, the radiation reflected by B at various values of ζ must come from different parts of the target. This effect is increased for higher values of D (broader curves) and by the fact that the radiation was taken at a glancing angle of 8° from the target face. Let us assume that the adjustments have been correctly made and that therefore when crystal B is reflecting the tip of the peak for a line, the radiation reflected comes from the most intense part of the focal spot. As B is rocked to either side of this position, the radiation reflected will have a different initial intensity if the focal spot is finite in extent. We have calculated that if the distribution of intensity in the focal spot in the particular tube used is such that at a distance of 0.43 mm from the center of the spot the intensity has fallen to $\frac{1}{2}$ that at the center, a 10 percent decrease in rocking curve width in the (2, 2) position can be explained. This corresponds to a diameter of 0.86 mm for the most intense part of the focal spot. The region of discoloration of the target appeared to be about 2.5 mm in diameter so that this explanation does not seem obviously impossible. If in later work it is found that this decrease of wave-length width with increasing D persists when a broad focus tube is used and rays taken at a large glancing angle from the target this explanation must be abandoned.

From Table VI we conclude that there is no significant variation of the width of MoKα_1 from 25 kv to 50 kv. The excitation voltage is 19.945 kv, but from intensity considerations it was not possible to take measurements below 25 kv. This indicates that the observed width is not due to satellites.

We obtained no evidence of satellites of Mo$K\alpha_1$ or α_2 from our experiments.[25]

Table VII indicates that the width of Mo$K\alpha_2$ is slightly greater than Mo$K\alpha_1$. The observed difference between the widths of the two lines is however close to the experimental error and we cannot positively assert that there is a difference in width.

The half width at half maximum to be expected from the classical theory of an oscillating electron damped by the electromagnetic radiation emitted is[26]

$$\Delta\lambda = \frac{2\pi e^2}{3mc^2} \tag{20}$$

where e is the electronic charge in e.s.u., m the electronic mass and c the velocity of light. Eq. (20) gives $\Delta\lambda = 5.9\times10^{-13}$ cm. Our measured value of W_λ for Mo$K\alpha_1$ is 1.47×10^{-12} or 2.5 times as large. If we call τ the time required for the vibrations of the electron to decrease to $1/e$ of their initial amplitude,

$$\tau = \frac{3mc\lambda^2}{4\pi^2e^2} = \frac{\lambda^2}{2\pi c}\,\frac{1}{\Delta\lambda}. \tag{21}$$

Using $\Delta\lambda = 1.47\times10^{-12}$ we find $\tau = 1.8\times10^{-16}$ seconds, which gives the order of magnitude of the life of a molybdenum atom excited to the K state.

Ehrenberg and Mark,[3] using diamond crystals, found $W_\lambda = 0.204$ X. U. for Mo$K\alpha_1$ and 0.199 for Mo$K\alpha_2$. Ehrenberg and von Susich[4] found, using calcite, $W_\lambda = 0.19$ X. U. for Mo$K\alpha_1$. These observations were made using only the (1, 1) and (1, -1) positions.

Davis and Purks[25] observed the rocking curves in the (2, 2) and (3, 3) positions but did not give a definite value to the line width as they interpreted their curves as being composed of satellites. The present results may be considered as an extension of the work of Ehrenberg and Mark and Ehrenberg and von Susich. Their results are confirmed in the sense that a line width in excess of the classically predicted value was found. The lower value found here may be partially due to the limitation of the vertical divergence of the x-ray beam.

[25] Davis and Purks, Proc. Nat. Acad. Sci. **14,** 172 (1928). Allison and Williams, Phys. Rev. **35,** 149 (1930).

[26] W. C. Mandersloot, Jahrb. der Radioakt. und Elektron. **13,** 16 (1916), A. H. Compton, X-rays and Electrons, p. 56. The expression given here corresponds to full width at half maximum.