Table 5 (*cont.*)

| Salt | $W_s$ (eV) (equation 13) | $W_s$ (eV) (experimental) |
|---|---|---|
| LiBr | 1·68 | 1·80* |
| LiI | 1·47 | 1·34* |
| NaCl | 2·20 | 2·12* |
| NaBr | 2·11 | 1·68* |
| KCl | 2·15 | 2·22* |
| KBr | 2·06 | 2·53* |
| CsBr | 1·86 | 2·0† |
| CsI | 1·83 | 1·9† |

* Boswarva & Lidiard (1967);
† Boswarva (1967).

Table 6. $W_s$ *values*

| Salt | $W_s$ (eV) (equation 13) | $W_s$ (eV) (Theoretical) | $W_s$‡(eV) (Theoretical) |
|---|---|---|---|
| NaF | 2·59 | 2·517* | |
| NaI | 1·90 | 1·603* | |
| KF | 2·37 | 2·419* | |
| KI | 2·04 | 1·924* | 1·87 |
| RbF | 2·12 | 2·188* | — |
| RbCl | 2·03 | 1·984* | 2·17 |
| RbBr | 1·96 | 1·979* | 1·99 |
| RbI | 1·88 | 1·900* | 1·88 |
| CsF | 1·96 | 1·954† | — |
| CsCl | 1·89 | 1·784† | 1·06 (CaCl)<br>2·00 (NaCl) |

* Boswarva & Lidiard (1967);
† Boswarva (1967);
‡ Rao & Rao (1968).

The values of $W_s$ calculated from equation (13) for various alkali halides are given in Tables 5 and 6 and compared with the experimental values where available. Column 3 of Table 6, gives the nearest theoretical values of $W_s$ calculated by Boswarva & Lidiard (1967), while column 4 gives those calculated by Rao & Rao (1968) employing a modified Born model with a higher Van der Waals term. In view of the simple model used and the uncertainties in the experimental observations, the agreement is excellent.

Financial assistance to one of us (NGV) by the Ministry of Education is gratefully acknowledged.

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*Acta Cryst.* (1970). A**26**, 658

# General Method of Obtaining Best Helical Parameters from the Diffraction Pattern

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(*Received* 12 *September* 1969 *and in revised form* 20 *October* 1969)

A practical method of obtaining the best helical parameters $p/P$ and $p$, where $p$ is the rise per unit length along the screw axis and $P$ is the pitch of the helix, is given, which consists of a graphical method followed by a least-squares analysis, and is particularly useful when the helix is non-integral and when the diffraction pattern is complicated by the existence of other crystalline or amorphous phases. The extension of the method to a coiled coil is also described.

## 1. Introduction

A theory of diffraction by helical structures was given by Cochran, Crick & Vand (1952) (hereafter referred to as CCV) and has been successfully applied to various substances. A helical structure in which scattering units are arranged around a screw axis at a regular interval is fully described by three parameters $p$, $p/P$ and $r$, where $p$ is the rise per unit along the screw axis, $P$ and $r$ are the pitch and radius of the helix, respectively. The parameter $p/P$ represents the angle of rotation per unit in fractions of $2\pi$ and was called 'unit twist' by

Ramachandran (1960). The relation between these parameters and the diffraction pattern is fully described in the CCV theory. However, the method of obtaining the best parameters from the diffraction pattern has so far been discussed only by Ramachandran (1960). This report presents a new and more general solution to this problem with respect to two parameters, $p$ and $p/P$. The author has already reported a graphical method to find out $p/P$ (Mitsui, 1966).

## 2. Simple helix

The graphical method proposed in the previous paper is briefly summarized here. The basic equation is,

$$\zeta_i p = m_i + n_i(p/P) \tag{1}$$

where $\zeta_i$ is the height of the $i$th layer line from the equator in reciprocal space (in Å$^{-1}$), and $n_i$, $m_i$ are the integers relating to this layer line (for the meaning of these integers, see CCV). The quantity $\zeta_i p$, which is denoted by $\zeta_{\text{rel}}$, corresponds to the height of the layer line expressed in fractions of the height, $1/p$, of a 'Perutz line'. Graphical representation of equation (1), or the $\zeta_{\text{rel}} - p/P$ diagram, shows the *relative* distribution of various layer lines, each corresponding to a particular set of $(n,m)$, as a function of $p/P$. The best value of $p/P$ may be obtained as the one which gives the best agreements between the observed and theoretical values of $\zeta$'s and between the observed relative intensities and the values of assigned $n$'s.

The numerical method now presented gives the best values of not only $p/P$ but also $p$. It needs the assignment of $(n,m)$ [the $(n,m)$-assignment] to each observed layer line as a preliminary step. This will be most conveniently done by the graphical method mentioned above (Mitsui, 1966). In this context, however, the diagram shown in the previous paper should be modified so that $n$ on each layer line is replaced by a set of $(n,m)$. The best set of $(p,p/P)$ can be calculated by a least-squares method, that is, by minimizing the following quantity

$$S(p,p/P) = \sum_i w_i[\zeta_i p - \{m_i + n_i(p/P)\}]^2 \tag{2}$$

where $w_i$ is the weight attached to the $i$th observation. This leads to the solution,

$$p = \Delta_1/\Delta\,, \quad p/P = \Delta_2/\Delta \tag{3}$$

where,

$$\Delta = \begin{vmatrix} \sum_i w_i n_i \zeta_i, & \sum_i w_i \zeta_i^2 \\ \sum_i w_i n_i^2, & \sum_i n_i w_i \zeta_i \end{vmatrix},$$

$$\Delta_1 = \begin{vmatrix} \sum_i w_i n_i \zeta_i, & \sum_i w_i m_i \zeta_i \\ \sum_i w_i n_i^2, & \sum_i w_i m_i n_i \end{vmatrix},$$

$$\Delta_2 = \begin{vmatrix} \sum_i w_i \zeta_i^2, & \sum_i w_i m_i \zeta_i \\ \sum_i w_i n_i \zeta_i & \sum_i w_i m_i n_i \end{vmatrix}.$$

Discussion concerning the weights $w_i$ will be given in § 5. This method has recently been applied to diffraction patterns of bacterial pili (Mitsui & Poole, 1969).

## 3. Extension to a coiled coil

Ramachandran (1960) introduced the concept 'the unit twist' into the diffraction theory of the coiled coil (Crick, 1953*a*). Equation (14) of his paper, by changing his notation $\eta$ to $\zeta_{\text{rel}}$, is written

$$t_0 p + t_1 q + (t_1 + t_0)s + m = \zeta_{\text{rel}} \tag{4}$$

where $p,q,s$ and $m$ are the integers relating to the diffraction intensity (see Crick, 1953*a*). The quantities $t_0$ and $t_1$ are the unit twists of the major helix ($N_0/M$) and of the minor helix ($N_1/M$), respectively, where $M$

Table 1. *Possible combinations of p, q, s and m under the restriction,* $|p| \le 2$, $|q| \le 2$, $|s| \le 1$ *and* $0 \le H[\equiv 0{\cdot}278\ (q+s)+m] \le \frac{1}{2}$

| | Gradient $(p+s)$ for $p=$ | | | | | | Permissible Segment at $t_0=0$ | |
|---|---|---|---|---|---|---|---|---|
| $s$ | −2 | −1 | 0 | 1 | 2 | $q$ | $m$ | $(H)$ |
| −1 | −3 | −2 | −1 | 0 | 1 | −2 | 1 | 0·166 |
| | | | | | | −1 | 1 | 0·444 |
| | | | | | | 0 | none | — |
| | | | | | | 1 | 0 | 0 |
| | | | | | | 2 | 0 | 0·278 |
| 0 | −2 | −1 | 0 | 1 | 2 | −2 | 1 | 0·444 |
| | | | | | | −1 | none | — |
| | | | | | | 0 | 0 | 0 |
| | | | | | | 1 | 0 | 0·278 |
| | | | | | | 2 | none | — |
| 1 | −1 | 0 | 1 | 2 | 3 | −2 | none | — |
| | | | | | | −1 | 0 | 0 |
| | | | | | | 0 | 0 | 0·278 |
| | | | | | | 1 | none | — |
| | | | | | | 2 | none | — |

is the number of scattering units in the identity period $c$, $N_0$ is the number of rotations made by the major helix in $c$, and $N_1=N_1'-N_0$, $N_1'$ being the number of rotation in $c$ made by the minor helix in the rotating frame which rotates along with the major helix. $\zeta_{\rm rel}$ is defined in the same way with the simple helix, that is, $\zeta_{\rm rel}\equiv\zeta h$, where $h=c/M$. Strictly speaking, there is another integer parameter $d$ (Crick, 1953*a*), but this parameter is set to zero because only this value can give rise to layer lines of appreciable intensities. The modification for non-zero $d$ is easy. A graphical representation of equation (4) gives the *relative* distribution of various layer lines, each corresponding to a particular set of $(p,q,s,m)$, as a function of $t_0$ and $t_1$. An example of such a diagram ($\zeta_{\rm rel}-t_0$ diagram) is shown in Fig. 1. In this case, $t_1$ is fixed to $\frac{5}{18}=0{\cdot}278$ ($\alpha$-helix). A diagram

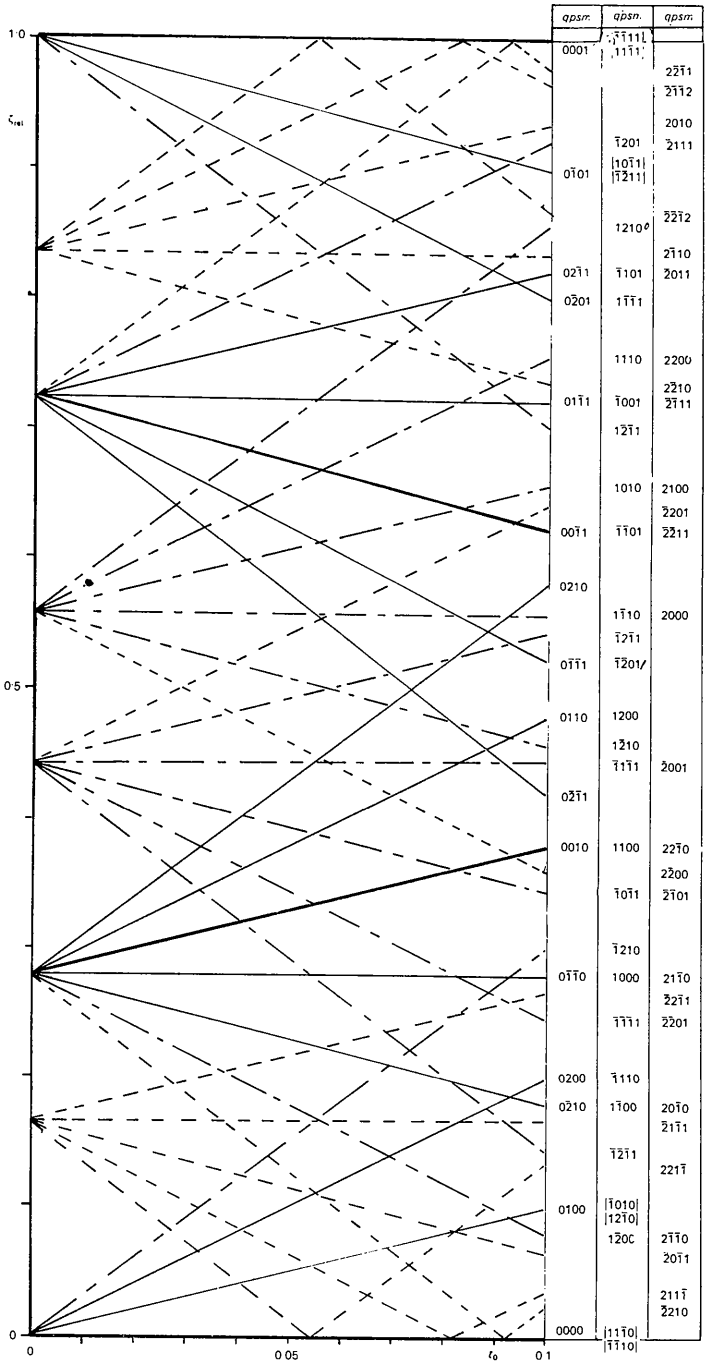


Fig. 1. $\xi_{\rm rel}-t_0$ diagram. —— layer line containing $q=p=0$. —— layer line with minimum $q=0$ .-·-·- layer line with minimum $|q|=1$. ------- layer line with minimum $|q|=2$.

with fixed $t_0$ is also possible. The diagram in the special case $t_0=0$, is nothing but a $\zeta_{rel}-p/P$ diagram for a simple helix. The procedure of finding out the best values of $t_0$ and $t_1$ is similar to that of a simple helix, except that the survey is now two-dimensional.

The method of preparing a $\zeta_{rel}-t_0$ diagram is explained by taking Fig. 1 as an example. As is evident in Fig. 1, there are 'mirror' planes corresponding to $\zeta_{rel}=0{\cdot}5n$ ($n=0, \pm 1, \ldots$). Since, by these mirrors, the signs of integers $p, q$ and $s$ are changed and $m$ is changed to $m'=-m+n$, only the layer lines with $0 \leq (q+s)t_1+m \leq \frac{1}{2}$ are independent. For simplicity, let us introduce the restriction $|p| \leq 2$, $|q| \leq 2$ and $|s| \leq 1$, so that only the prominent layer lines are considered. All the possible combination of $p, q$ and $s$ are shown in Table 1. In contrast with the simple helix, up to three different sets* of $(p,q,s,m)$ contribute to the same layer line at any value of $t_0$. Note that there is a relation $p-q=$ constant between these sets. In Fig. 1 the sets $(p,q,s,m)$ are denoted in the order of $q,p,s,m$, since $q$ is the dominant factor in determining the intensity provided $t_0$ is small. For the same reason, different types of lines are used for different minimum $|q|$ values. Layer lines which contain a set of $(p,q,s,m)$ with $p=q=0$ are shown by bold lines to indicate the potential meridional reflexions.

In the same way as in the simple helix, a set of observed $\zeta$'s are compared with the theoretical ones on a series of $\zeta_{rel}-t_0$ diagrams with various $t_1$. This leads to the assignment of a correct set $(p,q,s,m)$ to each layer line. Once this has been done, the best values of $t_0$, $t_1$ and $h$ are obtainable as the ones which make the following quantity minimum.

$$S=\sum_i w_i[\zeta_i h-\{t_0(p_i+s_i)+t_i(q_i+s_i)+m_i\}]^2 . \quad (5)$$

The solution is,

$$h=\Delta_h/\Delta , \quad t_0=\Delta_{t_0}/\Delta , \quad t_1=\Delta_{t_1}/\Delta ,$$

where

$$\Delta = |\Delta_1,\Delta_2,\Delta_3| , \quad \Delta_h = |\Delta_0,\Delta_2,\Delta_3|$$
$$\Delta_{t_0} = |\Delta_1,\Delta_0,\Delta_3| , \quad \Delta_{t_1} = |\Delta_1,\Delta_2,\Delta_0| ,$$

with

$$\Delta_1 = \begin{pmatrix} \sum_i w_i(p_i+s_i)\zeta_i \\ \sum_i w_i(q_i+s_j)\zeta_i \\ \sum_i w_i\zeta_i^2 \end{pmatrix},$$

$$\Delta_2 = \begin{pmatrix} \sum_i w_i(p_i+s_i)_2 \\ \sum_i w_i(p_i+s_i)(q_i+s) \\ \sum_i w_i(p_i+s_i)\zeta_i \end{pmatrix},$$

$$\Delta_3 = \begin{pmatrix} \sum_i w_i(p_i+s_i)(q_i+s_i) \\ \sum_i w_i(q_i+s_i)^2 \\ \sum_i w_i(q_i+s_i)\zeta_i \end{pmatrix},$$

$$\Delta_0 = \begin{pmatrix} \sum_i w_i m_i(p_i+s_i) \\ \sum_i w_i m_i(q_i+s_i) \\ \sum_i w_i m_i\zeta_i \end{pmatrix}.$$

These formulae will be useful if well resolved diffraction patterns of the coiled coil structure become available.

## 4. The advantage of the method

The advantage of the use of 'the unit twist' and 'rise per scattering unit', in place of 'the identity period' and 'the number of residues or turns per identity period', has been discussed by Ramachandran (1960) and Dickerson (1964). The advantages of the present *method* may be summarized as follows:

(*A*) By adopting a graphical method as the first step, it became very easy (1) to judge whether or not the pattern in question is that from a helical structure, (2) to distinguish between reflexions from two or more coexisting crystal phases, if any [such as the $\beta$-phase in $\alpha$-poly-L-alanine fibers (Brown & Trotter, 1956)] and (3) to identify 'abnormal' reflexions (such as the reflexion from distorted side chains of poly-$\gamma$-benzylglutamates (Mitsui, Iitaka & Tsuboi, 1967)].

(*B*) In the succeeding least-squares method, all the layer lines are treated on equal terms and no special dependence on the Perutz line or 'turn' layer line appears. This is quite in contrast with various methods proposed thus far, and is more reasonable, because, for polymers in general, these two layer lines are not always measured with especially high precision. The present method is applicable even if the Perutz line and/or 'turn' layer line is not observable.

## 5. Additional considerations

*On the weighting scheme*

An estimation of the weight factor appeared in equations (2) and (3) is discussed below. Consider the simplest geometry with the fiber axis normal to the incident beam (the wavelength $\lambda$) and with the cylindrical film (radius $R$) with its axis parallel to the fiber axis. Starting from the equations $\zeta=\sin\beta/\lambda$, $\tan\beta=y/R$, where $y$ is the height of the layer line from the equator on the film, we get,

$$\Delta\zeta=\{\Delta y[1-(\lambda\zeta)^2]^{3/2}-\Delta R\lambda[1-(\lambda\zeta)^2]\}/\lambda R \quad (7)$$

where $\Delta y$ and $\Delta R$ are the errors accompanying $y$ and $R$, respectively. Since, for a fiber diffraction pattern,

* Three is the number under the restriction assumed for the moment. It is infinite in general.

$\Delta R$ is usually much smaller than $\Delta y$, a reasonable weighting scheme will be obtained by setting $w_i = [1-(\lambda\zeta_i)^2]^{-3/2}$. $w_i$ increases rapidly if $\lambda\zeta_i$ is not small enough. Practically, however, the tilted axis method is more frequently used for $\lambda\zeta_i \gtrsim 0{\cdot}3$. Although general treatment for this case is complicated, a rough estimation may be given by considering the simplest case in which (1) the cylindrical film (radius $R$) is used with its axis normal to both the incident beam and fiber axis and (2) the fiber axis is tilted so that the meridional point of the layer line in question lies on the reflexion sphere. Starting from $\zeta = 2\sin\theta/\lambda$, $2\theta = y/R$, where $y$ is the height of the reflexion (this should be on the meridian of the photograph) and neglecting $\Delta R$ again, we get

$$w_i' = [1-(\lambda\zeta/2)^2]^{-1/2}\,.$$

The variation of $w_i'$ is not appreciable within the range, $\zeta\lambda = 0 \sim 1{\cdot}0$, which is practically important. Non-systematic factors such as the diffuseness of individual reflexions may be more important in deciding $w_i'$s.

*Extinction rules for a multistrand coiled coil*

The fact that coiled coil structures are very likely to occur as a multistrand rope (Crick, 1953*b*) must be taken into account for assigning $(p,q,s,m)$. Let us consider the simplest case in which each strand is related by a rotational symmetry only. Using the revised formula of Fraser, MacRae & Miller (1964), it is easy to get the extinction rule that only the layer lines with $q-p-d=kN$ ($k=0, \pm 1, \ldots$) appear for the $N$ strand coiled coil structure (Mitsui, 1968). If $d$ is set to 0 as in the previous section, we have $q-p=kN$. Similar considerations for the simple helix have already been made by Klug, Crick & Wyckoff (1958).

The author wishes to express his sincere gratitude to Professor Y. Iitaka of the University of Tokyo, and Professor G. N. Ramachandran of the University of Madras for valuable discussions.

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*Acta Cryst.* (1970). A**26**, 662

# Application of the Symbolic Addition Procedure in Neutron Diffraction for Non-centrosymmetric Crystals

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(*Received* 30 *December* 1969)

For non-centrosymmetric crystals containing both positive and negative scatterers of neutrons, the symbolic addition procedure has been tested as a means of obtaining phases of neutron reflexions. Test calculations were done for two structures, α-resorcinol and methyl GAG.2HCl.$H_2O$, which have already been studied by neutron diffraction using conventional methods. It is found that this procedure yields the phase angles with reasonable accuracy. The average error in phases for α-resorcinol was 14° and the $F_o$ Fourier synthesis with these phases revealed the position of all the positive scatterers and three out of six hydrogen atoms. The average error in methyl GAG.2HCl.$H_2O$ was 40° and only 10 positively scattering atoms out of 16 could be clearly seen in the Fourier map. For both the structures an $F_o$ map was found to be superior to an $E$ map. When the contribution of the negative scatterers to the total neutron scattering is less than 25%, it has been shown that the symbolic addition method will apply for crystals containing up to 100 atoms per unit cell.

## Introduction

In an earlier paper (Sikka, 1969) the author has shown that in centrosymmetric crystals, the application of the symbolic addition procedure (Karle & Karle, 1966) determines correctly the signs of about 95% of the neutron structure factors (with $|E_h| \geq 1{\cdot}5$) when the contribution of the negatively scattering atoms to the