

of low negative and positive density were found throughout the unit cell, but the interesting fact remains that the highest peaks were found in the spaces between the heavy atoms. This is particularly the case for the C-C bonds, while the terminal C-O bonds in the side chains have very small or absent residuals. To illustrate the situation the residual electron density in the planes of the rings is shown in Fig. 8. Similar effects have been reported by Hartman & Hirshfeld (1966) and have been more thoroughly discussed by O'Connell, Rae & Maslen (1966).

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The Use of Neutron Anomalous Scattering in Crystal Structure Analysis. I. Non-Centrosymmetric Structures

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A method for solving the phase problem *ab initio* in crystal structure studies by neutron diffraction has been suggested. This method is based on the anomalous scattering of thermal neutrons by certain nuclei. Using the data collected at two neutron energies, the process of phase determination is carried out in two steps: (i) the location of the position of the anomalous scatterer and (ii) the correlation of the phase of the structure factor with the phase of the anomalous scatterer. The method gives unique solution of the phases. The expressions deduced are general and can be used for X-ray anomalous scattering also.

1. Introduction

Direct methods of sign determination* which are based on the positivity of scattering matter are not applicable to neutron diffraction. Nor can the heavy atom method be used, as the scattering lengths of various nuclei do not differ appreciably. For these reasons the use of neutron diffraction in crystallography has been restricted to the location and the refinement of position

of light atoms (from the point of view of X-ray scattering) in a structure for which the main features are known from X-ray diffraction work. The possibility of solving the phase problem *ab initio* in neutron diffraction studies stems from the fact that some nuclei (e.g. ^{113}Cd , ^{149}Sm , ^{151}Eu and ^{157}Gd) show anomalous scattering in the thermal neutron range (Peterson & Smith, 1961, 1962). Ramaseshan (1966) pointed out that anomalous dispersion effects in neutron scattering are much more pronounced than in X-ray scattering and hence can be used effectively in solving the structures provided the

* See a recent paper by Karle (1966).

experimental problems associated with the collection of data are solved. Thus writing the scattering length in the form $b = b_0 + b' + ib''$, the ratios b'/b_0 and b''/b_0 can be as large as 6 and 10 respectively for ^{113}Cd (cf. the X-ray case where mostly $f'/f_0 \approx f''/f_0 \approx 0.15$).

Fig. 1 shows that by suitably choosing the neutron energy one can get $(b_0 + b')/b_0 \approx 7$, for ^{113}Cd , i.e. a scattering length which is greater than that of other nuclei by a factor of about 7. This amounts to having a heavy atom in the structure.

What is perhaps of importance is the fact pointed out by Ramaseshan (1966) that large anomalous dispersion in nuclei like ^{113}Cd , ^{149}Sm , ^{151}Eu and ^{157}Gd can make it possible to use neutron diffraction for solving the structure of large molecules. The success of the anomalous dispersion methods depends on observing significant differences, ΔI , between the intensities of inverse reflexions hkl and $\bar{h}\bar{k}\bar{l}$. In the case of X-ray anomalous scattering, the structure of vitamin B₁₂ mono-acid has been solved with $\langle \Delta I \rangle / \langle I \rangle \approx 0.06$. ($\langle \rangle$ indicates the root mean square value). If $\langle \Delta I \rangle / \langle I \rangle \approx 0.10$ is taken as the criterion for a structure that can be handled by anomalous dispersion methods, it turns out that a structure containing about 2000 atoms per ^{113}Cd can be solved.

The aim of the present paper is to show that by using the data collected at two neutron energies it is possible to locate the position of the anomalous scatterer and determine the phase unambiguously. The results obtained are general and can be applied to X-ray anomalous scattering also.

2. Determination of the position of the anomalous scatterer

In handling the phase problem by anomalous dispersion methods, the first step is to locate and refine the position of the anomalous scatterer (A -scatterer). The position of A -scatterers which are invariably 'heavy atoms' in the case of X-ray scattering may be determined by Patterson synthesis, but the location of the heavy atom vector in a Patterson synthesis becomes increasingly difficult as the number of light atoms increases. However, in the case of neutron scattering the A -scatterer need not necessarily be a 'heavy atom' for certain neutron energies and thus location of the A -scatterer becomes difficult even in structures of moderate complexity. A method which employs the combination of two sets of data collected at two neutron energies has been suggested here for locating the position of A -scatterers. The two sets of data are combined to give $|F_A|^2$, the contribution due to the A -scatterer alone. Obviously, a Patterson synthesis with $|F_A|^2$ will contain only the A -scatterer vectors. In effect the method is similar to those described by Harding (1962), Kartha & Parthasarathy (1965), Matthews (1966) and Singh & Ramaseshan (1966) which employ the combination of isomorphous and anomalous dispersion data. However, the 'two wavelength method' is super-

ior to the combination of isomorphous and anomalous data because one does not have to depend on the availability of isomorphous pairs. Moreover, lack of exact isomorphism is always a factor to be borne in mind in choosing the isomorphous pairs.

Let us consider a structure with n_A A -scatterers, all of the same type and n_N normal scatterers (N -scatterer) in the unit cell. Let the scattering length of an A -scatterer be denoted by

$$\begin{aligned} b_A &= b_0 + b' + ib'' \\ &= b(r) + ib(i) \end{aligned}$$

where $b(r) = (b_0 + b')$ and $b(i) = b''$.

The structure factor $F_1(\mathbf{H})$ for neutron-energy E_1 (associated de Broglie wavelength λ_1 is given by $\lambda_1 = h/\sqrt{2E_1M}$, h is Planck's constant and M is the mass of the neutron),

$$F_1(\mathbf{H}) = F_N + F_{A1} + F'_{A1}$$

where

$$\begin{aligned} F_N &= \sum_{j=1}^{n_N} b_{Nj} T_{Nj} \exp 2\pi i \mathbf{H} \cdot \mathbf{r}_{Nj} \\ F_{A1} &= \sum_{j=1}^{n_A} b_j(r) T_{Aj} \exp 2\pi i \mathbf{H} \cdot \mathbf{r}_{Aj} \\ &= b(r) \sum_{j=1}^{n_A} T_{Aj} \exp 2\pi i \mathbf{H} \cdot \mathbf{r}_{Aj}, \end{aligned}$$

since A -scatterers are all of the same type. And

$$F'_{A1} = b_1(i) \sum_{j=1}^{n_A} T_{Aj} \exp 2\pi i \mathbf{H} \cdot \mathbf{r}_{Aj}$$

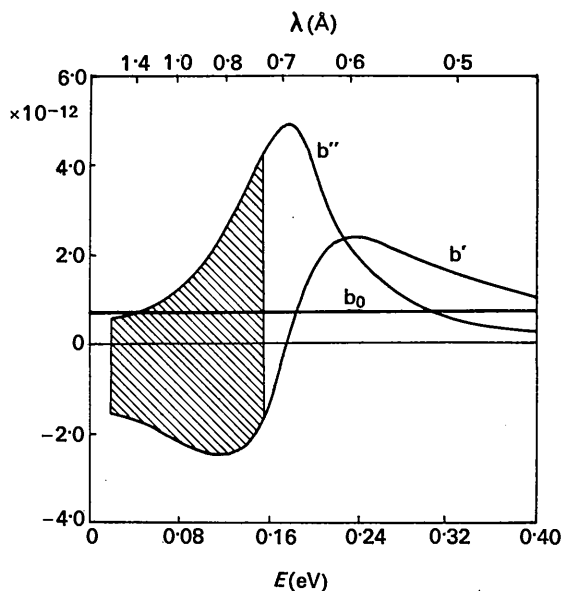


Fig. 1. The variation of b' and b'' for ^{113}Cd with wavelength in the vicinity of the resonant wavelength. The shaded part shows the region where E_1 and E_2 can be chosen conveniently so that $b_1(r) = b_2(r)$. (See Appendix.)

$$T_{Nj} = \exp\left(-B_{Nj} \frac{\sin^2\theta_1}{\lambda_1^2}\right)$$

$$T_{Aj} = \exp\left(-B_{Aj} \frac{\sin^2\theta_1}{\lambda_1^2}\right).$$

Now

$$\begin{aligned} |F_1(H)|^2 &= \mathbf{F}_1(\mathbf{H}) \cdot \mathbf{F}_1^*(\mathbf{H}) \\ &= (\mathbf{F}_N + \mathbf{F}_{A1} + \mathbf{F}_{A1}') \cdot (\mathbf{F}_N^* + \mathbf{F}_{A1}^* + \mathbf{F}_{A1}'^*) \\ &= |F_N|^2 + |F_{A1}|^2 + |F_{A1}'|^2 + 2|F_N||F_{A1}| \cos \varphi \\ &\quad + 2|F_N||F_{A1}'| \cos \varepsilon + 2|F_{A1}||F_{A1}'| \cos \psi \end{aligned}$$

where φ , ε and ψ are $\mathbf{F}_N\mathbf{F}_{A1}$ (angle between \mathbf{F}_N and \mathbf{F}_{A1}), $\mathbf{F}_N\mathbf{F}_{A1}'$ and $\mathbf{F}_{A1}\mathbf{F}_{A1}'$ respectively. For only one type of A -atom, $\psi = 90^\circ$ and $\varepsilon = (90 - \varphi)$. Thus

$$\begin{aligned} |F_1(H)|^2 &= |F_N|^2 + \{b_1^2(r) + b_1^2(i)\}|x|^2 \\ &\quad + 2|F_N|b_1(r)|x| \cos \varphi + 2|F_N|b_1(i)|x| \sin \varphi. \end{aligned} \quad (1)$$

where

$$\begin{aligned} |x| &= \left\{ \sum_{j=1}^{n_A} T_{Aj} \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Aj} \right\}^2 \\ &\quad + \left\{ \sum_{j=1}^{n_A} T_{Aj} \sin 2\pi \mathbf{H} \cdot \mathbf{r}_{Aj} \right\}^2; \end{aligned}$$

similarly,

$$\begin{aligned} |F_1(\bar{H})|^2 &= |F_N|^2 + \{b_1^2(r) + b_1^2(i)\}|x|^2 \\ &\quad + 2|F_N|b_1(r)|x| \cos \varphi - 2|F_N|b_1(i)|x| \sin \varphi. \end{aligned} \quad (2)$$

Similar expressions for $|F_2(H)|^2$ and $|F_2(\bar{H})|^2$ may be written and numbered equations (3) and (4) respectively.

Now we define $|F_{m1}(H)|^2$, $|F_{m2}(H)|^2$, ΔI_1 , and ΔI_2 as follows,

$$\begin{aligned} |F_{m1}(H)|^2 &= \frac{1}{2}[|F_1(H)|^2 + |F_1(\bar{H})|^2] \\ &= |F_N|^2 + \{b_1^2(r) + b_1^2(i)\}|x|^2 \\ &\quad + 2|F_N|b_1(r)|x| \cos \varphi \end{aligned} \quad (5)$$

$$\begin{aligned} |F_{m2}(H)|^2 &= \frac{1}{2}[|F_2(H)|^2 + |F_2(\bar{H})|^2] \\ &= |F_N|^2 + \{b_2^2(r) + b_2^2(i)\}|x|^2 \\ &\quad + 2|F_N|b_2(r)|x| \cos \varphi \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta I_1 &= [|F_1(H)|^2 - |F_1(\bar{H})|^2] = \\ &= 4|F_N|b_1(i)|x| \sin \varphi \end{aligned} \quad (7)$$

$$\begin{aligned} \text{and } \Delta I_2 &= [|F_2(H)|^2 - |F_2(\bar{H})|^2] = \\ &= 4|F_N|b_2(i)|x| \sin \varphi. \end{aligned} \quad (8)$$

Combining equations (7) and (8) we get,

$$\frac{\Delta I_1}{2b_1(i)} = \frac{\Delta I_2}{2b_2(i)} = 2|F_N||x| \sin \varphi = \delta. \quad (9)$$

It may be noted that $\Delta I_1/\Delta I_2 = b_1(i)/b_2(i) = \text{constant}$. Since the absorption is quite different for the two wavelengths, this will provide a check on the accuracy of the data.

The first term in equation (5) gives rise to $N-N$ peaks in a Patterson synthesis computed with $|F_{m1}(H)|^2$ as coefficient; the second and third terms give rise to $A-A$

and $A-N$ peaks respectively. In order to be able to locate the $A-A$ peaks it is essential to eliminate $A-N$ and $N-N$ peaks which tend to mask $A-A$ peaks. Ramaseshan (1966) suggested that if the neutron energies are so chosen that $b_1(r) = -b_2(r)$, then a Patterson function with $[|F_{m1}(H)|^2 + |F_{m2}(H)|^2]$ as coefficient will contain only $A-A$ and $N-N$ peaks; the background due to $A-N$ peaks will be eliminated. However, a simple estimation shows that in a structure containing a large number of N -atoms, $N-N$ peaks give rise to a background which is more serious than that due to $A-N$ peaks. It is therefore necessary to eliminate both $A-N$ and $N-N$ peaks.

Expression for $|x|^2$

We shall now derive an expression for $|x|^2$ in terms of $|F_{m1}(H)|^2$, $|F_{m2}(H)|^2$, δ , $b_1(r)$, $b_1(i)$, $b_2(r)$ and $b_2(i)$.

Eliminating φ between equations (5) and (7) and using equation (9) we get,

$$\begin{aligned} |F_N|^4 - 2|F_N|^2[|F_{m1}(H)|^2 + \{b_2^2(r) - b_2^2(i)\}|x|^2] \\ + [|F_{m1}(H)|^2 - \{b_1^2(r) + b_2^2(i)\}|x|^2]^2 + \delta^2 b_2^2(r) = 0. \end{aligned} \quad (10)$$

Similarly equations (6), (8) and (9) give,

$$\begin{aligned} |F_N|^4 - 2|F_N|^2[|F_{m2}(H)|^2 + \{b_2^2(r) - b_2^2(i)\}|x|^2] \\ + [|F_{m2}(H)|^2 - \{b_2^2(r) + b_2^2(i)\}|x|^2]^2 + \delta^2 b_2^2(r) = 0. \end{aligned} \quad (11)$$

Subtracting equation (11) from (10) gives,

$$\begin{aligned} 2|F_N|^2\{[|F_{m1}(H)|^2 - |F_{m2}(H)|^2] + \{b_2^2(r) - b_2^2(i)\} \\ - (b_2^2(r) - b_2^2(i))\}|x|^2\} = [|F_{m1}(H)|^2 - \{b_1^2(r) + b_2^2(i)\}|x|^2]^2 \\ - [|F_{m2}(H)|^2 - \{b_2^2(r) + b_2^2(i)\}|x|^2]^2 + \delta^2\{b_1^2(r) - b_2^2(r)\}. \end{aligned} \quad (12)$$

Now multiplying equations (5) and (6) by $b_2(r)$ and $b_1(r)$ respectively and subtracting the resulting equations we have,

$$\begin{aligned} [b_2(r)|F_{m1}(H)|^2 - b_1(r)|F_{m2}(H)|^2] = \\ \{b_2(r) - b_1(r)\}[|F_N|^2 + [b_2(r)\{b_1^2(r) + b_2^2(i)\} \\ - b_1(r)\{b_2^2(r) + b_2^2(i)\}]|x|^2]. \end{aligned} \quad (13)$$

Eliminating $|F_N|^2$ between (12) and (13) we have,

$$P|x|^4 - 2Q|x|^2 + R = 0, \quad (14)$$

where

$$\begin{aligned} P &= \{b_1(r) - b_2(r)\}^2 [2\{b_1^2(i) + b_2^2(i)\} \\ &\quad + \{b_1(r) - b_2(r)\}^2] + \{b_2^2(i) - b_2^2(r)\}^2 \end{aligned}$$

$$\begin{aligned} Q &= \{b_1(r) - b_2(r)\}^2 [|F_{m1}(H)|^2 + |F_{m2}(H)|^2] \\ &\quad + \{b_1^2(i) - b_2^2(i)\}\{F_{m1}(H)|^2 - |F_{m2}(H)|^2\} \end{aligned}$$

$$R = \{F_{m1}(H)|^2 - |F_{m2}(H)|^2\}^2 + \delta^2\{b_1(r) - b_2(r)\}^2.$$

It is obvious that P , Q and R are always positive and therefore equation (14) will always have two positive roots $|x_+|^2$ and $|x_-|^2$ given by

$$|x_{\pm}|^2 = Q/P \pm (Q^2 - RP)^{1/2}/P. \quad (15)$$

If we substitute $b_2(r) = b_2(i) = 0$, it is equivalent to combining isomorphous and anomalous dispersion data. In this case equation (15) reduces to equation (11) of Singh & Ramaseshan (1966).

Interpretation of two solutions

The physical significance of the two values of $|x|^2$ as obtained from equation (14) is that, in general, there are two sets of values of $|x|$, $|F_N|$ and φ for a given set of $|F_1(H)|^2$, $|F_1(\bar{H})|^2$, $|F_2(H)|^2$ and $|F_2(\bar{H})|^2$. Two possible values of $|F_N|$ and φ can be calculated as follows:

Subtracting equation (6) from (5) we get,

$$|F_{m_1}(H)|^2 - |F_{m_2}(H)|^2 = \\ \{[b_1^2(r) + b_1^2(i)] - [b_2^2(r) + b_2^2(i)]\}|x|^2 \\ + 2|F_N||x|\{b_1(r) - b_2(r)\} \cos \varphi$$

or

$$|F_N(\pm)| \cos \varphi(\pm) = \\ \{[|F_{m_1}(H)|^2 - |F_{m_2}(H)|^2] - \{b_1^2(r) + b_1^2(i) - \\ - (b_2^2(r) + b_2^2(i))\}|x_{\pm}|^2\} / 2|b_1(r) - b_2(r)||x_{\pm}|, \quad (16)$$

and from equation (9),

$$|F_N(\pm)| \sin \varphi(\pm) = \delta/2|x_{\pm}|. \quad (17)$$

Thus the values of $|F_N|$ and φ corresponding to $|x_+|$ and $|x_-|$ can be obtained from equations (16) and (17).

For illustration computations were made in a hypothetical case with $b_1(r) = 2.0$, $b_1(i) = 1.0$, $b_2(r) = 1.0$, $b_2(i) = 1.0$, $\varphi = 60^\circ$, $|F_N| = 4.0$ and $|x| = 0.50$. These give $|F_1(H)| = 4.972$, $|F_1(\bar{H})| = 4.217$, $|F_2(H)| = 4.686$, $|F_2(\bar{H})| = 3.878$. Thus, if we start with these as the values of the observed structure amplitudes we get from equations (15), (16) and (17) $|x_+| = 3.95$, $|F_N(+)| = 5.581$, $\varphi(+)=175^\circ 18'$ and $|x_-| = 0.50$, $|F_N(-)| = 4.0$, $\varphi(-) = 60^\circ$.

Choice of the correct solution

The next step is to choose the correct solution of equation (14). If the structure contains n_A anomalous scatterers (all of the same type), then $|x_m|^2$, the maximum possible value of $|x|^2$ is n_A^2 when n_A nuclei scatter all in phase. Thus if $|x_+|^2 > n_A^2$ the only acceptable solution is $|x_-|^2$. If, however, $|x_+|^2 < n_A^2$, both $|x_+|^2$ and $|x_-|^2$ are acceptable solutions by this criterion. In such cases the ambiguity remains unresolved.

As the quantity $(Q^2 - PR)$ tends to zero, $|x_+|^2$ and $|x_-|^2$ tend to be equal. One may come across cases where $|x_+|^2$ and $|x_-|^2$ are nearly equal. This makes the selection of the correct root difficult. In such cases it is better to take Q/P , the mean value of the two roots for $|x|^2$.

Unique solution of $|x|^2$

If the two neutron-energies are so chosen that $b_1(r) = b_2(r)$ and $b_1(i) \neq b_2(i)$ (it is clear from Fig. 1 that such a choice is certainly possible) then

$$P = \{b_1^2(i) - b_2^2(i)\}^2 \\ Q = \{b_1^2(i) - b_2^2(i)\} \{|F_{m_1}(H)|^2 - |F_{m_2}(H)|^2\}$$

and $R = \{|F_{m_1}(H)|^2 - |F_{m_2}(H)|^2\}^2$.

This leads to $(Q^2 - RP) = 0$ and therefore the two roots are coincident and are given by,

$$|x_+|^2 = |x_-|^2 = Q/P. \quad (17)$$

It may be noted that this result* can be obtained directly by subtracting equation (6) from equation (5).

Owing to the practical difficulty in selecting the neutron-energies E_1 and E_2 for which $b_1(r) = b_2(r)$, one may have a case $b_1(r) \simeq b_2(r)$. It is rather fortunate that the factor $\{b_1(r) - b_2(r)\}$ occurs in the expressions of P , Q and R as squares and, therefore, equation (17) can be used without introducing much error even if $b_1(r)$ and $b_2(r)$ are slightly different.

As P depends only on the scattering lengths it may appear that P can be made zero by suitably selecting E_1 and E_2 . In such a case equation (14) will have only one root $|x|^2 = R/2Q$. However, since P is the sum of three positive terms, it can be made zero only when the three terms are separately zero which cannot be done except in a trivial case $E_1 = E_2$.

Refinement of the thermal and positional parameters

Once $|x|$ is determined, a Patterson function with $|x|^2 b_1^2(r)$ as coefficients will give the positions of A -scatterers. A comparison of $|x|$ calculated from the known positions of A -scatterers with those obtained from equation (15) will reveal the reflexions for which the root has been wrongly chosen. If equation (17) is used this comparison is not necessary. The values of $|x|$ obtained this way can be used to refine the thermal and positional parameters of A -scatterers.

3. Unique solution of the phases

It can be easily shown (Ramachandran & Raman, 1956) that the phase $\alpha_{A_1}(H)$ of the A -scatterer contribution to the structure factor is related to the phase $\alpha'_1(H)$ of $|F'_1(H)|$ by,

$$\alpha'_1(H) = \alpha_{A_1} + \theta_1, \quad (18)$$

(see Fig. 2) where θ_1 is given by

$$\sin \theta_1 = \Delta I_1/4|F'_1(H)||F''_{A_1}| = \delta/2|F'_1(H)||x| \quad (19)$$

and

$$|F'_1(H)| = [\frac{1}{2}\{|F_1(H)|^2 + |F_1(\bar{H})|^2\} - |F''_{A_1}|^2]^{\frac{1}{2}}.$$

θ_1 determined from equation (19) will have two values θ_1 and $(180^\circ - \theta_1)$. Thus there is a twofold ambiguity in $\alpha'_1(H)$ calculated from equation (18). In X-ray anomalous dispersion work this ambiguity has been resolved by various indirect methods (Ramaseshan, 1963).

Here it has been shown that the use of data collected at two neutron energies yields a unique solution of $\alpha'_1(H)$.

Referring to Fig. 2, φ and θ_1 are related by,

$$|F_{A_1}|/\sin(\varphi - \theta_1) = |F'_1(H)|/\sin \varphi.$$

or

$$\sin(\varphi - \theta_1) = |F_{A_1}|/|F'_1(H)| \sin \varphi. \quad (20)$$

* The authors are grateful to the referee for drawing their attention to the fact that when $b_1(r) = b_2(r)$, a difference even Patterson function (Okaya, Saito & Pepinsky, 1955) also leads to similar results.

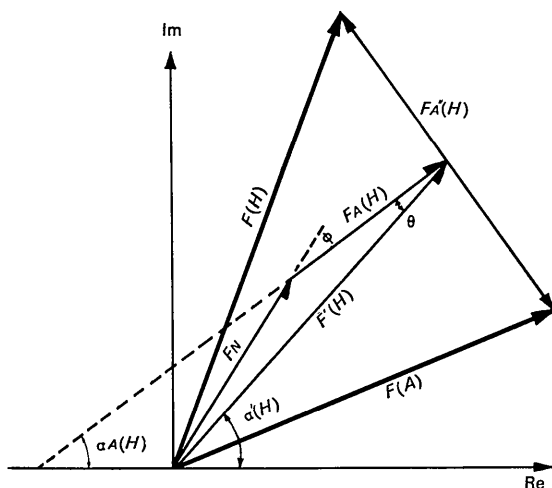


Fig. 2. Argand diagram representing $F(H)$ and $F(\bar{H})$.

Combining equations (19) and (20) we get

$$\cos \theta_1 = [\delta \cot \varphi / 2|x| + |F_{A1}|] / |F'_1(H)|. \quad (21)$$

Equations (5), (6) and (9) can be combined to give

$$\cot \varphi = \frac{\{|F_{m1}(H)|^2 - |F_{m2}(H)|^2\} - \{(b_1^2(r) + b_1^2(i)) - (b_2^2(r) + b_2^2(i))\}|x|^2}{\{b_1(r) - b_2(r)\}\delta}. \quad (22)$$

On substituting the value of $\cot \varphi$ from equation (22) in equation (21) we have,

$$\cos \theta_1 = \frac{\{|F_{m1}(H)|^2 - |F_{m2}(H)|^2\} - \{(b_1^2(r) + b_1^2(i)) - (b_2^2(r) + b_2^2(i))\}|x|^2}{2\{b_1(r) - b_2(r)\}|F'_1(H)||x|} + \frac{|F_{A1}|}{|F'_1(H)|}. \quad (23)$$

In case $b_1(r) = b_2(r)$, equations (5) and (6) give,

$$|F_{m1}(H)|^2 - |F_{m2}(H)|^2 = \{b_1^2(i) - b_2^2(i)\}|x|^2$$

and equation (23) reduces to,

$$\cos \theta_1 = \frac{-\{b_1(r) + b_2(r)\}|x| + 2|F_{A1}|}{2|F'_1(H)|}. \quad (24)$$

Since $\sin \theta_1$ and $\cos \theta_1$ are known from equations (19) and (23) respectively, θ_1 and hence $\alpha'_1(H)$ is known. Similarly $\alpha_2(H)$ can also be obtained.

4. Conclusion

Thus we see that combination of the data collected at two neutron-energies makes it possible to determine and refine the thermal and positional parameter of the anomalous scatterer in large molecules - a process which is normally difficult. Further, the phases of the reflexions can be determined unambiguously.

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APPENDIX

It has been shown in § 2 that if E_1 and E_2 are so chosen that $b_1(r) = b_2(r) = b(r)$ and $b_1(i) \neq b_2(i)$, $|x|^2$ can be determined uniquely. A method has been indicated to calculate such pairs of E_1 and E_2 .

Measurement of the scattering and absorption cross-section of ^{113}Cd and ^{149}Sm (Brockhouse, 1953) shows

that the one-level Breit-Wigner formula is valid. It can be shown from the one-level Breit-Wigner theory that,

$$b' = \frac{1}{2} \frac{gw\lambda_0\Gamma_n(E-E_0)}{(E-E_0)^2 + \Gamma^2/4} \quad (i)$$

and

$$b'' = b(i) = \frac{1}{4} \frac{gw\lambda_0\Gamma_n\Gamma}{(E-E_0)^2 + \Gamma^2/4}, \quad (ii)$$

where g is a spin weighting factor, w is the isotopic abundance, which is unity for a resonant isotope, λ_0 is the wavelength at resonance divided by 2π , Γ_n is the neutron width, Γ is the total width, E is the energy of measurement and E_0 the resonance energy. Substituting the numerical values (Brockhouse, 1953) for various parameters in equations (i) and (ii) we get

$$b' = \frac{A(E-E_0)}{(E-E_0)^2 + B}$$

and

$$b'' = \frac{C}{(E-E_0)^2 + B},$$

where A , B , C and E_0 , have values respectively 0.278×10^{-12} , 0.0032 , 1.565×10^{-14} and 0.178 eV for ^{113}Cd and 0.250×10^{-12} , 0.0014 , 0.920×10^{-14} and 0.096 eV for ^{149}Sm .

The two sets of values of E for which $b_1(r) = b_2(r) = b'$ can be calculated from the equations

$$(E_{1,2} - E_0) = 0.139/b' \pm \{[0.139/b']^2 - 0.0034\}^{\pm} \text{ for } ^{113}\text{Cd}$$

and

$$(E_{1,2} - E_0) = 0.125/b' \pm \{[0.125/b']^2 - 0.0014\}^{\pm} \text{ for } ^{149}\text{Sm}.$$

It is clear from Fig. 1 that such a pair, E_1 and E_2 , can be chosen on either side of the resonance energy ($E_0 = 0.178$). However, the smaller-energy side (the shaded region) is preferable to the greater-energy side because of the convenient working wavelength and the large flux of neutrons from the pile. This region corresponds to the X-ray wavelength range from Mo $K\alpha$ to Fe $K\alpha$.

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