

The action of the helium in this case is usually interpreted as quenching the higher vibrational levels of the excited molecules before they radiate. This is feasible, since the masses of the H₂ molecule and the He atom in this case are nearly equal. This is not the complete explanation, however. The observations have all been made on the transitions where the initial levels are all about 112,000 cm⁻¹ above the ground state of H₂. Reference to column 7, Table I, will show that this is about the limit of the excitation of He₂*. Since the vibrational levels are separated by about 2000 cm⁻¹, the excitation of the various electronic states in the range of 112,000 cm⁻¹ is more probable than excitation of higher vibrational levels of a low-lying electronic state.

The level $1s\sigma 2s\sigma^3\Sigma_g^+$, 95,226 cm⁻¹ above the ground state of H₂, which is responsible for the hydrogen continuum, may have many vibrational levels excited. This coupled with the "quenching" action of helium may account for discrepancy between Smith's⁸ measurements of the intensity

distribution of the hydrogen continuum produced in helium and hydrogen mixtures, and those of Coolidge⁹ produced in pure hydrogen by controlled electron impact.

NEON MOLECULES

In most of the references listed in this paper, data of enhanced spectra in neon mixtures are also given. Enhancement appears at energies slightly higher than that caused by He₂* and possibly over a longer range of energies. This is probably caused by neon metastable molecules. However, discussion of these effects must be deferred until more information is available, about either the attractive or the repulsive state in neon.

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The Determination of X-Ray Diffraction Line Widths

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The methods which have been suggested for correcting x-ray diffraction line widths for geometrical effects are reviewed. Experimental data are presented for two samples of finely-divided NiO and MgO which show that neither the Warren nor the Jones correction method is valid for *these particular specimens*. A direct Fourier transform procedure is given which permits calculation of the corrected diffraction line width for all experimental cases.

INTRODUCTION

IT is well known in x-ray diffraction studies that the size of the diffracting crystals determines to a certain extent the sharpness or diffuseness of the observed diffraction line. With the usual type of diffraction cameras, the diffraction broadening is noticeable with crystal sizes in the range of 400–500 Å and becomes more pronounced as the crystal size is reduced. Numerous applications of this broadening have been made in the past in determining the crystal sizes present in experimental systems.

It has been shown¹⁻³ that the angular breadth β of a diffraction line should be given by

$$\beta = C\lambda/L \cos \theta, \quad (1)$$

where C is a constant, λ the x-ray wave-length, L the size of the crystal, and θ the Bragg angle corresponding to the diffraction line under study. In this expression, either the "half-width" (total width at half maximum) or the "integral width"

¹ P. Scherrer, *Kolloidchemie* (Zsigmondy, 1920), third edition, p. 387.

² W. H. and W. L. Bragg, *Crystalline State* (The Macmillan Company, New York, 1933), p. 189.

³ A. L. Patterson, *Phys. Rev.* **56**, 972–982 (1939).

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(area under diffraction peak divided by peak maximum) definitions of β can be used. The value of the constant C (commonly referred to as the Scherrer constant) will depend upon the definition of β , as Patterson³ and others have shown.

The most recent and reliable calculations of the Scherrer constant for crystals of cubic symmetry have been made by Patterson,³ Stokes and Wilson,^{4,5} and Murdock.⁶ These investigators have shown C to depend upon the crystal shape and the diffraction line indices, and in all cases to be not far removed from unity.

Before applying Eq. (1) to experimental data, it is necessary to correct the observed diffraction line widths for geometrical effects (finite specimen size, divergence in incident x-ray beam, absorption in specimen, etc.) which contribute to the observed broadening. Some of the earlier proposed methods for making these corrections have been reviewed by Clark.⁷ These correction procedures are incomplete in spite of being rather involved and lead to the possibility of considerable error in the final result.

More recently Jones⁸ has suggested a mixture method which furnishes a direct experimental determination of the necessary geometrical corrections. In the Jones method, the material (A) of unknown crystal size is intermixed with a second material (B) whose crystals are very large (larger than 1000Å) and hence whose diffraction broadening is negligible. The widths of the diffraction lines of (B) can then be considered the geometrical width contributing to the observed width of (A). This is so because the same geometrical conditions were present during the simultaneous irradiation of both (A) and (B). There are certain precautions which must be taken to insure the equivalence of geometrical effects for (A) and (B) as Taylor⁹ has pointed out. These include: (1) a mass absorption coefficient for (B) not far removed from that of (A) and (2) a crystal size for (B) which is not large enough that its diffracted radiation would suffer an absorption (including

⁴ A. R. Stokes and A. J. C. Wilson, Proc. Camb. Phil. Soc. **38**, 313 (1942).

⁵ A. R. Stokes and A. J. C. Wilson, Proc. Camb. Phil. Soc. **40**, 197-198 (1944).

⁶ C. C. Murdock, Phys. Rev. **63**, 223 (1943).

⁷ G. L. Clark, *Applied X-Rays* (McGraw-Hill Book Company, Inc., New York, 1940), third edition, pp. 490-499.

⁸ F. W. Jones, Proc. Roy. Soc. **166A**, 16-43 (1938).

⁹ A. Taylor, Phil. Mag. **35**, 215-229 (1944).

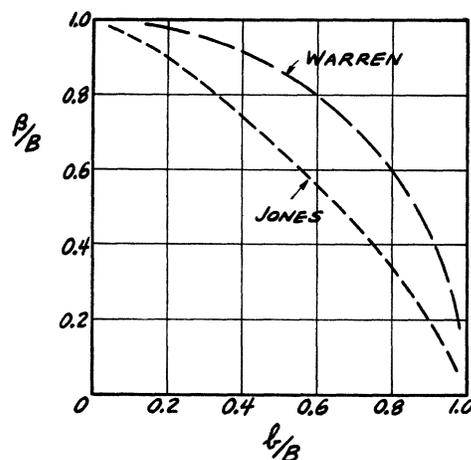


FIG. 1. Curves for correcting observed diffraction line width for geometrical width.

extinction) different from that characterized by the mixture composition.

Jones⁸ has worked out a procedure for applying the corrections obtained by this mixture method. After correcting all of the diffraction line widths for the presence of the $K\alpha$ doublet, the pure diffraction width β is obtained from the true width¹⁰ B of material (A) and from the true width b of material (B) through use of a correction curve. This correction curve is shown as the Jones curve in Fig. 1. Since B and b are known from experimental data, the pure diffraction width β can be evaluated from the curve in this figure.

Warren,¹¹ on the other hand, has proposed a different correction curve from that by Jones and his is also included in Fig. 1. In comparing the two curves, it is seen that a considerable difference in results can be obtained by the two methods, especially if the experimental data fall in the range of b/B values above 0.4. Unfortunately with samples of crystal size 100Å or larger and with the usual cylindrical type of diffraction camera, the experimental data generally fall in this unfavorable region of b/B and hence there is uncertainty in the result because of the differences in the correction curves.

The present paper deals with observations on two samples of finely divided materials, NiO and

¹⁰ True width corresponds to the diffraction line width after the doublet correction has been applied to the observed width.

¹¹ B. E. Warren and J. Biscoe, J. Am. Ceramic Soc. **21**, 49 (1938).

MgO, and is intended to show the differences between the results obtained by the two correction methods. It is seen in Fig. 1 that the two curves show a different dependence upon b/B values and this suggests a means for selecting one over the other. Since for any sample the true diffraction broadening β should be independent of experimental conditions, a study of β_W (calculated according to the Warren curve) and β_J (calculated according to the Jones curve) should indicate a preference between the two methods.

In addition to the Warren and Jones procedures for correcting the observed diffraction line for geometrical effects, there is a resolution procedure available which enables a direct evaluation of the diffraction width. Such an evaluation has been carried out for the present materials and comparisons will be made in a later section with the results obtained by the correction methods. We proceed first to a study of the direct resolution procedure for evaluating the pure diffraction width.

DIRECT EVALUATION OF THE DIFFRACTION WIDTH

Jones⁸ has shown that the function $k(x)$ representing the observed intensity of diffraction as a function of the distance x from the center of the diffraction line can be obtained from

$$k(x) = \int_{-\infty}^{\infty} g(u)f(x-u)du, \quad (2)$$

where g represents the distribution of intensity across a line possessing no diffraction broadening and f corresponds to the intensity distribution which would have been obtained with an infinitely narrow and perfectly collimated x-ray beam and an infinitely small specimen. The function k would, for example, represent the observed profile of the diffraction line of material (A) above, while g would represent the material (B) line profile. It is desired to evaluate the function f from experimental data for k and g . This can be performed conveniently by use of Fourier transform theory.¹²

¹²The present problem is very similar to that encountered in determining the shape of x-ray emission lines from the rocking curves obtained with double crystal spectrometers. A general treatment of the spectrometer problem has been given by L. P. Smith (Phys. Rev. **46**, 343-351 (1934)) and the present treatment can be considered as a simplified

We let K , G , and F be the Fourier transforms of k , g , and f as defined by equations of the form

$$K(t) = (2/\pi)^{1/2} \int_0^{\infty} k(x) \cos xtdx. \quad (3)$$

Only the cosine transforms need be considered here since all of these functions are symmetrical about their origin points. It follows from Eq. (2) that¹³

$$F(t) = K(t)/G(t) \quad (4)$$

and hence

$$f(x) = (2/\pi)^{1/2} \int_0^{\infty} F(t) \cos xtdt. \quad (5)$$

Thus when k and g are known, a straightforward process is available for determining the function f from which the diffraction width can be easily obtained. The general process is rather cumbersome since it involves finding transforms for three functions which are known only numerically and not analytically. However, it has been found from experimental data that the functions k and g can be closely approximated by simple analytical functions (within experimental error) and this serves to simplify the numerical work greatly. Several special cases are given in the following.

Case I: When

$$g(x) = \exp(-m^2x^2) + \sigma \exp(-n^2x^2)$$

and

$$k(x) = \exp(-p^2x^2) + \tau \exp(-q^2x^2). \quad (6)$$

It follows that

$$G(t) = \frac{1}{\sqrt{2}m} \exp\left(-\frac{t^2}{4m^2}\right) + \frac{\sigma}{\sqrt{2}n} \exp\left(-\frac{t^2}{4n^2}\right) \quad (7a)$$

and

$$K(t) = \frac{1}{\sqrt{2}p} \exp\left(-\frac{t^2}{4p^2}\right) + \frac{\tau}{\sqrt{2}q} \exp\left(-\frac{t^2}{4q^2}\right), \quad (7b)$$

and hence $f(x)$ can be obtained by insertion of

and specialized one applicable to the conditions found in this type of investigation.

¹³E. C. Titchmarsh, *Introduction to the Theory of Fourier Integrals* (Oxford University Press, New York, 1937), p. 51.

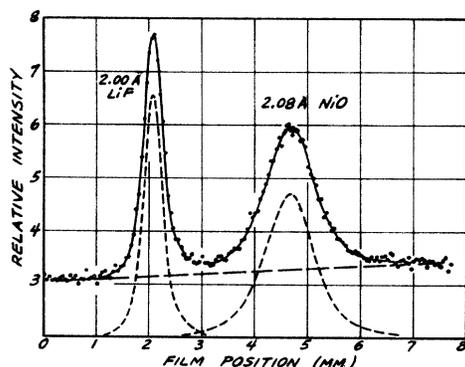


FIG. 2. Intensity distribution over typical NiO and LiF diffraction lines.

Eq. (7) into Eq. (4) followed by the evaluation of Eq. (5).

For this particular case F can be evaluated directly from the parameters given in Eq. (6) and hence only one transformation is necessary. If additional exponential terms are needed to represent either k or g above, the solution is still available after carrying out one transformation.

Case II: When

$$g(x) = \exp(-m^2x^2)$$

and

$$k(x) = \exp(-p^2x^2) + \tau \exp(-q^2x^2). \quad (8)$$

It follows that

$$F(t) = \frac{m}{p} \left\{ \exp(-r^2t^2) + \frac{\tau p}{q} \exp(-s^2t^2) \right\} \quad (9)$$

where

$$r^2 = \frac{m^2 - p^2}{4m^2p^2} \quad \text{and} \quad s^2 = \frac{m^2 - q^2}{4m^2q^2},$$

and hence

$$f(x) = \frac{m}{\sqrt{2}p} \left\{ \frac{1}{r} \exp\left(-\frac{x^2}{4r^2}\right) + \frac{\tau p}{q} \frac{1}{s} \exp\left(-\frac{x^2}{4s^2}\right) \right\}. \quad (10)$$

Thus the function representing the diffraction line profile free of geometrical contributions can be written directly in terms of the parameters of

(8). Moreover if our interest is confined to the integral width of this diffraction line, this can also be obtained directly as

$$\begin{aligned} \beta &= \frac{1}{f(0)} \int_{-x}^x f(x) dx \\ &= 2\sqrt{\pi} rs \left[\frac{1 + \tau p/q}{s + r\tau p/q} \right]. \end{aligned} \quad (11)$$

Thus the pure diffraction width may be obtained by mere evaluation of the parameters describing the observed diffraction lines.

Case III: When

$$g(x) = \exp(-m^2x^2)$$

and

$$k(x) = \exp(-p^2x^2). \quad (12)$$

It follows that

$$f(x) = \frac{m}{\sqrt{2}p} \frac{1}{r} \exp\left(-\frac{x^2}{4r^2}\right) \quad (13)$$

and that

$$\beta = 2\sqrt{\pi} r. \quad (14)$$

This expression for the integral width is identical with that obtained by the Warren correction method with B and b obtained from Eq. (12).

EXPERIMENTAL TECHNIQUE

Samples of finely divided NiO and MgO were used as specimens in the present study. Both oxide samples were prepared by heating in air the respective carbonates, one hour at 750°F for NiO and six hours at 1200°F for MgO. A series of x-ray photograms for each of these samples was taken under various experimental conditions. Most of the photograms were taken in cylindrical type diffraction cameras (radii 28.8 and 71.7 mm) with powder specimens packed into small glass capillaries.

Pulverized LiF and NaCl were used as calibration materials to provide diffraction lines possessing no diffraction broadening. These calibration materials were obtained by grinding single crystal fragments of the halide until microscopic examination showed the final powder particle size to be of the order of one micron and smaller. Crystals of such size would, of course, produce no observable diffraction broadening. Careful mixing

of the calibrating material with the oxide samples was performed to insure equivalence of geometrical effects during the x-ray examination.

Thin-walled glass capillaries of various diameters between 0.3 and 0.8 mm were used as specimen holders along with different conditions of primary x-ray beam collimation. Filtered radiation from both copper and cobalt target x-ray tubes was used. By changing the conditions of beam collimation, specimen size, x-ray wavelength and camera radius, it was possible to obtain data covering quite a range of b/B values. Some data were also taken in a Brentano "focusing" spectrometer type of instrument and these data combined with those taken in the cylindrical cameras covered a b/B range from 0.25 to about 0.8.

Specimen mixtures of NiO-LiF and MgO-NaCl were used in the experimental investigation. With the NiO-LiF mixture, the 2.08A-NiO diffraction line (200) and the 2.00A-LiF diffraction line were selected for study. These two lines were sufficiently close together so that the width of the LiF line could be considered the geometrical width present at the NiO line position. A microphotometer trace showing the intensity distribution across a typical pair of these lines is given in Fig. 2. After resolving the individual peaks from the background, the observed widths b_0 and B_0 (using Jones' notation) were determined for the LiF and NiO peaks, respectively. Similar data were taken for the 2.10A-MgO line and the 1.99A-NaCl line in MgO-NaCl specimen mixtures.

Integral peak widths (in which the area under the peak is divided by the peak maximum) have been used exclusively in the present investigation. It has been found that such widths are to be preferred experimentally to half-width values because of their greater internal consistency.

TABLE I. Results of Fourier transform determinations of the diffraction width.

NiO (All values expressed in terms of 10^{-2} radians)	MgO
$\beta = 1.33$	1.57
1.40	1.34
1.40	1.61
1.34	1.37
1.31	1.20
1.41	1.43
1.51	1.38
Average = 1.39 ± 0.05	1.41 ± 0.10

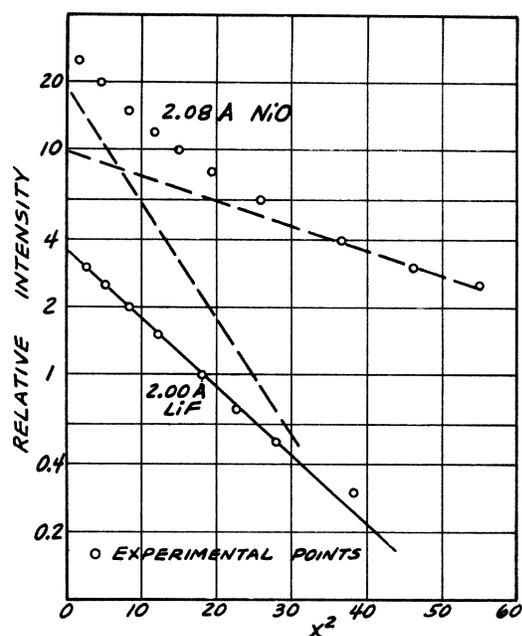


FIG. 3. Graph showing relative intensity *versus* distance from center of line squared (arbitrary units) for NiO and LiF diffraction lines.

Moreover integral widths would appear to be of more significance when a distribution of crystal sizes is encountered in the specimen. All crystal sizes would be contributing to the integral width value in a known degree of weighting⁸ whereas this would not be the case with half-width values.

ANALYSIS OF EXPERIMENTAL DATA

The data analysis by the Fourier transform procedure will be considered first. It has been found that the experimental curves, such as given in Fig. 2, can be represented sufficiently closely by the analytical functions (8) corresponding to Case II above. Figure 3 shows a semi-logarithmic plot of the intensity *versus* distance squared from center of line for a pair of NiO-LiF diffraction lines. The representation of the NiO line by the sum of two straight lines and the LiF line by one straight line indicates the applicability of the conditions described in Case II.

The Fourier transform analysis has been applied to fourteen sets of data (covering a wide range of geometrical conditions) for the two specimens with the results given in Table I. The standard deviations have been calculated from the internal consistency of the data. It is purely

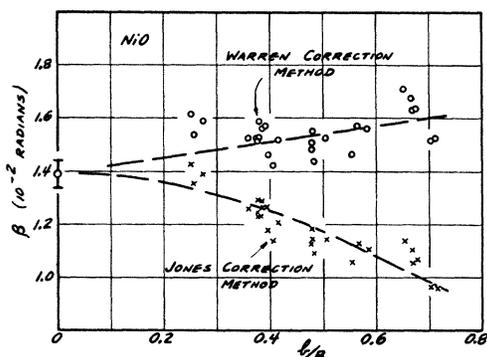


FIG. 4. Variation of the pure diffraction width of 2.08A-NiO line with geometrical conditions. The point plotted on the ordinate axis is that taken from Table I. All values are on the basis of an x-ray wave-length of 1.54A.

fortuitous that the two average values are close together since there is no connection between their crystal sizes.

In applying the Warren and Jones correction methods to the data, it was first necessary to correct for the presence of the $K\alpha$ doublet. This was done by the method outlined by Jones.⁸ In general this correction was small because of the small separation of the doublet components at these angles of diffraction. These corrected width values, b and B , were then used to determine the pure diffraction widths β_w and β_j from the curves of Fig. 1.

Figures 4 and 5 show the pure diffraction widths for the 2.08A-NiO line and the 2.10A-MgO line plotted against b/B values. There is considerable spread among the experimental points but nevertheless definite trends in the data can be seen. Also shown in Figs. 4 and 5 along the ordinate axes are the average values for the pure diffraction widths as given in Table I. Since both the Warren and Jones correction curves intersect at a common value along the ordinate axis, the data calculated by the correction methods should likewise show the trend toward a common intersection representing the true diffraction width. The curves through the experimental points in these figures have been drawn with this in mind although the data are not sufficiently significant to warrant selection of a particular curve shape. The intersection point would be, of course, the value to be inserted into Eq. (1) in determining the crystal size.

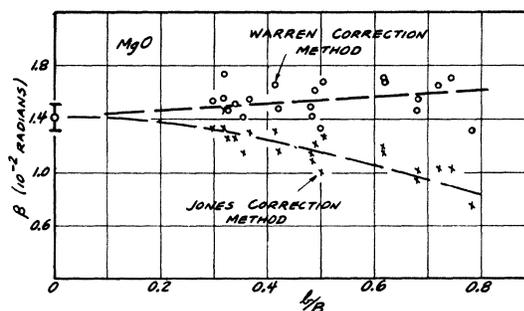


FIG. 5. Variation of the pure diffraction width of the 2.10A-MgO line with geometrical conditions. The point plotted on the ordinate axis is that taken from Table I. All values are on the basis of an x-ray wave-length of 1.54A.

DISCUSSION OF RESULTS

It would appear from the sequence of data shown in Figs. 4 and 5 that neither the Warren nor the Jones correction curve was the most suited for these particular specimens. An intermediate correction curve would have been more suitable. Such a correction curve, applicable for all cases covered by the conditions given in Eq. (8), could of course be constructed. If the diffraction lines had been of shape characterized by Case III above, the Warren method would have been acceptable. It is to be emphasized that other specimens may show diffraction line shapes different from those for the present specimens because of differences in crystal size distribution. Thus the optimum correction curve depends upon the particular line shapes encountered experimentally.

Of course, the best procedure in determining crystal sizes is that of obtaining experimental data under conditions where the correction to be applied is small, namely, small values of b/B . If this is not possible or feasible, as is the case with crystal sizes in the upper range of measurable sizes, then it would appear necessary for best results to study the diffraction line shapes. In any event the Fourier transform procedure is a direct one applicable to all cases.

ACKNOWLEDGMENTS

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