

ANALYSIS OF CRYSTAL ATOMS ON THE BASIS OF X-RAY DIFFRACTION*

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Introduction

In principle it is obvious that properties of crystal atoms can be studied by X-ray diffraction. In practice this is a question of an extreme refinement of the analysis. The structure must be known, and the experimental data on the diffraction intensities must be very accurate to make the treatment of the problem reasonable.

We can, thus, assume in this context that the experimental information is given as a set of structure amplitudes F_j . In crystallographic studies this is often the end of an analysis rather than the starting point. One might think that further analysis would be trivial, because we have the basic relationship

$$(1) \quad \rho(\mathbf{r}) = \frac{1}{V} \sum_j F_j e^{-2\pi i \mathbf{b}_j \cdot \mathbf{r}_j} \quad ; \quad F_j = \int_V \rho(\mathbf{r}) e^{2\pi i \mathbf{b}_j \cdot \mathbf{r}} d^3\mathbf{r}$$

* This article contains the two lectures
"Significance of reciprocity in crystallography" and
"Crystal atoms from the point of view of X-ray diffraction" given at the congress.

between the charge density and the structure amplitudes of the crystal. The only problem seems to be, how do the experimental errors and the termination problem affect the results. We are, however, not so much interested in values of the charge density but in the physics behind. There are many kinds of phenomena involved, charge transfer, bonding, dynamics etc. which we should like to study, and this makes the further analysis a problem. We shall discuss general principles of such an analysis, its goal and the requirements we must put on it, and then study how these considerations apply on our particular problem, the study of crystal atoms.

2. Two directions of approach

Analysis is a central problem of physics in general. It is the point where theory and experiment meet. Practically speaking, its purpose is to extract information from the data. Since information must be expressed in terms of some parameters, we can define the analysis roughly as a *proper parametrization of the experimental information*. The attribute "proper" is clearly important. Its meaning, however, depends on the case treated, and a detailed discussion will be necessary to make clear its contents.

The two counterparts, the theory and the experiment are always both involved in the analysis. The results necessarily include two kinds of statements: definition of the theoretical model used, and statements concerning deviations of the experimental results from the model. Correspondingly we may use two kinds of parameters, those of the model and some others which express directly the nature of experimental information. We can, thus, approach the problem from two different directions, from the model or from the data, depending on the nature of parameters we are using in the treatment.

The first approach is, more or less, fitting of model parameters. In the second approach we try to find the essential features of the experimental information - to separate the signals from noise - in order to get a direct parametrization of it.

The phenomena we are discussing in this context are governed by quantum mechanics. If we were able to perform a complete quantum mechanical calculation we should obtain a very accurate result, which could be used even to check our experiments. However, nobody thinks to check the validity of quantum mechanics by crystallography. All of the models we can use are highly approximate. What we can and should do with our experiments is to test the validity of the approximate concepts used in order to obtain better understanding of their nature and, thus, to improve our ability to treat complex systems. A good fit is no end in itself. It is much more important to have a well defined approximate model; and a good experiment is expected to measure deviations from this model.

In our problem a natural primary model is a crystal built from rigid theoretical atoms in harmonic thermal motion. Some fitting procedure will fix the mean nuclear positions and the Debye-Waller factors of the model atoms.

If this leads to agreement with data within experimental accuracy, the model explains the data. The present problem of analysis arises when this is not the case, i.e. when the model is not sufficient, and the data contain more information than just values of the primary parameters. In treatment of this excess information a difference can be made between the two approaches.

Let us think as an example estimation of the atomic charges, cf. Kurki-Suonio and Salmo (1971) (hereafter KSS). One current method is to build model crystals from atoms in different states of ionization and to look for the best fit with the low scattering angle data. Here the ionic state is treated clearly as a parameter of the first kind. It is also possible to conclude the state of ionization by scrutiny of the electron counts in different regions of the unit cell. This is an approach of the second type, because the electron count of a given region is obtained from the experimental structure amplitudes by a definite algebraic procedure, and it is therefore just a piece of experimental information in form of a special parameter.

Continuation of the first approach to obtain more information of the atoms would involve improvement of the model by adoption of new parameters. We may, for instance, introduce unharmonicity of motion and changes in the atomic wave functions properly parametrized. Each additional parameter will improve the fit until it is complete. There are several suggestions, how to proceed, but, it is not clear what is the most appropriate way of choosing parameters. Therefore, at this stage of the problem the second approach, direct study of the experimental information, will be useful, and we shall concentrate on it. The problem is, how to find the most proper way of direct parametrization of the experimental information, how to choose the parameters to make possible a successful analysis.

3. Clarity, reliability and totality

Physical inquiry is the primary motiv of the analysis. It is essential that the analysis gives answers to our questions. The information must therefore be expressed in form of parameters which have a concrete meaning from the point of view of the physical problem studied and of the model used. This is the requirement of *clarity*, which the parameters must fulfil to have interpretational value.

In our problem this requirement means that we should use parameters characterizing single atoms of the crystal. However, only the free atom is a well defined entity. If we want to speak of an atom as a part of a larger system we need an independent definition of the atom in that system. The interest is then concentrated on comparison of this atom with the free one. In other words, we want to find parameters describing properly the changes which the free atoms undergo when packed together to form a solid. This may involve charge transfer from one atom to another, so that the electron count of the atom is an obvious parameter. Other changes can be called deformations.

There is an important conceptual difference between the crystal atom and the

free atom. Any division of the crystal into atoms is artificial and the atomic definition can never be unique. Therefore interpretation of data in terms of the atomic model must necessarily contain statements on this conceptual indeterminacy. This will appear as indeterminacy of the values of parameters obtained. It has nothing to do with the experimental inaccuracy, but it is a piece of experimental information concerning the usability of the atomic concept.

If we take the requirement of clarity seriously, each parameter used in the analysis, and the value obtained for it, should imply an independent well defined statement of some relevant property of the atom. This clearly means that we ought to get along with a small number of mutually independent parameters; otherwise the information is not well analyzed.

Nature brings up the questions we want to ask, the data determine those we are allowed to ask. This gives us the second requirement, the requirement of *reliability*: we must adopt parameters which can be evaluated reliably from the data. They must not depend strongly on unknown structure amplitudes and must not be sensitive to their errors, random or systematic. In the 4th section we shall study in detail the explicit consequences of this requirement.

Finally, the analysis should lead to an interpretation of the data in terms of the parameters. This will be obtained if it is possible to exhaust the available experimental information by the set of parameters. This is the requirement of *totality*. It is fulfilled when no more independent information can be extracted from the data. It is not easy to judge by certainty when this situation is achieved. Obviously, this will be the case, if the data can be completely reconstructed from the parameters obtained. If this reconstruction is not exact we ought to be able to check whether the differences have the nature of pure random fluctuations or not. On the other hand, if it is exact, our parameters have not accomplished any separation of information from errors, which a good analysis should be able to do. Thus we encounter here the problem of constraints and their effect on signal shape: by appropriate application of our knowledge about the system we ought to be able to distinguish weaker signals from the background noise and, thus, to improve the degree of totality of our analysis.

Totality alone can certainly be achieved by using many parameters. But, if we let the two first conditions determine our choice of parameters, it will be a difficult requirement. We cannot be sure beforehand how well it will be satisfied. The degree of totality can be checked only afterwards, and in this way it is, more or less, a measure of the final success of the analysis.

These three requirements form a basis on which we can judge the relative merits of different methods of analysis, and we can use them as a guidance when we seek better methods. If we could satisfy all of them simultaneously in our present problem, we were able to transform all information contained in the set $\{F_{\text{obs}}\}$ into quantitative statements on deviations of crystal atoms from theoretical free atoms. If it is not possible to make this analysis total, the data will give us also some information on the nature of the deficiency of the atomic model.

4. Reciprocity and reliability

Reciprocity means conventionally the relation between the real *space* and the Fourier or reciprocal space. The charge distribution lies in the real space of the position vector \mathbf{r} , while the geometry of scattering is defined by the scattering vector \mathbf{b} which is a vector of the reciprocal space. Reciprocity refers to the fact that, qualitatively speaking, the scales of these two spaces as defined by the real lattice and the reciprocal lattice are reciprocal.

We may also understand reciprocity as the relation of the charge distribution $\rho(\mathbf{r})$ and its scattering amplitude $f(\mathbf{b})$, which define the physical *system* in the real and reciprocal space, respectively. They are related through the Fourier transformation

$$(2) \quad \rho(\mathbf{r}) = \int f(\mathbf{b}) e^{-2\pi i \mathbf{b} \cdot \mathbf{r}} d^3 b \quad ; \quad f(\mathbf{b}) = \int \rho(\mathbf{r}) e^{2\pi i \mathbf{b} \cdot \mathbf{r}} d^3 r \quad ,$$

and therefore a sharply peaked $\rho(\mathbf{r})$ has a flat $f(\mathbf{b})$ and vice versa.

Here we take a third view. We connect the reciprocity with *quantities* or parameters representing properties of the system.

We restrict the treatment on a class of quantities which can be called *linear parameters*. A linear parameter X is uniquely defined, independent of the system, by its *distribution* $\gamma_x(\mathbf{r})$ in real space or its distribution $q_x(\mathbf{b})$ in reciprocal space. The value of X in any system is then given by the integral

$$(3) \quad X = \int \gamma_x(\mathbf{r}) \rho(\mathbf{r}) d^3 r = \int q_x(\mathbf{b}) f(\mathbf{b}) d^3 b \quad .$$

The two distributions are related by the Fourier transformation

$$(4) \quad \gamma_x(\mathbf{r}) = \int q_x(\mathbf{b}) e^{2\pi i \mathbf{b} \cdot \mathbf{r}} d^3 b \quad ; \quad q_x(\mathbf{b}) = \int \gamma_x(\mathbf{r}) e^{-2\pi i \mathbf{b} \cdot \mathbf{r}} d^3 r \quad .$$

They are therefore reciprocal to each other in the same way as the charge distribution and its scattering amplitude. A sharply local quantity is nonlocal in reciprocal space and vice versa. The widths of the two distributions are, more or less, inversely proportional.

Let us look, for instance, the three quantities:

1. Charge density at a point
2. average charge density at distance R from the origin
3. the electron count in a sphere of radius R ,

which can be defined by the distributions shown in table 1. They present three different degrees of locality in real space. The first quantity is strictly local, concentrated on one point, the second is uniform on a spherical surface, and the third is uniformly distributed in the volume of a sphere. Their reciprocal distributions demonstrate clearly the nature of the reciprocity. The first one is completely nonlocal, uniform in the whole reciprocal space, while the two others show different degrees of localization around the origin, fig. 1.

Table 1. Examples of real and reciprocal distributions γ and q of quantities X .

X	$\gamma_X(r)$	$q_X(b)$	$q_X(b \rightarrow \infty)$
$\rho(r_0)$	$\delta(r - r_0)$	$\exp(-2\pi i b \cdot r_0)$	~ 1
$\rho_0(R)$	$\frac{\delta(r - R)}{4\pi r^2}$	$\frac{\sin 2\pi R b}{2\pi R b}$	$\sim b^{-1}$
$\int \rho(r) d^3r$ sphere	$\begin{cases} 1; r \leq R \\ 0; r > R \end{cases}$	$4\pi R^3 \frac{j_1(2\pi R b)}{2\pi R b}$	$\sim b^{-2}$

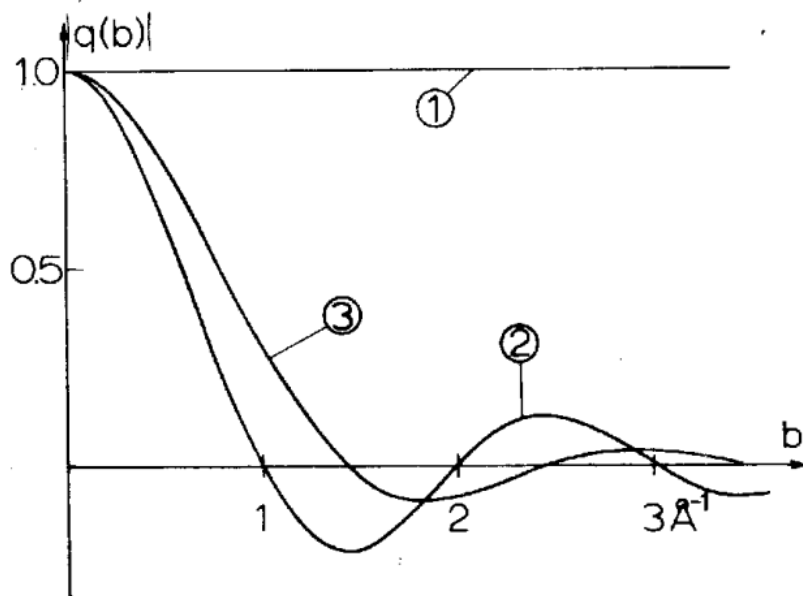


Figure 1. Reciprocal distributions 1. of the charge density at a point r_0 , 2. of the average charge density on a spherical surface of radius $R=0.5 \text{ \AA}$ and 3. of the electron count in the same sphere.

If the system is a crystal, the scattering amplitude is a lattice of δ -functions and the second integral in eq. (4) gets the form of a series

$$(5) X = \frac{1}{V} \sum q_x(\mathbf{b}_j) F_j$$

where the summation runs through the reciprocal lattice. Thus, the reciprocal distribution tells us the importance of different structure amplitudes in calculation of the value of X for the crystal. Its behaviour is therefore decisive in the problem of reliability.

This problem resolves naturally into two parts: the effect of experimental uncertainties and the residual term problem. If we do not think about the experimental difficulties, then, in principle, the first problem is far simpler, because it concerns a finite number of terms. The rate of convergence depends on the asymptotic behaviour of the reciprocal distribution. In this respect the three examples of table 1 represent different orders of magnitude.

Because the asymptotic behaviour of the Fourier transform reflects the degree of discontinuity of the function, the microstructure of the real distribution seems to determine the difficulty of the termination problem. However, we must take into account the whole region beyond a fixed finite cutoff, determined by the X-ray wave length, rather than just the behaviour at infinity. We should also note that in all three of our examples series (5) will converge only due to the strong asymptotic decrease of the structure amplitudes. They have normally considerable values at the cutoff and, thus, the residual term will be large in any case. On the other hand, it can be assumed that the theoretical free atom model provides asymptotically reliable values. Therefore, in practice, the terms closely beyond the cutoff will be most important in the termination problem, and the degree of the reliability of X will in the first place depend on the values of its reciprocal distribution in that region of the reciprocal space.

In our examples this means that below some critical radius there will be no substantial difference in the reliability of these three quantities. Suppose the cutoff is at about $b = 1.0 \text{ \AA}^{-1}$ (1.2 \AA^{-1} is the limit of CuK α -radiation). From fig. 2 we see then that the radius must be about 0.5 \AA or larger to make the two last quantities essentially more reliable than $\rho(r_0)$.

More generally, we can conclude from the reciprocity that non-local quantities, or quantities with wide distributions in real space will be essentially more reliable than the more local ones. To make this statement more accurate we need a more quantitative definition for the reciprocity.

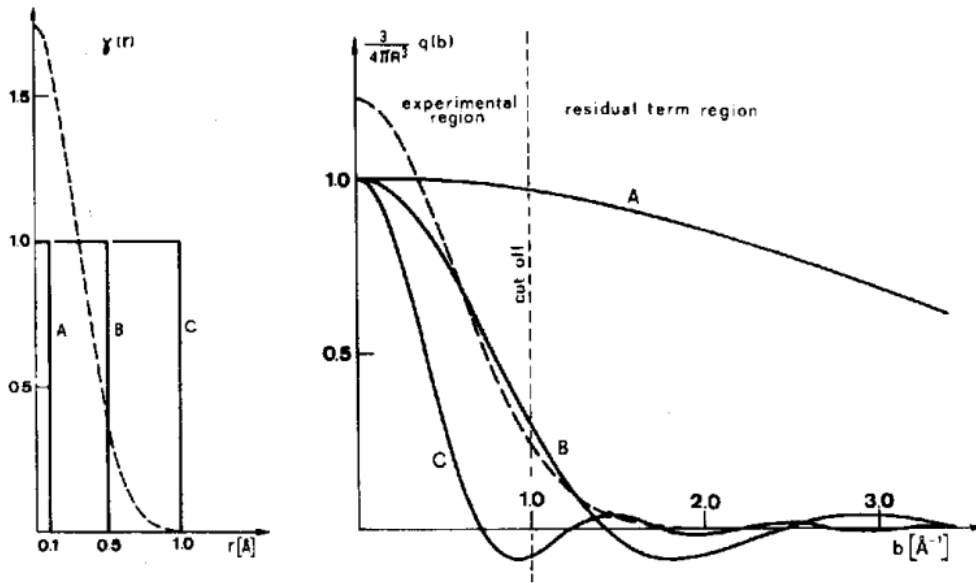


Figure 2. Distributions $\gamma(r)$ and $q(b)$ of the electron count in a sphere for three different radii. The dashed curves are Gaussians with 3-dimensional least squares fit to the case B.

The conventional "uncertainty relation"

$$(6) \quad \Delta r \Delta b \geq \frac{3}{4\pi}$$

of the Fourier transformation applies naturally on the distributions $\gamma(r)$ and $q(b)$, with the normal definitions

$$(7) \quad (\Delta r)^2 = \langle (r - \langle r \rangle)^2 \rangle ; \quad (\Delta b)^2 = \langle (b - \langle b \rangle)^2 \rangle ,$$

$$(8) \quad \langle f(r) \rangle = \frac{\int f(r) |\gamma(r)|^2 d^3 r}{\int |\gamma(r)|^2 d^3 r} ; \quad \langle g(b) \rangle = \frac{\int g(b) |q(b)|^2 d^3 b}{\int |q(b)|^2 d^3 b}$$

However, it does not represent a quantitative reciprocity theorem because of the inequality sign. For instance, in all three of our examples we have an infinite Δb , although $\Delta r = 0$ only for the first one. This again shows the dominant role of the

“microstructure”. To get forward we ought to define in some way the large-scale or macroscopic behaviour of distributions which clearly also obeys some kind of a reciprocity theorem.

Here we refer to well known properties of the Fourier transformation:

First, *the harmonic oscillator wave functions are form invariant in the Fourier transformation*: If

$$(9) \psi_n(\mathbf{r}) = a^{3/2} f(a\mathbf{r}) \quad \left(a^2 = \frac{m\omega}{\hbar} \right)$$

is an arbitrary n quantum state of an isotropic three dimensional harmonic oscillator, its Fourier transform is given by the expression

$$(10) \varphi_n(\mathbf{b}) = \int \psi_n(\mathbf{r}) e^{2\pi i \mathbf{b} \cdot \mathbf{r}} d^3 r = i^n A^{3/2} f(A\mathbf{b})$$

where

$$(11) Aa = 2\pi$$

Gaussian is the most simple example corresponding to $n = 0$.

Secondly, *an n quantum state of a harmonic oscillator obeys the “uncertainty equation”*

$$(12) \Delta r \Delta b = \frac{1}{2\pi} \left(n + \frac{3}{2} \right) .$$

Thirdly, *least squares fit is conserved in the Fourier transformation*. If $g(\mathbf{r})$ is the Fourier transform of $G(\mathbf{b})$, this theorem says

$$(13) \int |g(\mathbf{r}) - \gamma(\mathbf{r})|^2 d^3 r = \int |G(\mathbf{b}) - q(\mathbf{b})|^2 d^3 b .$$

Particularly, if $g(\mathbf{r})$ is the Gaussian with the best least squares fit to the distribution $\gamma(\mathbf{r})$, then $G(\mathbf{b})$ will be that Gaussian which has the best fit to the corresponding reciprocal distribution $q(\mathbf{b})$, cf. fig. 2.

It is obviously possible to define the macroscopic behaviour of a distribution, for

instance, as that Gaussian which has the best least squares fit to the distribution. The macroscopic widths $\Delta_M r$ and $\Delta_M b$ of the two distributions of a quantity X would correspondingly be equal to Δr and Δb of their best fit Gaussians. With these definitions we have the exact reciprocity theorem

$$(14) \quad \Delta_M r \Delta_M b = \frac{3}{4\pi} .$$

This is mathematically valid for any quantity with a square integrable distribution. It cannot be applied, for instance, to any δ -function distribution, but this is no essential limitation because use of strict δ -functions is never necessary.

There are, however, important practical limitations. Gaussian definition of the macroscopic behaviour will be reasonable only for distributions which have some resemblance to a Gaussian behaviour. The electron count of a sphere is clearly a positive case having

$$\Delta r = \sqrt{\frac{3}{5}} R \approx 0.77 R ; \Delta b = \infty$$

but

$$\Delta_M r = 0.70 R \quad \text{and} \quad \Delta_M b = 0.34 \frac{1}{R} .$$

Any distribution with a harmonic angular dependence $K_l(\theta, \varphi)$ of order $l > 0$, would represent an obviously negative example, since the best fit Gaussian would be identically zero. In such a case an appropriate definition of the macroscopic behaviour and the macroscopic width can be based in a similar way on the function

$$Ca^{3/2} (ar)^l \exp(-\frac{1}{2} a^2 r^2) K_l(\theta, \varphi)$$

which is the most simple harmonic oscillator wave function with the relevant angular behaviour and corresponds to an l quantum state. This leads to the reciprocity theorem

$$(14') \quad \Delta_M r \Delta_M b = \frac{1}{2\pi} \left(l + \frac{3}{2} \right) .$$

It is not possible to put the reciprocity theorem in a general form which would be satisfactory for all possible cases simultaneously. These considerations show, however, that the concept of reciprocity in macroscopic sense, as we need it, is not merely qualitative. We can make the practical conclusion that integral parameters are more reliable than the local ones. To be more concrete, if the cutoff is at about $b = 1 \text{ \AA}^{-1}$, then only quantities with a $\Delta_M r > 0.4 \text{ \AA}$ can belong to the class of the best possible reliability. The condition is necessary but not sufficient. Only a closer study of the reciprocal distribution will make clear the nature of the residual term problem for any particular quantity. It gives, however, a suggestion of the type of parameters we should seek. Because the atoms have radii of the order of 1 \AA it is obvious that we can derive from the data integrated properties of atoms much more accurately than their charge distributions in detail, and we should tend to describe the crystal atoms in terms of such parameters rather than by density maps.

5. Atomic definition

The assumption that the crystal is composed of atoms means in this context, that the composite charge density of the crystal is the sum of atomic contributions

$$(15) \rho(\mathbf{r}) = \sum \rho_n(\mathbf{r} - \mathbf{r}_n) ,$$

where \mathbf{r}_n is the mean nuclear position of the n^{th} atom and the summation runs over all atoms; and that the crystal structure amplitudes are certain linear combinations of the atomic factors at relevant scattering angles

$$(16) F_j = \sum f_n(\mathbf{b}_j) e^{2\pi i \mathbf{b}_j \cdot \mathbf{r}_n} ,$$

with n running through the atoms of one unit cell.

For a model crystal there seems to be no problem since we start from known theoretical atoms and we are, thus, going from right to left in eqs. (15) and (16). This construction is misleading, because in reality the composite system is primary and the problem is to decompose the left hand sides of eqs. (15) and (16) into atomic contributions which is not possible without some underlying atomic definition. The definition must arise from the properties of the crystal. The free atom is a completely different system and cannot provide a basis for this purpose. As known by experience, superposition of free atoms gives a good approximation for the composite charge density of the crystal. This, however, does not necessarily mean that the free atoms would represent the crystal atoms. They just correspond to one possible way to decompose the structure, but there is no *a priori* reason why we should prefer this particular way. This applies also to the model crystal, because we must use our

definitions consistently.

As emphasized in sec. 3, it is clear that no unique definition can be given for the crystal atoms. It is also obvious that no distant parts of the charge distribution can be assigned to one atom; an electron cannot be said to belong to an atom for any other reason than for being close enough to its nucleus. We call this the *requirement of locality*, which the atomic definition must fulfil to be physically reasonable. This means simply that we should define the atom as the charge distribution peak at the relevant position. The problem is where to draw the limit, but this is just an expression of the conceptual indeterminacy of the atom. The definition cannot be more accurate.

It is easiest to keep track on the requirement of locality by looking at the radial charge density

$$(17) 4\pi r^2 \rho_0(r) = \int_{4\pi} \rho(r) r^2 d\Omega = 4\pi r^2 \frac{1}{V} \sum F_j \frac{\sin 2\pi b_j r}{2\pi b_j r}$$

around the atomic positions. Figures 3, 4 and 5 show four examples: the radial densities of Ca and F ions in CaF_2 , NH_4 and Cl ions in NH_4Cl and the atoms in diamond and silicon according to the data of Togawa (1964), Pesonen (1971), Göttlicher and Wölfel (1959) and Hattori, Kuriyama, Katagawa and Kato (1965), hereafter T, P, GW and HKKK respectively.

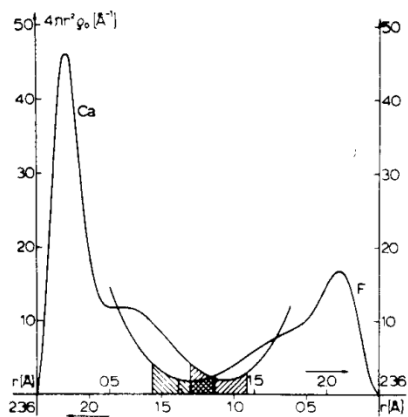


Figure 3. Radial charge densities $4\pi r^2 \rho_0(r)$ of Ca and F in CaF_2 with an indication of the integrated electron counts of the peaks, as calculated from the T data. (From an unfinished work by Ruuskanen and Kurki-Suonio (RKS).)

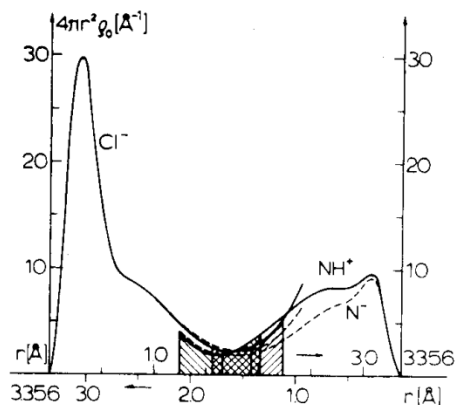


Figure 4. Radial charge densities $4\pi r^2 \rho_0(r)$ of NH_4 and Cl in NH_4Cl as calculated from the P data. The dashed curves correspond to a model built of N^- and Cl^- . (From a preliminary analysis).

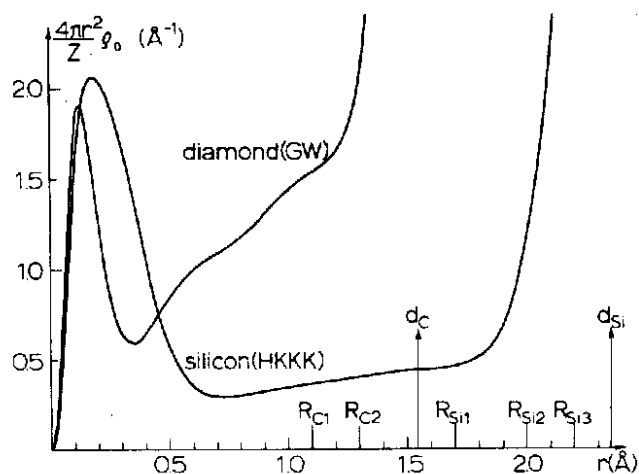


Figure 5. Radial charge density $4\pi r^2 \rho_0(r)/Z$ of an atom in diamond and silicon as calculated from the GW and HKKK data. (Figure 1 of KSR).

To obtain these curves Gaussian representations were used for the atomic factors at large $\sin \theta/\lambda$ and the Debye Waller factors of the Gaussian crystal were chosen such that the difference series $\Delta\rho_0$ was flat at the atomic centra. The radial charge density (17) was calculated for the Gaussian crystal on the basis of the analytic expression and these values were corrected by a difference series with coefficients $F_{\text{Obs}} - F_{\text{Gauss}}$. This procedure corresponds to the method used by Hosemann and Bagchi (1953, 1962) for charge density calculations, and it is expected to yield pure experimental results with termination errors minimized. According to the preceding section the quantity (17) fulfils the requirement of reliability for $r > 0.4 \text{ \AA}$, and it is justified to believe that in those regions the significance of the results depends only on the accuracy of the experimental values F_{Obs} .

As seen from figs. 3 to 5 the radial charge density (17) shows clearly the relation of an atom to its surroundings and, thus, the possibilities to define the crystal atom as an independent entity. The distance of the minimum is *the radius of the best separation* of the atom from its surroundings. The distribution within this radius behaves essentially as a distribution centered at the relevant nucleus, and it is natural to take it as the operational definition of the atom, or the 'effective atom' in the sense of X-ray diffraction. The value of the radial density at the minimum is a measure of the conceptual uncertainty of this definition.

The figures show also the characteristic difference between the atoms of ionic compounds and covalent crystals for which our definition, more or less, falls down because of the pronounced bond contribution. Fig. 4 shows also for comparison the situation in a model crystal built from free ions Cl^- and N^- . The ions of the real crystal are more compact and thus better definable than the atoms of the model crystal.

To demonstrate the need for such a simple atomic definition we shall discuss more closely the determination of the ionic state of crystal atoms in the light of relevant literature, cf. KSS.

6. The ionic state

The determination of ionic state by X-diffraction was proposed already by Debye and Scherrer (1918). They suggested a procedure where the information obtained from low angle data was extrapolated to zero scattering angle. The classical book of Compton (1926) presents another, somewhat more sophisticated method based on the charge distribution. By these two works the initiative was given to development of two basically different methods which can be called the extrapolation method and the integration method corresponding to two different principles followed in dividing the crystal into atoms. The extrapolation methods correspond to a decomposition of the structure amplitudes into atomic factors according to eq. (16) and an extrapolation to zero scattering angle. The integration methods involve some division of the charge density according to eq. (15) into atomic contributions and a subsequent integration to count the electrons.

In fifties severe difficulties were realized leading to a wave of critical articles. The criticism culminated in the completely negative conclusion by Bijvoet and Lonsdale (1953), that it is impossible to determine the ionic state by X-ray diffraction. They referred particularly to the extrapolation method. Applications of the integration method led to a similar development. The critical articles of Black (1955), Taylor (1954) and Black and Taylor (1958) ended up with an equally pessimistic view.

Cochran (1958, 1961), however, took the question up again emphasizing the necessity of careful definitions of the concepts. And it was shown in an article by Calder, Cochran, Griffiths and Lowde (1962) that the distribution of charges in LiH, which was the original cause of the whole discussion, does indicate single ionization of the components.

These are the main points of the long history, and it is only left to show, why and in which sense some positive statements are possible.

It is essential in this problem that we want to study the changes of atoms when they become a part of a solid. Information of these changes is included in the low angle behaviour of the scattering factors. Extrapolation involves necessarily an assumption of the low angle behaviour. Most often it is the free-atom-like behaviour we assume; direct comparison of data with different atomic models is nothing but a free-atom-like extrapolation. But this is contrary to what we know and to what we try to get out from our analysis. There is no space left for the experimental information if the low angle behaviour is fixed beforehand by extrapolation.

The impossibility of the extrapolation method is obvious if we look at the structure factors of different models with different states of ionization. The differences are often extremely small, almost always smaller than the experimental errors, so that it is hopeless to stare at their fit with the experimental values. One has tried to avoid the problem by electron diffraction, where the differences in the lowest order structure amplitudes are strongly enhanced. It is then possible to see, which of the models has best fit with the low angle data, but the procedure is still not more

reliable because the low angle behaviour will not be that of the free atoms.

It is instructive to note that this problem concerns even the most obvious ionic crystals such as alkali halides. The structure amplitudes, say, of $K^0 Br^0$ and $K^+ Br^-$ model crystals are all almost equal. This, however, does not indicate that the atomic charges of the crystal are indeterminate but just that the atomic charges of the free model atoms have little correlation to the charges of the atomic peaks. If it would not be possible to see that KBr is composed of ions, then X-ray diffraction would not be worth much.

The same problem appears in connection of the integration method, if we look at the difference series and try to make conclusions on the basis of deviations of the integrated electron counts from model values. For instance, Weiss (1966) states in his book that there are very little differences in the electron counts of $Mg^0 O^0$, $Mg^{+1} O^{-1}$ and $Mg^{+2} O^{-2}$ model crystals. This of course is due to the fact that they have almost equal structure amplitudes. Fig. 6 shows the same situation in $K^0 Br^0$ and

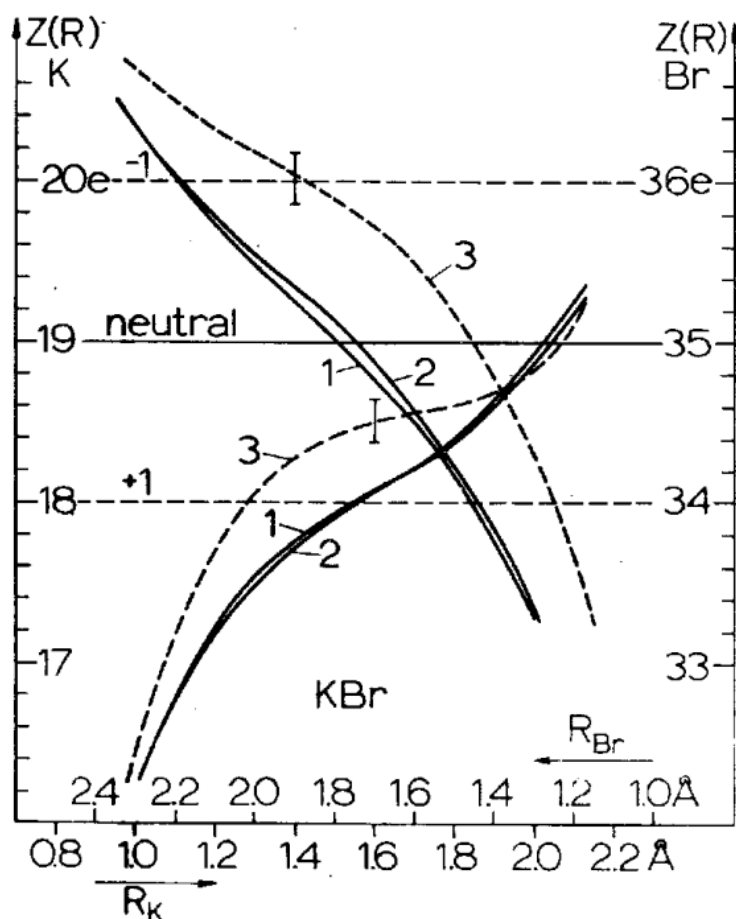


Figure 6. Integrated electron counts in spheres around K and Br atoms in KBr. The curves correspond to 1. $K^0 Br^0$ model crystal, 2. $K^+ Br^-$ model crystal, 3. experimental data of Meisalo and Inkinen (1967). (Fig. 1 of KSS).

$K^+ Br^-$ model crystals. Again, this does not imply any conclusion on the atomic charges of the real crystal.

It is misleading to think, for instance, that $K^0 Br^0$ represents a crystal with neutral atoms. We had better realize that it is an artificial model lacking some essential features of a crystal. It should be understood only as a model for the composite charge distribution, and the free atoms, from which it is formally built, have no relevance in it. It cannot provide reasonable atomic parameters for comparison with experimental values. Its main role is just to provide *estimates for residual terms*, so that we shall be able to calculate the integrated charges or any other quantities X from the experimental data.

This is demonstrated by table 2 showing some experimental atomic charges calculated on the basis of the local definition of the preceding section or, simply, the electron counts within the radius of best separation. We observe that the state of ionization comes out directly from the data. Similarly, integration of the areas of the peaks in figs. 3 and 4 gives correct electron counts of Ca^{++} , F^- , NH_4^+ and Cl^- . The corresponding values for different model crystals serve just for demonstration of the irrelevance of the free atom parameters.

Table 2. Degrees of ionization n^+ and n^- of the atoms in some crystals as obtained from electron counts corresponding to the local definition of crystal atoms. The derivative dn/dr is a relative measure of the conceptual indeterminacy. (Kurki-Suonio and Salmo 1971).

	neutral model		ionic model		experimental				
	n^+	n^-	n^+	n^-	n^+	$\frac{dn^+}{dr}$	n^-	$\frac{dn^-}{dr}$	$n^+ - n^-$
KBr	+0.8	-0.2	+1.0	-0.4	+0.45	0.6	-1.15	1.4	1.6
NaF	+0.9	-0.2	+0.9	-0.6	+0.85	1.4	-0.75	2.0	1.6
LiF	+0.9	-0.3	+1.0	-0.6	+0.95	1.0	-0.70	1.8	1.65
MnO	+1.8	-0.2	+2.0	-1.2	+2.0	4.0	-1.7	4.0	3.7
CoO	+1.5	-0.1	+1.9	-1.0	+2.0	2.6	-0.7	3.2	2.7
NiO	+1.3	0.0	+1.9	-1.0	+2.1	5.4	-1.8	5.0	3.9

The ionic state expresses only one, though important, property of the atoms. To obtain a complete description of the experimental information we need more parameters. The atomic charge is a typical one and the preceding discussion applies in

many respects to the whole analysis. Particularly, the same dualism dominates all of the historical development: conclusions are based either on charge density or on comparison of scattering factors. There is also the same temptation to misuse theoretical free atom parameters; and the same cure can be recommended: careful definition of basic concepts and use of purely experimental values for the parameters i.e. the full series (5) instead of difference series, which can be realized e.g. by Gaussian procedures similar to that explained in connexion of series (17).

7. Charge density analysis

The conventional analysis in terms of charge density fits in our general scheme. The values $\rho(\vec{r}_0)$ at all points \vec{r}_0 of the unit cell form its basic set of linear parameters. The main advantage is, that it gives a clear and concrete view on the situation in crystal. This is, however, not enough to satisfy our requirement of clarity. It uses an infinite number of parameters, none of which is very informative from the point of view of crystal atoms. It can lead to definite statements of the crystal atoms only through a visual survey of the maps drawn, which means some kind of an integration by eye.

From the point of view of reliability these quantities are the worst one can think, because the reciprocal distribution is uniform over the whole reciprocal space. Only the totality is fulfilled completely. The charge distribution is just another way to represent the data, and that is why it is so useful in preliminary study of the nature of the information.

To avoid difficulties caused by the ultimate locality Weiss (1966) proposed the use of charge distributions with density values $\bar{\rho}(\vec{r}_0)$ averaged over a small cube. The real distribution of this quantity is constant within the cube and zero outside. This certainly improves the reliability, but rather large cubes are required before this really matters, cf. fig. 2. According to sec. 4 the edge should be at least of the order of 1.0 \AA if the data extend to 0.5 \AA^{-1} in $\sin \theta/\lambda$. This would yield strongly smoothed charge distribution maps with a somewhat questionable interpretational value.

8. Atomic factor analysis

The atomic scattering factors refer directly to the single atoms. There seems to be a direct connexion between them and the experimental structure amplitudes through eq. (16). This has given rise to studies where "experimental atomic factors" are derived from the data by simple algebra, interpolation and extrapolation. This procedure is, however, bound to the behaviour of the theoretical atomic factors in a way which, strictly speaking, leads to misuse of the parameters of the free model atoms just as explained in sec. 6, and, consequently, to misinterpretation of data, cf. also Kurki-Suonio (1970). The point is again that the method leaves the atoms undefined;

it merely correlates them in some vague manner to the formal constituents of the model. Therefore, the results do not represent the experimental information in a definite sense.

The unsatisfactory nature of such procedures has led to a search for alternative methods. The first idea (Kurki-Suonio 1959) was to try analysis in terms of the scattering amplitude

$$(18) f_T(\mathbf{b}) = \int_T \rho(\mathbf{r}) e^{2\pi i \mathbf{b} \cdot \mathbf{r}} d^3r$$

of a region T . For any region T and any value of \mathbf{b} this is a linear parameter. We can also apply directly the local definition of an atom to obtain from eq. (18) its experimental atomic factor with a certain conceptual indeterminacy. The result coincides at $\mathbf{b} = 0$ with the atomic charge defined in the previous section.

The reciprocal distribution of $f_T(\mathbf{b}_0)$ is

$$(19) q(\mathbf{b}) = \int_T e^{2\pi i (\mathbf{b}_0 \cdot \mathbf{b}) \cdot \mathbf{r}} d^3r$$

If T is a sphere of radius R centered at the origin we get

$$(20) q(\mathbf{b}) = 4\pi R^3 \frac{j_1(2\pi R|\mathbf{b} - \mathbf{b}_0|)}{2\pi R|\mathbf{b} - \mathbf{b}_0|}$$

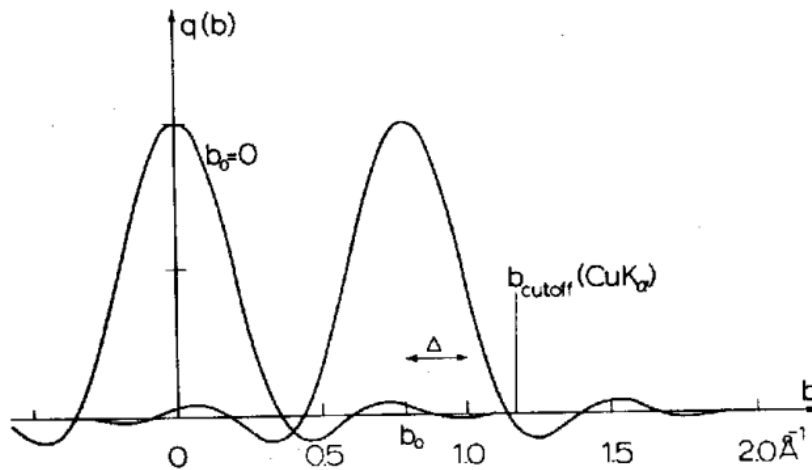


Figure 7. The reciprocal distribution of the scattering amplitude $f_T(\mathbf{b}_0)$ of a charge distribution within a sphere of radius $R = 2.0 \text{ \AA}$ for $\mathbf{b}_0 = 0$ and $\mathbf{b}_0 \neq 0$ along the straight line through the point \mathbf{b}_0 in the reciprocal space.

From its behaviour, fig. 7, we easily see the reliability of f_T . It is for any b_0 the same spherically symmetric function in 3-dimensions centered at b_0 . When b_0 approaches the cutoff value of data i.e. the surface of a sphere with the radius b_{cutoff} , the main peak of this distribution is gradually displaced into the residual term region. The region T must have atomic dimensions, and for small b_0 $f_T(b_0)$ is therefore of the highest class of reliability. With increasing b_0 the reliability keeps first practically unchanged, until b_0 exceeds the value $b_{\text{cutoff}} - \Delta$, where Δ is the width of the main peak and is smaller for larger regions. Then the reliability starts going down rapidly until at b_{cutoff} it is of about the same quality as that of the local charge distribution and finally at $b_0 = b_{\text{cutoff}} + \Delta$ there is no information about $f_T(b_0)$ in the data. This shows what we mean by saying somewhat loosely that the analysis is kept in the reciprocal space and that therefore we obtain f_T reliably up to b_{cutoff} but not beyond.

Analysis based on estimation of atomic factors by eq. (18) has been applied to a number of crystals with simple structures. Figures 8 to 13 show two typical examples:

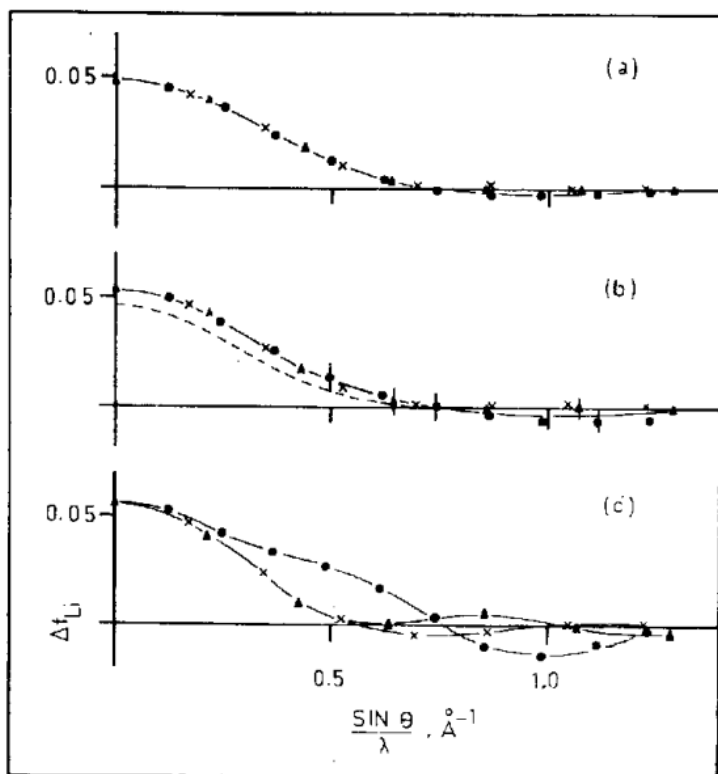


Figure 8. Differences between experimental and theoretical f_T values for a Li-centered sphere with the radius $R = 0.63 \text{ \AA}$ (a), $R = 0.78 \text{ \AA}$ (b), $R = 0.92 \text{ \AA}$ (c) in the crystallographic directions $[h00]$ (solid circles), $[hh0]$ (crosses) and $[hhh]$ (triangles). In fig. 8 (b) the standard deviation calculated from experimental errors has been entered for a few points. The broken curve in fig. 8 (b) is obtained with a scale factor lower by 1% (Fig. 4 of M1).

the results on LiF by Merisalo and Inkinen (MI) (1966) and the analysis of CaF₂ by Kurki-Suonio and Meisalo (KSM) (1966). These results are obtained by difference series calculations. They, thus, represent deviations of the atomic factors from those of the model crystal. Their dependence on the radius expresses the nature of the conceptual uncertainty. Figs. 8 and 11 indicate relative compression of the positive ion. From figs. 9, 10, 12, 13, we see that the fluorine ions possess, at least in LiF, a significant nonsphericity.

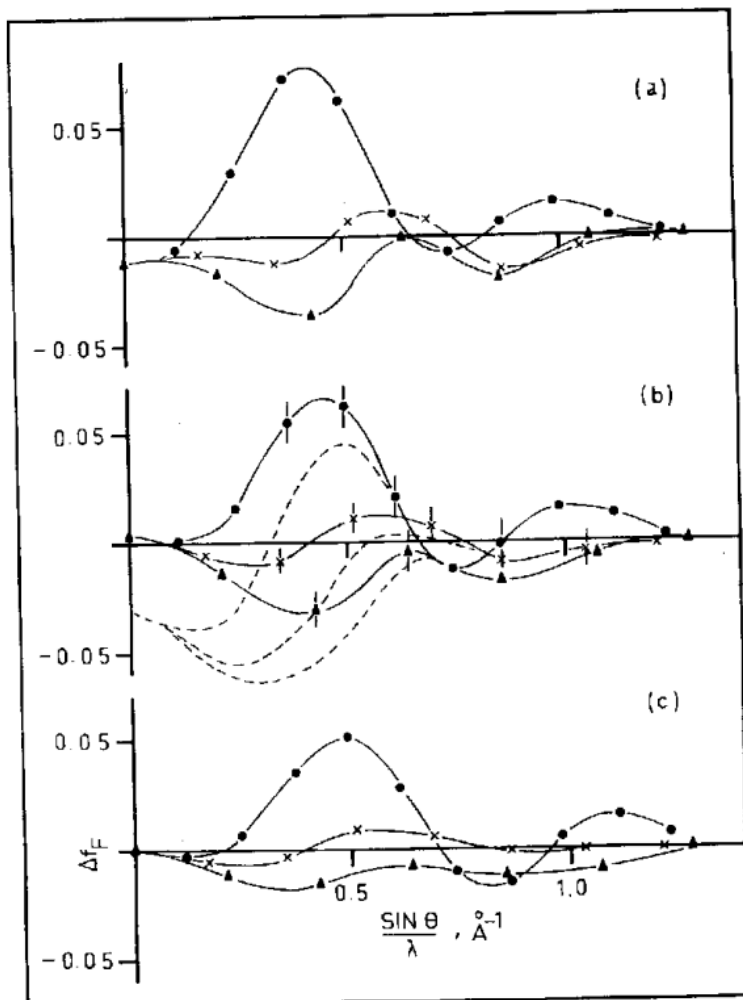


Figure 9. Differences between experimental and theoretical f_T values for an F-centered sphere with the radius $R = 1.38 \text{ \AA}$ (a) $R = 1.23 \text{ \AA}$ (b), $R = 1.09$ (c). The symbols are the same as those in fig. 8. In fig. 9 (b) the standard deviation calculated from experimental errors has been entered for a few points. The broken curves in fig. 9 (b) are obtained with a scale factor lower by 1 % (fig. 5 of MI).

These analyses are not quite satisfactory in conceptual sense, because only difference series are calculated and not the experimental atomic factors themselves.

Still, the nonsphericities of the crystal atoms are quantitatively described, because they are negligible in the model. Even this need not be true always, since generally the overlapping may produce some nonsphericities of the peaks in the model crystal. In LiF and CaF₂ structures this would affect specifically the results in [100] and [111] directions, respectively, due to the nearest neighbours.

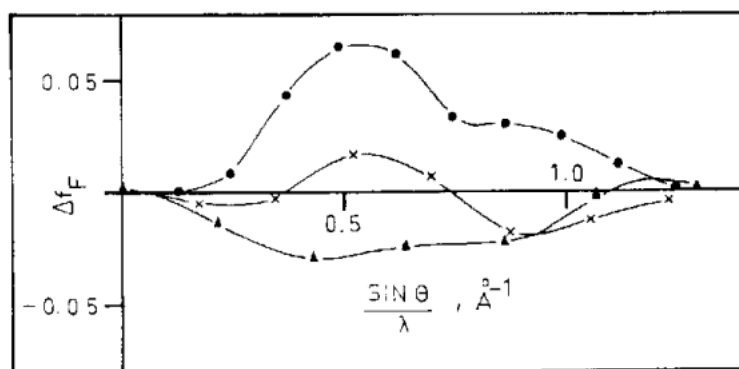


Figure 10. The effect on fig. 9 (b) of dividing the coincident reflections in the ratio of the intensities measured by Krug, Witte and Wölfel (1955). (Fig. 6 of MI).

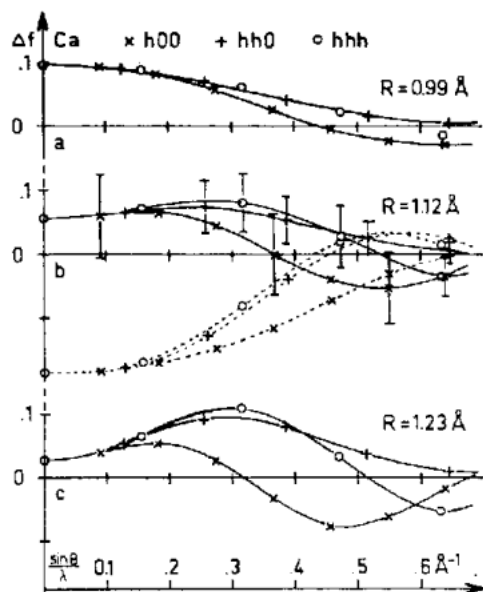


Figure 11. The difference between the experimental and theoretical atomic factor f_T of the calcium ion calculated in main crystallographic directions using three spheres of different sizes. The dotted curves are obtained with the original scale which was lower by 2 %. (Fig. 2 of KSM)

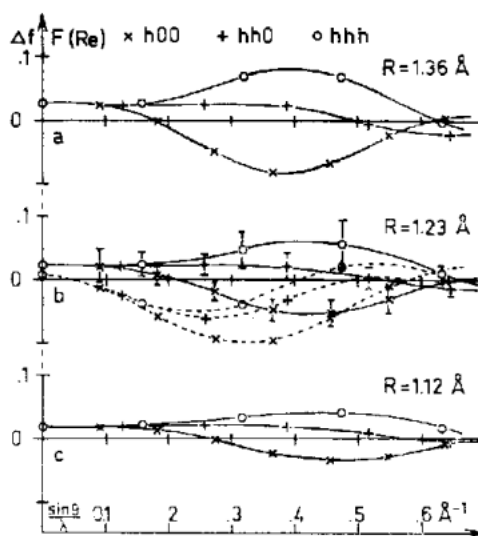


Figure 12. The real part of the difference between the experimental and theoretical atomic factor f_T of the fluorine ion calculated in main crystallographic directions using three spheres of different sizes. The dotted curves are obtained with the original scale. (Fig. 3 of KSM).

Comparison of figs. 9 and 10 shows a specific feature of powder data. No information is obtained about the differences of the coincident reflexions, and a damping of the nonsphericity in the results follows.

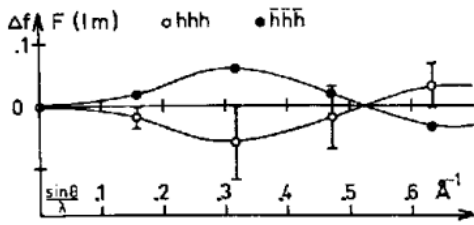


Figure 13. The imaginary part of the experimental atomic factor f_T of the fluorine ion at $(1/4, 1/4, 1/4)$ calculated using a sphere of radius $R = 1.23 \text{ \AA}$ (fig. 4 of KSM).

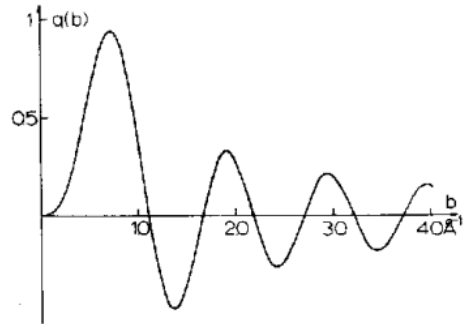


Figure 14. The radial behaviour of the reciprocal distribution of the third order radial density ρ_3 ($R = 1.0 \text{ \AA}$).

Although this analysis refers more directly to the atoms and is based on much more reliable parameters than the charge density analysis it is rather complicated and obviously not satisfactory from the point of view of the requirement of clarity. In principle, we are still working with an infinite number of parameters: the values of $f_T(\mathbf{b})$ at all different points \mathbf{b} . These do not yield immediate concrete statements without a thorough survey. The method also requires treatment of the scattering factor for each atom separately in a number of different crystallographic directions, and, in case of noncentral site symmetry (e.g. fluorine in CaF_2), calculation of the real and imaginary parts separately. Partly due to this complication this analysis was never completed to a point where the degree of its totality could be seen.

9. Use of harmonic expansions

The next step towards more analysed information was the idea to make use of symmetry (Kurki-Suonio and Meisalo 1967, Kurki-Suonio 1967, 1968, Dawson 1967 a, b, c, 1969). Each atom necessarily obeys the point symmetry of its position in the crystal environment. We can, thus, write the atomic charge distribution and the atomic scattering factor in form of harmonic series

$$(21) \quad \rho(\mathbf{r}) = \sum \rho_n(r) K_n(\theta_r, \varphi_r)$$

$$(22) \quad f(\mathbf{b}) = \sum f_n(b) K_n(\theta_b, \varphi_b)$$

where $K_n(\theta, \varphi)$ are harmonics of the relevant symmetry. The first term is spherical and the others represent deviations from sphericity with increasing complication of the angular behaviour with the order.

The radial density $\rho_n(r_0)$ is a linear parameter. The spherical term ρ_0 was treated in sec. 4 as an example. The others have very similar nature with a radial δ -function distribution, except that the angular behaviour is given by the corresponding harmonics. The reciprocal distribution of $\rho_n(r_0)$ is

$$(23) \quad q_n(\mathbf{b}) = \frac{4\pi}{A_n} j_n(2\pi r_0 b) K_n(\theta_b, \varphi_b) \quad ; \quad A_n = \int |K_n|^2 d\Omega \quad .$$

Figure 14 shows as an example the behaviour of q_3 . In all orders q_n has the same asymptotic behaviour $q_n \sim b^{-1}$ corresponding to the radial δ -function nature of the real distribution, but as we see also by comparison of figs. 1 and 14, the damping of oscillations gets slower and, consequently, the reliability of $\rho_n(r_0)$ at fixed r_0 decreases with increasing n , in accordance with the less favourable reciprocity relation (14').

Although the reliability is not as good as that of integrated quantities, the radial densities, particularly $\rho_0(r)$, may be useful quantities in giving a concrete view of the shape of the charge distribution around the atomic peak, cf. figs. 3, 4, 5.

If $f(\mathbf{b})$ corresponds to the charge distribution in a spherical region of radius R in accordance with our local definition of the crystal atom, the radial scattering factors $f_n(b_0)$ are linear parameters with the distributions

$$(24) \quad \gamma_n(r) = \begin{cases} \frac{4\pi i^n}{A_n} j_n(2\pi b_0 r) K_n(\theta_r, \varphi_r) & ; \quad r \leq R \\ 0 & ; \quad r > R \end{cases}$$

$$(25) \quad q_n(\mathbf{b}) = \frac{(4\pi)^2 R^3}{A_n} \frac{x j_{n+1}(x) j_n(x_0) - x_0 j_{n+1}(x_0) j_n(x)}{x^2 - x_0^2} K_n(\theta_b, \varphi_b)$$

$$\text{with } x = 2\pi b R \quad , \quad x_0 = 2\pi b_0 R .$$

Two features of the reciprocal distributions (25) should be noted. First the distributions are peaked at a spherical shell of radius b_0 , provided the radius of the region used is large enough, cf. figs. 15,16. Therefore these quantities resemble the scattering amplitude $f_T(\mathbf{b})$ of a given region in that they are of the highest class of reliability up to same value b_0 close to b_{cutoff} . So, the analysis is again "kept in the reciprocal space". This property manifests itself very concretely in the fact that even truncated series (5) gives good values for the radial scattering amplitudes below the point of termination (Kurki-Suonio 1968). Secondly, the effect of the reciprocity condition (14') getting less favourable is again observed, fig. 17. For a given size of the spherical region $q_n(\mathbf{b})$ gets broader with increasing n , causing a gradual loss of reliability of $f_n(b)$. Finally, at a fixed value of n it falls suddenly down indicating that the data do not contain any information of the high order components within the atomic sphere. For $R = 1 \text{ \AA}$ this limit is at about $n = 5$ as seen from fig. 17.

Figures 18 and 19 show results of a difference series calculation of the radial atomic factors for Ca and F in CaF_2 on the basis of the T data (a) and of the T + WWW data (b).

Addition of the weak reflexions affects the spherical components, while the 4th order component corresponding to a cubic deformation is unchanged. The higher orders are insignificant. The antisymmetric tetrahedral component ($n = 3$) in fluorine seems also to be too small to be observed.

This analysis has distinct advantages as compared to the previous one. First, the information is in a more concise form. Once we have the radial structure amplitudes we immediately know the behaviour of the scattering amplitude in all directions. Moreover, only few terms are significant in series (22).

Secondly, the information is in a more concrete or more analysed form. The spherical effects are clearly separated from the nonsphericities, which allows statements on the average effect of the crystalline field on the atoms and separately about the shape of the atoms or the effects of possible bond formation.

This separation of the spherical and nonspherical information is useful also when we study the possible systematic errors. Most of the difficult problems in the improvement of experimental accuracy concern mainly the spherical behaviour, i.e. they depend on the scattering angle, but not on the direction of the scattering vector. Thus, for experimental reasons the nonspherical information is more reliable than the spherical one. It may be that the spherical components tell us more about the experiment than about the atoms. Figure 20 demonstrates this situation. It shows the radial scattering factors of silicon atoms in a silicon crystal as calculated from the HKKK and GW data. We observe a significant difference in the spherical behaviour, which must be due to the different experiments, but we also see that, at least qualitatively, the significant nonspherical terms of the third and fourth order are equal. Also, figs. 18 and 19 indicate that the two data on CaF_2 combined are mutually not quite consistent as to the spherical behaviour.

Thirdly, the use of the difference series, which in principle causes conceptual

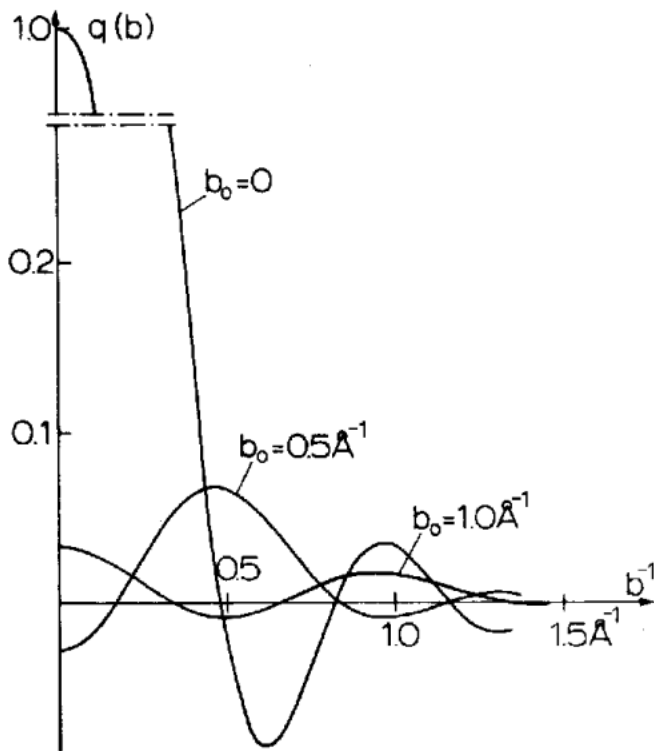


Figure 15. The reciprocal distribution of the spherical average scattering amplitude $f_0(b_0)$ of the charge distribution within a sphere of radius $R = 1.50 \text{ \AA}$ for different values of b_0 .

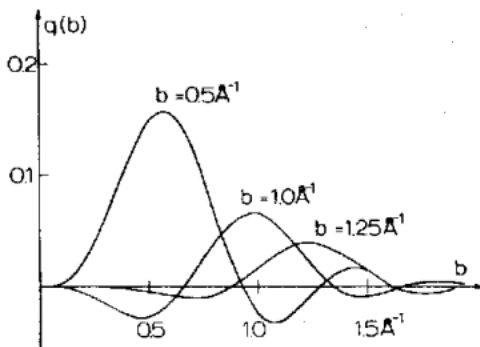


Figure 16. The radial behaviour of the reciprocal distribution of the third order radial scattering amplitude $f_3(b_0)$ of the charge distribution within a sphere of radius $R = 1.50 \text{ \AA}$ for different values of b_0 .

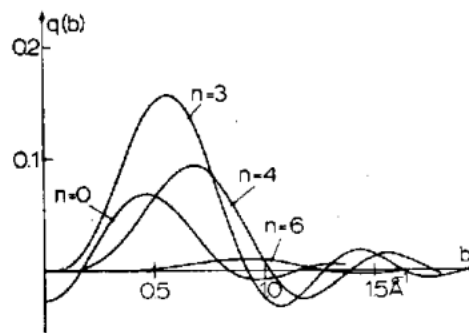


Figure 17. The radial behaviour of the reciprocal distributions of the radial scattering amplitudes $f_n(b_0 = 0.5 \text{ \AA}^{-1})$ of the charge distribution within a sphere of radius $R = 1.50 \text{ \AA}$ in different orders.

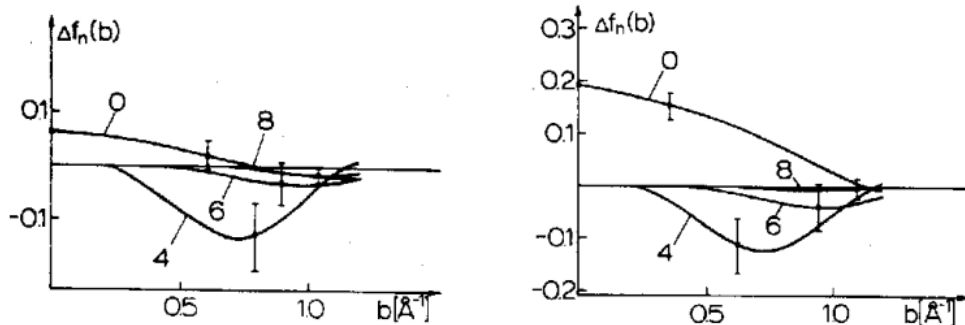


Figure 18. The radial atomic factor of Calcium in CaF_2 within the radius $R = 1.48 \text{ \AA}$. Results of a single difference series calculation from the T data (a), and from the T + WWW data (b). (From RKS).

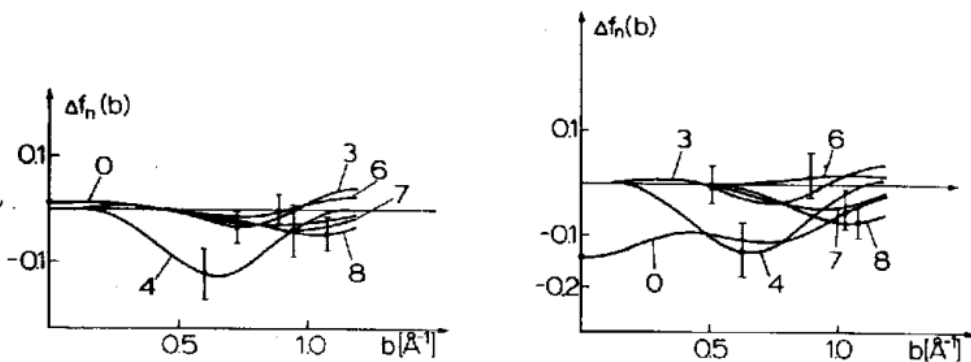


Figure 19. The radial atomic factors of fluorine in CaF_2 within the radius $R = 1.67 \text{ \AA}$. Results of a single difference series calculation from the T data (a), and from the T + WWW data (b). (From RKS).

indeterminacy, is now more safe in the case of nonsphericities. The averaging of the behaviour over all directions causes that we must have quite large a sphere before the effect of overlapping of neighbouring atoms has any influence on the radial atomic factors, cf. Kurki-Suonio (1968). Therefore the difference series gives directly the experimental results for the nonsphericities. This naturally does not apply on the spherical component.

Also in the study of nonsphericities there is a feedback on the problem of experimental accuracy. The physical requirement of low order harmonic behaviour can be used as a criterion for judgement of the quality of the data. If the data indicate considerable higher order components they are probably just too inaccurate to contain information about the nonsphericities. This can be controlled rapidly for any data, and the criterion will thus spare a lot of time and effort.

For instance, the T data on CaF_2 even when completed with the WWW weak reflections are adequate. According to fig. 20 the same is true for the two data on Silicon. The GW data for diamond, fig. 21, seem extremely good, while it is no use to make such an analysis of the De Marco and Weiss (DMW) (1965) data on Germanium,

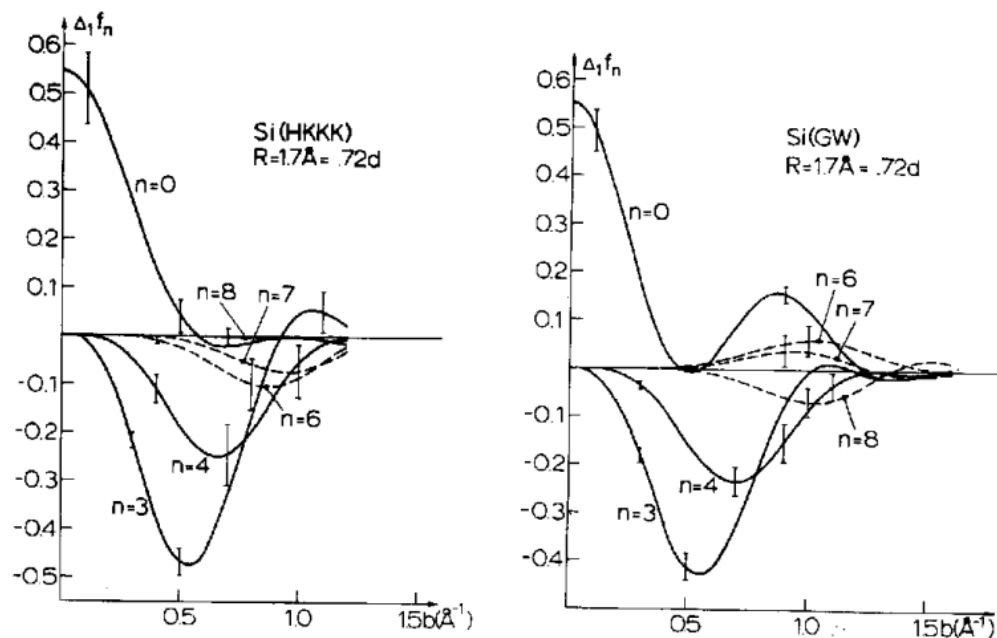


Figure 20. The radial atomic factors $\Delta_1 f_n$ of a crystal atom in silicon calculated with a sphere of radius $R = 1.7 \text{ \AA}$ from the HKKK data (a), and from the GW data (b). The error bars show the experimental standard errors. (Figures 3 and 4 of KSR).

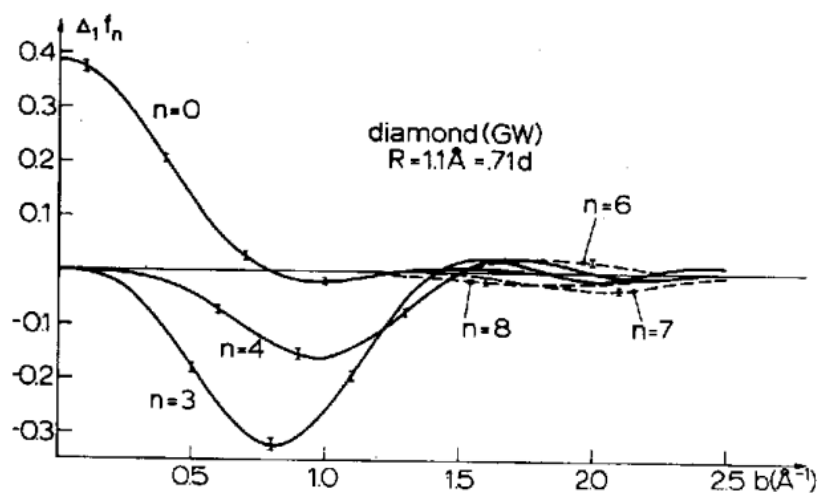


Figure 21. The radial atomic factors $\Delta_1 f_n$ of carbon in diamond calculated from the GW data with a sphere of radius $R = 1.1 \text{ \AA}$. The error bars show the experimental standard errors. (Fig. 2 of KSR).

fig. 22, cf. Dawson (1967 d). This is quite natural since the relative contributions of nonsphericities to the experimental intensities are much smaller in case of heavier atoms.

There is still one interesting feature. The size of the atom, or of the sphere used for analysis restricts essentially the behaviour of radial scattering factors. It will put a definite lower limit for the size of details occurring in the resulting curves. This is analogous to the restriction into low order harmonics, which requires a systematic angular behaviour of the structure amplitudes. Both requirements together accomplish here a separation of the systematic behaviour of the data from statistical fluctuations. They are constraints, which define the signal shape so that we can better distinguish the signal from the noise.

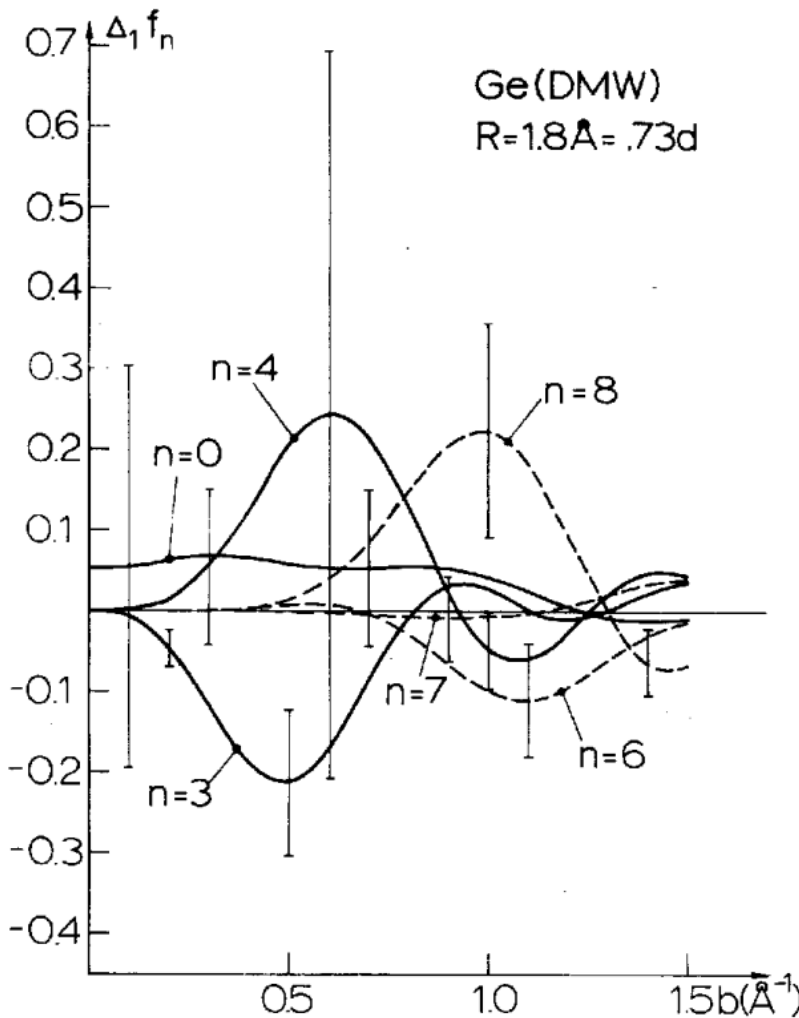


Figure 22. The radial atomic factors $\Delta_1 f_n$ of a crystal atom in germanium calculated from the DMW data. The error bars show the experimental standard errors. (Fig. 6 of KSR).

Because of this systematic it will also be possible to get estimates for unobserved reflexions. One interesting example is the reflexion (222) of diamond. Fig. 23 shows the independence of the experimental information of the presence of this reflexion in the data. This indicates that the other structure amplitudes, more or less, determine its value. In fact, we get for it in this way values which are slightly larger than the observed ones, cf. KSR.

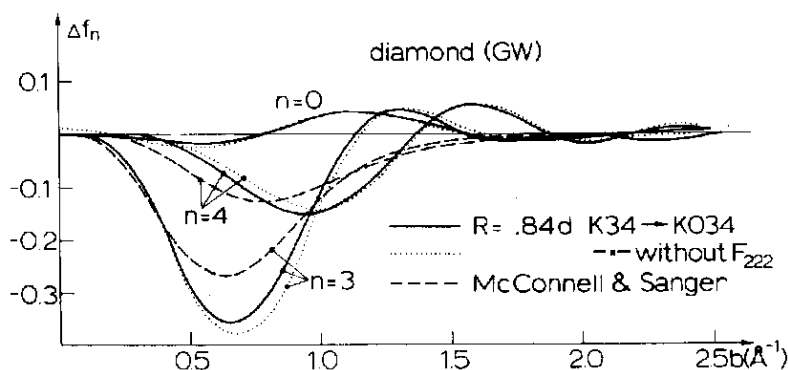


Figure 23. The radial atomic factors $\Delta f_0, f_3/i$ and f_4 of carbon in diamond according to the GW data. Results of an iterative calculation with and without F_{222} (solid and dotted lines, respectively). The broken lines show the results of the MCS parametric analysis. (Fig. 14 of KSR).

At last, it is interesting to see how well this analysis satisfies the requirement of totality. The question is, whether we can interpret the whole set of data in terms of local atoms with low order harmonic angular behaviour. We can argue that both of these requirements are physically reasonable. Therefore, if this analysis is not total, there will be some charge distribution which does not fit in the mere conceptual indeterminacy of atoms but definitely cannot be attached to any atom.

The degree of totality can be checked by adding the deviations obtained for the radial scattering factors to the model and by comparing the resulting prepared model with the data. However, a single correction is not necessarily sufficient. If the neighbouring spheres overlap, their common regions are counted twice and the corrections may be in error. Termination errors and deficiencies of data, such as low angle reflexions not measured or coincident reflexions, may also give errors which make another correction on the basis of the residual differences necessary. We are thus led to an iterative procedure.

By iteration we finally come to a situation where one further calculation gives negligible residual corrections. This final prepared model is, thus, consistent with the

data. The totality of this analysis in case of CaF_2 is shown by fig. 24. We see that the T data are exhausted of information. They can be reproduced from the results of analysis. The combined data cannot be completely reproduced, but still the residual differences are so small that we can consider the analysis practically total.

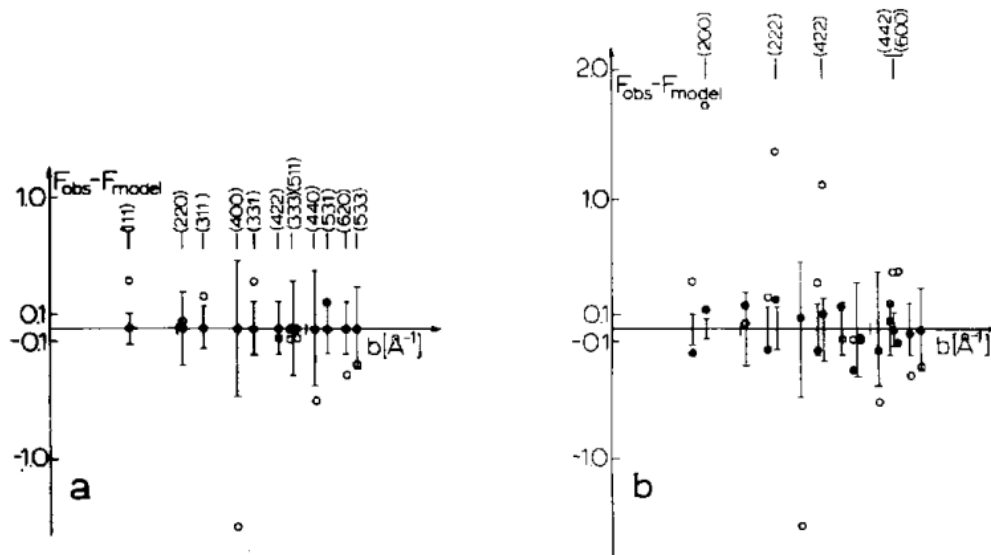


Figure 24. The deviations of the experimental structure amplitudes of CaF_2 from the original theoretical model (open circles) and from the final model (solid circles) obtained by an iterative harmonic analysis of the T data (a) and of the T + WWW data (b), as compared with the experimental uncertainties. (From RKS).

It is natural that in case of incomplete data we arrive easier at a prepared model which completely fits to the data. This indicates that in such cases the systematics is not strong enough to accomplish the separation of information from the statistical fluctuations. Therefore full advantage of the properties of this analysis is obtained only in case of as complete data as possible.

Diamond gives another interesting example, because there we definitely have covalent bonding. From fig. 25 we observe that the results of iteration are almost total only when extremely large spheres are used. Thus, even these data can be interpreted in terms of atoms with low order harmonic behaviour, which is an extremely simple model. This is, however, possible only if we allow a very strong overlapping of the atoms.

In spite of the favourable properties of this analysis there is one point of criticism left. The angular behaviour is well analysed, but the radial one is expressed in terms of

infinite number of parameters, the values of $f_n(b_0)$ at different b_0 . Again further inspection is necessary before the experimental information can be expressed in form of clear and concrete statements.

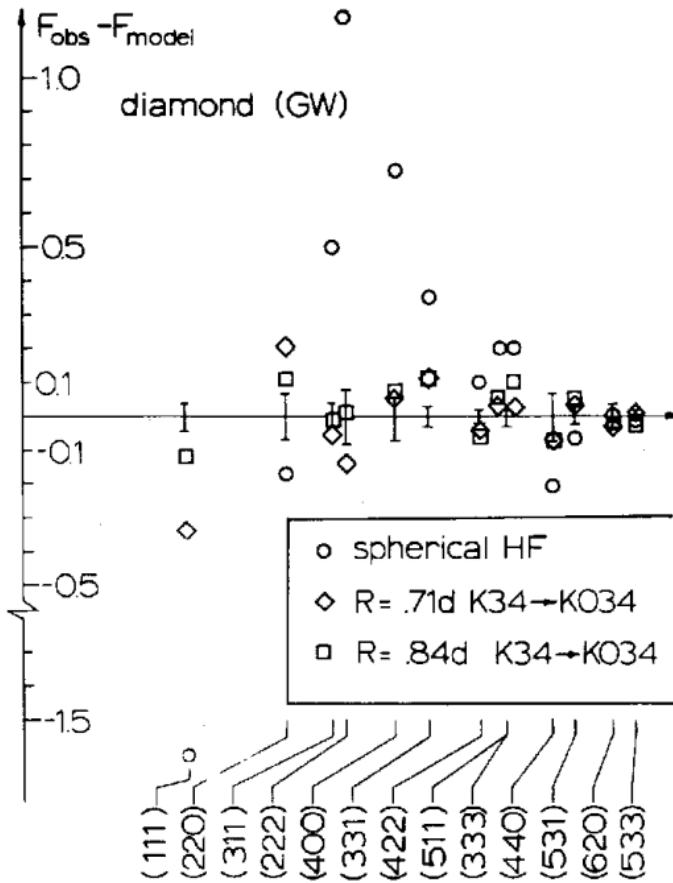


Figure 25. The deviations of the GW structure amplitudes of diamond from the spherical Hartree-Fock atomic model and from final models obtained by an iterative harmonic analysis with two different radii, as compared with the experimental uncertainties (Fig. 12 of KSR).

10. Radial parameters

The requirement of locality restricts strongly the behaviour of the radial scattering amplitudes. Particularly the nonspherical components contain obviously little experimental information. Their large scale behaviour reflects just the geometry of the crystal structure. The question is, how to parametrize this scant radial information properly to take full advantage of the geometrical constraint and, thus, accomplish "separation of the signal".

A natural characterization of a deformation component of an atom would be given by its "strenght" and "range". They can be defined as the number of electrons displaced from the negative lobes of K_n to the positive ones or

$$(26) Z_n = C_n \int_0^\infty \rho_n(r) r^2 dr = \frac{\Gamma(\frac{n+3}{2})}{i^n \pi^{3/2} \Gamma(\frac{n}{2})} C_n \int_0^\infty f_n(b) \frac{db}{b}$$

where $C_n = \int_{K_n > 0} K_n d\Omega$, and as the expectation value $\frac{1}{Z_n} \langle r \rangle_n$ of r in this

component defined by

$$(27) \langle r \rangle_n = C_n \int_0^\infty \rho_n(r) r^3 dr = \frac{\Gamma(\frac{n+4}{2})}{i^n \pi^{5/2} \Gamma(\frac{n-1}{2})} C_n \int_0^\infty f_n(b) \frac{db}{b^2}$$

Values of these parameters are easily obtained by numerical integration of the results of the harmonic analysis described in the previous section. For instance, for carbon and silicon atoms in diamond and silicon crystals we get from the results of KSR the values of Table 3. In fact, these parameters have a direct relationship to the parameters used by Dawson (1967 b, c, d) and by McConnell and Sanger (1970). And comparison of these two analyses indicates strongly that these parameters give a total description of the nonspherical information.

Table 3. Strenght Z_n and range $\langle r \rangle_n / Z_n$ of the third and fourth order deformations of crystal atoms in diamond and silicon corresponding to the results of the iterative harmonic analysis of Kurki-Suonio and Ruuskanen and to the parametric analysis of Dawson and McConnell and Sanger.

Crystal	analysis/data	Z_3	$ \langle r \rangle_3 / Z_3 $	Z_4	$ \langle r \rangle_4 / Z_4 $
diamond $a=1.544 \text{ \AA}$	KSR/GW	0.338	0.605d	-0.127	0.554d
	D/GW	0.347	0.657d	-0.170	0.657d
	MCS/GW	0.323	0.655d	-0.177	0.655d
silicon $a=2.352 \text{ \AA}$	KSR/HKKK	0.500	0.63 d	-0.315	0.60 d
	KSR/GW	0.617	0.65 d	-0.167	0.405d
	D/HKKK	0.508	0.682d	-0.269	0.682d
	MCS/HKKK	0.498	0.685d	-0.351	0.685d

The spherical component seems to offer a more difficult problem. On the other hand, the procedure, by which table 3 was produced, including iteration and final numerical intergration is already too complicated to be satisfactory. We should note therefore that the expectation values

$$(28) \langle r^k \rangle_n = C_n \int_0^R r^k \rho_n(r) r^2 dr$$

are linear parameters, and they can, thus, be calculated directly from series of the type (5). They can be used as such in connexion of the local definition of a crystal atom. They also constitute a natural generalization of the parameters (26) and (27) corresponding to $k = 0$ and $k = 1$, respectively. They include the atomic charge treated in sec. 6 as a special case with $k = n = 0$. Further we can note that the cases $n = 0, k = -1$ and $n = 0, k = 2$ are related to the Coulomb energy and the diamagnetic susceptibility, respectively, (cf. e.g. Sirota 1967).

The parameters (28) are integrals over the atomic region and we can therefore expect them to have the best possible reliability. This can be seen in more detail from figs. 26 and 27 showing the reciprocal distributions of $\langle r^k \rangle_0$ and $\langle r^0 \rangle_n = Z_n$, respectively. We see that $\langle r^{-2} \rangle_0$ is less reliable, obviously due to the singularity of its real distribution, and we expect this to be the case always when $k = -n - 2$ (the lowest

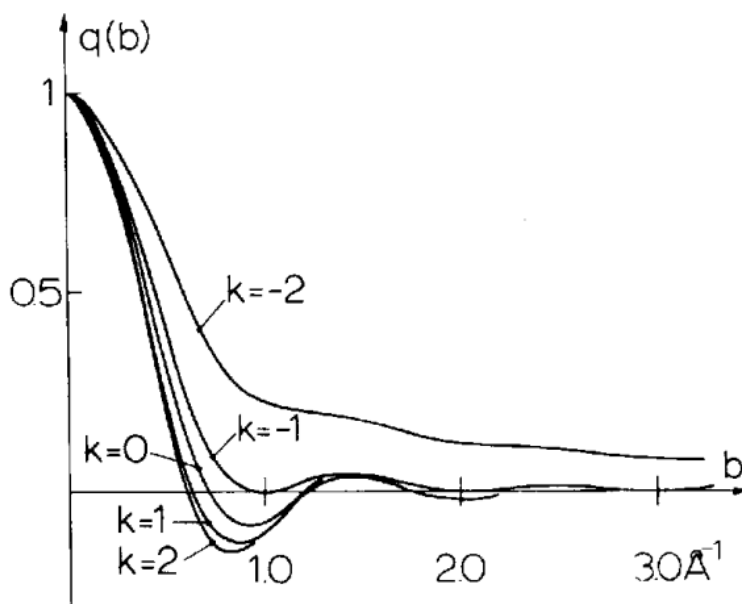


Figure 26. The reciprocal distributions of the moments $\langle r^k \rangle_0$ of the charge distribution within a sphere of radius 1.0 Å.

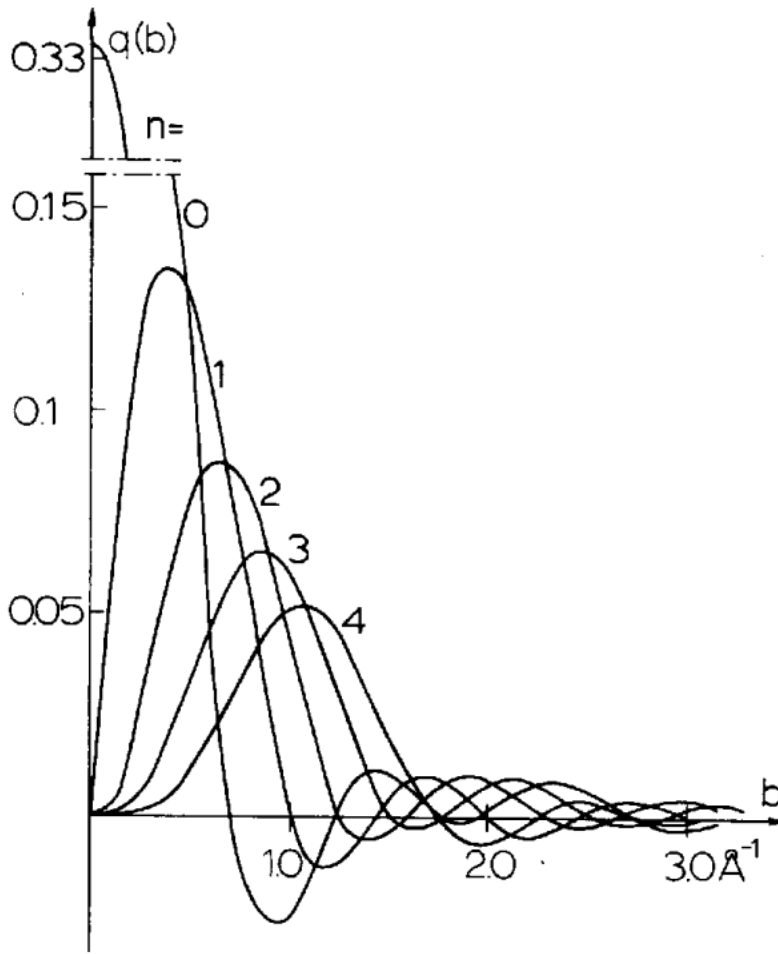


Figure 27. The reciprocal distributions of the electron counts Z_n taking part in different terms of the harmonic expansion of the charge distribution within a sphere of radius 1.0 \AA .

possible value of k in eq. (28)). On the other hand, the reciprocal distribution moves farther with increasing n causing a decrease of reliability. This again corresponds to the reciprocity condition (14') getting less favourable and agrees well with all we have stated about the damping of information about higher order components.

These parameters summarize in integral form the properties of an atom. No complete analysis based on them is yet done, but on the basis of their properties discussed and the earlier developments described few low order parameters will be sufficient to exhaust the experimental information, and "the analysis of the second type" seems to arrive here at a point where it satisfies the requirements of clarity and reliability in the sense defined, and the degree to which totality is not fulfilled will show the insufficiency of the atomic model to explain the diffraction data.

References

- Bijvoet, J.M. and Lonsdale, K., *Phil. Mag.* **44** (1953) 204.
Black, P.J., *Phil. Mag.* **46** (1955) 155.
Black, P.J. and Taylor, W.H., *Rev. Mod. Phys.* **30** (1958) 55.
Calder, R.S., Cochran, W., Griffiths, D. and Lowde, R.D., *J.Phys. Chem. Solids* **23** (1962) 621.
Cochran, W., *Rev. Mod. Phys.* **30** (1958) 47.
Cochran, W., *Nature* **191** (1961) 60.
Compton, A.H., *X-Rays and Electrons*, Ch. V § 73. Van Nostrand (1926).
Dawson, B., *Proc. Roy. Soc. A* **298** (1967a) 255.
Dawson, B., *Proc. Roy. Soc. A* **298** (1967b) 264.
Dawson, B., *Proc. Roy. Soc. A* **298** (1967c) 379.
Dawson, B., *Proc. Roy. Soc. A* **298** (1967d) 395.
Dawson, B., *Acta Cryst. A* **25** (1969) 12.
Debye, P. and Scherrer, P., *Phys. Z.* **19** (1918) 474.
De Marco, J.J. and Weiss, R.J. (DMW), *Phys. Rev. A* **137** (1965) 1869.
Göttlicher, S. and Wölfel, W. (GW), *Z.Elektroch.* **63** (1959) 891.
Hattori, H., Kuriyama, H., Katagawa, T. and Kato, N. (HKKK), *J.Phys. Soc. Japan* **20** (1965) 988.
Hosemann, R. and Bagchi, S.N., *Nature* **171** (1953) 785.
Hosemann, R. and Bagchi, S.N., *Direct Analysis of Analysis of Diffraction by Matter*, Ch XIII 6, 7. North-Holland, Amsterdam (1962).
Krug, J., Witte, H. and Wölfel, E., *Z. Phys. Chem., Neue Folge* **4** (1955) 36.
Kurki-Suonio, K., *Ann. Acad. Sci. Fenn. A VI* **31** (1959).
Kurki-Suonio, K., *Ann. Acad. Sci. Fenn. A VI* **263** (1967).
Kurki-Suonio, K., *Acta Cryst. A* **24** (1968) 379.
Kurki-Suonio, K., *Acta Cryst. A* **26** (1970) 458.
Kurki-Suonio, K. and Meisalo, V. (KSM), *J. Phys. Soc. Japan* **21** (1966) 122.
Kurki-Suonio, K. and Meisalo, V., *Ann. Acad. Sci. Fenn. A VI* **241** (1967).
Kurki-Suonio, K. and Ruuskanen, A. (KSR), *Ann. Acad. Sci. Fenn. A VI* **358** (1971).
Kurki-Suonio, K. and Salmo, P. (KSS), *Ann. Acad. Sci. Fenn. A VI* **369** (1971).
McConnell, J.F. and Sanger, P.L., *Acta Cryst. A* **26** (1970) 83.
Meisalo, V. and Inkinen, O., *Acta Cryst.* **22** (1967) 58.
Meisalo, M. and Inkinen, O. (MI), *Ann. Acad.Sci.Fenn. A VI* **207** (1966).
Pesonen, A. (P), *Ann. Acad. Sci. Fenn. A VI* **378** (1971).
Ruuskanen, A. and Kurki-Suonio, K. (RKS), unfinished work.
Sirota, N.N., *Chemical Bonds in Semiconductors and Solids*, Consultants Bureau, New York (1967).
Taylor, W.H., *Acta Met.* **2** (1954) 684.

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- Togawa, S. (T), *J.Phys.Soc.Japan* **19** (1964) 1696.
Weiss, A., Witte, H. and Wölfel, E. (WWW), *Z.Phys. Chem.* **10** (1957) 98.
Weiss, R.J., *X-Ray Determination of Electron Distributions*, North Holland, Amsterdam (1966).

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