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The use of neutron anomalous scattering in crystal-structure analysis. II. Centrosymmetric structures. By

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The methods for locating the positions of the anomalous scatterers in a centrosymmetric structure and determining the signs of the reflexions using the data collected at two neutron energies are given. The results are general and can be used for X-ray anomalous scattering as well.

In an earlier publication (part I, Singh & Ramaseshan, 1968*a*) the authors have suggested a method of locating the position of the anomalous scatterers and determining the phases of the non-centrosymmetric structure factors using the data collected at two neutron energies. A similar approach for centrosymmetric structures is reported in this communication.

The notation used here is the same as in part I (Singh & Ramaseshan, 1968*a*).

Location of the anomalous scatterers

Let us consider a centrosymmetric structure containing n_A identical anomalous scatterers with their scattering lengths of the form $b_0+b'+ib''$ and n_N normal scatterers. The structure factor is given by

$$F(\mathbf{H})=F_N(\mathbf{H})+F_A(\mathbf{H})+iF''_A(\mathbf{H}) = \mathscr{F}(\mathbf{H})+iF''_A(\mathbf{H}) \quad (1)$$

where

$$\mathscr{F}(\mathbf{H})=F_N(\mathbf{H})+F_A(\mathbf{H})$$

$$F_A(\mathbf{H})=b(r)\mathbf{x}$$

$$F''_A(\mathbf{H})=b(i)\mathbf{x}$$

$$\mathbf{x}=2\sum_{j=1}^{n_A}\cos 2\pi\mathbf{H}\,.\,\mathbf{r}_{Aj}\exp\left[-\left((B_{Aj}\,.\,\frac{\sin^2\theta}{\lambda^2}\right)\right]$$

$$F_N(\mathbf{H})=2\sum_{j=1}^{n_A} b_{Nj}\cos 2\pi\mathbf{H}\,.\,\mathbf{r}_{Nj}\exp\left[-B_{Nj}\frac{\sin^2\theta}{\lambda^2}\right].$$

Following the procedure indicated in an earlier publication (Singh & Ramaseshan, 1968*a*), equation (1) can be rewritten for two neutron energies E_1 and E_2 as follows:

$$|F_N(H)|^2+2b_1(r)\mathbf{x}F_N(\mathbf{H}) + \{b_1^2(r)+b_1^2(i)\}|x|^2-|F_1(H)|^2=0 \quad (2)$$

$$|F_N(H)|^2+2b_2(r)\mathbf{x}F_N(\mathbf{H}) + \{b_2^2(r)+b_2^2(i)\}|x|^2-|F_2(H)|^2=0 \quad (3)$$

On eliminating $|F_N(H)|^2$ between (2) and (3) and noting that $[\mathbf{x}F_N(\mathbf{H})]^2=|x|^2|F_N(\mathbf{H})|^2$ we get

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

where

$$P=\{b_1(r)-b_2(r)\}^2[2\{b_1^2(i)+b_2^2(i)\} + \{b_1(r)-b_2(r)\}^2]+\{b_1^2(i)-b_2^2(i)\}^2$$

$$Q=\{b_1(r)-b_2(r)\}^2[|F_1(H)|^2+|F_2(H)|^2] + \{b_1^2(i)-b_2^2(i)\}\,[|F_1(H)|^2-|F_2(H)|^2]$$

$$R=\{|F_1(H)|^2-|F_2(H)|^2\}^2.$$

Equation (5) can be obtained from equation (14) of Singh & Ramaseshan (1968*a*) by letting $|F_{m1}(H)|^2=|F_1(H)|^2$, $|F_{m2}(H)|^2=|F_2(H)|^2$ and $\delta=0$.

The roots of equation (5) are

$$|x_\pm|^2=\frac{Q}{P}\pm\left[\frac{Q^2}{P^2}-\frac{R}{P}\right]^{1/2}. \quad (5)$$

Thus for a given set of values of $|F_1(H)|^2$ and $|F_2(H)|^2$ two values of $|x|^2$ and $|F_N(H)|^2$ are possible. To understand the physical significance of the two roots let us consider a case with $b_1(i)=b_2(i)=0$; equation (5) then gives

$$|x_+|^2=\{|F_1(H)|+|F_2(H)|\}^2/\{b_1(r)-b_2(r)\}^2 \quad (6a)$$

$$|x_-|^2=\{|F_1(H)|-|F_2(H)|\}^2/\{b_1(r)-b_2(r)\}^2 \quad (6b)$$

Further, writing equation (1) for two neutron energies and subtracting one from the other we have for $b_1(i)=b_2(i)=0$

$$F_1(\mathbf{H})-F_2(\mathbf{H})=\{b_1(r)-b_2(r)\}\mathbf{x}$$

or

$$|F_1(H)|S(F_1)-|F_2(H)|S(F_2)=\{b_1(r)-b_2(r)\}\mathbf{x}\,. \quad (7)$$

$S(F_1)$ and $S(F_2)$ are the signs of $F_1(\mathbf{H})$ and $F_2(\mathbf{H})$. It is well to note that if $b_1(i)$ and $b_2(i)$ are not zero, $F_1(\mathbf{H})$ and $F_2(\mathbf{H})$ have phases different from 0 and π. In such cases we can only talk of the signs of $\mathscr{F}_1(\mathbf{H})$ and $\mathscr{F}_2(\mathbf{H})$.

On comparing equation (7) with (6*a*) and (6*b*) we find that $|x_+|^2$ and $|x_-|^2$ are the correct solutions for the cases $S(\mathscr{F}_1)\neq S(\mathscr{F}_2)$ and $S(\mathscr{F}_1)=S(\mathscr{F}_2)$ respectively.

It can be easily shown that $S(\mathscr{F}_1)\neq S(\mathscr{F}_2)$ occurs when

$$S(N)\neq S(x)$$

and

$$|b_1(r)\mathbf{x}|>|F_N(H)|>|b_2(r)\mathbf{x}|$$

for

$$b_1(r)>b_2(r)\,. \quad (8)$$

In the case of X-ray anomalous scattering the changes in scattering factors due to change in wavelength are not large and therefore the reflexions with $S(\mathscr{F}_1)\neq S(\mathscr{F}_2)$ will be very weak. In the case of neutron anomalous scattering these changes may be quite large. In such cases the reflexions with $S(\mathscr{F}_1) \neq S(\mathscr{F}_2)$ may be strong but the number of such reflexions is limited owing to the small probability of condition (8) being satisfied. Thus $|x_-|^2$ will represent the correct roots for most reflexions. The change of sign however can occur more frequently if scattering length for one of the energies, say E_2, is negative [*i.e.* $b_2(r)$ is negative and further for the sake of discussion we shall assume again that $b_2(r) < b_1(r)$]. The conditions to be satisfied for such a change are

$$|b_2(r)\mathbf{x}| > |F_N(H)| \quad \text{if} \quad S(N) = S(x)$$

or

$$|b_1(r)\mathbf{x}| > |F_N(H)| \quad \text{if} \quad S(N) \neq S(x)$$

In practice it seems advantageous to choose the neutron energies such that $b_1(r)$ and $b_2(r)$ are of the same sign.

For structures with large 'heavy atom' ratio, the position of the anomalous scatterer can be determined by an ordinary Patterson synthesis or synthesis with $|F_1(H)|^2 + |F_2(H)|^2$ (Ramaseshan, 1966). The latter is known to contain only $A-A$ and $N-N$ vectors if the neutron energies are chosen so that $b_1(r) = -b_2(r)$. As the 'heavy atom' ratio decreases, an increasing background is provided by the $N-N$ vectors. For a small 'heavy atom' ratio, $A-A$ vectors can hardly be distinguished from the $N-N$ vectors. It is in such cases that the present method is particularly useful. Further for a structure with small 'heavy atom' ratio, cases with $S(\mathscr{F}_1) \neq S(\mathscr{F}_2)$ are not many and $|x_-|^2$ represents the correct root for most reflexions.

Equation (4) has coincident roots if E_1 and E_2 are chosen so that $b_1(r) = b_2(r)$ and $b_1(i) \neq b_2(i)$. The roots are then given by

$$|x_+|^2 = |x_-|^2 = Q/P \;.$$

Thus there is no ambiguity in the determination of $|x|^2$. However in such a case the signs of the reflexions cannot be determined [see equation (9)].

A Patterson synthesis with $b_1^2(r)\,|x_-|^2$ as coefficients will yield the positions of the anomalous scatterers. A comparison of the calculated $|x|^2$ values with those obtained from equation (4) will indicate the cases in which a wrong solution has been chosen. Once such corrections have been made $|x_-|^2$ values from equation (4) can be used to refine the thermal and the positional parameters of the anomalous scatterers.

The sign determination

On subtracting equation (3) from (2) we get,

$$2F_N(\mathbf{H})\,\{b_1(r) - b_2(r)\}\mathbf{x} = \{|F_1(H)|^2 - |F_2(H)|^2\} - [\{b_1^2(r) + b_1^2(i)\} - \{b_2^2(r) + b_2^2(i)\}]\,|x|^2 \,. \quad (9)$$

Thus, **x** being known, $F_N(\mathbf{H})$ can be determined. With this all the information necessary for solving a structure is complete. A Fourier synthesis with $F_N(\mathbf{H})$ as coefficients will reveal the position of the normal scatterers.

As pointed out in the previous section, the choice of two neutron energies such that $b_1(r) = b_2(r)$ and $b_1(i) \neq b_2(i)$ leads to unique solution of $|x|^2$. However on letting $b_1(r) = b_2(r)$ in equation (9) the term containing $F_N(\mathbf{H})$ vanishes and equation (9) becomes an identity. Thus $F_N(\mathbf{H})$ cannot be determined under these conditions. However, from equation (2) or (3), both of which are identical under the condition $b_1(r) = b_2(r) = b(r)$, we get

$$|F_N(\mathbf{H})| = -b(r)\mathbf{x} \pm [b^2(r)|x|^2 + \{|F_1(H)|^2 - (b_1^2(r) + b_1^2(i))\,|x|^2\}]^{1/2}.$$

These two roots correspond to the two cases (i) $F_N(\mathbf{H})$ having the same sign as $b(r)\mathbf{x}$ and (ii) $F_N(\mathbf{H})$ having a sign opposite to that of $b(r)\mathbf{x}$. However this ambiguity cannot be resolved.

Thus an attempt to combine the data at two neutron energies to give $|x|^2$ leads to two possible solutions [equation (5)]. The correct roots can be chosen indirectly and a Patterson synthesis with these will give the position of the anomalous scatterers. Equation (9) can then be used to determine $F_N(\mathbf{H})$.

Equation (6) leads to a unique solution for $b_1(r) = b_2(r)$ and $b_1(i) \neq b_2(i)$ but $F_N(\mathbf{H})$ cannot be determined from equation (9). This situation is similar to that encountered in the noncentrosymmetric case (Singh & Ramaseshan, 1968*b*) wherein such a choice of radiation gives $|x|^2$ unambiguously but the ambiguity in the phase remains unresolved

References

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