samples, then the width of the 033 reflexion must have the same trend. The correlation coefficient $r = 0.79$ for the width of the 011 and 033 reflexions confirms this to a large degree.

Conclusions

From our measurements of the form, position and half-height widths of reflexions from chrysotile asbestos fibres of different origins, the following results are shown:

1. Within the limits of error there is no difference in the wall thickness and the mean diameter of the cylindrical lattice among our 15 samples. The average wall thickness was found to be 155 ± 1 Å, and the average mean diameter less than 280 ± 2 Å, probably about 234 ± 1 Å. (Confidence limits are equal to the estimated values of the r.m.s. deviation of averages.)

2. From the form of reflexion there is strong evidence in favor of Whittaker's model of distribution of cylindrical azimuthal boundaries separating silica-brucite double layers. However, the form of reflexion 031 suggests that there may be a reason for considering a model with less than the maximum number of cylindrical azimuthal boundaries per elementary fibre, perhaps similar to the one dealt with in TF1, Fig. 5(b).

3. The most interesting feature is the presence of axial disorder which causes the equatorial reflexion of

both $h0l$ and $0kl$ types to display larger 'particle size' than the higher layer line reflexions. There is an indication of a correlation in the number of the cylindrical axial boundaries and the planar axial boundaries in our samples. We believe that the dark radial lines on the electron micrographs in the paper of Maser, Rice & Klug (1960), Figs. 2(c) and 3, confirm our finding of the presence of planar boundaries.

4. We could find no apparent close correlation between tensile strength and type or number of misfit boundaries, which suggests that interfibre binding may be an important factor in tensile strength.

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On the Information about Deformations of the Atoms in X-ray Diffraction Data

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The information which can be obtained about the shape of crystal atoms by X-ray diffraction is studied in light of a model calculation. The electron density of an atom is treated as a Fourier invariant expansion in terms of harmonic oscillator wave functions adapted to the crystal symmetry. Definite limits for the observability of the terms are set by the experimental cutoff in $\sin\theta/\lambda$, and by the volume of the atom. As a consequence, details smaller than a critical size cannot be seen either in the electron density or in the atomic factor. Experimental errors are such that the atomic factor rather than the electron density reveals the significant deformations. Termination effects are studied in a model crystal: deformations are inserted and a truncated set of structure amplitudes is analysed. Here series were used for the radial coefficients ϱ_i, f_i in the harmonic expansions $\Sigma\varrho_i(r)_i K(\theta,\varphi)$ and $\Sigma f_i(b) K_i(\theta,\varphi)$ for the electron density and the scattering factor of a sphere. The radial scattering factors are well reproduced up to the cutoff value of the reciprocal vector, while a fair representation of the radial densities can be reached only by a long series. The termination does not significantly mix components with different angular behaviour. Reasonable contributions from neighbouring atoms have no major effect on the radial scattering factors or densities. Therefore the factors f_i calculated for a slightly 'too large' sphere will lead to a proper interpretation of the electron distribution in terms of deformed atoms.

1. Introduction

The concept of atomic deformation refers to the idea that we are analysing the structure of the crystal in terms of separate atoms. Actually it is surprising how well the separate atom model works in spite of the interactions between the atomic electrons in the solid state. Still to day almost all experimental diffraction data on crystals can be explained by models built from free atoms vibrating about their lattice sites. Only recent

improvements in experimental technique have been able to show deviations from such models. However, as Cochran (1961) has noted, care is needed in talking about single atoms in the solid state. One needs some practical definition for this concept, and definitions which are reasonable in different connexions need by no means be identical. In connexion with X-ray diffraction work the definition of an atom must be based in the first place on the electron density function

$$\varrho(\mathbf{r}) = \frac{1}{V} \sum_j F_j \exp(-2\pi i \mathbf{b}_j \cdot \mathbf{r}), \qquad (1)$$

since the experiments refer to it giving more or less directly the Fourier coefficients F_j. In real crystals there are always parts of the electron distribution, such as local bonds or metallic electrons, which cannot be uniquely shared among the atoms. Only in an ideal ionic crystal would there be no uncertainty in dividing it into atoms.

To be physically reasonable the definition of a crystal atom must have certain locality. It is obvious that the distribution peak which corresponds to a certain atom will be the main contents of that atom. It is also reasonable to attach the entire peak to that atom since the overlapping of peaks due to thermal motion is normally very small, and it would be senseless to attach electrons in the immediate vicinity of one nucleus to another atom. The possible definitions can therefore differ only in the way in which the distribution between the peaks is treated. Also by deformation we mean in this connexion deformation of these distribution peaks, without any reference to its physical origin.

The proposition that the atom be understood as the contents of a suitable region represents a limiting case in its exaggeration of locality. Its mathematical simplicity makes it, however, sometimes rather useful (Kurki-Suonio, 1959, 1962). In ionic crystals, where the electron density often falls to very small values between the ions, all reasonable definitions of the atoms must be practically equal. Also this idea is certainly as correct as any other definition. The situation is different in the case of metals and covalent bonds. The uncertainty – or freedom – in the definition is considerable, and the strict local separation will be a rather superficial limiting case among the possibilities. Some overlapping atom models, such as those used by Dawson (1967b,c,d) to explain the covalent bond in diamond and related substances, will then be more natural. The justification of such divisions of the distribution into separate atoms lies, however, merely in their success in describing the situation in simple terms.

A risk in another extreme is hidden in the traditional separation of structure amplitudes into atomic scattering factors. It is included in the mathematical statement of Hosemann & Bagchi (1962), that any set of experimental structure amplitudes can be explained in terms of spherical 'atoms', except possibly coincident reflexions. Also, we get information only at a finite number of discrete points in reciprocal space and the values of atomic factors everywhere else can formally be chosen at will. If applied uncritically this can lead to quite absurd definitions of the atoms, *e.g.* distant parts of a distribution may get attached to the same atom. The cutoff is one aspect of this question causing essential limitation of the experimental information. It is, however, possible to define a limited class of physically reasonable residual terms (Kurki-Suonio, 1962). The non-unique interpretation of the structure amplitudes in terms of atomic factors and the apparently arbitrary behaviour of atomic factors between the reciprocal lattice points form a more sophisticated problem. Actually, they are just an expression of our uncertainty about how the crystal atoms should be defined. Again the general physical knowledge about atoms will be rather restrictive. Particularly we shall demonstrate in § 3 that the volume of atoms will essentially limit the reasonable choice of the atomic factors. An exhaustive interpretation of structure amplitudes in terms of spherical atomic factors may therefore prove impossible even though no coincident reflexions have been measured. This is the formal basis which makes it reasonable to speak of non-sphericities of the atoms.

Doubts have been expressed to the effect that the atomic deformations are such fine details of the structure that the information about them just cannot be observed in diffraction data (*e.g.* Kitajgorodskij, 1957, 1961). It is, however, not immediately clear what should be understood by 'details' in this connexion. The experimental information is local in reciprocal space, and any effect which is large enough somewhere in the region $b < b_{\text{cutoff}}$ will be seen. The complementarity relation between the locality in **b** space and the locality in **r** space causes local phenomena of **b** space to be widely spread in **r** space, and *vice versa*. An observable effect may well seem insignificant in real space and even large local effects in the electron density can be invisible in the scattering factors. The deformations occur in the outer shells of the atoms and they are rather large-scale phenomena. If enough electrons altogether take part in them they will certainly be observable.

For the present experimental technique the best resolution seems to be about 0·1 electron per unit cell in simple crystals. In view of several theoretical scattering factor calculations, *e.g.* those of McWeeny (1951, 1952, 1953, 1954), Freeman (1959), Weiss & Freeman (1959), Watson & Freeman (1961) and Dawson (1964b), one would expect displacements of this order to occur. In fact, this is also found in some cases where the proper analysis of experimental values has been performed. For instance, the analysis of Dawson (1967b,c) yields 0·087 and 0·127 electron per bond, corresponding to 0·35 and 0·51 electron per unit cell, taking part in nonspherical phenomena in diamond and silicon respectively. The results obtained by the group in Helsinki (*e.g.* Merisalo & Inkinen, 1966; Järvinen & Inkinen,

1967; Meisalo & Inkinen, 1967) for several ionic crystals also indicate phenomena of this order of magnitude, as well as the work of Weiss & DeMarco (1965) and DeMarco & Weiss (1965) and some others.

Thus, in general, we can expect to obtain information about such solid state effects from X-ray studies. Its presence in the data may, however, be difficult to observe. The deviations of structure amplitudes caused by the deformation need not be large in order to be significant as a whole. The information may be hidden in a complicated systematics of many small differences, perhaps only of the order of experimental error (*cf.* Kurki-Suonio & Meisalo, 1966).

Proper methods of analysis are necessary for detection and analysis of such information. Dawson (1967*a*) has recently emphasized the importance of improved methods of analysis to make possible the adequate separation of this information from experimental data. In subsequent papers (Dawson, 1967*b,c,d*; Dawson, Hurley & Maslen, 1967; Dawson & Willis, 1967) some examples of such an analysis are given. Earlier, one such method was proposed by the author (Kurki-Suonio, 1959, 1962) on account of the studies of Korhonen (1953, 1955, 1956). Several applications (*e.g.* Merisalo & Inkinen, 1966; Järvinen & Inkinen, 1967; Meisalo & Inkinen, 1967) have shown that it can unravel information which is difficult to observe by conventional methods. A more complete treatment of the problem will be possible by a new suggestion (Kurki-Suonio & Meisalo, 1967).

The aim of this work is to elucidate more closely the nature of the information concerning deformations. Special attention will be paid to how the spatial boundedness affects its nature and how the cutoff and finite accuracy of measurements restrict the information that can be obtained. For this purpose we constructed models for different types of deformation and studied to which extent they were reproduced by proper analysis of a truncated set of structure amplitudes.

2. The basic functions

The angular dependence of atomic deformations is most properly treated in terms of spherical harmonics $K_l(\theta, \varphi)$ adapted to the symmetry of the atomic position in the crystal, or lattice harmonics (Altmann & Cracknell, 1965; Altmann & Bradley, 1965). Their adoption is motivated by both mathematical and physical arguments (Kurki-Suonio & Meisalo, 1967; Dawson, 1967*b,c,d*). Therefore we shall express the electron density and the scattering factor of the atom as harmonic expansions

$$\varrho(\mathbf{r}) = \sum_{l\alpha} \varrho_{l\alpha}(r) K_{l\alpha}(\theta, \varphi); f(\mathbf{b}) = \sum_{l\alpha} f_{l\alpha}(b) K_{l\alpha}(u, v), \quad (2)$$

where l is the order of harmonics, α refers to the possibility of having several independent harmonics of the same order, and r, θ, φ and b, u, v are the spherical coordinates of the vectors $\mathbf{r}$ and $\mathbf{b}$ respectively. The suit-

ability of this representation for diffraction analysis is especially emphasized by the Fourier invariance of the harmonics, which will establish a one to one correspondence between the terms of the two expansions (2). The radial functions in these expansion are related to each other through a Fourier–Bessel transformation

$$f_{l\alpha}(b) = 4\pi i^l \int_0^\infty \varrho_{l\alpha}(r) j_l(2\pi br) r^2 dr, \quad (3)$$

which depends only on the order l of the term.

To describe different types (l, α) of deformation we still need a proper set of radial functions. They can be taken somewhat arbitrarily, as stated by Dawson (1967*b*), mathematical simplicity being the main criterion.

The harmonic oscillator wave functions seem to be a most natural choice. They simplify the treatment of our problem essentially because of their Fourier invariance, which is stated by the theorem:

An arbitrary eigenfunction

$$\psi_n = a^{3/2} g(a\mathbf{r})$$

of the Schrödinger equation

$$\nabla^2 \psi + a^2 (2E - a^2 r^2)\psi = 0$$

with the eigenvalue $E = n + \frac{3}{2}$, has the Fourier transform

$$\varphi_n = \int \psi_n \exp (2\pi i \mathbf{b} \cdot \mathbf{r}) d^3 r = i^n A^{3/2} g(A\mathbf{b}),$$

where $Aa = 2\pi$.

We can now take the eigenfunctions separated in spherical coordinates and adapt the angular dependence to the symmetry needed. In this way we arrive at the functions

$$\varrho_{nl}(\mathbf{r}) = c R_{nl}(ar) K_l(\theta, \varphi), \quad n = l, l+2, l+4, \ldots, \quad (4)$$

where K_l is a lattice harmonic of order l and

$$R_{nl}(x) = x^l \exp (-x^2/2) L_{\frac{1}{2}(n-l)}^{l+\frac{1}{2}}(x^2), \quad (5)$$

where the functions L_m^k are the associated Laguerre polynomials

$$L_m^k(x) = \frac{1}{m!} e^x x^{-k} \frac{d^m}{dx^m} (e^{-x} x^{m+k}).$$

If (4) is taken to be a contribution to the electron density of the atom, the corresponding contribution to the scattering factor will be, according to the invariance theorem

$$f_{nl}(\mathbf{b}) = i^n Z R_{nl}(Ab) K_l(u, v);$$

$$Z = c(2\pi)^{3/2}/a^3, \quad A = 2\pi/a. \quad (6)$$

Thus we have different sets of radial functions R_{nl} for different angular dependences $K_l(\theta, \varphi)$. To avoid confusion we shall call l the type and $\frac{1}{2}(n-l)$, within each type, the order of deformation.

It should be noted that this invariance theorem includes the Fourier invariance of the spherical har-

monics as well as the invariance of the radial functions R_{nl} under the Fourier–Bessel transformation (3) in the form

$$\langle j_l \rangle_{nl} = 4\pi a^{3/2} \int_0^\infty R_{nl}(ar) j_l(2\pi br) r^2 dr =$$

$$(-1)^{\frac{1}{2}(n-l)} A^{3/2} R_{nl}(Ab) .$$

To see more closely the nature of the basic radial functions R_{nl} a set of them is shown in Fig. 1. They are given in the form $Z_{nl} R_{nl}(\sqrt{2\pi}x)$ which is a true invariant of the lth radial transformation, except for the phase factor. Therefore the curves serve also to illustrate the properties of the transformation. For each type and any constant a the functions $R_{nl}(ar)$, $n = l, l+2, l+4, \ldots$ form a complete orthogonal set of radial functions. They bear the usual characteristics of such sets, the $\frac{1}{2}(n-l)$ nodes due to the zeros of the Laguerre polynomials. The Gaussian factor dominates at large values of the variable and causes the functions to approach zero strongly. The pure Gaussian form is just a special case with $n = l = 0$. The locality of the deformation is defined more closely by the parameter a. With a suitable choice of it we can restrict the deformation to the region desired.

It is a well known property of the Fourier transformation that all changes which diminish the smoothness of the functions will cause their transforms to extend wider, and *vice versa*. This is also evident from the behaviour of the functions (4) and (6). If we let a increase in order to compress the deformation into a smaller region, the corresponding radial scattering factor will stretch farther according to the relation $aA = 2\pi$. The order of the function determines the rate of radial oscillations, the larger n the more oscillations. As a consequence, the scattering factors of deformations with higher n extend farther, if deformations lying in the same region are compared. The angular oscillation depends on the type of the function, and it has a similar effect. This is seen directly from Fig. 1, where curves of equal order and different types are compared (*cf.* Fig. 3 of Dawson, 1967*b*). When l increases the range of the deformation grows in both spaces simultaneously. Numerically this is demonstrated for instance by the rule $2\pi r_l b_l = l$ for the maxima r_l and b_l of the zero order deformation $R_{ll}(ar)$ and its transform $R_{ll}(Ab)$ respectively.

3. Limitations of observability

Now that we have fixed the basic functions, we can handle the electron density and the scattering factor of the atom as expansions in terms of these functions. Particularly in this case we have a Fourier invariant division of the atom into components (4) or (6). The restrictions caused by the locality of the atom and the experimental limitations on the obtainable information can now be seen by studying them for the different components separately.

First we note that a component n, l can evidently be observed and identified only if a sufficient part of even its last oscillation lies both below the cutoff in reciprocal space and inside the atomic region in real space. On account of the transformation properties discussed above, this criterion will allow only the first few components to be observed. This situation can also be understood to arise from two simultaneous restrictions. First, as known, the cutoff sets up a lower limit for the wavelength of oscillations, or more generally, for the dimensions of details, which can be observed in the electron density. Quite analogously the radius R of the atomic region defines a lower limit for details which can occur in the atomic scattering factor. Therefore only those few terms of the form (4), (6) can occur, the wavelength of which is long enough in both spaces at the same time.

The upper limits of n and l depend on b_{cutoff} and the radius R of the atomic sphere. These limits are not sharp, since the criterion is not accurate. Rather, the significance of the components is reduced by and by with increasing n and l. A better idea of this limitation can be obtained if one lists for instance all components which have their last maxima or minima in the desired regions. If this point is denoted by X_{nl} for the function R_{nl} in Fig. 1, then all components will be accepted for which $X_{nl}^2 < Rb_{\text{cutoff}}$. Other components either do not exist in the region of that atom or they cannot be observed because of the cutoff.

The non-spherical components represent in this formalism angular displacements of electrons as compared with the average spherical electron density. The preferred directions are given by the maxima of the corresponding harmonic function. The limitation of l means that components which describe the angular behaviour in too much detail, *i.e.* components having many maxima and minima, cannot be observed. If we
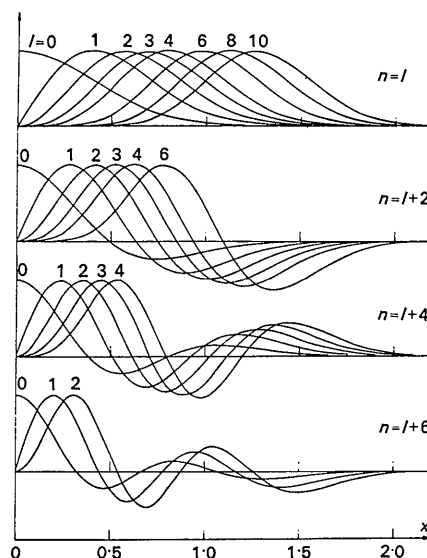

Fig. 1. Fourier invariant radial functions $Z_{nl} R_{nl}(\sqrt{2\pi}x)$.

consider, for instance, a measurement by Cu radiation, we have $b_{cutoff} \simeq 1\cdot2$ Å^{-1}. For an atom of medium size, with a radius $R = 1\cdot2$ to $1\cdot5$ Å, we then find from Fig. 1 that components with $l > 8$ are absolutely not observable. Also from a physical point of view the components with higher l are not expected to have any significance, since a component of type l can be caused only by valence electrons with angular momentum quantum number at least $\frac{1}{2}l$. For instance, a K_8 type deformation would provide the presence of g states, which in general are not expected to occur in significant extent.

The limiting order is different for different types. It determines the minimum size of details which can be seen in the radial behaviour of the electron density and the scattering factor of the corresponding type of deformation. The wavelength of R_{nl} will give a rough measure of it. In our example, no details at all can be seen in the components with $l > 3$, for which only the zero order ($n = l$) is possible. Even for the spherical case ($l = 0$) only the first three orders can be significant.
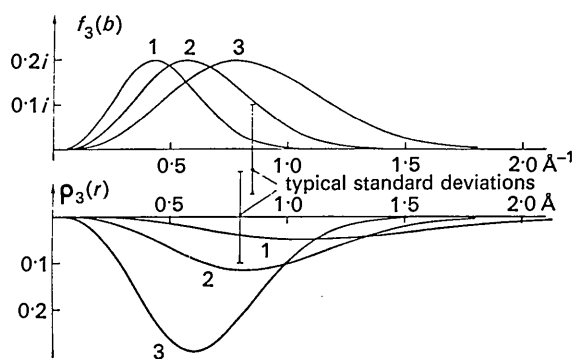

Fig. 2. The radial scattering factors and the corresponding radial electron densities of some K_3 type deformations with equal observability. A typical experimental uncertainty is indicated by an error bar.
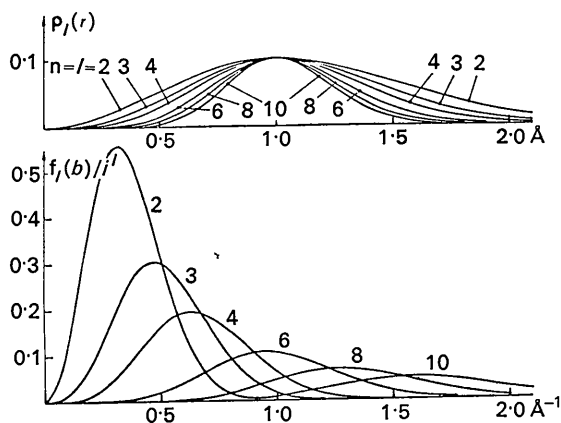

Fig. 3. The radial electron densities and the corresponding radial scattering factors of deformations with different angular behaviour and with equal apparent strength and range in real space.

This means that the details of the average spherical behaviour are invisible if they are smaller than about $\frac{1}{3}R \simeq 0\cdot4$ Å in real space or smaller than $\frac{1}{3}b_{cutoff} \simeq 0\cdot4$ Å^{-1} in reciprocal space. This means a strong restriction of possibilities to adapt spherical atomic factors to a given set of structure amplitudes. The atomic factor curves are 'stiff' and cannot be bent at will. This is why it may certainly be unnatural to interpret structure amplitudes by means of merely spherical atomic factors.

Thus, in general, it will not be realistic to search for much more than just the zero order term of each observable type of deformation. This will be enough for stating the existence of the component with certain angular dependence and for obtaining some parameters corresponding to Z and A of the function $f_{ll}(\mathbf{r})$. The first one will be a kind of strength of the deformation, which should be related to the number of electrons participating in the angular displacements, and the other one will be connected with its effective range. These results will certainly be independent of the particular set of basic radial functions used, e.g. the functions used by Dawson (1967b, c, d) in his analysis of diamond, silicon and germanium are therefore equally justified. Further details of the radial behaviour can scarcely be significant. Thus, the conclusions of Dawson very likely exhaust the information about the shape of the atoms included in the experimental structure amplitudes.

The limited accuracy is not yet explicitly included in these considerations. Qualitatively, its effect will be to prevent the observation of tiny components. Since the experimental information lies primarily in reciprocal space this restriction refers more directly to the atomic factor representation of the deformations. It is reasonable to assume that the observability of a component means that its scattering factor $f_{nl}(\mathbf{b})$ must exceed some minimum value. If the accuracy of the experimental structure amplitudes is, say, $\pm 0\cdot1$, then a component with a maximum $0\cdot2$ will certainly be significant. This will allow certain local inaccuracies roughly of the order of $0\cdot1$ Å^{-3} in the corresponding electron densities. Fig. 2 shows as an example deformations of type $l = 3$ with equal observability, represented in terms both of the atomic factors and of the electron density. These curves demonstrate very clearly that effects of equal magnitude in reciprocal space may seem to have very different significance if studied in real space. Obviously, a significant deformation may even be difficult to observe and it may easily be overlooked on inspection of the density maps. Moreover, this situation is expected to occur often, since the deformations appear in the outer part of the atomic region, and the radial densities ϱ_{nl} with their maxima in this region are the flattest ones. We come therefore to the conclusion that the analysis of deformations must be performed in reciprocal space, as far as possible, if we are to be able to judge their significance. The density maps serve then for useful visualization of the results.

Fig. 3 demonstrates another aspect of the meaning of the finite accuracy. It represents zero order $(n=l)$ deformations of different types, concentrated at a definite distance and having an equal apparent strength in real space. Their scattering factors are seen to lose their significance very rapidly with increasing l. Now, we expect from physical arguments that the deformations with higher l will, moreover, be much weaker than those with low l. The experimental errors will therefore be rather effective in hiding the deformations of higher l, even though the geometrical conditions discussed above should allow their observation.

4. Termination effects

The structure amplitudes F_j, or the Fourier coefficients, define the electron density of a crystal uniquely. The experimental cutoff will reduce this information, but most of the termination effects can be eliminated by using difference series, which is equivalent to taking a theoretical residual term (see e.g. Lipson & Cochran, 1957). The philosophy behind the difference methods is also discussed by the author (Kurki-Suonio, 1962). The information we are looking for will be found by studying the Fourier series (1) in the region of the atom. For simplicity we shall consider a spherical region. This is practical, because the radial coefficients $f_{l\alpha}(b)$ of the series (2) for the contents of a sphere can be expressed in an analytic form in terms of the structure amplitudes (Kurki-Suonio & Meisalo, 1967; Kurki-Suonio, 1967). In a difference series calculation this includes the assumption that outside the sphere the theoretical atom is correct, i.e. the overlap of atoms is properly described by the model. If this is true, the differences inside the sphere represent the deformations of the atom. (This is certainly not the case, if a considerable amount of covalent bonding is present and if the model atoms are spherical, as usual. We shall return to this question in the next section.)

To see the effect of the residual term on the information concerning atomic deformations we performed the following calculations. For simplicity we took a simple cubic crystal. Each atom is then in a cubic field and the angular factors $K_l(\theta, \varphi)$ in (2) are just the α-type cubic harmonics of von der Lage & Bethe (1947). All components with odd l and $l=2$ are identically zero, and in the lowest five orders $l=0,4,6,8,10$ there is only one term in each (Betts, Bhatia & Wyman, 1956). The radial coefficients ϱ_l and f_l are given by the series

$$\varrho_{l\alpha}(r) = \frac{4\pi(-i)^l}{VN_{l\alpha}} \sum_j F_j K_{l\alpha}(u_j, v_j) j_l(2\pi b_j r) \qquad (7)$$
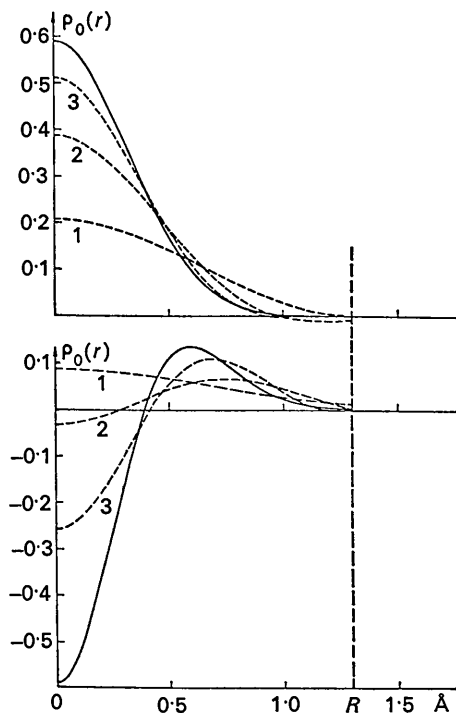
first derived by Atoji (1958), and

$$f_{l\alpha}(b) = \frac{16\pi^2}{VN_{l\alpha}} \sum_j F_j K_{l\alpha}(u_j, v_j) I_l(2\pi b, 2\pi b_j; R), \qquad (8)$$

where
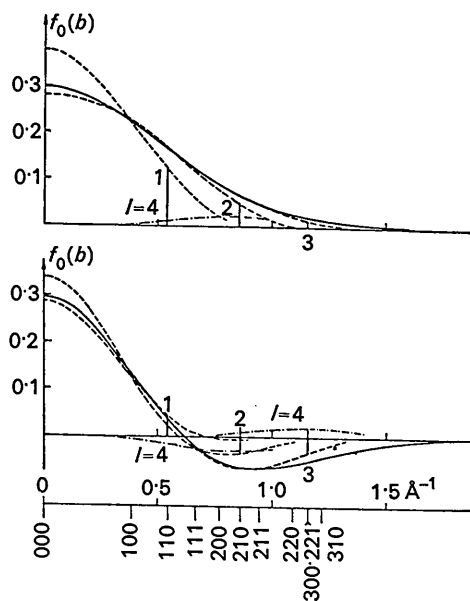
(a)

(b)

Fig. 4. Termination effects in spherical components $n=l=0$ and $n=2$, $l=0$ (a) in reciprocal space and (b) in real space; ———— the model function [0·3 $R_{00}(2b)$ and 0·2 $R_{20}(2b)$]; ———— the spherical component as reproduced by the truncated series; —·—·— non-spherical components due to termination. The labelling of ϱ curves refers to the numbering of cutoffs indicated by vertical lines attached to the scattering factor curves at b of the last term included.

$$I_l(x,y;R)= \int_0^R j_l(xr)j_l(yr)r^2dr=$$

$$\frac{R^2}{x^2-y^2}\,[xj_{l+1}(xR)j_l(yR)-yj_l(xR)j_{l+1}(yR)]$$

and

$$N_{l\alpha}= \int_{(4\pi)} K_{l\alpha}^*(\theta,\varphi)K_{l\alpha}(\theta,\varphi)d\Omega$$

(Kurki-Suonio, 1967). If the notation of Kurki-Suonio & Meisalo (1967) is used for the cubic harmonics K_l we have $C_0=1$, $C_4=32\cdot8125$, $C_6=2408\cdot656$, $C_8=9258\cdot691$, $C_{10}=448736\cdot96$ for $C_l=4\pi/N_l$. The lattice constant was chosen to be $2\cdot6$ Å and the radius of one atom $R=1\cdot3$ Å. To simulate a difference series calculation we assumed that the deviation of the atom from the theoretical one was represented by one of our model functions (4) and (6). The contributions of this deformation to the structure amplitudes were then calculated and used as coefficients of the series (7) and (8). To get a general view of the convergence properties this procedure was repeated for a whole set of different functions and with different cutoff limits. In each case Z was chosen to make the deformation observable as compared with a reasonable experimental accuracy and A was taken so that no significant parts of the deformation remained outside the atomic sphere. In this way we could check, how well the information lying inside a sphere will be reproduced in the analysis. Typical examples of the results are given in Figs. 4, 5, 6. The Figures (a) show the reproduction of the atomic factor components f_0, f_4 and f_6 by truncated series (8). The Figures (b) show the corresponding curves $\varrho_0(r)$, $\varrho_4(r)$ and $\varrho_6(r)$.

As a general observation we found that the termination effects are of a very simple nature in the atomic factor calculations. The truncated series (8) tends to follow a function which is equal to the model $f_l(b)$ up to the cutoff limit and zero beyond that, rounding off the discontinuity at b_{cutoff}. This behaviour is observed already by a very small number of terms as indicated by the Figures. It can be understood by our earlier qualitative argument, that in this way the analysis is kept in reciprocal space, where the residual term is locally separated from the experimental information (Kurki-Suonio & Meisalo, 1967). As the only exception we observe some piling up of cutoff error near the origin $b=0$ in the case of spherical deformations [see Fig. 4(a)].

The truncated series (7) gives a much worse approximation of the radial electron densities $\varrho_l(r)$. The termination errors resemble those of the ordinary Fourier series and spoil the picture to a large extent. Only near the surface of the sphere is the representation somewhat more satisfactory.

Another important and very useful property is that the termination does not mix different types of deformation significantly. This was controlled explicitly by calculating all radial functions ϱ_l and f_l with $l=$

0, 4, 6, 8, 10 for each particular model with the same cutoff limits as before. In every case all irrelevant components were negligible. The dotted lines in Figs. 4(a), 5(a), 6(a) show all such components that can be seen at the scale used. In the electron density there were some more components which should have been visible in Figs. 4(b), 5(b), 6(b). None of them has any true significance.

We conclude that by series (8) the information about deformations inside a sphere can be extracted in the most pure form. If significant values of the difference series (8) are found for any type of deformation, then this component does exist (without any reference to its origin or interpretation), and the curve obtained gives a fair representation of its contribution to the atomic factor below the cutoff limit. Because of the termination effects it may, however, be impossible to conclude how far the components do extend beyond the cutoff. This is a mathematical point of view. Physically one may argue that the deformations are such smooth phenomena in the rather wide region of the outer electron shells that all essential information about them lies at small b values. If one can rely upon such arguments, this uncertainty will not be so important. All components of about the same order of magnitude can be observed simultaneously. One dominant component may, however, prevent a reliable observation of the others, if the uncertainty about its continuation beyond the cutoff is large compared with the values of other components. This concerns especially components with neighbouring values of l.

5. On the role of overlap

The restriction of the considerations to the contents of a sphere is mathematically a very simple solution of our problem. The justification for this procedure is evident only if the reasonable division of the electron density into atoms does not provide considerable overlap in addition to what is present in the theoretical model used. One will often meet cases where its applicability is not immediately clear. It may, however, be possible to find, even for covalent bonds, a simple interpretation in terms of separate deformed atoms. This is clearly demonstrated by the succesful analysis of the bonds in diamond, silicon and germanium (Dawson, 1967b, c, d) which could be properly described by overlapping K_3 and K_4 components of the atoms.

By use of the series (8) one can get a good picture of the contents of a sphere, as is shown in the preceding section. Therefore it will be useful to know how the overlapping components are reflected in the results of such an analysis. For this purpose we extended our studies to cases with considerable overlap. The same models were used as before, except for values of A which were chosen to produce a reasonable overlap of neighbouring atoms in the model crystal. In the light of Dawson's results and our considerations in § 3 we believe that such models cover, well enough for

X-ray diffraction analysis, all cases where the density does not vanish between neighbouring atoms.

Again we derived at first the structure amplitudes F_j corresponding to the model deformations. Then the different components around one atom were computed with the use of the series (7) and (8). In each case all structure amplitudes greater than 10^{-5} were included; hence the results are well guarded against termination errors. In addition to the normal close packing radius $R_1 = 1\cdot3$ Å we used a 'too large' radius $R_2 = 1\cdot5$ Å, which clearly extends to the region of the nearest neighbours but contains the model deformation more completely.

Two cases, $n = l = 4$ and $n = l = 6$, are presented in Fig. 7(a),(b) respectively as typical examples of the calculations. (Compare also Fig. 8 where a similar calculation is presented for the spherical case $n = 2, l = 0$.) The situation is shown both in reciprocal space and in real space. The radial behaviour f_l and ϱ_l is given for the model deformations themselves and for all components of deformation arising from them in the crystal atoms, as far as they are visible in the scale of the figures. To get an idea of the extent of overlapping we show also the corresponding electron densities $\varrho(x, 0, 0)$ along the connecting line of two neighbouring atoms.

Again, a general observation is that different types of deformation are largely independent. This can be seen both in ϱ_l and in f_l. The original behaviour of each component is well reproduced in spite of the overlap. In reciprocal space the reproduction by the too large sphere is good. The smaller sphere is evidently somewhat too small compared with the range of the model deformations. Also, all irrelevant components are weak, especially inside the smaller sphere. But even in the larger one the mixing of components is not strong enough to produce any misleading features. The worst interactions are here between the same components as in the termination effects. Overlapping components with a definite l will produce weak deformations with neighbouring values of l. Again the interaction is strongest between $l = 4$ and $l = 0$. Especially, overlapping K_4 components will make the number of electrons in the atomic sphere to increase, as is indicated by the rise of f_0 at $b = 0$. These rather favourable properties can be explained by noting that the overlapping concerns only a small solid angle, and each radial function represents the averaged behaviour in the full 4π solid angle.

These results indicate that the method of calculating the scattering factor differences for a sphere can be useful also in cases with considerable amount of covalent bonding. They also suggest that one should rather use 'too large' spheres in such an analysis to obtain the best result. The existence and approximate strength of different types of deformation can be detected in this way.

By application of the same procedure to spherical components we wanted to find out to what extent non-

spherical deformations of the distribution peaks can be caused by mere overlapping, since it has been suggested that this might be the only interpretation of such observations (Hosemann & Bagchi, 1962; Hovi, 1959).
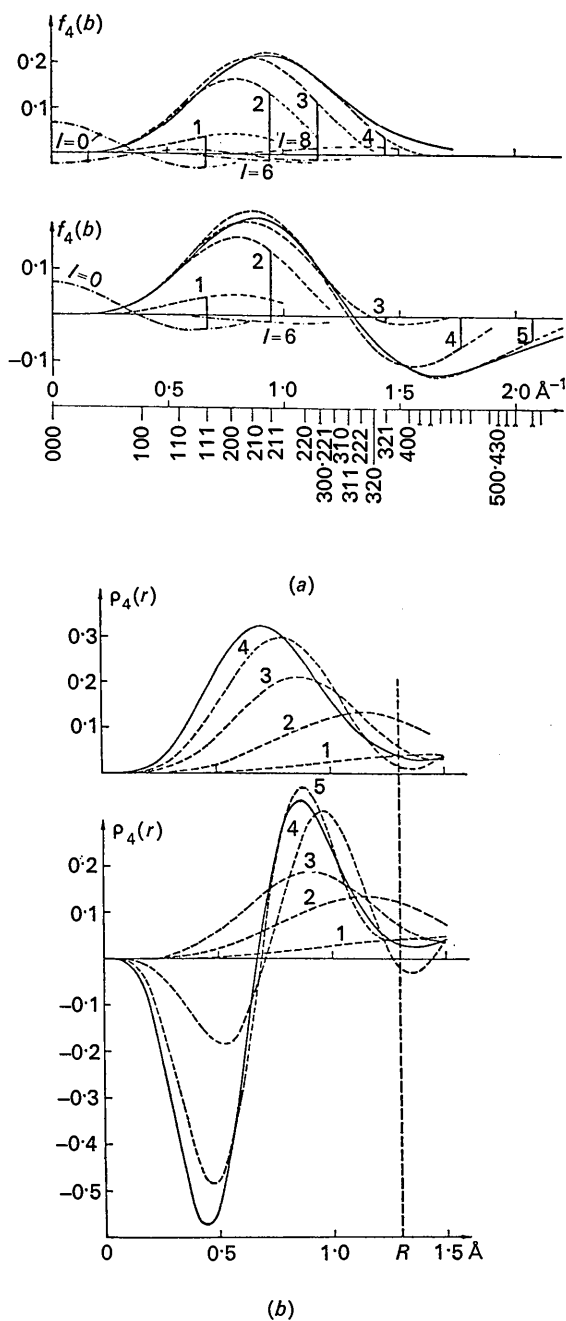

Fig. 5. Termination effects in deformations $n = l = 4$ and $n = 6$, $l = 4$ (a) in reciprocal space and (b) in real space; ———— the model deformation [$(0\cdot1$ $R_{44}(2\cdot2b))$ and $0\cdot04$ $R_{64}(1\cdot8b)$]; – – – – the K_4 component as reproduced by the truncated series; –·–·–·– irrelevant components due to termination. The labelling of ϱ curves refers to the numbering of cutoffs indicated by vertical lines attached to the f curves.

An example is given in Fig. 8. The results show that almost no aspherical features will occur without the presence of non-sphericities in the atoms themselves. Of course, the overlapping may be rather large in
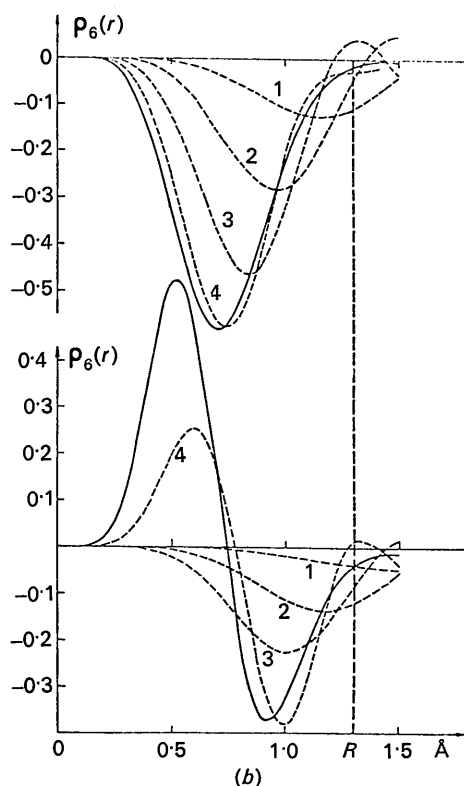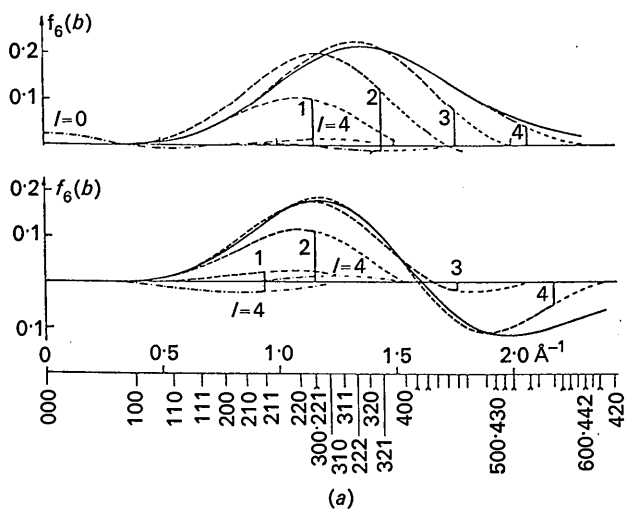

Fig. 6. Termination effects in deformations $n=l=6$ and $n=8$, $l=6$ (a) in reciprocal space and (b) in real space; —— the model deformation [0·02 $R_{66}(1\cdot8b)$ and 0·006 $R_{86}(1\cdot7b)$]; ———— the K_6 component as reproduced by the truncated series; —·—·— irrelevant components due to termination. The labelling of ϱ curves refers to the numbering of cutoffs indicated by vertical lines attached to the f curves.

reality, when, for instance, some metallic crystal is built from free atoms. To check the validity of this conclusion we therefore calculated this effect also for theoretical Cu and Fe crystals using the Gaussian representations for their atomic factors (Kurki-Suonio, Meisalo, Merisalo & Peltola, 1966).* The structure of Cu is f.c.c. with a lattice constant $d_{Cu}=3\cdot608$ Å. Fe is b.c.c. with $d_{Fe}=2\cdot8664$ Å. A temperature factor of the form $\exp(-B\sin^2\theta/\lambda^2)$ was adopted with $B_{Cu}=0\cdot4$ Å² and $B_{Fe}=0\cdot36$ Å² corresponding to room temperature. In both cases the overlap is rather strong. As a measure we can use the amount of electrons coming from the neighbours to one atomic sphere. A direct calculation from the Gaussian expressions gives 0·48 e in Cu and 0·85 e in Fe for close packed spheres with $R_{Cu}=1\cdot275$ Å and $R_{Fe}=1\cdot24$ Å. If one then calculates the radial functions $f_l(b)$ for the first few cubic harmonics one finds that the maximum deviation of the strongest component f_4 from zero is only 0·009 for Cu and 0·014 for Fe. If we take larger spheres, this number will naturally increase. Radii larger by 0·2 Å lead to corresponding maxima of 0·033 for f_4 in Cu and 0·051 in Fe, which still are only of the order of reasonable experimental error. In the light of these figures it seems obvious that non-sphericities discovered by the use of series (8) cannot be caused by mere overlap in any significant extent.

6. Discussion

It is clear that one must have an extraordinarily good set of experimental structure amplitudes up to a certain minimum cutoff, before the search for deformations will be reasonable at all. It is an experimental fact that the deformations are only tiny effects in the intensities. If this first condition is fulfilled there should in principle be no absolute obstacles for performing such an analysis for each atom separately.

Our considerations strongly suggest that this analysis should be done in terms of atomic scattering factors. First, the experimental information lies primarily in the reciprocal space and its observability does not guarantee distinct effects in the electron density. Secondly, the convergence properties are much more favourable for scattering factor calculations than for the electron density, as shown in § 4. In the atomic factors one can really see the experimental information in a pure form, because the termination effects are concentrated in the vicinity of the cutoff. A series of the type (8) will be a suitable tool for such an analysis, at least if used as a difference series. The strict separation of the atom, made in the derivation of the series, will not produce insurmountable difficulties in interpretation of the results, even if overlapping of atoms occurs, e.g. covalent bonding. The considerations of § 5 suggest the use of slightly too large spheres in this analysis.

* Note a misprint: one of the parameters a_i for Cu should be 0·09470 instead of 0·94701.

The simple nature of the termination effects is a remarkable advantage also for estimation of the accuracy of results. Because of the approximate local separation of experimental information and the residual term the significance of different atomic factor components below the cutoff is mainly determined by the experimental accuracy alone. For series (8) the effect of non-systematic errors can easily be handled by conventional methods. All systematic errors must, of course, be studied separately. It should be noted that many of them refer specially to the average spherical behaviour f_0 and will therefore not essentially affect the reliability of non-spherical features. Errors which only depend on $\sin \theta / \lambda$ certainly belong to this category. The independence of different types of deformation in termination means here a valuable simplification. Many sources of error affect the results also indirectly by increasing our uncertainty about the residual term or about the choice of theoretical atomic factors, e.g. the temperature parameters, in difference series calculations. Now, however, since termination does not mix different types of deformation, the errors affecting only the spherical components cannot produce significant inaccuracies in the others, even through the residual term. This result is in accordance with our earlier statements (Kurki-Suonio & Meisalo, 1966).

It is true that our considerations are rather limited, since only one particular case with a high symmetry is handled. Perhaps in lower symmetries there will be some more mixing of the neighbouring components in termination as well as in overlapping. If the equilibrium nuclear position of the atom is not determined by the geometry of the crystal, a stronger coupling will arise between even and odd components. This is a kind of phase problem. The even components constitute the symmetric part of the electron density and are due to the real parts of the structure amplitudes, while the odd ones correspond to the antisymmetric distribution or the imaginary parts. It is provided in the derivation of series (7) and (8) that the origin coincides with the centre of the atom. An uncertainty about the position of the atom leads to an uncertainty regarding the phases of the structure amplitudes used in these series. Dawson (1964a) has studied the nature of this interaction and its consequences, pointing out that conventional methods of refinement are equivalent to an artificial minimization of the antisymmetric distribution or the odd components and will therefore lead to erroneous parameters. The interactions between different types of deformation will also depend on the positions of nearest neighbours. For instance, in an f.c.c. lattice the interaction between $l=6$ and $l=0$ will be somewhat stronger than in the simple cubic or b.c.c. lattices, simply because $K_6(\theta,\varphi)$ has a deep minimum in the [110] direction. However, these differences between different structures can be considered more or less as subtleties. They certainly do not affect the general features, which showed up in our example and which guarantee the usefulness of series (8) in analysis of deformations.
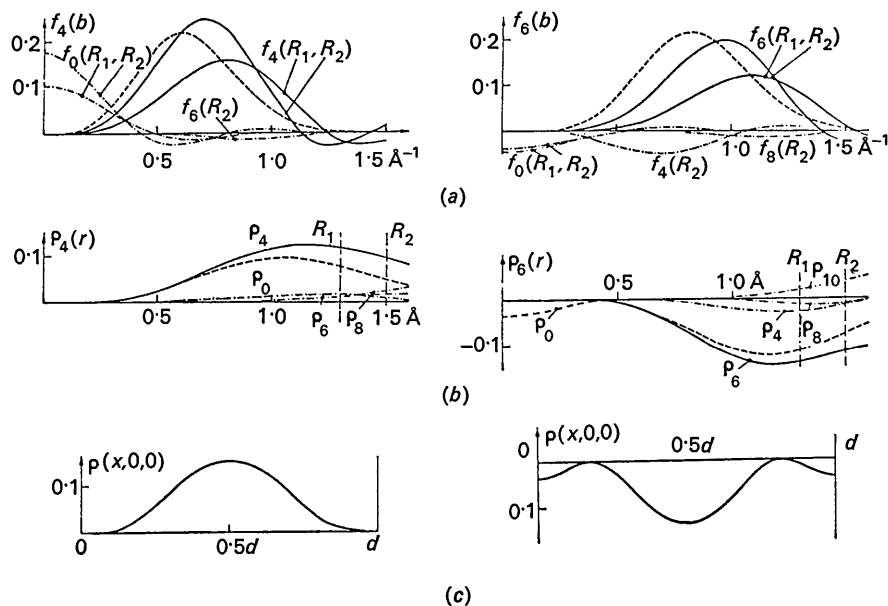

Fig. 7. Effect of overlap (a) on the scattering factor and (b) on the electron density of atoms in a simple cubic lattice and (c) the corresponding contribution to the electron density along the connecting line of neighbouring atoms; – – – – the model deformation inserted to produce the overlap [$f_4 = 0 \cdot 1$ $R_{44}(3 \cdot 3b)$, $f_6 = 0 \cdot 02$ $R_{66}(3b)$]; ——— the corresponding deformations of crystal atoms; –·–·–· irrelevant components due to overlap. The scattering factor curves refer to the contents of a sphere with close packing radius R_1 or of another with a 'too large' radius R_2 as indicated by the labelling.

The physical interpretation or the origin of the features obtained is another question. The non-sphericities can be caused by real deformations due to electronic wave functions (McWeeny, 1951, 1952, 1953, 1954; Freeman, 1959; Weiss & Freeman, 1959; Watson & Freeman, 1961; Dawson, 1964b, etc). They may also be due to vibrations of the atom (Dawson, 1967a,b,c,d; Dawson, Hurley & Maslen, 1967; Dawson & Willis, 1967). Finally, such effects can also be produced by some systematic errors, such as preferred orientation in powder measurements, which favour certain crystallographic directions. Therefore, one must be critical in judging the quality of the measurements. In any case, if something is observed which exceeds the limits of known experimental error, then the information is there, and its source must be found.

The calculations in this work were performed with the Elliott 803 computer at the Department of Nuclear Physics of the University of Helsinki and partly with the Elliott 503 computer of the Finnish State Computer Centre. The necessary programs were written by the author in Algol. For spherical Bessel functions a special procedure of Gautschi (1964) was used. A straightforward computation from recurrence relations would lead to exceptional piling up of rounding errors (Gautschi, 1967). A corresponding difficulty was not present in the calculation of associated Laguerre polynomials of the orders needed.

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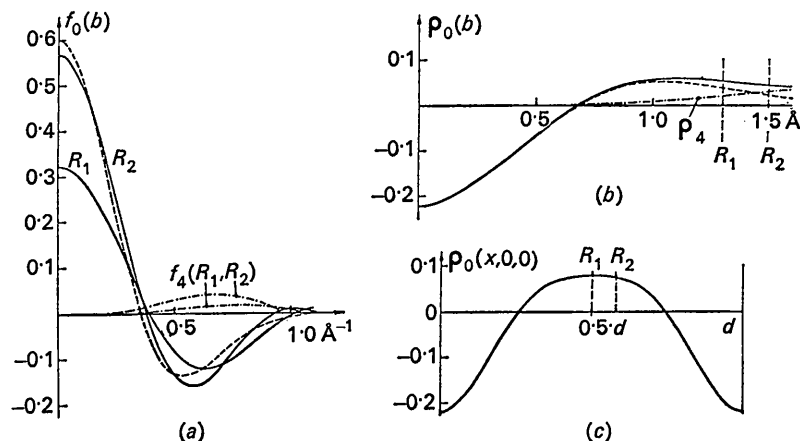KURKI-SUONIO, K. & MEISALO, V. (1966). *J. Phys. Soc. Japan*, **21**, 122.

Fig. 8. Effect of overlapping spherical distributions (a) on the scattering factor and (b) on the electron density of atoms in a simple cubic lattice and (c) the corresponding contribution to the electron density along the connecting line of neighbouring atoms; – – – – the model contribution $f_0 = 0.4\, R_{20}(3.5\,b)$ inserted to produce the overlap; ——— the corresponding spherical component in crystal atoms; –·–·– deformations produced by the overlap. The scattering factor curves refer to the contents of a sphere with close packing radius R_1 or of another with a 'too large' radius R_2 as indicated by the labelling.

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Relativistic Hartree-Fock X-ray and Electron Scattering Factors

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Kinematic X-ray and electron scattering factors, found with the use of relativistic Hartree–Fock atomic fields, are tabulated for 76 atoms and ions. Parametric fits to these are given in the range of $\sin \theta/\lambda$ from 0·0 to 2·0 Å^{-1}. A method is developed to obtain the electron structure factor for forward scattering for a crystal containing ionized atoms.

Introduction

A relativistic Hartree–Fock (R–HF) atomic wave function calculation has been programmed by Coulthard (1967). Results have been obtained by him and by the present authors for 76 atoms and ions. The calculation yields, among other data, the total charge densities $\varrho(r)$ and atomic potentials $\varphi(r)$. From these, kinematic scattering factors for X-rays and electrons, $f_X(s)$ and $f_{el}(s)$, have been found by using the equations

$$f_X(s) = 4\pi \int_0^\infty r^2 \varrho(r) \frac{\sin(4\pi sr)}{(4\pi sr)} dr \qquad (1)$$

and

$$f_{el}(s) = \frac{8\pi^2 m_0 e}{h^2} \int_0^\infty r^2 \varphi(r) \frac{\sin(4\pi sr)}{(4\pi sr)} dr, \qquad (2)$$

where $s = \sin \theta/\lambda$ Å^{-1}.

Equation (2) was used only for neutral atoms. The case of ions will be dealt with separately. For asymmetric atoms, Harada & Kashiwase (1962) found $\underset{s\to 0}{\mathrm{Lt}} f_{el}(s)$ depends on the direction in which the limit is taken. A single value is obtained in the present case, since the atom is considered as being spherically symmetrical.

A brief comparison, for mercury, between the R–HF scattering curves and those found from some other atomic models has been given previously (Doyle & Turner, 1967). Work by several authors (see Byron &

Joachin, 1967*a,b*) has taken some account of correlations between electrons in the atom. However, since this deals only with a few light atoms, the present tabulation may prove useful. The inclusion of correlations might be expected to decrease $f_X(s)$ for medium s, and to increase $f_{el}(s)$ for small and medium s. Except for the lightest atoms, the most sophisticated tables previously available were those based on the non-relativistic Hartree–Fock model by Freeman (1959) for lighter atoms, and on the Dirac–Slater model (relativ-
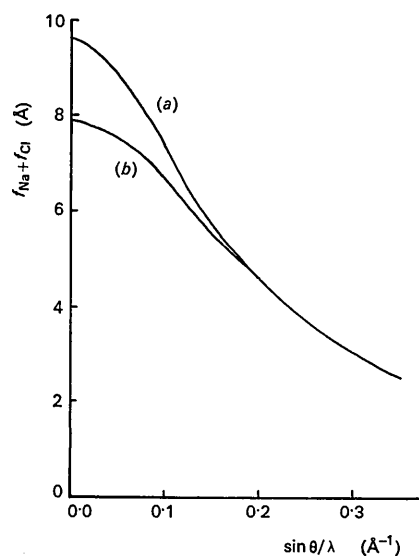

Fig. 1. $f_{Na}(s) + f_{Cl}(s)$ for (a) neutral and (b) ionized atoms.

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