

CHAPTER 2

**Determination of crystal structures by x-ray diffraction methods:
Theoretical backgrounds and experimental technique.**

2.1. INTRODUCTION.

The structure determination of the crystalline state seems to be one way to obtain general information about conformation and packing of the molecules in the crystalline state. The interactions as well as the steric conditions, which are manifested in the crystal structure can sometimes explain the formation of the LC states as temperature changes.

A large scale of systematic investigation is needed to obtain detailed knowledge in this field of liquid crystal research. Although in the past 15 years, a large number of papers are published on this subject, the available data are not yet sufficient for the derivation of general ideas or laws. A preliminary survey of the present knowledge of the solid-mesophase relationships has been given by Bryan¹. The transformation from the solid to the nematic phase is characterised by the breakdown of the positional order of the molecules but not of the orientational order. But Leadbetter² has, however, pointed out that although this is true of at least the majority of the cases so far known, it is a generalisation which must at this stage be treated with caution. Hence we find it very promising to undertake the project of determining the crystal and molecular structure of a number of alkenyl nematogenic compounds, the properties of which have been studied in liquid crystalline phase. I have successfully solved two structures. One of the structures have already been published³ in MCLC and the other one is communicated.

2.2. X-RAY DIFFRACTION BY CRYSTALS.

In the analysis of crystal structures by x-ray diffraction, the dimensions of the unit cell are determined by observing the positions and intensities of the diffraction maxima. To locate the positions of individual atoms in the unit cell, the intensities must be measured and analysed. Most important equation relating the

positions of the atoms to the structure factor is given by,

$$F_{hkl} = \sum_{j=1}^N f_j \exp 2\pi i (hx_j + ky_j + lz_j) \quad (2.1)$$

Where f_j is the scattering factor or form factor of the j^{th} atom and x_j , y_j and z_j are the fractional co-ordinates of the j^{th} atom in a unit cell containing N atoms. The observable quantity I is proportional to $|F|^2$.

Now the atoms in the unit cell are the positions of the high electron density $\rho(x,y,z)$, so \bar{F}_{hkl} can be expressed as

$$\bar{F}_{hkl} = \int_V \rho(x,y,z) \exp 2\pi i (hx + ky + lz) dv \quad (2.2)$$

where V is the volume of the unit cell. Then by Fourier transform we have ,

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} \exp -2\pi i (hx + ky + lz) \quad (2.3)$$

We could have directly derived the crystal structure by making a Fourier summation, if F_{hkl} values could be determined from diffraction experiment. From experiments we can have structure amplitude $|F_{hkl}|$, but not the phases and this lack of information constitutes the phase problem in crystallography.

In general there are four methods to overcome the phase problem, e.g. (1) Patterson function, (2) Direct method, (3) Isomorphous replacement technique and (4) Anomalous scattering method.

Since we have determined the structure of two compounds using Direct methods, only this method will be described in detail.

2.3 INTENSITY DATA COLLECTION

All the intensity data have been collected with an ENRAF - NONIUS CAD4 automatic single crystal diffractometer using CuK_α radiation monochromated by a graphite monochromator. The intensity data is collected by $\omega - 2\theta$ scan mode. The measured value of the intensity is given by,

$$I_{\text{raw}} = \frac{A}{n} (C - R.B) \quad (2.4)$$

where A = attenuation factor (26.55 for CuK_α).

n = an integer varying from 8 to 24 as mentioned earlier.

C = Total count.

R = Ratio of scan time to background counting time.

B = Total background count.

The standard deviation $\sigma(I)$ calculated on the basis of counting statistics is given by

$$\sigma(I_{\text{raw}}) = \frac{20.166}{n} A (C + R^2 B)^{1/2} \quad (2.5)$$

2.4 Intensity Data Reduction

The relationship between $|F_o|$ and $I^{1/2}$ depends on a number of factors, primarily geometric which relates to the individual reflection and to the apparatus used to measure the intensity. The proportionality can be written as

$$|F_{(hkl)}| = \left(\frac{KI}{L_p} \frac{hkl}{p} \right)^{1/2} \quad (2.6)$$

K is called the scale factor, which is normally constant for a given set of measurements and is usually obtained at a later stage.

In our case the incident beam is partially polarized during monochromatization by reflection from the basal plane of a graphite crystal and P takes the form,

$$P_{hkl} = P_{\text{erf}} \frac{\cos^2 2\theta_m + \cos^2 2\theta_{hkl}}{1 + \cos^2 2\theta_m} + (1 - P_{\text{erf}}) \frac{\cos^2 2\theta_m + \cos^2 2\theta_m}{1 + \cos^2 2\theta_m} \quad \text{--- (2.7)}$$

Where P_{erf} = Constant depending on the crystal used in the monochromator (0.5 in our experiment).

θ_m = Bragg angle of reflection from the monochromator crystal.

The Lorentz factor⁴⁻⁶ L depends on the precise measurement technique used and for our diffraction data it is given by,

$$L_{hkl} = \frac{1}{\sin^2 \theta_{hkl}} \quad (2.8)$$

Temperature Factor

It has been shown theoretically and practically that the change in scattering power of the atoms in a crystal due to thermal vibrations can be given by the expression,

$$f_o^{-B(\sin^2 \theta)/\lambda^2}$$

where B is related to the mean-square amplitude (\bar{u}^2) of atomic vibration by,

$$B = 8\pi^2 \bar{u}^2$$

By using the method introduced by A.G.C. Wilson⁷ one can obtain an overall value of B and at the same time, places all the observed intensities on an approximately absolute basis.

Wilson showed that average absolute structure factor depends only on what is in the cell and not where the atoms are located and hence for a random distribution of N atoms in the unit cell,

$$\langle |F|^2 \rangle = \sum_{j=1} f_j^2 \quad (2.9)$$

Dividing entire reciprocal space observed into annular zones of equal S^2 ($S = \sin\theta/\lambda$), $\langle |F_{\text{obs}}|^2 \rangle$ is determined for each of them and $\sum_{j=1}^N f_{\text{obs}}^2(S_{\text{mid}})$ is calculated using the mean value of S^2 for

each zone. Since $|F_{\text{obs}}|^2$ is usually known on an arbitrary scale, we may write

$$\langle |F_{\text{obs}}|^2 \rangle = K \langle |F|^2 \rangle \quad (2.10)$$

where $\langle |F|^2 \rangle$ is the average absolute structure factor. To separate out thermal motion in the crystal, we write,

$$\langle |F|^2 \rangle = \sum_{j=1}^N f_j^2 = \sum_{j=1}^N f_{\text{oj}}^2 \exp(-2B_j S^2) \quad (2.11)$$

Assuming B same for all atoms,

$$\langle |F|^2 \rangle = \exp(-2BS^2) \sum_{j=1}^N f_{\text{oj}}^2 \quad (2.12)$$

Substituting the equation (2.12) in equation (2.10) we get,

$$\langle |F_{\text{obs}}|^2 \rangle = K \exp(-2BS^2) \sum_{j=1}^N f_{\text{oj}}^2$$

$$\ln \frac{\langle |F_{\text{obs}}|^2 \rangle}{\sum_{j=1}^N f_{\text{oj}}^2} = \ln K - \frac{2BS \sin^2 \theta}{\lambda^2} \quad (2.13)$$

The plot of $\ln \langle |F_{\text{obs}}|^2 \rangle / \sum_{j=1}^N f_{\text{oj}}^2$ against $\sin^2 \theta / \lambda^2$ called the wilson

plot is, therefore, a straight line except for the scattering due

to experimental errors and furnishes us with intercept of $\ln K$ and a slope of $-2B$.

When instead of random distribution of atoms, groups of atoms with known geometry (such as benzene ring) are present in the structure, they may be included in the expression for average intensity even knowing nothing about their positions and orientations. When G groups of known geometry are present, the k^{th} of which contains M_k atoms, we may write using the scattering formula of Debye⁸,

$$\langle |F|^2 \rangle = \sum_{k=1}^G \sum_{i=1}^{M_k} \sum_{j=1}^{M_k} f_i f_j \frac{\sin 2\pi r_{ij} s_{ij}}{2\pi r_{ij} s} + \sum_{j=1}^N f_j^2 \quad (2.14)$$

Where r_{ij} is the distance between the i^{th} and j^{th} atoms of the k^{th} group and $S = S_{\text{mid}}$ as before. The plot in this case is known as Debye plot and gives a better straight line fit for obtaining B and K .

It is often advantageous to use a k -curve. For this purpose, $K(S_{\text{mid}})$ is computed for each zone of S^2 mentioned above, as

$$K(S_{\text{mid}}) = \frac{\sum_{j=1}^N \epsilon \sum_{o_j} f_{oj}(s)}{\sum |F_o|^2(s)} \quad (2.15)$$

where ϵ is a small integer depending on the space group⁹. A least squares procedure is used to fit a best smooth analytical function usually $\ln K = A + B^c$ to experimental points. When $c = 2.0$, the curve is the same as Wilson's plot.

After scaling the data and estimating the temperature factors we try to postulate a trial structure by direct methods.

2.5 DETERMINATION OF TRIAL STRUCTURE BY DIRECT METHOD.

The crystal structure of relatively small molecules of up to 100 independent atoms are readily determined from the diffraction intensities by means of Direct-Method techniques.¹⁰⁻¹⁴

From a diffraction experiment it is possible to derive the amplitude of a complex quantity, the structure factor, which may be written as,

$$F(\bar{h}) = |F(\bar{h})| \exp\{i\phi(\bar{h})\} \quad (2.16)$$

If the positions of the atoms in the unit cell were known then the values of the structure factors could be found from,

$$F(\bar{h}) = \sum_{j=1}^N f_j \exp 2\pi i \bar{h} \cdot \mathbf{r}_j \quad (2.17)$$

where f_j is the scattering factor for the j^{th} atom. The problem in structural crystallography is that of finding the atomic positions when usual experiments only give $|F_{\bar{h}}|$. If structure factors were known in both amplitude and phase then the electron density could be calculated at all points of the unit cell from ,

$$\rho(\bar{r}) = 1/v \sum_{\bar{h}} |F(\bar{h})| \cos(2\pi \bar{h} \cdot \bar{r} - \phi_{\bar{h}}) \quad (2.18)$$

Direct methods of solving crystal structures are those methods which attempt to find the phases directly by mathematical processes from the measured x-ray intensities.

2.6 Unitary and Normalised Structure Factors

For direct methods it is an advantage to work with unitary structure factors for which the fall off with increasing scattering angle has been removed. The unitary structure factor is defined as,

$$U(\bar{h}) = \frac{F(\bar{h})}{\sum_{j=1}^N f_j} \quad \text{so that } |U(\bar{h})| \leq 1$$

Writing the unitary scattering factor as

$$n_j = \frac{f_j}{\sum_{j=1}^N f_j}$$

We may write,

$$U(\bar{h}) = \sum_{j=1}^N n_j \exp 2\pi i (\bar{h} \cdot \bar{r}_j) \quad (2.19)$$

Another corrected structure factor of great theoretical importance is the normalized structure factor given by,

$$|E(\bar{h})|^2 = \frac{|F(\bar{h})|^2}{\varepsilon(\bar{h}) \sum_{j=1}^N f_j^2}$$

Where $\varepsilon(\bar{h})$ takes into account the effect of space group symmetry. Now if f be the common shape for all atoms then $f_j = Z_j f$.

$$E(\bar{h}) = \varepsilon(\bar{h})^{-1/2} \frac{F(\bar{h})}{\left(\sum_{j=1}^N Z_j^2 f^2 \right)^{1/2}} = \varepsilon(\bar{h})^{-1/2} \sum_{j=1}^N \left(\frac{Z_j}{\sigma_2^{1/2}} \right) \exp 2\pi i (\bar{h} \cdot \bar{r}_j) \quad \text{---(2.20)}$$

where $\sigma_m = \sum Z_j^m$. $E(\bar{h})$ is called the normalised structure factors because of its property $\langle |E(\bar{h})|^2 \rangle = 1$. This relationship shows

that the average of E^2 can be carried out regardless of θ . The same is not true, however, of either $|F(h)|^2$ or $|U(h)|^2$ and this simplification is one of the main reasons why E 's are preferred for use in direct method.

2.7 SOME RELATIONS INVOLVING THE MAGNITUDES AND THE PHASES.

Harker-Kasper Inequalities.

In 1948 Harker and Kasper¹⁵ using Cauchy inequality relation derived the following inequality relation between magnitudes and phases of unitary structure factors,

$$U(\bar{h})^2 \leq 1/2 [1 + U(2\bar{h})] \quad (2.21)$$

If we denote the sign of $U(\bar{h})$ by $S(\bar{h})$ which can have the values either +1 or -1, then this relationship can be written as

$$S(\bar{h}) S(\bar{h}') S(\bar{h} + \bar{h}') = 1 \quad (2.22)$$

A development made by Karle and Hauptman¹⁶ in the form of an inequality does depend on the non-negativity of electron density. For a centro-symmetric structure where $U(\bar{h}) = U(-\bar{h})$ gives,

$$1 - U(\bar{h})^2 - U(\bar{k})^2 - U(\bar{h}-\bar{k})^2 + 2U(\bar{h})U(\bar{k})U(\bar{h}-\bar{k}) \geq 0$$

from which, if the U 's are sufficiently large, it may be shown that,

$$S(\bar{h}) S(\bar{k}) S(\bar{h} - \bar{k}) = 1 \quad (2.23)$$

A significant step in the development of direct methods was done by Sayre¹⁷.

The electron density is given by the summation,

$$\rho(\bar{r}) = 1/v \sum_{\bar{h}} F(\bar{h}) \exp -2\pi i(\bar{h} \cdot \bar{r})$$

and we may write,

$$\rho(\bar{r})^2 = 1/v \sum_{\bar{h}} G(\bar{h}) \exp -2\pi i(\bar{h} \cdot \bar{r}) \quad (2.24)$$

where $G(\bar{h})$ is the Fourier coefficient of the squared density.

If the structure consists of equal resolved atoms, then both $\rho(\bar{r})$ and $\rho(\bar{r})^2$ will show equal resolved peaks. If the scattering factors of the squared atoms is represented by g and that of the normal atoms by f then,

$$F(\bar{h}) = \frac{f}{gv} \sum_{\bar{h}'} F(\bar{h}') F(\bar{h} - \bar{h}') \quad (2.25)$$

This is Sayre's equation, and is an exact relationship between structure factors for equal and resolved atoms.

For a centro-symmetric structure it might be assumed that a large product on the right hand side of equation (2.25) was likely to have the same sign as $F(\bar{h})$. This leads to the relationship that for large structure factors

$$s(\bar{h}) s(\bar{h}') s(\bar{h} - \bar{h}') = +1 \quad (2.26)$$

This was the sign relationship given in the papers by Cochran¹⁸ and Zachariason¹⁹. Expression for probability of equation(23) was given Cochran and Woolfson²⁰. This is for an equal atom structure.

For non-centrosymmetric crystals, the main phase determining formula are the sum of angles formula,

$$\phi_3(\bar{h}, \bar{k}) = \phi(\bar{h}) - \phi(\bar{k}) - \phi(\bar{h} - \bar{k}) = 0 \quad (\text{modulo } 2\pi) \quad (2.27)$$

and the tangent formula,

$$\tan\phi(\bar{h}) = \frac{\sum_{\bar{k}} K(\bar{h}, \bar{k}) \sin [\phi(\bar{h} - \bar{k}) + \phi(\bar{k})]}{\sum_{\bar{k}} K(\bar{h}, \bar{k}) \cos [\phi(\bar{h} - \bar{k}) + \phi(\bar{k})]} \quad (2.28)$$

Structure Invariant and Semi-Invariant.

A structure invariant is defined as a quantity which is independent of the choice of origin in the unit cell.

The intensities of reflections, $|F(\bar{h})|^2$ s are structure invariants. However, the structure factor itself is not structure invariant, otherwise the phase problem would not exist in crystallography. The structure factor $F(\bar{h})$ is given by,

$$F(\bar{h}) = |F(\bar{h})| \exp i\phi(\bar{h}) = \sum_{j=1}^N f_j \exp 2\pi i (\bar{h} \cdot \bar{r}_j) \quad (2.29)$$

With shift Δr of the origin, the equation(2.29) changes to

$$\begin{aligned} F'(\bar{h}) &= \sum f_j \exp 2\pi i [\bar{h} \cdot (\bar{r}_j - \Delta\bar{r})] \\ &= |F(\bar{h})| \exp -2\pi i (\bar{h} \cdot \Delta\bar{r}) \exp i\phi(\bar{h}) \end{aligned} \quad (2.30)$$

Thus we see that the phase changes by $-2\pi i(\bar{h} \cdot \Delta\bar{r})$ while the amplitude is invariant.

In a similar way it can be shown that $|F(\bar{h})|^2$ is structure invariant.

Individual phases depends on the structure and choice of origin, some combinations of them is a structure invariant.

For example if $h_1 + h_2 + h_3 = 0$, then $\phi(h_1) + \phi(h_2) + \phi(h_3)$ is a structure invariant for every space group. It follows directly from the fact that $F(\bar{h}) F(\bar{k}) F(-\bar{h}-\bar{k})$ is an invariant,

$$\begin{aligned} F'(\bar{h})F'(\bar{k})F'(-\bar{h}-\bar{k}) &= F(\bar{h}) \exp -2\pi i(\bar{h} \cdot \Delta\bar{r}) F(\bar{k}) \exp -2\pi i(\bar{k} \cdot \Delta\bar{r}) \\ &\quad F(-\bar{h}-\bar{k}) \exp 2\pi i[(\bar{h} \cdot \Delta\bar{r}) + (\bar{k} \cdot \Delta\bar{r})] \\ &= F(\bar{h}) F(\bar{k}) F(-\bar{h}-\bar{k}) \end{aligned} \quad (2.31)$$

Since the moduli of the structure factors are invariant themselves, the angular part of $F(\bar{h}) F(\bar{k}) F(-\bar{h}-\bar{k})$ is also an

invariant i.e.. $\phi(h) + \phi(k) + \phi(-h-k)$ is an invariant or $\phi_3 = \phi(h) + \phi(k) + \phi(-h-k)$ is an invariant.

Knowledge of the actual values of ϕ_3 or reliable estimates of ϕ_3 would strengthen direct method procedures enormously. Direct methods mostly use $|\phi_3| = 0$ for large values of $E_3 = N - 1/2 |E(h) E(k) E(-h-k)|$.

The quartet structure invariant relationship is given by

$$\phi_4 = \phi_H + \phi_K + \phi_L + \phi_{-H-K-L} \quad (2.32)$$

The value of ϕ_4 is not only dependent on $E_4 = N^{-1} |E_H E_K E_L E_{-H-K-L}|$ but also on the cross term $|E_{H+K}|$, $|E_{H+L}|$ and $|E_{K+L}|$. In case the cross terms are large $\phi_4 = 0$.

The structure semi-invariants are quantities which do not change value by transfer from one special origin to another. The structure semi-invariants originate from space group symmetry. In any space group any structure invariant is also a structure semi-invariant, but in general the converse is not true. A complete theory concerning this subject is given in a series of papers by Hauptman and Karle²¹⁻²³ and by Schenk^{24,25}.

We have solved crystal structures of two different compounds. The first one belongs to centro-symmetric space group and its structure was determined by using the program SIMPEL. The program SIMPEL estimates phases using symbolic addition procedure. It is a complete direct method system, which may enter with $|F|$ and may produce an E-map of the structures. The unique part of SIMPEL is formed by a series of routines, successively gathering the relationships and determining a starting set, carrying out a symbolic addition, finding the correct numerical values for the symbols and finally executing a numerical phase extension and refinement.

The symbolic-addition method starts with collecting n phase relationships for m unknown phases where $m \ll n$. Then origin

defining phases are selected and a number of other unknown phases is given a symbolic phase. These starting reflections are chosen such, that in principle all other phases can be reached from this set via the phase relationship. Then a phase propagation is carried out, using throughout the symbolic phases. With the extended phase set as basis, the numerical values of the symbols are then determined through Figures of Merit. In most cases an additional tangent extension is carried out, followed by a Fourier summation, which is expected to show the structures.

2.8 Starting Set Determination.

The determination of the starting set begins with a convergence procedure similar to that devised by Germain, Main and Woolfson²⁶. This procedure searches for that reflection which is the weakest linked to the other reflections by means of the phase relations and then this reflection is removed from the set of reflections. At the same time all its phase relations are removed from the collection of phase relationships. This process is repeated until no reflections are left in the set. Any time the reflection is removed without having phase relationships linking it with other phases, this reflection has taken to be starting set. Since a starting set reflections with large $|E|$ are preferred, the use of triplets and quartets generally leads to very good starting set. The second set is a few cycles of symbolic addition using quartets and triplets, employing very strict acceptance criteria, and not allowing relations among the symbolic phases. This leads to a much larger starting set.

The next step is the extension of starting set. This is done in SIMPEL using triplet relations only. It is very essential that no errors are included during this process and therefore, the criteria used to accept a symbolic phase for a reflection are very strict, in particular in the beginning. In, general, no single indication

will be accepted unless it belongs to the ten to fifteen strongest triplet relationships. For multiple indications giving rise to the symbolic phase, high acceptance limits are applied. In general, this precautions make sure that the resulting set of symbolic phases contains the correct solution.

Figures of Merit.

With the extended group of phased reflections as input numerical values for the symbols are calculated using a number of figures of merit (FOM's).

Apart from the separate FOM's also a combined FOM is calculated, which mostly discriminates the correct solution without difficulties.

After determining the symbols all symbolically phased relations can get numerical phase. These phases are then used as starting point for numerical phase extension, because in general the number of phased reflections is yet insufficient to calculate a good E-map. In the centrosymmetric case this is achieved by means of a \sum_2 refinement and extension.

Thus SIMPEL produces a set of E-values with phases, which can be fed into an E-map calculating program with subsequent interpretation.

Eventually the atomic positions can be tested and be refined by a fast diagonal least squares program.

2.9 Refinement of the structure :

The trial structure thus obtained is, however, an approximate one. The positional and thermal parameters describing the model along with the scale factor for reducing the observed structure factors, have to be refined. An agreement between the calculated structures factors F_c and those observed, F_o , indicates the degree of refinement. The most common method of assessing the agreement

is calculating the residual or reliability index of the form,

$$R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|} \quad (2.33)$$

the summation being over all the reflections.

Another form of the residue of common use is

$$R_w = \left[\frac{\sum W (|F_o| - |F_c|)}{\sum W |F_o|^2} \right]^{1/2} \quad (2.34)$$

where the weight,

$$W = \frac{1}{\sigma^2(F_o)}$$

$\sigma(F_o)$ being the standard deviation of F_o .

Generally for refinement of a crystal structure we adopt following three methods, e.g., (i) Fourier synthesis, (ii) Difference fourier synthesis and (iii) Least square refinement. The fourier synthesis gives the refined co-ordinates of the atoms and also tends to reveal the position of any atom which is not included in computing the structure factors. The difference fourier map is very useful for locating H-atoms towards the final stages of refinement procedure. Difference fourier synthesis is free from series termination effect which arises due to limitation in the amount of data being collected.

The method of least square :

An analytical method of refinement of great power and generality is that based on the principle of least squares. In this case the quantity most commonly minimised is

$$D = \sum_{hkl} W_{hkl} (|F_o| - |KF_c|)^2 \quad (2.35)$$

where W_{hkl} is the weight of the observations and \sum_{hkl} indicates summation over all the observed reflections. To obtain the least

square fit, it will be necessary to consider the parameters P as variables which may be adjusted to minimise D . This is a straight forward minimization problem which is treated by differentiating the right side of equation (2.35) with respect to each of the parameters in turn and setting the derivation equal to zero. This gives, a equation of the type,

$$\sum_{r=1}^m W_r (f_{or} - f_{cr}) \frac{\delta f_{cr}}{\delta p_j} = 0 \quad (2.36)$$

A set of n equations in n unknowns called the normal equations. Solutions of these n equations gives directly the best values of the parameters p_j in the least-squares sense.

The second compound belongs to a noncentro-symmetric space group $P2_12_12_1$. Phases for this structure were estimated by generalised tangent procedures using the program GENTAN of XTAL system. GENTAN uses triplet and/or quartet structure invariant relationships in a general tangent formula to propagate and refine structure factor phases.

The first step in the GENTAN calculation is to specify sufficient phases to uniquely define the origin. The specification of phases to fix the cell origin may be done automatically or may be selected by the user. GENTAN provides for a wide range of starting and refinement options. From these phases additional values are determined through the application of the tangent formula to connect invariant relationship. When the space group is non-centrosymmetric this procedure is also used to specify the phases for fixing the enantiomorphic form of the structure.

Multiple phase sets may be initialised with permuted, magic integer or random starting phases. The extension and refinement of phases is simultaneous in the tangent process. There are two different methods for propagating phases in Gentan ; CASCADE and

BLOCK. Tangent weighting schemes include probabilistic²⁷, Hull-Irwin²⁸ statistical and Modified H-I Statistical weights. Refined phase sets are examined for correctness in terms of a variety of figures of merit. A combined figure-of-merit CFOM and an absolute measure of success parameters AMOS are used to sort the best phase sets. Calculation of the E-maps, interpretation of the structure and refinement are done in the usual methods.

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