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THE RESOLVING POWER ATTAINABLE IN X-RAY SPECTROSCOPY BY PHOTOGRAPHIC METHODS

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ABSTRACT

If w_c, the (half) range of glancing angle over which a crystal will reflect monochromatic x-rays, has been determined by the double spectrometer method, it is possible to calculate what resolving power is attainable from this crystal by photographic methods. Equations are set up giving the resolving power in terms of a, the slit width, and R, the distance from slit to photographic plate. Some results are: (1) No appreciable increase in resolving power is attainable by making $a/2R<\frac{1}{4}w_c$. (2) If $a/2R>3w_c$, the resolving power does not involve w_c. (3) The resolving power attainable in the first order is $1/2^{1/2}$ of that attainable in a double spectrometer with crystals of equal perfection. Equations are also derived by which observed line widths in photographic spectrometers may be corrected for slit and crystal diffraction pattern effects. The results are applied to recent experimental results with photographic spectrometers and it is shown that the width of Mo$K\alpha_1$ observed photographically is considerably greater than the values obtained by the double spectrometer.

INTRODUCTION

THE recently increasing use of the double crystal x-ray spectrometer has led to comparisons of its resolving power with that attainable in photographic x-ray spectroscopy.[1,2] A pair of crystals which are as nearly identical as possible (being two previously contiguous sides of a split crystal) can be investigated in parallel positions of the double spectrometer, and the angular width of glancing angle over which monochromatic radiation is reflected can be found. With this information it should be possible to calculate the resolving power attainable from one of the crystals if used in a photographic spectrometer of known slit width and slit-to-plate distance. Such a calculation will be reported in this paper, and extended to the consideration of measurement of line breadths by photographic methods.

THE WIDTH OF THE DIFFRACTION PATTERN FROM A SINGLE CRYSTAL

Let us at first represent the diffraction pattern from a single crystal in the general form

$$I_\xi = F(\xi) \tag{1}$$

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[1] Bergen Davis, Phys. Rev. **35,** 209 (1930).

[2] Valasek, Phys. Rev. **36,** 1523 (1930).

In this expression I_ξ is the intensity reflected from a crystal at a glancing angle whose deviation from a reference angle θ is ξ, divided by the intensity reflected when ξ is 0. In the Darwin-Ewald theory [3,4] this reference angle is

$$\theta = \theta_0 + \delta \sec \theta_0 \operatorname{cosec} \theta_0 \tag{2}$$

where

$$\sin \theta_0 = n\lambda/2d \tag{3}$$

and is in the center of the diffraction pattern. Here δ is the deviation of the index of refraction from unity, and n, λ, and d have their usual significance as in the Bragg equation. The function $F(\xi)$ is expressed as follows

$$F(\xi) = \left\{ \frac{\overline{\Delta\theta}}{2\xi - (4\xi^2 - \overline{\Delta\theta}^2)^{1/2}} \right\}^2 \text{ for } \xi < -\tfrac{1}{2}\overline{\Delta\theta}; \tag{4}$$

$$F(\xi) = 1 \text{ for } -\tfrac{1}{2}\overline{\Delta\theta} < \xi < \tfrac{1}{2}\overline{\Delta\theta}; \tag{5}$$

and

$$F(\xi) = \left\{ \frac{\overline{\Delta\theta}}{2\xi + (4\xi^2 - \overline{\Delta\theta}^2)^{1/2}} \right\}^2 \text{ for } \xi > \tfrac{1}{2}\overline{\Delta\theta}. \tag{6}$$

The expression for $\Delta\theta$ is

$$\Delta\theta = (4F\delta \operatorname{cosec} 2\theta)/Z \tag{7}$$

where F is the structure factor and Z the number of electrons in the unit cell.[5] The best experimental evidence for the nature of the function $F(\xi)$ comes from the shape of the rocking curves obtained in the parallel positions of the double crystal spectrometer. Such curves do not give $F(\xi)$ directly, but give a curve which may be represented as follows[6]

$$I_B = \int_{-\infty}^{\infty} F(\xi) F(\xi - \xi_B) d\xi. \tag{8}$$

In this equation I_B is the intensity reflected from crystal B when B is at a position whose angular deviation from the center of the rocking curve is ξ_B, divided by the intensity reflected when $\xi_B = 0$.

Since the work of Mark and Ehrenberg[7] it has been customary to evaluate the integral (7) on the assumption that $F(\xi)$ has the form

$$F(\xi) = e^{-(\log 2/w_c^2)\xi^2} \tag{9}$$

and not that predicted by the Darwin-Ewald theory as in Eqs. (4), (5), (6). It is seen that Eq. (9) represents a Gaussian error curve of half-width at half maximum w_c. If we assume that Eq. (9) gives the correct form of $F(\xi)$, we can carry out the integration of Eq. (8) with the result

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[3] Darwin, Phil. Mag. **27,** 325 and 675 (1914).

[4] Ewald, Phys. Zeits. **26,** 29 (1925).

[5] Allison and Williams, Phys. Rev. **35,** 1476 (1930).

[6] Schwarzschild, Phys. Rev. **32,** 162 (1928), Eq. (8) of this paper is Eq. (31) of Schwarzschild's paper with slightly different notation.

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

$$I_B = w_c\left(\frac{\pi}{2\log 2}\right)^{1/2} e^{-(\log 2/2w_c^2)\xi_\beta^2} \tag{10}$$

Thus the rocking curve on crystal B is also a Gaussian error curve, and if w is the half-width at half maximum of the observed curve, Eq. (10), the relation between w and w_c is

$$w = w_c(2)^{1/2}. \tag{11}$$

If, however, the diffraction pattern curves from a single crystal actually have the theoretical shape as predicted in Eqs. (4), (5), (6), the rocking curve of crystal B should not be of the Gaussian error curve shape, and the correct factor for finding the half width at half maximum of a single crystal diffraction pattern from that of the observed rocking curve is not $2^{1/2}$ as in Eq. (11).

The author has solved Eq. (8) for I_B, assuming F is of the Darwin-Ewald form, by graphical methods, thus obtaining the rocking curve predicted by the theory for parallel positions of the double spectrometer. The resulting curve differs markedly from the Gaussian error curve shape, and the half width at half maximum is approximately given by

$$w = 0.60\Delta\theta \tag{12}$$

where $\Delta\theta$ is defined by Eq. (7). The half width at half maximum of the theoretical single crystal curve (Eqs. (4), (5), (6)) is

$$w_c = 0.531\Delta\theta \tag{13}$$

hence on this basis the observed width on the double spectrometer and the diffraction pattern width are related by

$$w = 1.13w_c. \tag{14}$$

At the time of writing this paper, it is uncertain whether the diffraction pattern width for a single crystal should be calculated from the observed parallel position rocking curve widths by Eq. (14) or by Eq. (11). The experimental rocking curves are very closely of the Gaussian error curve form, and hence favor Eq. (11), although no detailed study of the shape in a single case has been carried out. We shall therefore use Eq. (11), as has been the general practice previously, with the provision that later developments may favor some other factor, as in Eq. (14).

THE RESOLVING POWER OF THE PHOTOGRAPHIC SPECTROMETER

Fig. 1 represents the essentials of a type of high resolving power photographic spectrometer which has been designed by Professor Siegbahn at the Univesity of Upsala and used there and at the University of Minnesota by J. Valasek.[2] Others have also used photographic apparatus of this type.[8] In the figure, x-rays from the target T fall upon the crystal, and a narrow band

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[8] Duane, Phys. Rev. **37**, 1017 (1931), also unpublished work by J. A. Bearden in this laboratory.

of the reflected rays is selected by the slit of width a. This bundle of x-rays falls on the photographic plate which is put at a distance R.

Let us assume the radiation to be monochromatic, of wave-length λ. The dotted line intersecting the photographic plate at O passes through the geometrical center of the slit aperture and makes a glancing angle θ with the crystal, where θ is the angle calculated from Eq. (2). We will select a point P at a distance x from O and calculate the intensity at this point. From the geometry of Fig. 1 it results that radiation can reach P which has been reflected from the crystal over a range of glancing angle from $\theta-(a-2x)/2R$ to $\theta+(a+2x)/2R$. Assuming a single crystal diffraction curve of the form of Eq. (9), we have then

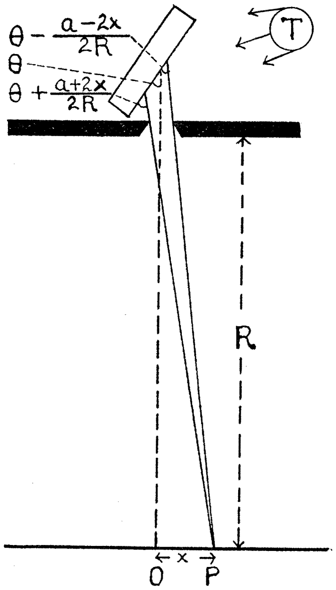

Fig. 1.

$$I_P = \int_{-(a-2x)/2R}^{(a+2x)/2R} e^{-(\log 2/w_c^2)\xi^2} d\xi. \tag{15}$$

Curves for various angular slit widths $(a/2R)$ obtained by graphical integration of this function are shown in Fig. 2. The abscissae of these curves are angular deviations from O, Fig. 1, and the ordinates are intensities. Several interesting conclusions may be reached from Fig. 2. Let us consider the curve for $a/2R = 1/4w_c$. Here the angular half width at half maximum of the impression on the photographic plate is simply w_c, which is the angular half width at half maximum of the crystal diffraction pattern, and the slit width does not contribute to the observed width at all. We may then state that the narrowness of the impression on the photographic plate, or in other words the resolving power of the instrument, is not increased by reducing the half angular width of the slit below approximately one-four of the half width at half maximum of the crystal used. In any given spectrometer this gives a lower limit to the slit width beyond which nothing is gained by narrowing the slit.[9]

In the other direction, at $a/2R=3w_c$, the half width of the impression on the photographic plate is just what one would expect from the slit dimensions and distance alone, namely, $a/2R$, and the diffraction pattern from the crystal plays no appreciable part.

In order to set up an expression for the resolving power, we must now decide at what angular separation two curves for slightly differing wavelengths would be resolved. The author wishes to make the suggestion here

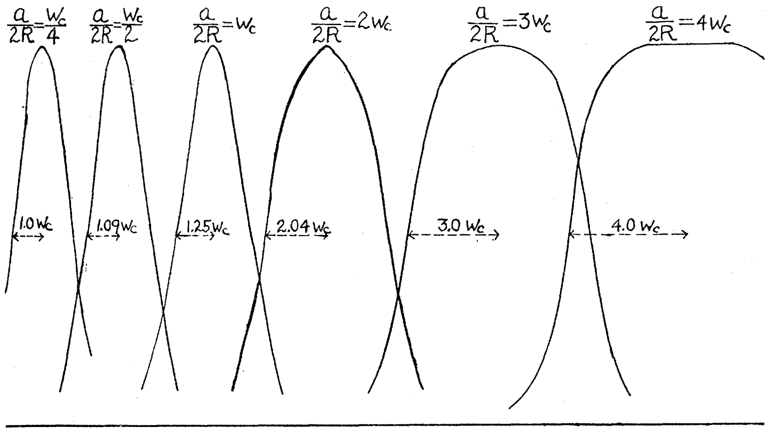

Fig. 2.

that two curves of the type of Fig. 2 shall be said to be resolved if the separation of their maxima is twice their half width at half maximum. In the case of the curves of Fig. 2 which do not greatly deviate from the Gaussian error curve shape, two such curves at the limit of resolution would have a dip between them of approximately 93 percent of the intensity at either maximum. This, of course, is an arbitrary definition of resolution, but is neither more or less so than the classical definition applying to the resolving power of gratings in the optical region. Now differentiating the Bragg equation to get the angular dispersion, we obtain

$$\frac{\lambda}{d\lambda}=\frac{\tan\theta}{2w}\,. \tag{16}$$

The highest resolving power attainable is obtained if $a/2R \leqq 1/4w_c$; here $w=w_c$ and we get

$$\frac{\lambda}{d\lambda}=\frac{\tan\theta}{2w_c}\,. \tag{17}$$

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[9] If the single crystal diffraction pattern is not of the Gaussian error curve shape, but of the theoretical Darwin-Ewald form, this lower limit is reached somewhere between $a/2R=\frac{1}{4}w_c$ and $a/2R=w_c$, and considerably nearer the higher value than the lower.

If $a/2R \geqq 3w_c$ we have $w = a/2R$ and

$$\frac{\lambda}{d\lambda} = \frac{R \tan \theta}{a}. \tag{18}$$

COMPARISON WITH THE MAXIMUM RESOLVING POWER ATTAINABLE IN THE DOUBLE SPECTROMETER

If the vertical divergence of the beam of x-rays in the double spectrometer is sufficiently great, it may cause a diminution of resolving power. The calculation of the shape of the rocking curve which combines this geometrical effect with the diffraction pattern widths of the crystals is considerably more difficult than in the photographic case previously considered. One can, however, calculate the two effects separately and estimate the extent to which geometrical effects lower the resolution. The calculation has been carried out, and it is quite possible, using calcite crystals in the (1, 1) position, to limit the vertical divergence to the point where geometrical effects do not enter appreciably, and yet to have sufficient intensity in the beam for measurement.[10] In the (2, 2) position this is much less easily possible due to the much lower value of w_c in the second order. However, the maximum resolving power is attainable only by eliminating geometric effects and we will assume this has been done. If the instrument were operating with a perfectly monochromatic beam of x-rays the half width at half maximum in any position (n_A, n_B) would be given by

$$w = (w_A^2 + w_B^2)^{1/2} \tag{19}$$

where w_A and w_B are the values of w_c corresponding to the orders of reflection n_A and n_B. According to the assumption in the second section of this paper the rocking curve would be of Gaussian error curve shape. We have postulated that two such curves are resolved if separated by twice the half width at half maximum, or $2w$. The dispersion is

$$D \equiv \frac{d\theta_B}{d\lambda} = \frac{n_A}{2d \cos \theta_A} + \frac{n_B}{2d \cos \theta_B} \tag{20}$$

if the sign of n_B is chosen according to a convention suggested previously by Allison and Williams. Using Eqs. (19) and (20) we find

$$\frac{\lambda}{d\lambda} = \frac{D\lambda}{2w} = \frac{D\lambda}{2(w_A^2 + w_B^2)^{1/2}} \tag{21}$$

Eq. (21) represents the highest resolving power attainable in the double spectrometer for any given values of n_A and n_B. This can actually be attained without too great loss of energy in the (1, 1) position, where 14.1 becomes

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[10] See Table V of the paper of Allison and Williams previously referred to. In the (1, 1) position the geometric half width at half maximum was 0.34″, whereas the rocking curve half width at half maximum due to crystal diffraction patterns was 3.0″. It would easily have been possible to decrease the vertical divergence further, but due to the large natural line width, nothing would be gained.

$$\frac{\lambda}{d\lambda}=\frac{(2)^{1/2}\tan\theta}{2w_c}\cdot \tag{22}$$

Here w_c is the half width at half maximum of the single crystal diffraction pattern in the first order, and θ is the corresponding glancing angle.

By a comparison of Eqs. (22) and (17) we see that the maximum resolving power attainable by the double spectrometer in the (1, 1) position is 1.4 times that obtainable photographically in the first order from the same crystals. This conclusion has been previously stated by Valasek.[2] It is, of course, futile to pretend that the equations for resolving power developed here will be of great importance to the investigator seeking to resolve a given pair of x-ray lines. Many other factors, such as their shapes, their relative intensities, and the acumen of the observer, enter. The real use of the equations is their ability to serve as a criterion of the relative resolving powers of different instruments and methods.

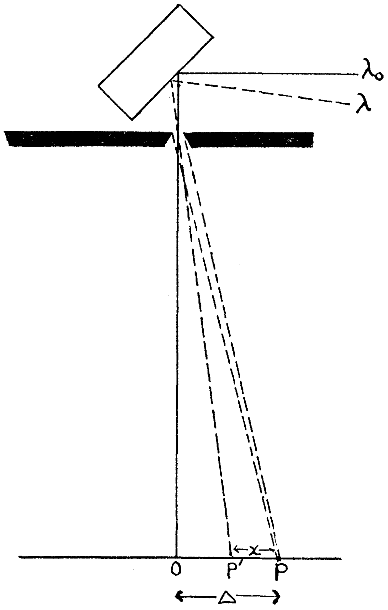

Fig. 3.

THE PHOTOGRAPHIC MEASUREMENT OF LINE BREADTHS

In order to set up equations for the measurement of line breadths photographically, we must solve the problem of Eq. (15) in the case in which the spectrum, instead of being monochromatic, consists of a continuous distribution of energy over a range of wave-lengths.[11] We will limit our considerations

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[11] Valasek has corrected his observed line widths by merely subtracting from them a value of the monochromatic width obtained by adding the angular slit width and the full width at half maximum of the observed rocking curve on the double spectrometer. In the opinion of the author, this method is open to criticism, and an attempt is here made to outline a better method of correction.

to a spectrum line and assume that the energy is dstributed in a Gaussian error curve, represented by

$$I_\lambda = e^{-(\lambda-\lambda_0)^2\log 2/w_\lambda^2} \tag{23}$$

where I_λ is the intensity of wave-length λ in terms of the maximum which occurs at λ_0, and w_λ is the half width at half maximum of the line. In Fig. 3 consider the intensity at point P on the photographic plate due to a wave-length range $d\lambda$ about λ. P' is the intersection on the photographic plate of a line passing through the center of the slit aperture and making a glancing angle θ on the crystal (Eq. (2)). If I_λ is the intensity of this wave-length in the original spectrum, an intensity $I_\lambda d\lambda$ will be derived from the spectral range $d\lambda$. This will be spread out on the photographic plate in an impression the width of which is determined from Eq. (15), and the contribution to the intensity at P may be written

$$dI_p = I_\lambda d\lambda \int_{-(a-2x)/2R}^{(a+2x)/2R} e^{-(\log 2)/wc^2)\xi^2} d\xi \tag{24}$$

where x is now the distance PP' and not OP as in Fig. 1. The integral in Eq. (24) will be one of the curves in Fig. 2; which one depending on the ratio $(a/2R)/w_c$ which is appropriate to the apparatus being used. Let us assume that this integral in a particular case is $F(x/R)$. Let $\overline{OP}/R$ in Fig. 3 be Δ, then if D is the angular dispersion,

$$x/R = \Delta - D(\lambda - \lambda_0) \tag{25}$$

and Eq. (24) becomes

$$dI_p = I_\lambda d\lambda F\{\Delta - D(\lambda - \lambda_0)\} \tag{26}$$

or

$$I_p = \int_{-\infty}^{\infty} I_\lambda F\{\Delta - D(\lambda - \lambda_0)\} d\lambda. \tag{27}$$

The extension of the limits of λ to $\pm\infty$ is justified by the narrowness of the lines compared to the spectral range which can get through the slit. Unless the form of $F(\Delta - D(\lambda-\lambda_0))$ is known, the problem cannot be carried out further. For suggestions as to the form of this function we may inspect Fig. 2. If we assume that for angular slit widths up to $a/2R = w_c$ the function can be sufficiently well represented by a Gaussian error curve we can get an approximate solution of Eq. (27). Setting

$$F\{\Delta - D(\lambda - \lambda_0)\} = e^{-\log 2/w^2\{\Delta - D(\lambda-\lambda_0)\}^2} \tag{28}$$

we obtain from Eq. (27) the result

$$I_p \sim e^{-\Delta^2\log 2/(w^2+w_\lambda^2D^2)} \tag{29}$$

in which a factor similar to that under the radicle sign in Eq. (10) has been omitted. If W is the half width at half maximum of the line as observed on the photographic plate, in angular units, it follows from Eq. (29) that

$$W = (w^2 + D^2w_\lambda^2)^{1/2} \tag{30}$$

APPLICATION TO EXPERIMENTAL RESULTS

Valasek[2] and Duane[8] have recently reported results obtained with high resolving power photographic spectrometers. In the case of Duane's work, the slit to plate distance R was 472.5 cm, but the slit width is not given, hence the resolving power cannot be calculated.

In Valasek's work results are given for measurements of Mo$K\alpha_1$, Mo$K\beta_1$, Ag$K\alpha_1$ and Cu$K\alpha_1$ in the first order from a high resolving power spectrometer constructed in Siegbahn's laboratory. Measurements in the second order for the $K\alpha$ lines of Fe, Ni, Co, and Cu are also given. Discussion here will be confined to the experiments on Mo$K\alpha_1$ in the first order, as for the other values so little is known at present about w_c that speculation is very precarious. We can, however, assume that the crystal used by Valasek had a w_c equal to that reported by Allison and Williams, and proceed to calculate the resolving power. The value of R was 296 cm, of a, 0.003 cm, hence $a/2R$ was 5.06×10^{-6}. Allison and Williams' value of w_c is 2.1 seconds of arc, or 1.02×10^{-5} radans. Hence $(a/2R)/w_c$ was 0.496 in Valasek's experiment. We now look to Fig. 2 to find the type of monochromatic impression on the photographic plate to be expected. We see that the curve will be of approximately Gaussian error curve shape and of angular width $w=1.09w_c=1.11\times10^{-5}$. Applying Eq. (16) we find that $\lambda/d\lambda=5350$. Valasek's own estimate of his resolving power is 4720. The maximum resolving power obtainable from a double spectrometer having equally good crystals in the (1, 1) position is is 8100.

We now proceed to the calculation of w_λ from the widths of the photometer curves observed by Valasek for the Mo$K\alpha_1$ line. We apply Eq. (30). Valasek's value of W observed was 0.20X.U. In order to apply Eq. (30) we must change the value of w in Eq. (30) to wave-lengths. The angular dispersion of calcite for Mo$K\alpha_1$ (1) is 34.28 seconds per X.U., hence the w of the preceding paragraph corresponds to 0.066 X.U. Applying Eq. (30) we find $w_\lambda=0.19$ X.U. for Mo$K\alpha_1$.

The value of w_λ calculated by this method is considerably larger than that calculated by Valasek from his own results (0.13 X.U.). If the method of treatment in this paper is valid, however, his method of correcting the observed W's, which consists in simply subtracting values of w from them, is erroneous.

The value of the half width at half maximum of Mo$K\alpha_1$ calculated here from Valasek's results (0.19 X.U.) is considerably larger than that obtained by the most recent results by the double spectrometer method. The value obtained by Allison and Williams was 0.147 X.U., and recently Mark and von Susich[12] have obtained the values 0.163 and 0.144 X.U. with calcite and topas crystals respectively. The discrepancy between the photographic and ionization double spectrometer methods may be due to lateral spreading of the image on the photographic plate due to secondary x-rays, or to photoelectrons ejected from the plate substance. Also the effective slit width of the microphotometer used in taking the blackening curve would contribute to the estimated W, tending to increase it.

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[12] Mark and von Susich, Zeits. f. Physik **65**, 253 (1930).