

## The phase problem in neutron diffraction

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**Abstract.** The structure of any crystal can now be determined *ab initio* from the neutron Bragg intensity data alone, without recourse to the x-ray structural analysis. This has been made possible by the reduction in data collection times due to the availability of increased neutron fluxes at the samples and the extensive development of the phase determining procedures for neutron diffraction in the last 15 years. In this review, we describe the applications of direct methods, anomalous dispersion techniques and difference Patterson methods and discuss why these methods are applicable in neutron diffraction. Their limitations are also discussed. Some newer methods like resonance-modulated diffraction and use of 'Renninger effect' to measure the structure invariants are also touched upon.

**Keywords.** Neutron diffraction; Patterson method; anomalous dispersion techniques; direct methods.

### 1. Introduction

Neutron diffraction has distinct advantages in structural analysis of crystals: (i) to locate hydrogen atoms, thereby providing in hydrogen-bonded crystals a very precise stereochemical information about hydrogen bonds and (ii) to differentiate the neighbouring elements in the periodic table, say, nitrogen from carbon and oxygen, in crystals of organic and biological molecules. Lately the determination of deformation charge densities in organic molecules by combined x-ray and neutron studies has also become possible. For a recent review of the above applications of neutron diffraction see Chidambaram (1981).

Till late sixties, the neutron diffraction of a given crystal was studied only after analysis of its structure by x-rays. Once the x-ray non-hydrogen skeleton of the structure was available, the phase problem really did not exist in neutron diffraction. This is because, from neutron scattering length considerations (see table 1) a typical organic crystal containing C, H, N, Cl and O atoms etc may be assigned a formula,  $C_p H_q$ . Then the average contribution of non-hydrogen atoms to neutron intensities

$$\sigma_x = \frac{P(0.66)^2}{P(0.66)^2 + Q(0.372)^2} \quad (1)$$

for  $P = Q$  case is 0.7. For this  $\sigma_x$ , 92% of phases evaluated from non-hydrogen atom positions only, according to the theory of Ramachandran and Parthasarathy (1965), should be within  $90^\circ$  of the true phases, a criterion which usually leads to the final structure. In an actual case, carbon monoxide derivative of myoglobin (Norvell *et al* 1975), the true and the calculated phases with omission of hydrogen atoms differed on the average by  $31^\circ$  up to  $1.8 \text{ \AA}$  Bragg resolution.

Two reasons can be attributed for not carrying out neutron structure determinations *ab initio*. First, because of low incident neutron fluxes from nuclear reactors ( $\sim 10^4$  neutrons/cm<sup>2</sup>/sec at the sample) in earlier times, the neutron Bragg intensity

**Table 1.** Neutron scattering amplitudes for some elements.

Z	Element	$b(10^{-12} \text{ cm})$
1	H	-0.372
	$b_+$	1.04
	$b_-$	-4.07
1	D	0.67
6	C	0.6626
7	N	0.940
8	O	0.58
17	Cl	0.98
48	$^{113}\text{Cd}$	$0.725 + 4.507i$
		(at $\lambda = 0.678 \text{ \AA}$ )
62	$^{149}\text{Sm}$	$0.795 + 6.051i$
		(at $\lambda = 0.915 \text{ \AA}$ )
66	Dy	1.69
	$^{164}\text{Dy}$	4.94
92	U	0.85

\*  $b_+$  for  $I + \frac{1}{2}$  and  $b_-$  for  $I - \frac{1}{2}$  compound nucleus states.

data collection was very time-consuming compared to x-rays. Second, because of the differences in which x-rays and neutrons interact with the atoms making up the crystals, it was suspected that the customary phasing methods of x-rays like the heavy atom technique, direct methods etc could not be employed in neutron diffraction. However, with the advent of high flux reactors ( $\sim 10^6$ – $10^7$  neutrons/cm<sup>2</sup>/sec at the sample) and building of automatic four-circle diffractometers, the neutron Bragg intensity data collection times have been drastically reduced and full three-dimensional data are now routinely recorded (see Sequeira *et al* 1978). These have motivated many attempts to solve the crystal structures directly from neutron data. These have been quite successful and have shown that the direct methods and anomalous dispersion techniques of x-rays can be applied in neutron diffraction as well. Since this volume is dedicated to Prof. Ramaseshan, it is appropriate here to review these successes, as he was the first to recognise the higher potential of neutron resonance scattering compared to the x-ray anomalous dispersion scattering for solving the phase problem. Before we do so, it is instructive first to examine the causes of the differences in x-ray and neutron phase problems in some detail.

## 2. Differences between x-ray and neutron phase problems

The differences arise from the fact that the scattering agents in atoms are different for the two radiations. Whereas the x-rays are essentially scattered by atomic electrons, the scattering centres for neutrons are predominantly the nuclei. The nuclear scattering length for neutrons can be written as

$$b = b_0 + b' + ib'' \quad (2)$$

The term  $b_0$  represents the hard sphere or potential scattering contribution and is

independent of neutron energy.  $b'$  and  $b''$  are the energy dependent resonance scattering contributions. In most cases,  $b''$  is negligible. It is this energy-dependent  $b'$  term which makes the neutron scattering amplitude an irregular but featureful function of the atomic number.

Expression (2) is similar to

$$f = f_0 + \Delta f' + i\Delta f'' \quad (3)$$

the x-ray scattering factor of the atom.  $\Delta f'$  and  $\Delta f''$  are significant only when the wavelength of the radiation is close to the absorption edge of this atom.

Neutron scattering amplitudes for some elements are given in table 1, from which many things are apparent.

### 2.1 Equal atoms

The neutron scattering factors for different nuclei are of the same order of magnitude and do not display as much variation as in the x-ray case, for which it changes by a factor of 90 from the hydrogen to the uranium atom. This, although conferring the major advantage to neutron diffraction for location of protons, leads to the fact that none of the nuclei present in the crystal will dominate the scattering of neutrons and hence there will be no heavy atoms for neutron diffraction. The variation in  $b$ 's for different elements is such that at the most, the neutron 'heavy atoms' are of strength equivalent to that of a Cl atom in a crystal containing C, H, O atoms etc. for the x-ray case\*†. Further, as the scattering amplitude of the hydrogen nucleus is comparable to other elements, there are more numbers of atoms to be located at the phasing stage in a neutron structure analysis. Consequently, the neutron Patterson map will be more overcrowded and difficult to interpret directly.

### 2.2 Negative scattering factors

The x-ray scattering factors are all positive while for neutrons, they are of both signs. This fact may be expected to have the following consequences:

(a) The neutron Patterson map will now contain both positive and negative vector peaks and hence some of them will be removed from the map by their overlap, thereby making difficult the deconvolution of the Patterson function with the help of superposition methods like the minimum and sum functions etc. However for small structures, this has not proved a serious drawback. The structures of potassium hydrogen chloromaleate (Ellison and Levy 1965) and  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  (Sikka and Chidambaram 1969) have been solved by the combination of symmetry minimum and minimum functions.

(b) The negativity of  $b$  also appears to rule out the possibility of using direct methods in neutron diffraction as hydrogen nucleus ( $b$  is negative) are present in almost every interesting crystal. This led Karle (1966) to propose the squared structure approach to

\*  $^{113}\text{Cd}$ ,  $^{149}\text{Sm}$ ,  $^{164}\text{Dy}$  etc. can act as heavy atoms for structures, say of 200 atoms per one heavy atom in the unit cell. However, they are of wrong type. They cannot be easily introduced into such structures and also their high absorption cross-sections for neutrons pose problems in data collection.

† In some of the structures *e.g.*  $\text{UO}_3(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Taylor and Muller (1965) and  $\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$  (Williams and Peterson 1969) which have been solved by the 'heavy atom' neutron Patterson method, this situation prevailed.

circumvent the difficulty caused by the negative scattering factors. He showed that from the observed neutron normalized structure factors ( $E_h$ ), it is possible to derive another set of normalized structure factors ( $V_h$ ) corresponding to a structure in which all the atoms scatter with the square of the original scattering factors but whose positions are the same as in the original structure. The scattering density would then become positive everywhere and the phase problem for this 'squared' crystal can be solved using the direct methods. The success of this approach was demonstrated by Ellison and Levy (1967), who used it to solve the structure of glycolic acid.

Sikka (1969, 1970), however, re-examined the consequences of the negativity of  $b$  for hydrogen atoms and found that these are not as serious, as assumed for the straight employment of direct methods in neutron diffraction. The amount of average neutron scattering from hydrogen atoms present in a crystal defined by

$$\sigma = \frac{\sum_{j=1}^H b_j^2}{\sum_{j=1}^N b_j^2} \quad (4)$$

is rarely more than 30% in a crystal. Up to this  $\sigma$ , the criterion for the application of direct methods in x-rays *i.e.* the normalized structure factors for actual and the squared structures ( $E_h$  and  $V_h$ ) should have the same sign or nearly equal phases, is very well satisfied in neutron diffraction for  $E_h \geq 1$  as shown in figure 1.

### 2.3 Isotopic differences

The neutron scattering amplitudes vary from isotope to isotope. This makes the difference Patterson technique\* more attractive for neutrons. This map now will

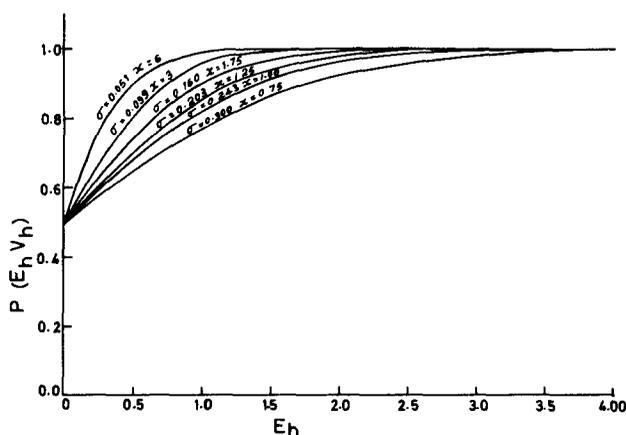


Figure 1. The probability  $P(E_h V_h)$  that  $E_h$  and  $V_h$  will be alike in sign for different  $E_h$  and  $\sigma$  or  $x (= P/Q)$  (from Sikka 1969).

\* Difference Patterson can in principle be utilized with polarised neutrons for crystals containing ordered magnetic atoms, for whom the scattering factors are neutron polarisation-dependent. As is well-known, for spin-up polarisation of neutrons, the scattering by the magnetic atom is proportional to  $(b + p)$  and for the spin-down case, it is proportional to  $(b - p)$ . Here  $p =$  magnetic atom form factor. For Ni,  $p = 0.13 \times 10^{-12}$  cm at  $\sin \theta/\lambda \approx 0$  compared to  $b = 1.02 \times 10^{-12}$  cm.

contain only  $RR$  and  $RO$  vectors ( $R$  = replaceable atoms,  $O$  = other atoms) with peak heights  $(b_{R1}^2 - b_{R2}^2)$  and  $[(b_{R1} - b_{R2}) \times b_0]$  and since  $b_{R1}$  and  $b_{R2}$  can be of opposite sign,  $RO$  vectors can get strengthened. However, one has to know the positions of the  $R$  atoms to recover the structure from the difference Patterson map. Again as these will not be heavy scatterers of neutrons, unlike in x-rays, these may be difficult to locate.

A neat application of the isotopic replacement method is due to Johnson (1967) in 3 endo-phenyl-2-endo norbornanol (60 atoms in the asymmetric unit). For this compound the neutron intensity data were collected from two crystals—one containing hydrogen atoms and the other in which 4 of the hydrogen atoms had been selectively substituted by deuterium atoms. The replaceable atoms were first found by a  $(|F_H| - |F_D|)^2$  Patterson (similar to  $(\Delta|F|)^2$  synthesis of Rossmann (1961) for anomalous dispersion). A difference Patterson map  $(F_D^2 - F_H^2)$  helped to locate additional eight atoms and the remaining atoms were found by the usual Fourier synthesis.

### 2.4 Complex scattering amplitudes

The neutron scattering amplitudes for some nuclei like  $^{113}\text{Cd}$ ,  $^{149}\text{Sm}$ ,  $^{155,157}\text{Gd}$ ,  $^{135}\text{Xe}$  etc which have high resonant absorption for thermal neutrons are complex and hence the anomalous dispersion method of x-rays becomes applicable in neutron diffraction (Peterson and Smith 1962). However, there are quantitative differences in the values of real and imaginary dispersion terms for the two radiations (Ramaseshan 1966; Dale and Willis 1966) as shown below for  $^{113}\text{Cd}$

	$b'/b_0$	$b''/b_0$
x-rays	$\sim 0.3$	$\sim 0.3$
Neutrons( $^{113}\text{Cd}$ )	7.4 at $\lambda = 0.55 \text{ \AA}$ -7.4 at $\lambda = 0.8 \text{ \AA}$	12.4 at $\lambda = 0.68 \text{ \AA}$

The neutron values of these ratios are an order of magnitude higher\* than for the x-rays and can be varied significantly by a variation in wavelength (figure 2). This larger

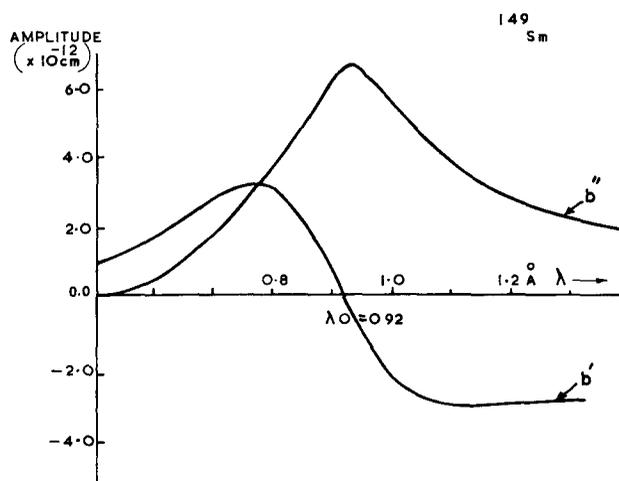


Figure 2.  $b'$  and  $b''$  for  $^{149}\text{Sm}$  vs  $\lambda$  ( $\text{\AA}$ ).

\* These ratios for  $^{149}\text{Sm}$ ,  $^{157}\text{Gd}$  and  $^{135}\text{Xe}$  are even higher

anomalous dispersion effect for neutrons can, therefore, be used to tackle more complex structures than are possible by x-ray anomalous dispersion method. The power of this technique is shown in figure 3, taken from Sikka and Rajagopal (1975), by high average values of the Bijvoet ratios:

$$\begin{aligned} \langle \delta \rangle &= \langle \Delta I / I \rangle \\ \Delta I &= \left| |F(hkl)|^2 - |F(\bar{h}\bar{k}\bar{l})|^2 \right| \\ I &= 0.5 \left[ |F(hkl)|^2 + |F(\bar{h}\bar{k}\bar{l})|^2 \right] \end{aligned} \quad (5)$$

for hypothetical structures containing  $N$  atoms and one resonant atom (natural Sm in this case, containing 13%  $^{149}\text{Sm}$  resonant isotope). Note that in the x-ray case, structures have been solved when  $\langle \delta \rangle$  has been as low as 0.1.

### 3. Applications and status of direct and anomalous scattering methods in neutron diffraction

#### 3.1 Direct methods

The application of direct methods ( $\Sigma_1$ ,  $\Sigma_2$  tangent formulas, and cosine and sine invariants methods etc) for neutron diffraction both for centrosymmetric and non-centrosymmetric structures is now an accepted fact. So far, about 25 structures have been solved by this technique and these have not revealed any significant differences between the application of direct methods in x-ray and neutrons. The errors in phases (figure 4) determined by this technique are similar for the two radiations ( $\langle |\phi_0 - \phi_{\text{TAN}}| \rangle_{\text{av}} = 28^\circ$  for the neutron study of  $L_3$ -threonine (Ramanadham *et al* 1973) compared to the value  $22^\circ$  for x-ray study of alkaloid Panamine (Karle and Karle

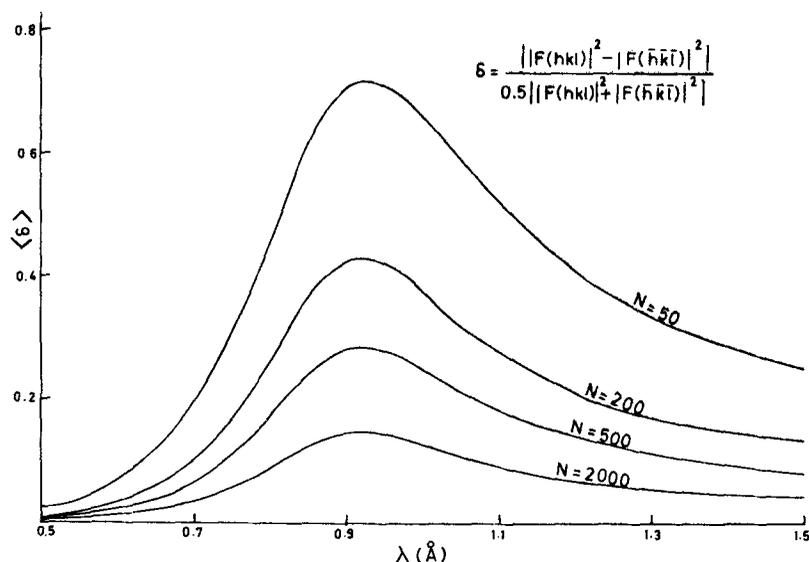
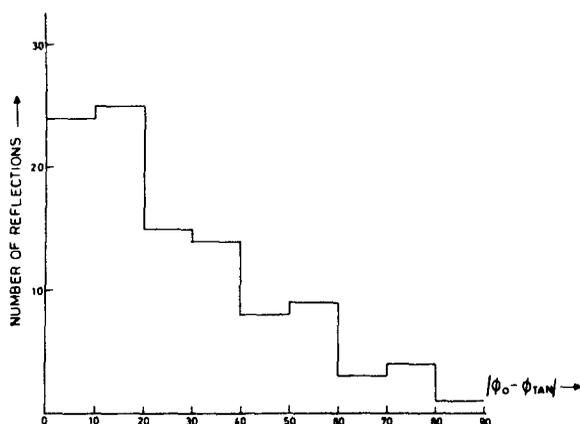


Figure 3. Variation of  $\langle \delta \rangle$  vs  $\lambda$  for crystals containing one natural Sm atom and  $N$  other atoms (from Sikka and Rajagopal 1975).



**Figure 4.** Frequency distribution of the error  $\langle |\phi_0 - \phi_{TAN}| \rangle$  for non-centrosymmetric neutron reflections in *L*-threonine (from Ramanadham *et al* 1973).

1966)). The largest structure solved using neutron data, by routine application of the program MULTAN (Germain *et al* 1971), up-to-date, is that of Melampodin containing 54 atoms in the asymmetric unit (Bernal and Watkins 1973). Out of the 22 largest maxima on the *E* map of this structure, only four were spurious. In view of the above, it may now be said that direct methods can be applied in a neutron structure analysis for almost any crystal to which they are applicable in x-rays.

### 3.2 Anomalous dispersion method

In spite of the higher power of this technique in neutron structure analysis for large crystals like proteins (as discussed in § 2.4), the method has not lived up to its early promise. So far, the method has been tested on six small structures

- |   |                              |
|---|------------------------------|
| (i) $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$                            | (MacDonald and Sikka 1969),  |
| (ii) $\text{Sm}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$                          | (Sikka 1969a),               |
| (iii) $\text{NaSm}(\text{EDTA}) \cdot 8\text{H}_2\text{O}$                          | (Koetzle and Hamilton 1975), |
| (iv) $\text{Cd}(\text{tartrate}) \cdot 5\text{H}_2\text{O}$                         | (Sikka and Rajagopal 1975),  |
| (v) $\text{Cd-Histidine} \cdot 2\text{H}_2\text{O}$                                 | (Bartunik and Fuess 1975),   |
| (vi) $\text{agua}(\text{L-glutamato})\text{Cd}(\text{II}) \cdot \text{H}_2\text{O}$ | (Flook <i>et al</i> 1977),   |

and one protein,  $^{113}\text{Cd}$  myoglobin (Schoenborn 1975). The method is beset with the following difficulties, especially for complex crystals.

3.2a. *Phase ambiguity resolution*: It is well known that phases determined by the anomalous dispersion method at a single wavelength for a crystal have two fold ambiguity:

$$\phi = \phi_A + \frac{\pi}{2} \pm \theta, \quad (6)$$

$$\cos \theta = \frac{|F(hkl)|^2 - |F(\bar{h}\bar{k}\bar{l})|^2}{4|F'_A| |F''_A|}. \quad (7)$$

In the x-ray case, this ambiguity is resolved or circumvented by (i) the heavy atom method (Ramachandran and Raman 1956), (ii) the double-phase Fourier synthesis method (Ramachandran 1964), (iii) the sine-Patterson method (Okaya *et al* 1955) and (iv) the two wavelength method (Raman 1959; Ramaseshan *et al* 1957). For neutron diffraction as the anomalous site is a light weight from scattering point of view, method (i) cannot be used. Attempts by Schoenborn to use this method in  $^{113}\text{Cd}$  myoglobin did not yield good results. Methods (ii) and (iii) have successfully been applied in  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$  (see figure 5),  $\text{Cd}(\text{tartrate}) \cdot 5\text{H}_2\text{O}$  and  $\text{agua}(\text{L-glutamato}) \text{Cd}(\text{II}) \cdot \text{H}_2\text{O}$  (see figure 6). But for large molecules, these methods may not be applicable. This is because, if hydrogen atoms are present in the structure (this will be almost so in every large crystal), then because of their negative scattering length, they will give peaks of opposite polarity in the positive and negative images of the structure which are present in Fourier or Patterson maps of the crystal due to these two methods and thus cause confusion in picking out the correct structure. The limitations of the two wavelength method (successful in  $\text{Sm}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Na Sm}(\text{EDTA}) \cdot 8\text{H}_2\text{O}$ ) have been examined by Sikka (1969b). If the phase ambiguity has to be resolved then the two wavelengths chosen for data collection have to be on the opposite side of the resonance. For Cd, this is not practicable ( $\lambda_1 < 0.68 < \lambda_2$  and at  $\lambda_1$ , the incident neutron flux will be low, scattered intensity will also be less ( $\propto \lambda^3$ ) and there will be intense overlapping of reflections) unless a hot source coupled with the reactor is used. The best anomalous scatterer for the two wavelength method seems to be  $^{157}\text{Gd}$  (see figure 7). It has resonance at 1.6 Å. However, no structure containing this isotope has been studied so far.

Another method suggested to circumvent the phase ambiguity is to use the tangent formula of direct methods (Sikka 1973). The basis of this is that in a tangent formula calculation, if the input phases are within  $45^\circ$  of their true values, the tangent formula will determine and refine the phases to a correct set. Now this input set of phases can be obtained in two ways from the anomalous dispersion data.

(i) One can use the two-wavelength method for resolving the phase ambiguity for a limited set of reflections as suggested by Bartunik and Fues (1975). For Cd Histidine  $\cdot 2\text{H}_2\text{O}$ , these authors could measure the phases utilizing anomalous dispersion, with  $\langle |\phi_0 - \phi_{\text{ANM}}| \rangle_{\text{av}}$  of only  $2.3^\circ$ .

(ii) The centroid of the two phases,  $\phi_1$ , and  $\phi_2$  given by formula (6) can also be used. As pointed out by Sikka (1973) and others, the errors in phases by choosing the centroid will be limited to  $90^\circ$  and there will be reasonable number of reflections with errors less than  $45^\circ$ . Weighted tangent-formula calculations for L-aspartatocadmium(II) trihydrate ( $\text{P}2_12_12_1$ ) as given in table 2, demonstrate the success of this approach.

3.2b. *Location of the anomalous scatterer.* In all the above methods for ambiguity resolution of phases, prior knowledge of the position of the anomalous scatterer is implied. Again the task of locating these atoms in neutrons is more difficult than for x-rays (see § 2.1). The position of the anomalous scatterer can, in principle, be found by the two wavelength methods (for which  $b_R(\lambda_1) = b_R(\lambda_2)$ )\* of Singh and Ramaseshan (1968) and Sikka (1969c). Singh and Ramaseshan's method is an analytical method which combines data at these two-wavelengths to give  $F^2_A$ , the contribution due to the

\*  $b_R = b_0 + b'$ , the total real part of scattering from the anomalous atom.

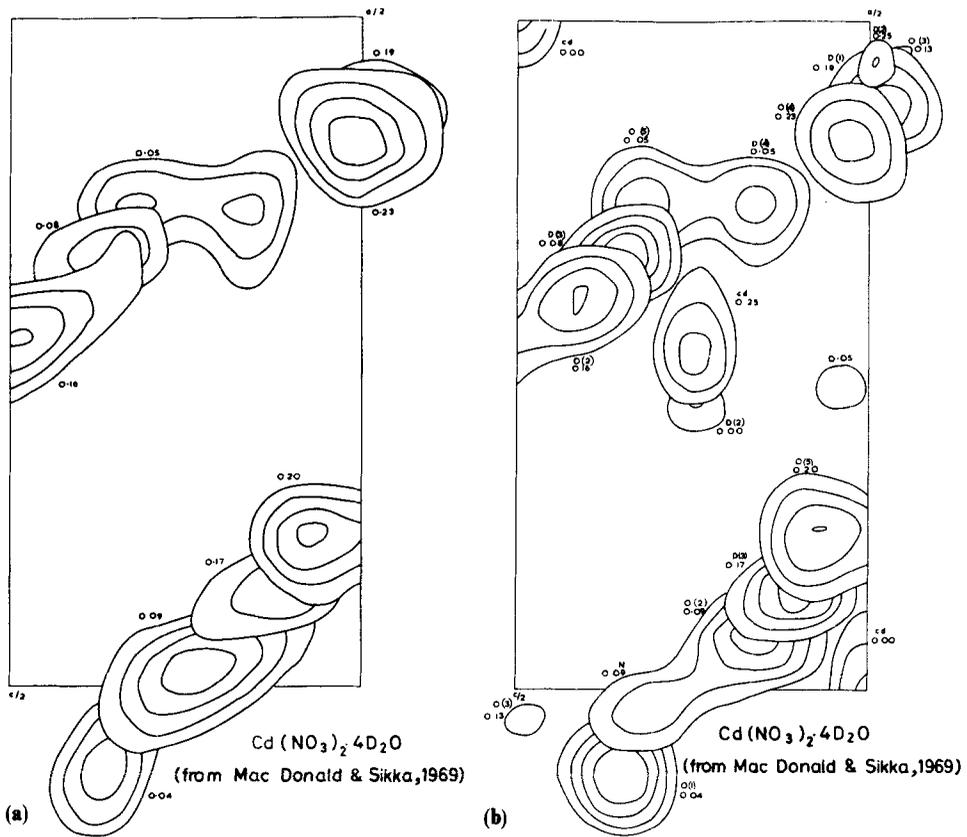


Figure 5.  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$  (a) Double phased Fourier synthesis (b) Anomalous dispersion Fourier synthesis (from Macdonald and Sikka 1969).

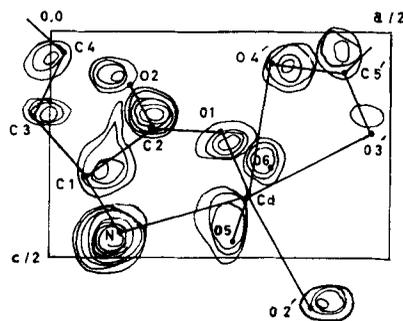


Figure 6. Composite map of the sum function of sine Patterson map of aqua (L-glutamato)  $\text{Cd}(\text{II}) \cdot \text{H}_2\text{O}$  (from Flook *et al* 1977).

anomalous atoms alone. The position of the anomalous atoms can then be determined by a Patterson synthesis with  $F_A^2$  as coefficients. This method has been tested by Koetzle and Hamilton (1975) on  $\text{NaSm}(\text{EDTA}) \cdot 8\text{H}_2\text{O}$ . Sikka's method is based on the cosine synthesis of Okaya and Pepinsky (1961). However, when the anomalous scatterer is

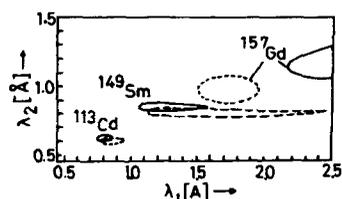


Figure 7. Optimum wavelength regions for  $^{157}\text{Gd}$ ,  $^{149}\text{Sm}$  and  $^{113}\text{Cd}$  for two different absorption factors (from Jauch and Dachs 1981).

Table 2. Tangent formula refinement results on L-aspartatocadmium(II) trihydrate for circumventing the phase ambiguity in neutron anomalous dispersion method.

Set number	Input set	Number of reflections in the input	$\delta$ limit	Weight assigned in first cycle	$\langle  \phi_0 - \phi_{\text{TAN}}  \rangle$ for acentric reflections	Number of centric reflections with wrong phase
1	$\phi_0$	144	—	1	22.4°	2
2	$\phi_c$	88	90°	$ \cos \delta $	22.5	3
3	$\phi_c$	88	90	$ \cos \delta ^2$	22.5	1
4	$\phi_c$	17	20	$ \cos \delta $	24.7	4

$\delta$  is the half angle of the phase ambiguity in (6) and (7).  $\phi_c$  is the centroid phase,  $\phi_0$  is the true value of phase and  $\phi_{\text{TAN}}$  is the one calculated by the tangent formula. Out of 144 reflections, 90 were acentric.

$\langle |\phi_0 - \phi_{\text{TAN}}| \rangle$  is the average error after 7 cycles of refinement.

$^{113}\text{Cd}$ , both these methods require the use of one neutron wavelength of about 0.7 Å, which as pointed above is not very practicable. The method which has shown more promise is the  $(\Delta|F|)^2$  synthesis of Rossmann (1961), used by Sikka and Rajagopal (1975) in  $\text{Cd}(\text{tartrate}) \cdot 5\text{H}_2\text{O}$  and by Schoenborn (1975) in Cd myoglobin. For the latter structure, the Harker section at  $\lambda = 1.25 \text{ \AA}$  is shown in figure 8. The Patterson density is, clearly, much higher at the Cd–Cd vector site.

Recently, a novel way to integrate the techniques of direct methods and anomalous dispersion technique for x-rays has been attempted by Hauptman (1982) which avoids the prior determination of the anomalous dispersion sites. It will be interesting to extend this approach to neutron diffraction also.

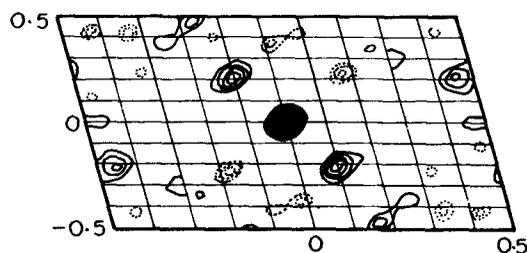


Figure 8. Harker section for Cd myoglobin at  $\lambda = 1.25 \text{ \AA}$  for  $(\Delta|F|)^2$  synthesis (from Schoenborn 1975). The densest peak is the Cd–Cd vector peak.

#### 4. Some new techniques

None of the techniques described below has been used in an actual structure analysis but the physics underlying them is attractive.

##### 4.1 Resonance modulated diffraction

This method has been suggested by Hayter *et al* (1974). It is based on the fact that the neutron scattering lengths of some nuclei are spin-dependent (see table 1 for the hydrogen nucleus). If these nuclei in crystals can be polarised, then the neutrons, which are parallel to the direction of nuclear polarisation, see a coherent scattering amplitude of  $b^+$  and the neutrons, which are anti-parallel, will be scattered with amplitude  $(b^+ + 2b^-)/(2I + 1)$  (Schermer and Blume 1968). Now if the intensity data are recorded from unpolarized and polarized crystals, the phase problem can be solved by utilizing the difference Patterson technique.

Since, for the hydrogen nuclei,  $b^+$  and  $b^-$  are large, this technique according to Hayter (1976) opens up the possibility of using these hydrogens as heavy atoms for phase determination. Experiments so far (using microwaves for polarizing hydrogens at 1.5°K) have only demonstrated the nuclear polarization effects on Bragg intensities and no actual structure determination has been carried out yet.

##### 4.2 Three-beam method of Post (1977) for x-rays

Post (1977, 1979) has demonstrated that, in principle, the phase problem in x-ray diffraction can be resolved if the Renninger effect, in which three Bragg planes simultaneously reflect giving out three diffracted beams, is made use of. For in this case, according to the dynamical theory, the interactions among these beams are coherent and their intensities will contain information about the phases. Post, using a single crystal of  $\text{Al}_2\text{O}_3$ , has experimentally shown that the intensity distributions are indeed dependent upon the products  $F_H F_K F_{H-K}$  ( $H = (h_1 k_1 l_1)$ ,  $K = (h_2 k_2 l_2)$  and  $H-K$ , the difference), the structure invariants\* as the theory predicts.

The above method can be employed in neutron diffraction also, as the dynamical theory is common to both x-rays and neutrons (Shull 1973). The four-circle diffractometers in conjunction with position sensitive neutron detectors or the film methods in neutron diffraction (Hohlwein 1975) can be employed to measure these intensity distributions. However, it remains to be seen even for x-rays, whether the method will be useful for imperfect crystals, such as are usually employed for crystal structure analysis.

#### Acknowledgement

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\* The phases of these structure invariants (products of structure factors the sum of whose indices are zero) are invariant to the choice of the origin and a knowledge of a few of these is enough to initiate the use of direct methods for the solution of phase problem.

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