For increasing values of the edge length there is a very noticeable decrease of the scattered intensity, as Fig. 12 shows very clearly.

5. Conclusion

The existence of lines or regions of discontinuity in the ordered structure of homogeneously oriented nematic liquid-crystal layers makes possible the setting up of dislocations of various kinds. We have shown that the shape of the small-angle scattering curves is mainly determined by the kind of dislocation configuration exhibited by homogeneously oriented nematic liquid crystals. As a consequence we have made a complete examination of the shape of the neutron scattering curves at very small scattering vectors, of the order of $0{\cdot}05 \sim 0{\cdot}1$ nm^{-1}, for the most significant cases of dislocation configurations.

This study gives a partial guide to the construction and the interpretation of scattering relations for any kind of possible dislocation configuration in homogeneously oriented nematic liquid crystals, *e.g.* for stationary straight edge dislocations, moving edge dislocations, oscillating edge dislocations, curved dislocations and dislocation networks.

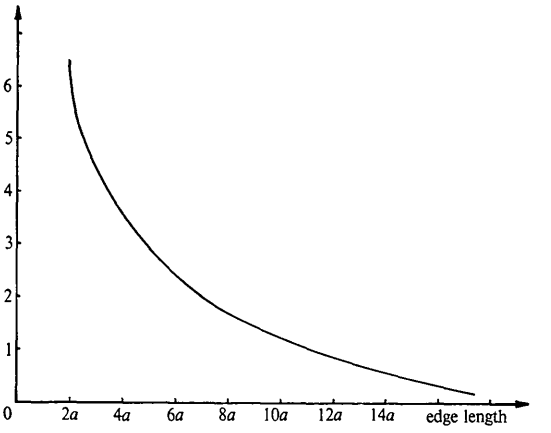

Fig. 12. Behaviour of the peak value of the scattered intensity *versus* the edge length $2a$ of the regular hexagon of a plane regular hexagonal Frank dislocation network (The scattering vector has been taken parallel to the y axis). For the parameters for the MBBA homogeneously oriented nematic liquid crystal see Fig. 11.

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Statistical Bias in Least-Squares Refinement

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(*Received* 20 *February* 1976; *accepted* 14 *May* 1976)

Statistical fluctuations in counting rates *etc.*, as well as defects in the structural model, can introduce bias in the estimation of parameters by least-squares refinements. Of the residuals in common use, only unweighted $R_2 = \sum(I_o - I_c)^2$ is free from statistical bias. Order-of-magnitude estimates of the bias can be derived, but it seems better to avoid it by adjusting the weights. To the second order, refinement of R_2 is unbiased if the intensity used in calculating the usual weights is not I_o but $\frac{1}{3}(I_o + 2I_c)$. There seems to be no simple method of avoiding bias in R_1.

Introduction

Estimates of quantities obtained by or from physical measurements may differ from the true values for one or more of three reasons.

(i) Systematic errors (defects in the model). In crystallographic investigations these may include incorrect allowance for absorption or extinction, incorrect assumptions about atomic scattering factors or thermal motion, overloading of counters or amplifiers, and so on (Shoemaker, 1968; Wilson, 1973).

(ii) Random errors. In crystallographic investiga-

tions statistical fluctuation in counting rates is likely to be the largest random error, but there can be irregular backlash in positioning mechanisms, and so on.

(iii) Unnoticed inappropriateness of mathematical techniques, whereby random errors, of mean value zero in the raw data, become a systematic bias in the derived quantities.

The present note is concerned with the third of these sources of error.

Correlation of weights and intensities

Wilson (1974), in the course of an investigation of the effects on crystallographic parameters of the neglect of dispersion, noticed that least-squares refinement of the overall scaling factor led to results that were systematically low by an amount $\frac{1}{2}R_1$ when the residual

$$R_1 = \sum w_1(|F_o| - |F_c|)^2 / \sum w_1 F_o^2 \qquad (1)$$

was used, the w_1 being weights. On the other hand, Lomer & Wilson (1975) found that statistical fluctuations did not produce a systematic bias in values of the overall scaling factor when the residual

$$R_2 = \sum w_2(I_o - I_c)^2 / \sum w_2 I_o^2 \qquad (2)$$

was used, the w_2 being weights. Both calculations rested on an implicit assumption that the weights are not functions of I_o or I_c. The use of unweighted residuals is not uncommon, but more frequently weights are assigned that are intended to be the reciprocals of the variances of $(F_o - F_c)$ or $(I_o - I_c)$. These variances arise largely from statistical variations in the counting rates, thus depending on the background intensity and the intensity of the reflexion being measured, and often empirical additions are included, in order to make the distribution of the observed values of $(F_o - F_c)/\sigma(F)$ or $(I_o - I_c)/\sigma(I)$ conform to a theoretical model. For a Poisson distribution of counts the variance of I is proportional to I, so that for R_2 the variances should be a linear function of I, the constant term arising from the background and non-X-ray sources. The true background and the true intensity of reflexion are unknown, so that in estimating the weights the observed values are used, giving weights something like

$$w_2 = (a_h + b_h I_o)^{-1}, \qquad (3)$$

where a_h and b_h are independent of the measured intensity, but may be functions of the Bragg angle or the indices of reflexion. Different investigators have used somewhat different forms; for typical examples see Shoemaker (1968), Abrahams & Keve (1971), and Sudarsanan & Young (1974). All have in common the property that the number used for the weight of the *hkl* reflexion is functionally dependent on the number used for F_o or I_o, thus introducing a correlation between the weight and the difference in structure factor or difference in intensity.

One can now see why least-squares refinements making use of these residuals can produce systematic biases from statistical fluctuations of mean value zero. If I_o is too small the weight is too large; if I_o is too large the weight is too small, but the effect is not as great; the effect of a negative fluctuation is not entirely compensated by an equal positive one, giving a kind of rectifier effect. Wilson (unpublished, and probably not worth publishing, in view of the result in the next section) made a number of estimates of the magnitude of the bias for scaling, temperature and positional parameters for different residuals and different weighting schemes. There were difficulties with convergence of series, especially with the positional parameters, but it seemed that the bias in the scaling factor and the overall temperature factor were usually proportional to R, and that the bias in the fractional coordinates would ordinarily be in the fifth decimal place, but might sometimes affect the fourth, particularly for atoms in unsymmetrical environments. Since the bias arose from the correlation of statistical fluctuations in the observed intensities in $(I_o - I_c)$ and in the weights, he attempted to avoid it by using I_c instead of I_o in (3) and variations on it. Bias, however, was not avoided, since there was now a correlation between the weights and I_c. In several specific cases it turned out to be half as great and of the opposite sign; this suggested that $\frac{1}{3}(I_o + 2I_c)$ as the intensity to be used in calculating the weights would remove the statistical bias. This conjecture turns out to be correct for R_2, as the following argument shows.

Refinement in R_2

In actual refinement procedures the denominators in (1) and (2) are either omitted or treated as constants while the parameters entering into the calculation of I_c are varied to minimize R. To simplify the notation, let us write I for I_o, H for I_c, and drop the subscript 2. The procedure is then to minimize

$$R = \sum w(I - H)^2 \qquad (4)$$

with respect to the parameters. Let x be the amount by which some desired parameter differs from its unbiased value. The residual may be expanded in powers of x:

$$R = R(0) + R_x x + \tfrac{1}{2}R_{xx}x^2 + \ldots, \qquad (5)$$

where the subscripts indicate differentiation and the derivatives are evaluated at $x = 0$. The value of x giving the minimum value of R is thus

$$x = -R_x/R_{xx} + \ldots, \qquad (6)$$

and the minimum value of R is not $R(0)$ but

$$R_{\min} = R(0) - \tfrac{1}{2}R_x^2/R_{xx} + \ldots. \qquad (7)$$

Since $dw/dx = (dw/dH)\,(dH/dx)$, differentiation of (4) gives

$$R_x = \sum [w_H H_x (I - H)^2 - 2w(I - H)H_x], \qquad (8)$$

$$R_{xx} = \sum [w_{HH} H_x^2 (I - H)^2 - 4w_H H_x (I - H^2) + w_H H_{xx}(I - H)^2 - 2w(I - H)H_{xx} + 2wH_x^2]. \qquad (9)$$

The important term in the expression for R_{xx} is the final one, as the others vanish with $(I-H)$, while it remains practically constant. For a well refined structure, therefore, it is sufficient to write

$$R_{xx}=2\sum wH_x^2 . \qquad (10)$$

The expression for R_x needs closer attention. If ε is the actual statistical fluctuation in a particular observed intensity, and δ is the actual amount by which the calculated intensity differs from the true value (because of defects in the model, incomplete refinement, *etc.*), $I-H=\varepsilon-\delta$, and (8) becomes

$$R_x=\sum [w_H(\varepsilon^2-2\varepsilon\delta+\delta^2)-2w(\varepsilon-\delta)]H_x . \qquad (11)$$

Expanding w as a power series in ε and δ and neglecting terms of third and higher orders in the small quantities gives

$$R_x=\sum [w_H\varepsilon^2-4w_H\varepsilon\delta+w_H\delta^2-2w\varepsilon-2w_I\varepsilon^2 +2w\delta+2w_I\varepsilon\delta+2w_H\delta^2+\ldots]H_x . \qquad (12)$$

The expected value (mean value over repetitions of the measurements) of ε is zero, and if the number of observations greatly exceeds the number of parameters to be determined the mean value of $\varepsilon\delta$ will also be zero. The expected value of the parameter is then, from (6),

$$\langle x\rangle=-\tfrac{1}{2}[\sum wH_x^2]^{-1}\sum [w_H\langle\varepsilon^2\rangle+3w_H\langle\delta^2\rangle -2w_I\langle\varepsilon^2\rangle+2w\langle\delta\rangle+\ldots]H_x . \qquad (13)$$

The terms in δ may be useful in discussions of bias arising from defects in the model and systematic errors, but our present concern is with the statistical bias arising from the terms in $\langle\varepsilon^2\rangle$. The coefficient of $\langle\varepsilon^2\rangle$ is

$$w_H-2w_I , \qquad (14)$$

so that if the functional form of w can be chosen so that

$$\frac{\partial w}{\partial H}=2\frac{\partial w}{\partial I} \qquad (15)$$

the coefficient of $\langle\varepsilon^2\rangle$ in each term in the sum in (13) will vanish and (to the second order in ε) x will not be biased by statistical fluctuations. This is achieved if w is any function of $(I+2H)$. In the final stages of refinement, therefore, it will be worthwhile to modify (3) to

$$w_2=(a_h+\tfrac{1}{3}b_hI_o+\tfrac{2}{3}b_hI_c)^{-1}, \qquad (16)$$

and similarly for its variants, modifications that should not greatly complicate the refinement program.

Refinement in R_1

Refinement in R_1 can be regarded as a special case of refinement in R_2 with weights

$$w_2=w_1(\sqrt{I_o}+\sqrt{I_c})^{-2}, \qquad (17)$$

where the w_1's are the weights that would have been used in R_1. As one might expect from the additional complexity, there seems to be no simple recipe for avoiding statistical bias in refinement in R_1 (except for modifications that turn it into an unnecessary complication of refinement in R_2), so it would perhaps be best to abandon it as a procedure when the highest attainable accuracy is desired.

Discussion

A disclaimer should be entered about what the proposal of replacing I_o by $\frac{1}{3}(I_o+2I_c)$ in the expressions for the weights does not do. It does not remove the statistical error in x arising from the statistical errors in the I_o [the errors mentioned under (ii) in the *Introduction*]. It does remove, to the second order in ε, biases of the type mentioned under (iii) of the *Introduction*. Third-order and higher terms have been neglected, and these may be of importance for the very weak reflexions. A previous paper (Wilson, 1973) was concerned with the conditions under which refinement of different residuals would give the *same* results, not the conditions under which they would provide *statistically unbiased* estimates, and correlations between ε and the weights were overlooked.

A familiar example of the use of a simple alteration to remove bias in an estimate is the substitution of $(n-1)$ for n in expressions for the variance or the standard deviation of the mean of a number of measurements [see, for example, Cramér (1945) p. 351, or Hamilton (1964) p. 40]. The use of biased estimators of crystallographic parameters may perhaps explain some of the difficulties encountered, for example, by Sudarsanan & Young (1974) in applying the error analysis of Abrahams & Keve (1971).

I am indebted to Dr S. C. Abrahams, Professor D. W. J. Cruickshank, Professor M. M. Woolfson and Professor R. A. Young for helpful discussions and correspondence.

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