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Anomalous Dispersion Effects in the Calculation of Electron Density

BY A. DEL PRA AND M. MAMMI

Institute of Organic Chemistry, University of Padova, Italy

AND G. FERRARIS

Institute of Mineralogy, University of Torino, Italy

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When anomalous scatterers are present the electron density function is complex, both for centrosymmetric and non-centrosymmetric crystals. By neglecting $\Delta f''$ in the calculation of the phase angles, the electron density map shows satellite maxima weighted according to $\Delta f''$ in positions defined by combinations of interatomic vectors, as in Ramachandran's β general synthesis. On the other hand, when $\Delta f''$ is accounted for, but the experimental data are not collected according to the point group symmetry, the electron density distribution calculated by the usual formulae shows maxima which are seriously affected both in position and shape. The errors are of the same type as those found in the least-squares refinement, when $\Delta f''$ is neglected.

Introduction

It is well known that the general expression for the X-ray atomic scattering factor, f , of an atom is complex (see, e.g., James, 1950):

$$f = f^0 + \Delta f' + i\Delta f'' = f^* + i\Delta f'' \quad (1)$$

where f^0 is calculated on the assumption that the electrons are 'free'; the terms $\Delta f'$ and $\Delta f''$ are functions of the binding energy of the electrons and of the energy of the incident X-rays. For wavelengths commonly used in X-ray structure analysis, the contributions of $\Delta f'$ and $\Delta f''$ are significant whenever 'heavy atoms' are present. In fact it was shown (Cruickshank & McDonald, 1967) that neglecting $\Delta f''$ in the determination of polar structures containing atoms heavier than oxygen (with Cu $K\alpha$ radiation), or sulphur (with

Mo $K\alpha$), the accuracy of the coordinates cannot be better than 0.005 Å, unless experimental data are collected in a proper way (Cruickshank & McDonald, 1967). The error in coordinates may be unexpectedly high, e.g. 0.05 Å for the z coordinate of the thorium atom in the structure of thorium nitrate pentahydrate (Ueki, Zalkin & Templeton, 1966). Furthermore, neglect of $\Delta f'$ and $\Delta f''$ generally affects the temperature parameters.

On the other hand, both a better agreement obtained between lengths of chemically equal bonds (see, e.g. McDonald & Cruickshank, 1967; Ferraris, 1969), and a comparison of X-ray and neutron diffraction results (cf. Ueki, Zalkin & Templeton, 1966) show that more reliable results are achievable after applying the anomalous dispersion correction. For most of the current structure analyses, however, these corrections

are not applied and, when they are, the procedure used is often not reported.

It must be noted that most of the anomalous scattering treatments in the literature deal with reciprocal space, taking this effect into account either in the calculation of structure factors or by correcting the experimental data in some way (least-squares stage). It seems therefore worth while to analyse the significance of the electron density function in the presence of anomalous scattering, its characteristics and validity, and which results are obtained in real space (electron density computation) when anomalous dispersion is accounted for in a complete, partial or in no way.

Mathematical relationships

(a) Structure factor

The general expression for the structure factor, derived from (1), is

$$F(\mathbf{H}) = F^0(\mathbf{H}) + F'(\mathbf{H}) + F''(\mathbf{H}) = F^r(\mathbf{H}) + F''(\mathbf{H}) \\ = |F(\mathbf{H})| \exp [i\alpha(\mathbf{H})] = A(\mathbf{H}) + iB(\mathbf{H}) \quad (2)$$

where

$$F^0(\mathbf{H}) = \sum_j f_j^0 \exp (2\pi i \mathbf{H} \cdot \mathbf{r}_j) = |F^0(\mathbf{H})| \exp [i\alpha^0(\mathbf{H})] \quad (3)$$

$$F'(\mathbf{H}) = \sum_j \Delta f_j' \exp (2\pi i \mathbf{H} \cdot \mathbf{r}_j) = |F'(\mathbf{H})| \exp [i\alpha'(\mathbf{H})] \quad (4)$$

$$F''(\mathbf{H}) = i \sum_j \Delta f_j'' \exp (2\pi i \mathbf{H} \cdot \mathbf{r}_j) \\ = |F''(\mathbf{H})| \exp [i\alpha''(\mathbf{H})] \quad (5)$$

$$A(\mathbf{H}) = \sum_j f_j^0 \cos (2\pi \mathbf{H} \cdot \mathbf{r}_j) \\ + \sum_j \Delta f_j' \cos (2\pi \mathbf{H} \cdot \mathbf{r}_j) \\ - \sum_j \Delta f_j'' \sin (2\pi \mathbf{H} \cdot \mathbf{r}_j) \quad (6)$$

$$B(\mathbf{H}) = \sum_j f_j^0 \sin (2\pi \mathbf{H} \cdot \mathbf{r}_j) \\ + \sum_j \Delta f_j' \sin (2\pi \mathbf{H} \cdot \mathbf{r}_j) \\ + \sum_j \Delta f_j'' \cos (2\pi \mathbf{H} \cdot \mathbf{r}_j). \quad (7)$$

From these equations it follows (see also Fig. 1) that

$$|F(\mathbf{H})| \neq |F(\bar{\mathbf{H}})|; |F^0(\mathbf{H})| = |F^0(\bar{\mathbf{H}})|; |F'(\mathbf{H})| = |F'(\bar{\mathbf{H}})|; \\ |F''(\mathbf{H})| = |F''(\bar{\mathbf{H}})|. \quad (8)$$

$$\alpha(\mathbf{H}) \neq \alpha^0(\mathbf{H}) \neq \alpha'(\mathbf{H}) \neq \alpha''(\mathbf{H}); \\ \alpha(\mathbf{H}) \neq -\alpha(\bar{\mathbf{H}}); \alpha^0(\mathbf{H}) = -\alpha^0(\bar{\mathbf{H}}); \\ \alpha'(\mathbf{H}) = -\alpha'(\bar{\mathbf{H}}); \alpha''(\mathbf{H}) = \pi - \alpha''(\bar{\mathbf{H}}). \quad (9)$$

For centrosymmetric structures and for any structures with all equal atoms, the relations (8) become identities. For centrosymmetric structures, (6), (7) and (9) can be rewritten

$$A(\mathbf{H}) = \sum_j f_j^0 \cos (2\pi \mathbf{H} \cdot \mathbf{r}_j) \quad (6')$$

$$B(\mathbf{H}) = \sum_j \Delta f_j'' \cos (2\pi \mathbf{H} \cdot \mathbf{r}_j) \quad (7')$$

$$\alpha(\mathbf{H}) \neq \alpha^0(\mathbf{H}) = \alpha'(\mathbf{H}) + m\pi = (\alpha''(\mathbf{H}) - \pi/2) + n\pi; \\ \alpha(\mathbf{H}) = \alpha(\bar{\mathbf{H}}); \alpha^0(\mathbf{H}) = \alpha^0(\bar{\mathbf{H}}); \alpha'(\mathbf{H}) = \alpha'(\bar{\mathbf{H}}); \\ \alpha''(\mathbf{H}) = \alpha''(\bar{\mathbf{H}}) \quad (9')$$

where m and n are integers.

It appears from the above considerations that the structure factor is a complex quantity whenever the scattering is anomalous. In this respect it may be noted that a numerically easy way to account for $\Delta f'$ and $\Delta f''$ is to write

$$f = |f| \exp (i\varphi) \quad (10)$$

where

$$|f| = [(f^r)^2 + (\Delta f'')^2]^{1/2} \quad (11)$$

and

$$\varphi = \text{tg}^{-1} \frac{\Delta f''}{f^r} \quad (12)$$

or, to a first approximation (Cruickshank & McDonald, 1967),

$$\varphi = \frac{\Delta f''}{f^r}. \quad (12a)$$

Then

$$F(\mathbf{H}) = \sum_j |f_j| \exp [i(2\pi \mathbf{H} \cdot \mathbf{r}_j + \varphi_j)]. \quad (13)$$

(b) Electron density

The linear property of Fourier transforms allows us to write

$$\varrho(\mathbf{r}) = T^{-1}[F(\mathbf{H})] \\ = T^{-1}[F^0(\mathbf{H})] + T^{-1}[F'(\mathbf{H})] + T^{-1}[F''(\mathbf{H})] \\ = T^{-1}[F^r(\mathbf{H})] + T^{-1}[F''(\mathbf{H})] \\ = \varrho^0(\mathbf{r}) + \varrho'(\mathbf{r}) + i\varrho''(\mathbf{r}) = \varrho^r(\mathbf{r}) + i\varrho''(\mathbf{r}). \quad (14)$$

Since both $T^{-1}[F^0(\mathbf{H})]$ and $T^{-1}[F'(\mathbf{H})]$ are real quantities, while $T^{-1}[F''(\mathbf{H})]$ is an imaginary one, $\varrho(\mathbf{r})$ must be a complex function; this is true for every space group. Writing the three components of such a function as Fourier series and taking into account the equalities (8) and (9), we obtain

$$\varrho(\mathbf{r}) = \frac{2}{V} \left\{ \sum_{\mathbf{H}}^{+\infty} |F^0(\mathbf{H})| \cos [2\pi \mathbf{H} \cdot \mathbf{r} - \alpha^0(\mathbf{H})] \right. \\ + \sum_{\mathbf{H}}^{+\infty} |F'(\mathbf{H})| \cos [2\pi \mathbf{H} \cdot \mathbf{r} - \alpha'(\mathbf{H})] \\ \left. - i \sum_{\mathbf{H}}^{+\infty} |F''(\mathbf{H})| \sin [2\pi \mathbf{H} \cdot \mathbf{r} - \alpha''(\mathbf{H})] \right\}. \quad (15)$$

The function $\varrho(\mathbf{r})$ may therefore be calculated using 'positive' \mathbf{H} coefficients only (*i.e.* coefficients having at least one of the three indices always non-negative) whenever the three components of the structure factor, $F^0(\mathbf{H})$, $F'(\mathbf{H})$ and $F''(\mathbf{H})$, are known.

On the contrary, in order to calculate $\varrho(\mathbf{r})$ as a function of the $F(\mathbf{H})$'s, one must also use negative \mathbf{H} 's:

$$\varrho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}}^{\pm\infty} |F(\mathbf{H})| \exp [i\alpha(\mathbf{H})] \exp (-2\pi i\mathbf{H} \cdot \mathbf{r}), \quad (16)$$

that is, on the basis of (2),

$$\begin{aligned} \varrho(\mathbf{r}) = \frac{1}{V} \left\{ \sum_{\mathbf{H}}^{\pm\infty} [A(\mathbf{H}) + A(\bar{\mathbf{H}})] \cos (2\pi\mathbf{H} \cdot \mathbf{r}) \right. \\ \left. + \sum_{\mathbf{H}}^{\pm\infty} [B(\mathbf{H}) - B(\bar{\mathbf{H}})] \sin (2\pi\mathbf{H} \cdot \mathbf{r}) \right\} \\ + i \frac{1}{V} \left\{ \sum_{\mathbf{H}}^{\pm\infty} [B(\mathbf{H}) + B(\bar{\mathbf{H}})] \cos (2\pi\mathbf{H} \cdot \mathbf{r}) \right. \\ \left. - \sum_{\mathbf{H}}^{\pm\infty} [A(\mathbf{H}) - A(\bar{\mathbf{H}})] \sin (2\pi\mathbf{H} \cdot \mathbf{r}) \right\}. \quad (17) \end{aligned}$$

With reference to (6) and (7) we have

$$\begin{aligned} A(\mathbf{H}) + A(\bar{\mathbf{H}}) &= 2 \sum_j^N f_j^r \cos (2\pi\mathbf{H} \cdot \mathbf{r}_j) \\ A(\mathbf{H}) - A(\bar{\mathbf{H}}) &= -2 \sum_j^N \Delta f_j'' \sin (2\pi\mathbf{H} \cdot \mathbf{r}_j) \\ B(\mathbf{H}) + B(\bar{\mathbf{H}}) &= 2 \sum_j^N \Delta f_j' \cos (2\pi\mathbf{H} \cdot \mathbf{r}_j) \\ B(\mathbf{H}) - B(\bar{\mathbf{H}}) &= 2 \sum_j^N f_j^r \sin (2\pi\mathbf{H} \cdot \mathbf{r}_j). \quad (18) \end{aligned}$$

It is evident from (18) that the real and imaginary parts of (17) correspond to $\varrho^r(\mathbf{r})$ and $\varrho''(\mathbf{r})$ of (14), respectively.

From (14) and from (3), (4) and (5) it may be concluded that each of the components $\varrho^0(\mathbf{r})$, $\varrho^r(\mathbf{r})$ and $\varrho''(\mathbf{r})$, is the inverse Fourier transform of the same structure, which, in the three cases, contributes with scattering factors f_j^0 , $\Delta f_j'$ and $\Delta f_j''$. The maxima of each of the $\varrho(\mathbf{r})$ components are in the same \mathbf{r}_j positions and their weight and shape correspond to the Fourier transform of f_j^0 , $\Delta f_j'$ and $\Delta f_j''$, respectively.

An obvious consequence of the above considerations is that neither $\varrho(\mathbf{r})$ nor $\varrho^r(\mathbf{r})$ represents the true electron density distribution in the crystal, their maxima being incorrectly weighted and shaped.

Calculation of electron density from experimental data

The experimental measurements give $|F_o(\mathbf{H})|$ values, corresponding to $|F(\mathbf{H})|$ in (2), and not the components $F^0(\mathbf{H})$, $F'(\mathbf{H})$ and $F''(\mathbf{H})$. Therefore, one cannot, in general, calculate an electron density distribution corresponding to $\varrho^0(\mathbf{r})$ of (14) directly from the experimental data.

In order to obtain an unbiased representation of the electron density the $|F_o(\mathbf{H})|$ values should be corrected to $|F^0(\mathbf{H})|$. Some approximate methods were proposed (Templeton, 1955; Patterson, 1963; Ibers & Hamilton, 1964) which employ calculated quantities, with an accuracy dependent on the stage of refinement and on the actual f^0 , $\Delta f'$ and $\Delta f''$ values used. A rather simple method is to take the difference between $F_o(\mathbf{H})$ and the calculated $F'(\mathbf{H})$ and $F''(\mathbf{H})$ vectors, by subtracting the terms which depend on $\Delta f'$ and $\Delta f''$ in (6) and (7), from $|F_o(\mathbf{H})| \cos \alpha(\mathbf{H})$ and $|F_o(\mathbf{H})| \sin \alpha(\mathbf{H})$, respectively. If $|F_o(\mathbf{H})|$ values are collected according to the point group symmetry of the crystal, only the $\Delta f'$ terms must be subtracted, on account of (17) and (18). For centrosymmetric space groups the coefficients $|F_o(\mathbf{H})| \cos \alpha(\mathbf{H})$ are used after the $\Delta f'$ term of (6) has been subtracted from them.

In each of the reported methods, corrections must be re-calculated at every stage of the refinement and, for non-centrosymmetric space groups, after the absolute configuration has been established. In most cases, however, experimental data are not corrected for anomalous dispersion by the above methods, even if this phenomenon is accounted for in the structure factor calculation. We wish, therefore, to examine which errors arise in the electron density depending on the procedure followed in processing the experimental data, *i.e.* whether (i) all or (ii) some of the reflexions in the limiting sphere are taken into account and whether (iii) the phases $\alpha(\mathbf{H})$ or (iv) $\alpha^0(\mathbf{H})$ are used, both for centrosymmetric and non-centrosymmetric structures.

Use of $|F_o(\mathbf{H})|$ and $\alpha(\mathbf{H})$

Let us suppose that only the $|F_o(\mathbf{H})|$ values of one hemisphere (\mathbf{H} positive) are available ($P1$ case), the

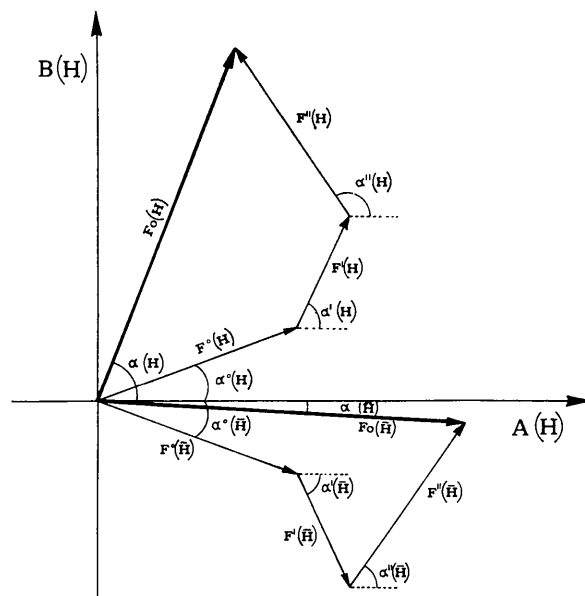


Fig. 1. Vector diagram representing equations (2) to (7).

true absolute configuration having been established. With the usual formulae, one may calculate the electron density real function derived from (16):

$$\varrho_0^x(\mathbf{r}) = \frac{2}{V} \sum_{\mathbf{H}}^{+\infty} |F_o(\mathbf{H})| \cos [2\pi\mathbf{H} \cdot \mathbf{r} - \alpha(\mathbf{H})]. \quad (19)$$

This function does not correctly represent the actual electron density, as far as the position and shape of the maxima are concerned. It differs from the real part in (14) or (15), namely from $\varrho^r(\mathbf{r})$, by

$$\begin{aligned} \varrho_0^x(\mathbf{r}) - \varrho^r(\mathbf{r}) &= \frac{2}{V} \sum_{\mathbf{H}}^{+\infty} |F_o(\mathbf{H})| \cos [2\pi\mathbf{H} \cdot \mathbf{r} - \alpha(\mathbf{H})] \\ &\quad - \frac{2}{V} \left\{ \sum_{\mathbf{H}}^{+\infty} |F^0(\mathbf{H})| \cos [2\pi\mathbf{H} \cdot \mathbf{r} - \alpha^0(\mathbf{H})] \right. \\ &\quad \left. + \sum_{\mathbf{H}}^{+\infty} |F'(\mathbf{H})| \cos [2\pi\mathbf{H} \cdot \mathbf{r} - \alpha'(\mathbf{H})] \right\} \\ &= \frac{2}{V} \sum_{\mathbf{H}}^{+\infty} \left\{ [A_o(\mathbf{H}) - A^0(\mathbf{H}) - A'(\mathbf{H})] \cos (2\pi\mathbf{H} \cdot \mathbf{r}) \right. \\ &\quad \left. + [B_o(\mathbf{H}) - B^0(\mathbf{H}) - B'(\mathbf{H})] \sin (2\pi\mathbf{H} \cdot \mathbf{r}) \right\} \\ &= \frac{2}{V} \sum_{\mathbf{H}}^{+\infty} \left\{ A''(\mathbf{H}) \cos (2\pi\mathbf{H} \cdot \mathbf{r}) \right. \\ &\quad \left. + B''(\mathbf{H}) \sin (2\pi\mathbf{H} \cdot \mathbf{r}) \right\}, \quad (20) \end{aligned}$$

that is,

$$\varrho_0^x(\mathbf{r}) - \varrho^r(\mathbf{r}) = \frac{2}{V} \sum_{\mathbf{H}}^{+\infty} |F''(\mathbf{H})| \cos [2\pi\mathbf{H} \cdot \mathbf{r} - \alpha''(\mathbf{H})]. \quad (21)$$

Equation (21) shows that $\varrho_0^x(\mathbf{r})$ is equal to $\varrho^r(\mathbf{r})$, which has maxima in the \mathbf{r}_j positions, plus a function that does not represent an electron density distribution of atoms in the \mathbf{r}_j positions, as shown by comparison with (15). Its maxima, with weights still depending on the $\Delta f''$ values, are in positions different from \mathbf{r}_j and their addition to the maxima of the $\varrho^r(\mathbf{r})$ function results in a shift of the atomic positions of the anomalous scatterers in the $\varrho_0^x(\mathbf{r})$ map, as indicated below.

We may conclude that the function calculated using $|F_o(\mathbf{H})|$ values with \mathbf{H} positive and $\alpha(\mathbf{H})$ phases is incorrect as regards both the shape and position of the maxima.

This is also true for centrosymmetric structures, if (19) is used, inasmuch as it corresponds to the real part of (17) after assuming $A(\mathbf{H}) = A(\bar{\mathbf{H}})$ and $B(\mathbf{H}) = -B(\bar{\mathbf{H}})$, instead of $B(\mathbf{H}) = B(\bar{\mathbf{H}})$. The correct real function to be calculated in the centrosymmetric case is

$$\varrho_0^x(\mathbf{r}) = \frac{2}{V} \sum_{\mathbf{H}}^{+\infty} A_o(\mathbf{H}) \cos (2\pi\mathbf{H} \cdot \mathbf{r}). \quad (22)$$

Obviously, when both positive and negative \mathbf{H} 's are available for summation (21), it turns out to be zero on the basis of (8) and (9), and therefore $\varrho_0^x(\mathbf{r}) = \varrho^r(\mathbf{r})$ both in the centrosymmetric and non-centrosymmetric cases.

As far as the extent of the previously described errors is concerned, it may be approximately estimated as follows.

By using the geometric phase $\alpha_i''(\mathbf{H})$ of the anomalous scatterers,

$$\alpha''(\mathbf{H}) = \alpha_i''(\mathbf{H}) + \frac{\pi}{2}, \quad (23)$$

summation (21) becomes

$$\sum_{\mathbf{H}}^{+\infty} |F''(\mathbf{H})| \cos \left[2\pi\mathbf{H} \cdot \mathbf{r} - \alpha_i''(\mathbf{H}) - \frac{\pi}{2} \right]. \quad (21')$$

(21') is a Fourier summation relative to the anomalous scatterers in which the phase of each term is shifted by $\pi/2$. It corresponds to X-rays being diffracted by crystallographic planes, each shifted by a quarter of a period in the direction of its scattering vector. This corresponds to the statement that, for any given reflexion, it is as if all the atoms were shifted in the direction of the \mathbf{H} vector by a quantity $\Delta\mathbf{r}$, such that

$$\mathbf{H} \cdot \Delta\mathbf{r} = \frac{1}{4}. \quad (24)$$

This means that the function which is added to $\varrho^r(\mathbf{r})$ to give the experimental $\varrho_0^x(\mathbf{r})$, has its maxima weighted by $\Delta f''$ and all shifted from the \mathbf{r}_j positions by the same average vector $\langle \Delta\mathbf{r} \rangle$, which results from the contribution of all the reflexions. Since \mathbf{H} and $\Delta\mathbf{r}$ are functionally independent, by averaging over all the reflexions (24) becomes

$$\langle \mathbf{H} \cdot \Delta\mathbf{r} \rangle = \langle \mathbf{H} \rangle \cdot \langle \Delta\mathbf{r} \rangle = \frac{1}{4}. \quad (25)$$

For $\langle \mathbf{H} \rangle$ (or $\langle \Delta\mathbf{r} \rangle$) we have

$$\langle \mathbf{H} \rangle = \frac{\int_v \mathbf{H} dV}{\int_v dV}. \quad (26)$$

When \mathbf{H} is limited to a hemisphere, it is easy to see that $\langle \mathbf{H} \rangle$ is a vector parallel to \mathbf{c} , with modulus $\frac{2}{3} S_{\max}$, where $S = 2 \sin \theta/\lambda$.

Therefore one obtains from (25)

$$\langle \Delta Z \rangle = \frac{2}{3 S_{\max}}. \quad (27)$$

Equation (27) represents the shift (in Å) of all the atoms in (21). In other words, only the $\langle \Delta\mathbf{r} \rangle$ component along the direction of the vector $\langle \mathbf{H} \rangle$ is effective in (21). Obviously, $\langle \mathbf{H} \rangle$ and hence $\langle \Delta\mathbf{r} \rangle$ are zero when the reflexions in the whole sphere are used.

The actual shift ΔZ_j of each atom in the $\varrho_0^x(\mathbf{r})$ map will result from the centre of gravity of the two contributing maxima, *i.e.*, that of $\varrho^r(\mathbf{r})$ in \mathbf{r}_j and that of (21) in $\mathbf{r}_j + \langle \Delta\mathbf{Z} \rangle$, weighted according to their relative weights f^r and $\Delta f''$:

$$\Delta Z_j = \langle \Delta Z \rangle \frac{\Delta f''}{f^r + \Delta f''}. \quad (28)$$

Finally, we note that the shift given by (27) and (28) is about the same as the systematic error in the Z

coordinate estimated, to a first-order approximation, by Cruickshank & McDonald (1967) in the case of least-squares refinement. The same kind of considerations reported by these authors on the vanishing of the coordinate errors when the reflexions are collected according to a tetrahedral arrangement of the spherical octants, also applies to the present case.

Use of $|F_0(\mathbf{H})|$ and $\alpha^0(\mathbf{H})$

If we carry out an electron density computation using, in a relation like (19), phases $\alpha^0(\mathbf{H})$ [or $\alpha^r(\mathbf{H})$] and $|F_0(\mathbf{H})|$ it may be deduced, on the basis of Ramachandran's β synthesis (Ramachandran, 1964), that the map will show maxima in the correct r_j positions but they are incorrect in shape and weight. Further, there are also satellite maxima, whose weights depend on the $\Delta f''$ values, in positions defined by combinations of interatomic vectors.

To a first order approximation we can write

$$\begin{aligned} |F_0(\mathbf{H})| \exp [i\alpha^0(\mathbf{H})] &= \frac{|F_o(\mathbf{H})| \cdot |F^0(\mathbf{H})|}{|F^0(\mathbf{H})|} \exp [i\alpha^0(\mathbf{H})] \\ &\simeq \frac{|F_o(\mathbf{H})|^2}{|F^0(\mathbf{H})|} \exp [i\alpha^0(\mathbf{H})]. \end{aligned} \quad (29)$$

If we assume that there are P and Q atoms in the unit cell having f^0 (or f^r) and $\Delta f''$ scattering factors respec-

tively (the Q atoms being in the same positions as the P atoms), the analogy with the β synthesis is evident by putting, according to the notation of Ramachandran,

$$F_o(\mathbf{H}) \rightarrow F_N \text{ and } F^0(\mathbf{H}) \rightarrow F_P \quad (30)$$

where $N = P + Q$.

Consequently, it must be noted that the same atoms, with the same $\Delta f''$ values, when packed in different structures, give rise to different spurious peaks and errors. Furthermore, there is, at present, no direct comparison between the magnitudes of these errors and of those described in the $|F_0(\mathbf{H})|$ and $\alpha(\mathbf{H})$ case.

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Absolute Measurement of Structure Factors of Si by Using X-ray Pendellösung and Interferometry Fringes

BY S. TANEMURA AND N. KATO

Department of Applied Physics, Nagoya University, Nagoya, Japan

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The absolute values of crystal structure factors $|F_g|$ of silicon were determined accurately for five low-order lattice planes, with probable errors of less than 0.05%. The principle of the measurement is to take the ratio of $|F_g|$ and $|F_0|$, which are geometrically proportional to the spacings of the Pendellösung and interferometric fringes respectively. Thus, this method is not only based on a principle appropriate for a truly absolute measurement, but the difficulty in determining the proportional factors is essentially eliminated, and the experimental errors can be reduced to about 0.1%. Some geometrical corrections, however, are required to attain an accuracy better than this. These corrections as well as the theoretical ones are discussed and the necessity of taking into account the effect of the nuclear Thomson scattering is pointed out. The consistency of the results was checked with respect to the following points; (i) $|F_g| = |F_{-g}|$, (ii) $|F_g|$ values being independent of whether the interference fringes in the direct beam or those in the Bragg-reflected beam are used, and (iii) the agreement of $|F_g|$ for different specimens. The atomic scattering factors $|f_g|$ standardized at 20°C are as follows; 111: 10.66₀, 220: 8.46₀, 333: 5.83₉, 440: 5.40₄, and 444: 4.16₈. A comparison is made with the values of other authors.

1. Introduction

One of the important topics in crystallography is the determination of accurate values of structure factors on an absolute scale. The methods can be classified in two

categories; (i) the methods based on the kinematical theory and (ii) those based on the dynamical theory of crystal diffraction. Obviously, the former is universal but cannot be very accurate, while the latter holds the possibility of obtaining very accurate values for limited