It does not appear useful to apply a similar analysis to other than first-row anions. The compounds are not so well described by the ionic model and complications arise from anion–anion bonding. For example, no simple pattern emerges from a comparable analysis of S^{2-} radii. It might be mentioned, however, that the behaviour of H^- closely parallels that of N^{3-}.

Conclusions

The main conclusions to be drawn from the results described in this paper are:

(1) it is not a satisfactory procedure to assume constant radii for anions, even in an isostructural series of compounds;

(2) variations of apparent anion radii can be correlated in an understandable way with Madelung potentials at anion sites;

(3) Madelung potentials at anion sites in simple crystal structures depend on the size (but not the charge) of the cations;

(4) to predict bond lengths in crystals, it is in general better to use empirical bond length–bond strength correlations (Brown, 1977) than to use tables of ionic radii.

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A Theoretical Comparison of the β, γ' and $2F_o - F_c$ Syntheses

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Abstract

A theoretical comparison of the β synthesis of Ramachandran & Raman [*Acta Cryst.* (1959), **12**, 957–964] with the weighted γ' and weighted $2F_o - F_c$ syntheses shows that, for partially known structures, the ratio of peak heights of the unknown atoms to those of the background is the same in all the syntheses. The β synthesis contains more background peaks than either the γ' or $2F_o - F_c$ syntheses. The $2F_o - F_c$ synthesis suppresses the peaks of wrongly positioned atoms most effectively and the γ' is the least effective. The syntheses which approach most closely the true electron density are the weighted $2F_o - F_c$ synthesis for non-centrosymmetric structures and the weighted γ' for centrosymmetric ones.

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Notation

F_N = structure factor of the complete structure
F_P = structure factor of the known atoms
F_Q = structure factor of the unknown atoms
F_W = structure factor of the wrongly positioned atoms
F_I = structure factor of all atoms included in a Fourier synthesis
φ_N, φ_P, φ_I = phases of F_N, F_P, F_I respectively
f_{N_i}, f_{P_i}, f_{Q_i}, f_{I_i} = scattering factors of the N, P, Q and I atoms
$\Sigma_N = \sum_{i=1}^{N} f_{N_i}^2$, similarly for Σ_P, Σ_Q and Σ_I

$$\sigma_1^2 = \frac{\Sigma_P}{\Sigma_N}, \quad \chi_1^2 = \frac{\Sigma_P}{\Sigma_I}$$

$\mathbf{x}_{P_i}$, $\mathbf{x}_{Q_i}$ = positions of the P and Q atoms

Introduction

When part of a crystal structure is known, there are many methods which make use of this information to determine the remainder of the structure. In particular, the α, β, γ, α', β' and γ' syntheses have been proposed by Ramachandran & Raman (1959) and Srinivasan (1961); see also Ramachandran & Srinivasan (1970). Of these, the α, β and γ' syntheses are the most worthy of consideration.

The Fourier coefficients of the α, β and γ' syntheses are:

$$\begin{aligned} &\alpha \text{ synthesis} && |F_N|^2 F_P, \\ &\beta \text{ synthesis} && |F_N|^2 / F_P^*, \\ &\gamma' \text{ synthesis} && |F_N| \exp i\varphi_P, \end{aligned}$$

where F_P^* = complex conjugate of F_P.

The α synthesis is a convolution of the Patterson function with the known part of the structure. Unlike the β and γ' syntheses, it does not give the electron density if $F_P = F_N$ and hence is expected to be less useful. This was confirmed in a recent comparison of the α and γ' syntheses by Nixon & North (1976). It is also less capable of suppressing peaks at wrong atomic sites than the β synthesis (Raman & Lipscomb, 1963; Kalyanaraman, Parthasarathy & Ramachandran, 1969; see also Ramachandran & Srinivasan, 1970) and so will not be considered further in this paper.

The γ' synthesis is the conventional synthesis used when part of the structure is known, usually weighted according to Woolfson (1956) or Sim (1959). The β synthesis, on the other hand, has not been so widely used. There are several reports that it is superior to the γ' (for example, Kartha, Ramachandran, Bhat, Madhavan Nair, Raghavan & Venkataraman, 1963; Chacko & Mazumdar, 1969; Ramachandran & Srinivasan, 1970) in that the peaks at the unknown atomic sites are almost of the same size as peaks at the known sites. For non-centrosymmetric structures, the γ' synthesis gives peaks at unknown sites of no more than half the weight of known peaks (Luzzati, 1953). However, this is not a valid criterion for the effectiveness of the syntheses. The peak heights at known atomic sites can be altered at will by adding a multiple of F_P to the Fourier coefficients. For example, a synthesis with $(2|F_N| - |F_P|) \exp i\varphi_P$ as coefficients has approximately the same peak heights at both known and unknown atomic positions. It is commonly used partly for this reason and its relationship to the γ' synthesis is obvious.

A better measure of the effectiveness of a Fourier synthesis to reveal the unknown part of the structure is the height of the required peaks above the background. In addition, it is desirable or even necessary for the synthesis to suppress peaks at the sites of wrongly included atoms. Both of these criteria will be considered in the following theoretical comparison of the β, γ' and $2F_o - F_c$ syntheses.

The β synthesis

For the sake of completeness, the results of the analysis of the β synthesis due to Raman (1959) will be reproduced here.

Using the relationship

$$F_N = F_P + F_Q, \tag{1}$$

the Fourier coefficients of the β synthesis can be expressed in terms of F_P and F_Q as:

$$\frac{|F_N|^2}{F_P^*} = F_P + F_Q + F_Q^* \exp 2i\varphi_P + \frac{|F_Q|^2}{F_P^*}. \tag{2}$$

Taking the Fourier transform of each of the terms in (2), it is clear that the β synthesis contains peaks of approximately equal weight at the sites of both the P and Q atoms. The last two terms in (2) contribute largely to the background.

The positions and weights of the background peaks can be determined by regarding the Fourier transform of $F_Q^* \exp 2i\varphi_P$ as the convolution of the transforms of F_Q^* and $\exp 2i\varphi_P$. Similarly, $|F_Q|^2/F_P^*$ is the Fourier transform of the convolution of the syntheses with coefficients $|F_Q|^2$ and $1/F_P^*$. Table 1 gives the peaks

Table 1. *Positions and strengths of peaks in the exp $2i\varphi_P$ and $1/F_P^*$ syntheses*

Synthesis	Peak positions	Scattering power
exp $2i\varphi_P$	$\mathbf{x}_{P_i} + \mathbf{x}_{P_j}$ all i and j	$f_{P_i} f_{P_j} / \Sigma_P$
$\frac{1}{F_P^*}$	$\mathbf{x}_{P_i}$	f_{P_i} / Σ_P
	$\mathbf{x}_{P_i} + \mathbf{x}_{P_j} + \mathbf{x}_{P_k}$ $i \neq k; j \neq k$	$-f_{P_i} f_{P_j} f_{P_k} / \Sigma_P^2$

present in the exp $2i\varphi_P$ and $1/F_P^*$ syntheses to a first approximation according to Raman (1959).

This leads immediately to the peaks in the β synthesis, to the same approximation, as set out in Table 2.

The γ' synthesis

In order to compare the γ' synthesis directly with the β synthesis, it is derived in the following way. Fig. 1 shows geometrical relationships among the three structure factors F_N, F_P and F_Q. From the cosine law,

$$|F_Q|^2 = |F_N|^2 + |F_P|^2 - 2|F_N||F_P| \cos\alpha, \quad (3)$$

where $\alpha = \varphi_N - \varphi_P$. The only unknowns in (3) are $|F_Q|^2$ and $\cos\alpha$. When they are replaced by their expectation values, (3) becomes

$$\langle|F_Q|^2\rangle = |F_N|^2 + |F_P|^2 - 2|F_N||F_P|\langle\cos\alpha\rangle, \quad (4)$$

where

$$\langle|F_Q|^2\rangle = \Sigma_Q \text{ (Wilson, 1942)},$$

and

$$\langle\cos\alpha\rangle = \frac{I_1(X)}{I_0(X)} \quad \text{(Sim, 1960)},$$

with

$$X = \frac{2|F_N||F_P|}{\Sigma_Q}.$$

Now put

$$|F_N|^2 = (F_P + F_Q)(F_P^* + F_Q^*), \quad (5)$$

and the coefficients of the *weighted* γ' synthesis can be obtained from (4) and (5) as

$$|F_N|\langle\cos\alpha\rangle \exp i\varphi_P = F_P + \frac{F_Q}{2} + \frac{F_Q^* \exp 2i\varphi_P}{2} + \frac{|F_Q|^2 - \langle|F_Q|^2\rangle}{2F_P^*}. \quad (6)$$

It is clear from this that the weighted γ' synthesis will contain peaks at the sites of the unknown atoms, but of only half the weight of the known peaks. However, a comparison of (6) with the β synthesis coefficients in (2) shows that the terms giving rise to the backgrounds of the two syntheses are virtually the same. What is more important to notice is that the ratio of the weights of the Q peaks to the background is *exactly the same* in both syntheses. The inclusion of $\langle|F_Q|^2\rangle$ in the final term in (6) removes the origin peak from the $|F_Q|^2$ Patterson function and this, in turn, removes the peaks in the bottom two rows of Table 2 from the synthesis. Thus, the weighted γ' synthesis contains the peaks shown in Table 3.

In order to give the P and Q peaks the same weight, the γ' synthesis can be altered to

$$(2|F_N|\langle\cos\alpha\rangle - |F_P|)\exp i\varphi_P = F_P + F_Q + F_Q^* \exp 2i\varphi_P + \frac{|F_Q|^2 - \langle|F_Q|^2\rangle}{F_P^*}. \quad (7)$$

This is normally referred to as the $2F_o - F_c$ synthesis. The peaks it contains are shown in Table 4 to the same approximation as that used for the β synthesis. The ratio of peak weights of the Q atoms to the background is identical in both the β and weighted $2F_o - F_c$ syntheses, but the latter contains fewer background

Table 2. *Peaks in the β synthesis for a non-centrosymmetric structure*

Term	Position	Scattering factor	Type
F_P	$\mathbf{x}_{Pi}$	f_{Pi}	known
F_Q	$\mathbf{x}_{Qi}$	f_{Qi}	wanted
$F_Q^* \exp 2i\varphi_P$	$\mathbf{x}_{Pi} + \mathbf{x}_{Pj} - \mathbf{x}_{Qk}$ all i,j,k	$f_{Pi}f_{Pj}f_{Qk}/\Sigma_P$	background
$\frac{\lvert F_Q\rvert^2}{F_P^*}$	$\mathbf{x}_{Pi} + \mathbf{x}_{Qj} - \mathbf{x}_{Qk}$ $j \neq k$	$f_{Pi}f_{Qj}f_{Qk}/\Sigma_P$	background
	$\mathbf{x}_{Pi}$	$f_{Pi}\Sigma_Q/\Sigma_P$	known
	$\mathbf{x}_{Pi} - \mathbf{x}_{Pj} + \mathbf{x}_{Pk}$ $i \neq j; j \neq k$	$-f_{Pi}f_{Pj}f_{Pk}\Sigma_Q/\Sigma_P^2$	background (known)

Table 3. *Peaks in the weighted γ' synthesis for a non-centrosymmetric structure*

Term	Position	Scattering factors	Type
F_P	$\mathbf{x}_{Pi}$	f_{Pi}	known
$\frac{1}{2}F_Q$	$\mathbf{x}_{Qi}$	$\frac{1}{2}f_{Qi}$	wanted
$\frac{1}{2}F_Q^* \exp 2i\varphi_P$	$\mathbf{x}_{Pi} + \mathbf{x}_{Pj} - \mathbf{x}_{Qk}$ all i,j,k	$f_{Pi}f_{Pj}f_{Qk}/2\Sigma_P$	background
$\frac{\lvert F_Q\rvert^2 - \langle\lvert F_Q\rvert^2\rangle}{2F_P^*}$	$\mathbf{x}_{Pi} + \mathbf{x}_{Qj} - \mathbf{x}_{Qk}$ $j \neq k$	$f_{Pi}f_{Qj}f_{Pk}/2\ \Sigma_P$	background

Table 4. *Peaks in the weighted $2F_o - F_c$ synthesis for a non-centrosymmetric structure*

Term	Position	Scattering factor	Type
F_P	$\mathbf{x}_{Pi}$	f_{Pi}	known
F_Q	$\mathbf{x}_{Qi}$	f_{Qi}	wanted
$F_Q^* \exp 2i\varphi_P$	$\mathbf{x}_{Pi} + \mathbf{x}_{Pj} - \mathbf{x}_{Qk}$ all i,j,k	$f_{Pi}f_{Pj}f_{Qk}/\Sigma_P$	background
$\frac{\lvert F_Q\rvert^2 - \langle\lvert F_Q\rvert^2\rangle}{F_P^*}$	$\mathbf{x}_{Pi} + \mathbf{x}_{Qj} - \mathbf{x}_{Qk}$ $j \neq k$	$f_{Pi}f_{Qj}f_{Qk}/\Sigma_P$	background

Table 5. *The scattering factors of peaks in various Fourier syntheses expressed as a ratio of those of the corresponding peaks in the true electron density*

For the weighted syntheses, the weighting factor, w, is different for centrosymmetric and non-centrosymmetric structures.

Synthesis	Coefficients	Peak	Non-centrosymmetric	Centrosymmetric
β	$\frac{\lvert F_N\rvert^2}{F_I^*}$	P	χ_1^2/σ_1^2	χ_1^2/σ_1^2
		Q	χ_1^2	$2\chi_1^2$
		W	$(1-\sigma_1^2)\,\chi_1^2/\sigma_1^2$	$(1-2\sigma_1^2)\,\chi_1^2/\sigma_1^2$
weighted γ'	$\lvert F_N\rvert w\, e^{i\varphi I}$	P	1	$(1+\chi_1^2)/2$
		Q	$\chi_1^2/2$	χ_1^2
		W	$1-\chi_1^2/2$	$(1-\chi_1^2)/2$
weighted $2F_o - F_c$	$2\lvert F_N\rvert w\, e^{i\varphi I} - F_I$	P	1	χ_1^2
		Q	χ_1^2	$2\chi_1^2$
		W	$1-\chi_1^2$	$-\chi_1^2$
weighted $nF_o - (n-1)F_c$	$n\lvert F_N\rvert w\, e^{i\varphi I} - (n-1)F_1$	P	1	$1-n/2(1-\chi_1^2)$
		Q	$n\chi_1^2/2$	$n\chi_1^2$
		W	$1-n\chi_1^2/2$	$1-n/2(1+\chi_1^2)$
weighted $F_o - F_c$	$\lvert F_N\rvert w\, e^{i\varphi I} - F_I$	P	0	$-(1-\chi_1^2)/2$
		Q	$\chi_1^2/2$	χ_1^2
		W	$-\chi_1^2/2$	$-(1+\chi_1^2)/2$

peaks. It is interesting that it has an exact relationship with the β synthesis, obtained from (2) and (7) as

$$(2\lvert F_N\rvert\langle\cos\alpha\rangle - \lvert F_P\rvert)\exp i\varphi_P = \lvert F_N\rvert^2/F_P^* - \langle\lvert F_Q\rvert^2\rangle/F_P^*. \quad (8)$$

Note that the β synthesis automatically gives a properly weighted known-atom Fourier.

The β synthesis with wrong atoms

Kalyanaraman, Parthasarathy & Ramachandran (1969) have investigated the effect of including wrong atoms in the β synthesis (see also Ramachandran & Srinivasan, 1970) and their results are repeated here.

Using the relationship

$$F_I = F_P + F_W, \quad (9)$$

where F_I is the structure factor of all the atoms included in the β synthesis, the coefficients of the β synthesis are now

$$\lvert F_N\rvert^2/F_I^* = F_P + F_Q + \frac{1}{F_I^*}(F_P F_Q^* + \lvert F_Q\rvert^2 - F_P F_W^* - F_Q F_W^*). \quad (10)$$

The peaks in this synthesis can be obtained by taking the Fourier transform of each term, making use of the peaks in the $1/F^*$ synthesis in Table 1. The scattering factors of the peaks at the sites of the P, Q and W atoms are presented in Table 5 compared with the corresponding peaks in the F_N synthesis, *i.e.* the true electron density. Clearly, the peaks of the wrongly included atoms are considerably suppressed and this is an important characteristic of the β synthesis.

The γ' synthesis with wrong atoms

The γ' synthesis may be derived in the same manner as previously. Fig. 1 shows the relationships among the structure factors involved. In addition to the relationships (1) and (9) we have

$$F_Q = F_W + F_Q'. \quad (11)$$

The cosine law in Fig. 1 gives

$$\lvert F_Q'\rvert^2 = \lvert F_N\rvert^2 + \lvert F_I\rvert^2 - 2\lvert F_N\rvert\lvert F_I\rvert\cos\beta, \quad (12)$$

where $\beta = \varphi_N - \varphi_I$. When the unknowns $\lvert F_Q'\rvert^2$ and $\cos\beta$ are replaced by their expectation values, (12) becomes

$$\langle\lvert F_Q'\rvert^2\rangle = \lvert F_N\rvert^2 + \lvert F_I\rvert^2 - 2\lvert F_N\rvert\lvert F_I\rvert\langle\cos\beta\rangle, \quad (13)$$

where

$$\langle\lvert F_Q'\rvert^2\rangle = \Sigma_N - \Sigma_I \quad \text{(Wilson, 1942),}$$

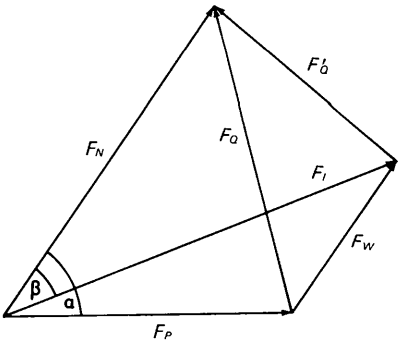

Fig. 1. Geometrical relationships among the structure factors F_N, F_P, F_Q, F_W, F_I mentioned in the text where $\alpha = \varphi_N - \varphi_P$ and $\beta = \varphi_N - \varphi_I$.

and

$$\langle \cos\beta \rangle = \frac{I_1(X)}{I_0(X)} \quad \text{(Sim, 1960),}$$

with

$$X = \frac{2|F_N||F_I|}{\Sigma_N - \Sigma_I}.$$

Equation (13) can now be rearranged to give the coefficients of the weighted γ' synthesis as

$$|F_N|\langle \cos\beta \rangle \exp i\varphi_I = |F_N|^2/2F_I^* - \langle |F_Q'|^2 \rangle/2F_I^* + F_I/2. \quad (14)$$

As before, this is closely related to the β synthesis and so a direct comparison is possible. The first term on the right hand side of (14) is the β synthesis itself. As this gives rise to all the required peaks and virtually all the background, it is obvious that the ratio of the weights of the Q peaks to the background is exactly the same for both syntheses. The second term removes some of the background peaks entirely as well as removing some density from the sites of the P and W atoms. The third term adds both P and W peaks to the synthesis at half weight. It is this third term which prevents the wrongly included atoms from being strongly suppressed in the weighted γ' synthesis. Clearly, wrong atoms will always reappear in the γ' synthesis with at least half weight. In this respect, the β synthesis is obviously superior. The peaks at the sites of the P, Q and W atoms can easily be obtained from those in the β synthesis and are shown in Table 5.

In order to give the P and Q peaks approximately the same weight, the weighted $2F_o - F_c$ synthesis can be used. This is derived from (14) to give

$$(2|F_N|\langle \cos\beta \rangle - |F_I|) \exp i\varphi_I = |F_N|^2/F_I^* - \langle |F_Q'|^2 \rangle/F_I^*. \quad (15)$$

It is identical to the β synthesis with the removal of some background peaks due to the $\langle |F_Q'|^2 \rangle$ term. This term also subtracts density from the W peaks so the $2F_o - F_c$ synthesis suppresses wrongly included atoms more than the β synthesis. This can be seen from the peak weights in Table 5.

Centrosymmetric structures

In addition to the results already mentioned, Table 5 also presents results for centrosymmetric structures.

If the structure is centrosymmetric, the $F_Q^* \exp 2i\varphi_P$ term in (2) becomes F_Q and the β synthesis is then

$$\frac{|F_N|^2}{F_P} = F_P + 2F_Q + \frac{|F_Q|^2}{F_P}. \quad (16)$$

That is, the Q peaks have doubled in weight and some of the background peaks have disappeared altogether. This also happens with the weighted γ' and the weighted $2F_o - F_c$ syntheses, which become respectively

$$|F_N| w s_P = F_P + F_Q + \frac{|F_Q|^2 - \langle |F_Q|^2 \rangle}{2F_P}, \quad (17)$$

and

$$(2|F_N| w - |F_P|)s_P = F_P + 2F_Q + \frac{|F_Q|^2 - \langle |F_Q|^2 \rangle}{F_P}, \quad (18)$$

where s_P is the sign of F_P and the weighting factor, w, in the centrosymmetric case is $\tanh(\frac{1}{2}X)$ (Woolfson, 1956) with X defined in (4).

In all of these syntheses, the ratio of the weights of the Q peaks to the background peaks is the same, but the β synthesis contains more background peaks.

Practical results

Some calculations were carried out on a one-dimensional crystal structure to test the predictions of the theory. Typical results are presented in Fig. 2 which shows the β, γ' and $2F_o - F_c$ syntheses for a ten atom structure. Of the ten atoms used in the calculation of F_I, nine were correctly positioned and one was wrong. The β and $2F_o - F_c$ syntheses are very similar when their backgrounds and densities at the Q and W peaks are compared. However, actual calculation of the r.m.s. deviation of the background from the mean showed that the β synthesis always had the greater background

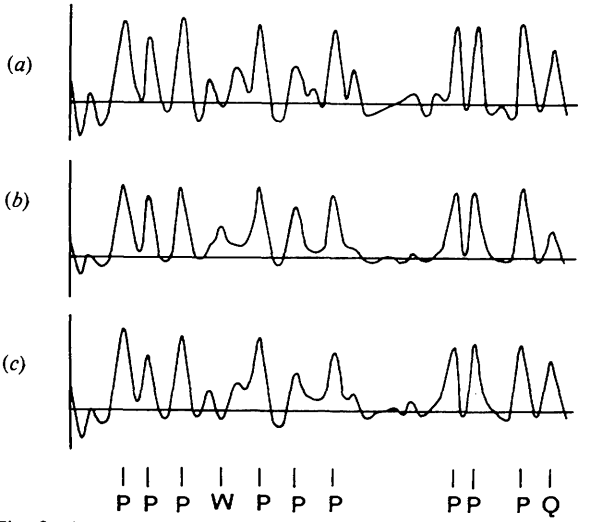

Fig. 2. A ten atom, non-centrosymmetric, one-dimensional structure. The positions of the P, Q and W peaks are shown. (*a*) β synthesis; (*b*) γ' synthesis; (*c*) $2F_o - F_c$ synthesis.

of the two. The density at the W peak is greater in the γ' synthesis than either the β or $2F_o - F_c$ and the Q peak is much smaller. It is clear from Fig. 2 that the greater density of the Q peak in both the β and $2F_o - F_c$ syntheses is achieved only by increasing the background and spurious peaks in proportion. That is, the signal to noise ratio is the same in both the γ' and $2F_o - F_c$ syntheses if the W peak is ignored.

Discussion

A comparison of equations (2), (6) and (7) shows that, for each of the three syntheses β, γ' and $2F_o - F_c$, the ratio of the terms giving rise to the required peaks and the background peaks is the same. Tables 3 and 4 indicate that both the γ' and $2F_o - F_c$ syntheses contain approximately PQN background peaks while Table 2 shows the β synthesis contains P^3 additional background peaks to the same approximation. For centrosymmetric structures, the Q peaks have twice the weight in relation to the background than for non-centrosymmetric for all three syntheses. Also, there are fewer background peaks in the centrosymmetric case – approximately PQ^2 for the γ' and $2F_o - F_c$ syntheses and $P^3 + PQ^2$ for β.

The synthesis which suppresses the peaks of wrongly included atoms most effectively is the weighted $2F_o - F_c$. The final term in (15) subtracts density from the sites of both P and W atoms as well as removing some background peaks from the β synthesis, which is the other term. This is also true for centrosymmetric structures, although in this case so much density is subtracted from the W peaks that they become negative in both the β and $2F_o - F_c$ syntheses. The γ' synthesis is the least effective at suppressing wrong atoms as seen by (14). The final term adds density to the P and W peaks making sure that the W peaks always appear with at least half weight. In addition, the required peaks never appear with more than half weight in this synthesis. This is not so for centrosymmetric structures where the minimum density of the W peaks is zero and the required peaks have a maximum density equal to the P peaks.

The syntheses which approach the true electron density most closely are the weighted $2F_o - F_c$ synthesis for non-centrosymmetric structures and the weighted γ' for centrosymmetric. In both cases they are better than the β synthesis as defined in (2), in that they contain fewer background peaks. Deisenhofer & Steigemann (1975) report that the $2F_o - F_c$ synthesis is better than either the γ' or the $3F_o - 2F_c$ syntheses in protein refinement. In addition, Jack, Ladner & Klug (1976) report that the $2F_o - F_c$ synthesis gave clear indications of wrongly placed atoms in the refinement of yeast phenylalanine transfer RNA. It is clear from the analysis in this paper why this should be so. If a computer is used to interpret maps at atomic resolution as proposed by Main & Hull (1978), it is important that the $2F_o - F_c$ synthesis be used rather than the γ' for non-centrosymmetric structures. This ensures that the P and Q peaks are of comparable weight and the W peaks are suppressed to approximately zero density. When the $2F_o - F_c$ synthesis is calculated for a structure with centrosymmetric projections, the coefficients corresponding to the projections should be calculated as for the γ' synthesis.

When only a small part of the structure is known, a single heavy atom for example, the $2F_o - F_c$ synthesis will not offer any advantage over the γ'. It will merely double the density everywhere except at the heavy atom position. Also, it is important that the observed and calculated structure factors should be on the same scale and this is not easy to achieve with sufficient accuracy until most of the structure is known. (Note that the β synthesis is much less sensitive to errors in scale.) The $2F_o - F_c$ synthesis is best for Fourier refinement when the absolute scale of F_o is accurately known. Not only will it suppress wrong peaks and show the missing atoms, but it will also move inaccurately placed atoms to their true positions. This can be seen in Fig. 3 which shows an atom on the left compared with the true electron density on the right. The density corresponding to the categories W, P and Q is marked. If the synthesis suppresses the W density completely and shows the Q density on the same scale as P, the atom will appear in the synthesis in its true position. If the W density is halved and the Q density is on only half the scale of P as in the γ' synthesis, the resulting electron density will show a broad peak whose centre is mid-way between the old and the true atomic positions. This is a well-known property of the γ' synthesis.

In general, the synthesis with $nF_o - (n-1)F_c$ as coefficients can be expressed as

$$n|F_N|\langle\cos\beta\rangle \exp i\varphi_I - (n-1)F_I = \frac{n(|F_N|^2 - \langle|F'_Q|^2\rangle)}{2F_I^*} - \frac{(n-2)}{2}(F_P + F_w), \quad (19)$$

with peaks as shown in Table 5. If n is not necessarily an integer, a value can be chosen which gives the P and Q peaks the same weight and reduces the density at W

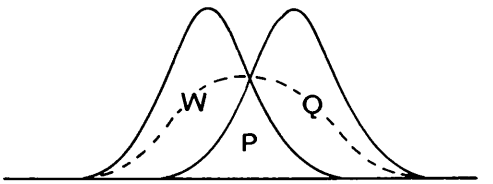

Fig. 3. The P, Q and W electron density corresponding to an inaccurately positioned atom. The atomic peak consists of areas W and P; the true electron density is given by areas P and Q. The dashed line shows the peak given by the γ' synthesis.

peaks to zero. From Table 5, this value of n is seen to be $2/\chi_1^2$ for non-centrosymmetric and $2/(1 + \chi_1^2)$ for centrosymmetric structures. The use of this obviously depends upon knowing or obtaining an estimate of the quantity χ_1^2, the proportion of correct to total scattering power included in the structure factor calculation. It can be seen from (19) that different values of n alter the density at the P and W peaks but do not change the density at the Q peaks in relation to the background.

The β synthesis is sensitive to small values of $|F_I|$ since these give rise to very large coefficients. Ramachandran & Ayyar (1963) (see also Ramachandran & Srinivasan, 1970) have proposed an empirical weighting scheme to deal with this. However, the weighting scheme does not increase the useful information in the synthesis beyond what is shown in this paper. The weighted $2F_o - F_c$ and weighted γ' syntheses are therefore a little easier to use than the β synthesis.

The theory presented here is a little optimistic in that atoms wrongly included in the $2F_o - F_c$ and γ' syntheses are not suppressed by as much as is predicted However, the comparison with the β synthesis is valid since the same approximations in the theory apply to all the cases considered.

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X-ray Scattering Intensities from a Shell Model for Silicon

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Abstract

Accurate theoretical intensities are presented for the phonon scattering at 295 K for Si. The one-phonon and n-phonon cross sections are shown for the principal symmetry directions and the total phonon scattering contours for a section of the $(10\bar{1})$ plane. Previous total phonon calculations have been confined to materials of simpler structure and to a coarser mesh of wavevectors. The Si cross sections show general features which are expected to be seen in a wide variety of materials. These include the behaviour of the scattering near forbidden reflexions, the behaviour in three essentially different kinds of zones and the behaviour close to Bragg peaks. Results are also presented for the temperature dependence of the harmonic Debye–Waller factor.

Introduction

In spite of the widespread interest in X-ray scattering from Si, accurate kinematic phonon X-ray scattering intensity calculations have not been reported even though reasonable lattice dynamical models have been

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