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**NONSPHERICAL
ANALYSIS OF CHARGE DENSITY**

BY

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Abstract

A method is presented for analysis of observed X-ray structure amplitudes in terms of nonspherical atoms. It is based on iterative calculation of the lattice harmonic components of the atomic factors. Locality and low order harmonic behaviour of the atomic charge densities are assumed providing thereby a criterion for adequacy of the data for nonspherical analysis.

In the examples of diamond and silicon components up to the fourth order are involved. Prepared models with practically complete fit to the data are obtained, provided that large overlapping of the atoms is allowed. The resulting radial atomic factors show artificial details but their average behaviour is well defined within uncertainties determined mainly by the experimental accuracy. The nonsphericities build up a systematics which makes the experimental information insensitive to omission of one of the reflexions, *e.g.* the weak F_{222} of diamond and silicon. The results support the justification of the corresponding parametric approach presented by DAWSON in 1967 except that his omission of the spherical component is a decisive defect.

1. INTRODUCTION

It has been proposed recently that lattice harmonic expansions of crystal atomic factors would provide a simple interpretation of crystal scattering factors F_j in terms of the separate atom model. DAWSON treated diamond, silicon and germanium as examples in refs. [1, 2, 3] and in a summarizing conference lecture [4]. A simple expression was assumed for the radial behaviour of the different harmonic components of the atomic charge density, and the parameters were adjusted by comparison with experimental structure factors. A least squares version of this analysis was presented by McCONNELL and SANGER [5]. KURKI-SUONIO and MEISALO [6, 7] suggested as an alternative direct evaluation of the radial functions from structure amplitudes.

In a subsequent paper KURKI-SUONIO [8] considered the possibilities of having such information in principle and of obtaining it in practice. Assuming locality as a basic property of the atomic definition, it was concluded that the available information decreases rapidly towards higher order harmonics, few first orders playing any role. It was also shown that a truncated set of structure amplitudes determines the atomic factor

components up to the cut off in $\sin\theta/\lambda$. Overlapping of neighbouring atoms was found to increase the indeterminacy of the components but not to destroy their significance: this statement is in fact decisive towards the nonspherical analysis having any value.

In this work we shall develop a direct method of nonspherical analysis on the basis of the suggestion of KURKI-SUONIO and MEISALO [6, 7], and shall study its properties. Diamond, silicon and germanium are obvious examples because they provide a direct comparison with the parametric approach of DAWSON [1, 2, 3] and McCONNELL and SANGER [5]. It will be interesting to see whether the direct analysis, without any *a priori* assumptions about the radial behaviour, will give equal results. In view of DAWSON's arguments in ref. [1] about the choice of radial functions and our statements in ref. [8] on the basically restricted nature of this type of information this ought to be the case.

The significance of the nonspherical analysis can be properly understood only if the indeterminacy of its results is known. By a direct calculation of components we probably get a better idea about the uncertainties of the atomic factor curves than by parameter fitting. Covalent bonding means that interpretation of the electron density in terms of atoms will require overlapping of the atomic densities, and the question about the uniqueness of the results will be important. By treating diamond, silicon and germanium as examples we therefore hope to shed some light on this problem.

On the other hand, the diamond structure is unfavourable for our method. Since at every step of analysis a limited spherical region is treated, the bond may cause some difficulties. Therefore we expect these examples to be instructive in showing the limitations of the method.

Further, this analysis leads to a discussion of the degree of internal consistency of the data, *i.e.* of the extent to which the experimental structure factors can be found to possess physically acceptable or reasonable behaviour. Our interest is specially directed to restrictions in the behaviour of the atomic factors, (*cf.* ref. [8]). In the following we shall deal with two aspects of this question:

First, consistency of the data is closely connected with their accuracy; errors are likely to cause inconsistency, therefore greater overall accuracy means normally a higher degree of consistency. This leads us to search for consistency criteria to indicate the reliability of the experimental values. Such criteria will help us judge what will be a reasonable degree of refinement of the analysis. DAWSON's »nonspherical standard of adequacy» is an example which by its very nature is suitable for nonspherical analysis. In a direct analysis we expect some modification of it to be useful.

Secondly, some of the structure amplitudes may be particularly difficult

to measure. In principle, however, they are fixed, more or less, by the others through the requirement of consistency. The famous weak reflection 222 of diamond structure is an interesting example. Sometimes it has been thought to be a unique indication of atomic deformation and much effort has been concentrated on measuring it. Study of the nonspherical consistency will now offer the possibility of seeing to what extent the information included in F_{222} is independent of the other reflections.

2. OUTLINE OF THE METHOD

At first we write the scattering amplitude of each atom in form of an expansion

$$(1) \quad f(\mathbf{b}) = \sum_{n\alpha} f_{n\alpha}(b) K_{n\alpha}(u, v),$$

which is a Fourier invariant division of the atom into harmonic components [6]. Here the scattering vector \mathbf{b} is denoted by (b, u, v) in spherical coordinates, and the functions $K_{n\alpha}$ form a complete orthogonal set of lattice harmonics for the atomic site symmetry. If the atom is defined as the contents of a sphere of radius R , the radial scattering factors can be written in the form of the series

$$(2) \quad f_{n\alpha}(b) = \frac{(4\pi)^2 R^3}{V A_{n\alpha}} \sum_j F_j K_{n\alpha}^*(u_j, v_j) \frac{x_j j_{n+1}(x) j_n(x_j) - x_j j_{n+1}(x_j) j_n(x)}{x^2 - x_j^2}$$

where $j_n(x)$ is the spherical Bessel function, $x = 2\pi Rb$, $A_{n\alpha} = \int K_{n\alpha}^* K_{n\alpha} d\Omega$, and the summation runs through all reciprocal lattice points \mathbf{b}_j [7]. The complex conjugate in eq. (2) plays no role in practice, since normally all $K_{n\alpha}$ are real.

The functions $f_{n\alpha}$ are real for even n and purely imaginary for odd n . In series (2) this is established by the parity theorem

$$K_{n\alpha}(-\mathbf{b}) = (-1)^n K_{n\alpha}(\mathbf{b}),$$

which shows that we can always combine terms by writing

$$(3) \quad F_{\mathbf{b}} K_{n\alpha}(\mathbf{b}) + F_{-\mathbf{b}} K_{n\alpha}(-\mathbf{b}) = \begin{cases} 2 \operatorname{Re}\{F_{\mathbf{b}}\} K_{n\alpha}(\mathbf{b}) & (n \text{ even}) \\ 2i \operatorname{Im}\{F_{\mathbf{b}}\} K_{n\alpha}(\mathbf{b}) & (n \text{ odd}). \end{cases}$$

The analysis will be based on some theoretical model built from separate atoms. The basic theoretical atomic factors $f_{\text{th}}(\mathbf{b})$ need not be spherical, but usually they are. Series (2) is used as a difference series with coefficients $\Delta F_j = F_o - F_{\text{th}}$ to evaluate the first order corrections $\Delta_1 f = \sum \Delta_1 f_{n\alpha} K_{n\alpha}$ to the theoretical atomic factors. The corrections are taken into account

only in those orders where they are of significant magnitude. All different atoms are treated similarly. This gives us a prepared model with atomic factors $f_{\text{pr}}^{(1)} = f_{\text{th}} + \Delta_1 f$ and structure amplitudes $F_{\text{pr}}^{(1)}$.

According to the meaning of series (2), this correction ought to remove all essential deviations of the theoretical charge density from the experimental one inside the spheres used. Another calculation with differences $\Delta_1 F = F_{\circ} - F_{\text{pr}}^{(1)}$ would then give $\Delta_2 f_{n\alpha}$ with negligible values, and the prepared atomic factors $f_{\text{pr}}^{(1)}$ would represent the results of analysis. If, however, the neighbouring spheres overlap, their common regions are counted twice and the corrections are in error. In such cases $\Delta_2 f_{n\alpha}$ might not be small enough and a new prepared model with structure amplitudes $F_{\text{pr}}^{(2)}$ can be constructed by using the prepared atomic factors $f_{\text{pr}}^{(2)} = f_{\text{th}} + \Delta_1 f + \Delta_2 f$. This can be repeated, which leads to an iterative procedure. In the case of the diamond structure iteration will be necessary, because considerable overlapping of the atomic densities will require the use of large spheres in the analysis.

Defects of experimental data, such as low angle reflexions not measured or coincident reflexions, may also make the iteration procedure necessary. The experimental information will thus leave the corresponding structure amplitudes arbitrary in certain limits. It is then reasonable to choose for them values which make the internal consistency of the experimental set $\{F_{\circ}\}$ as good as possible, although each model gives a slightly different basis for this choice. If we assume that the structure amplitudes can be exhaustively interpreted in terms of atomic factors (1), the unknown values must be taken as close as possible to the corresponding prepared values F_{pr} . Therefore the absent structure amplitudes are simply omitted from the difference series calculation, and the joint intensities of coincident reflexions are divided after each step in the same relationship as the »prepared intensities».

Of course, this procedure will be reasonable only if it converges. At the limit then we have prepared atomic factors in the form of expansion (1). These atomic factors are consistent with the experimental structure amplitudes in the sense that the differences $F_{\circ} - F_{\text{pr}}$ do not require any further corrections of the model inside the atomic spheres. Thus, they constitute an interpretation of the data in terms of separate deformed atoms.

There are several problems connected with the method itself, such as the role of the radii R , which are parameters of the method and whose basic function is to control the degree of locality in our treatment of the single atoms, this being basic to the method. The results of ref. [8] indicate that values larger than ordinary crystal radii are appropriate. The radii are also connected with the problem of convergence. It is clear at least that the procedure will diverge if the spheres are too large. The resulting model

will evidently depend on the radii R , and this leads us to study the range of different possible interpretations. Both the rate of convergence and the resulting model will certainly depend also on the number of harmonic components included in the iteration, on the quality of the experimental data used, and on the basic model. As a whole, these problems are too complicated to be treated thoroughly, therefore we simply hope to obtain a rough idea of their nature.

3. APPLICATION TO DIAMOND STRUCTURE

The atoms of the diamond structure fall naturally into two groups, denoted by A and B in ref. [1], depending on the orientation of the tetrahedrally located neighbours. Atom B is just the mirror image of A . Thus, their electron densities and scattering amplitudes are related by

$$(4) \quad \varrho_B(\mathbf{r}) = \varrho_A(-\mathbf{r}) ; f_B(\mathbf{b}) = f_A(-\mathbf{b}) = f_A^*(\mathbf{b}) .$$

Expansion (1) now takes the form

$$(5) \quad f_A = f_0 + f_3 K_3 + f_4 K_4 + f_6 K_6 + f_7 K_7 + \dots$$

where K_n are cubic harmonics. The expansion for f_B is obtained by changing the sign of the odd terms, which are imaginary. We shall normalize such that $\text{Max}\{K_n\} = 1 \geq |\text{Min}\{K_n\}|$, which gives for the lowest order harmonics

$$\begin{aligned} r^3 K_3 &= 3\sqrt{3}xyz \\ r^4 K_4 &= \frac{5}{2}(x^4 + y^4 + z^4 - \frac{3}{5}) \\ r^6 K_6 &= \frac{6 \cdot 9 \cdot 3}{3 \cdot 2}(x^6 + y^6 + z^6 - \frac{6}{11}K_4 - \frac{3}{7}) \\ (6) \quad r^7 K_7 &= -\frac{3 \cdot 3}{4}K_3(x^4 + y^4 + z^4 - \frac{5}{11}) \\ r^8 K_8 &= \frac{6 \cdot 5}{2}(x^8 + y^8 + z^8 - \frac{1 \cdot 2 \cdot 8}{1 \cdot 4 \cdot 8 \cdot 5}K_6 - \frac{8 \cdot 4}{1 \cdot 4 \cdot 3}K_4 - \frac{1}{3}) \\ r^9 K_9 &= -60.3367 [K_3(x^6 + y^6 + z^6) + \frac{2 \cdot 8}{1 \cdot 8 \cdot 7}K_7 - \frac{3 \cdot 5}{1 \cdot 4 \cdot 3}K_3] \\ r^{10} K_{10} &= -\frac{2 \cdot 8 \cdot 7 \cdot 7 \cdot 9 \cdot 3}{1 \cdot 2 \cdot 8 \cdot 0}(x^{10} + y^{10} + z^{10} - \frac{1 \cdot 8}{2 \cdot 4 \cdot 7}K_8 - \frac{6 \cdot 4}{5 \cdot 6 \cdot 1}K_6 - \frac{8 \cdot 4}{1 \cdot 4 \cdot 3}K_4 - \frac{3}{11}). \end{aligned}$$

By this choice the radial function f_n gives directly the maximum contribution of the n^{th} term to the atomic factor (5). This is practical, because we shall then get immediately an idea of the significance of each component obtained from series (2).

In order to make a close comparison with the parametric approach we shall analyse the same experimental values as studied in the refs. [1, 2, 3, 5] and shall adopt the same theoretical atomic factors as the basic models. Thus, for diamond we take the F_o values of GÖTTLICHER and WÖLFEL [9],

hereafter GW(C), completed with F_{222} corresponding to the measurements of RENNIGER [10] and WEISS and MIDDLETON, *cf.* ref. [1]. The theoretical atomic factors are those given in ref. [1] obtained by interpolation from the Hartree-Fock estimates of FREEMAN [11]. For silicon we have three different sets of structure amplitudes to compare: the powder data of GÖTTLICHER and WÖLFEL (GW) [9], the single crystal data of DEMARCO and WEISS (DMW) [12] and those of HATTORI, KURIYAMA, KATAGAWA and KATO (HKKK) [13] obtained from measurement of Pendellösung fringes completed with the DMW value of F_{222} . For germanium we use the data of DEMARCO and WEISS [12]. The theoretical atomic factors for Si and Ge are those given in refs. [2, 3] obtained from the Hartree-Fock calculation of CLEMENTI [14]. The necessary dispersion corrections are included in the experimental values in all cases.

As guidance for the choice of radius R we first calculated the average spherical electron density

$$(7) \quad \varrho_0 = \frac{1}{V} \sum F_j \frac{\sin 2\pi b_j r}{2\pi b_j r}$$

around one atom. Here a Gaussian representation was used for the atomic factor at large $\sin\theta/\lambda$. For Gaussian atoms ϱ_0 could be calculated analytically and the result was corrected by a difference series (7) with coefficients $F_0 - F_{\text{Gauss}}$. In this procedure termination errors are expected to be small in the interesting region between atoms, (*cf.* HOSEMANN and BAGCHI [15]). Fig. 1 shows the functions $[4\pi r^2/Z]\varrho_0(r)$ obtained for GW(C) and HKKK(Si). These curves give an idea of the separability of one atom

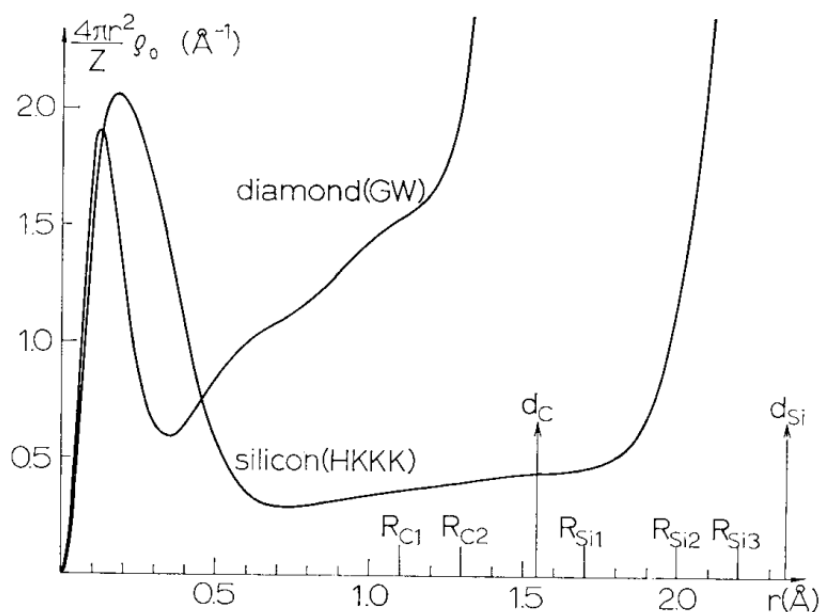


Figure 1. The average spherical charge density $(4\pi r^2/Z)\varrho_0(r)$ at an atom in diamond and silicon as calculated from the experimental structure amplitudes of Göttlicher & Wölfel (1959) and Hattori, Kuriyama, Katagawa & Kato (1965), respectively.

from its neighbours. In light of the discussion in ref. [8] we expect the neighbours not to contribute seriously to the series (2) until the radius R extends to the region of steeply increasing curve in fig. 1. This, however, does not necessarily mean that radii extending to that region would be unusable. Although the first step of the calculation will give a distorted picture, the iteration will still give a reasonable result provided it converges.

Anyhow, fig. 1 motivates the preliminary choice of radii: $R = 1.1 \text{ \AA} = 0.71d$ for diamond and $R = 1.7 \text{ \AA} = 0.72d$ for Si, where d is the nearest neighbour distance or 1.544 \AA and 2.352 \AA , respectively. By analogy we take $R = 1.8 \text{ \AA} = 0.73d$ for Ge with $d = 2.450 \text{ \AA}$. Difference series (2) calculated with these radii are shown in figs. 2 to 6 up to the eighth order. The error bars indicate the uncertainty corresponding to the experimental limits of error. For discussion of these figures we refer to the next section.

To carry through the iterations two different programs were written in ALGOL. In one of the programs, in accordance with DAWSON's analysis where no spherical corrections were included, only the nonspherical components $n = 3$ and 4 were corrected at each step. In the other program the spherical zeroth order was also included and treated similarly. We shall call these procedures K34 and K034, respectively. The \mathfrak{R} -factor, $\mathfrak{R} = 100 \sum |F_o| - |F_{\text{prep}}| / \sum |F_o|$, was used to follow the convergence and to indicate the fit of the prepared model with the data. To account for the coincident reflections in powder data a subprocedure was included, which divided the joint intensities in the same relationship as the intensities corresponding to the prepared model each time the new \mathfrak{R} -factor was smaller than the preceding one.

All calculations were performed with the Elliott 803 computer at the Department of Nuclear Physics of the University of Helsinki.

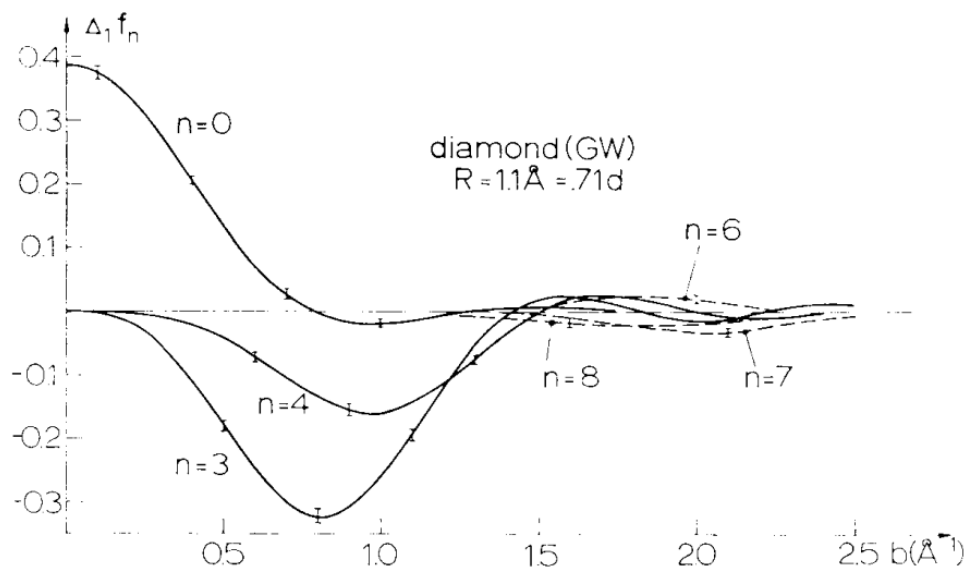


Figure 2. The radial scattering amplitudes $\Delta_1 f_n$ of an atom in diamond calculated from the GW data with a sphere of radius $0.71d$.

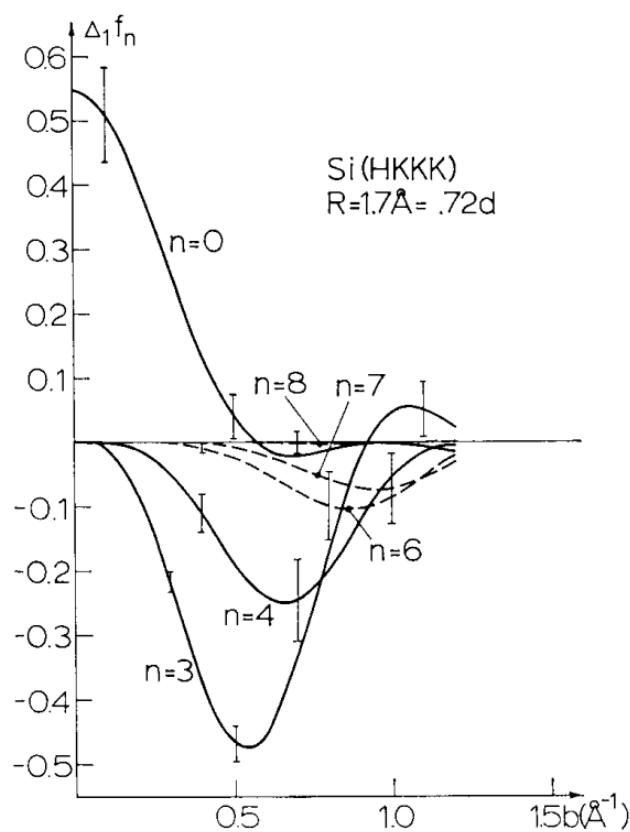


Figure 3. The radial scattering amplitudes $\Delta_1 f_n$ of a crystal atom of silicon calculated from the HKKK data with a sphere of radius $0.72d$.

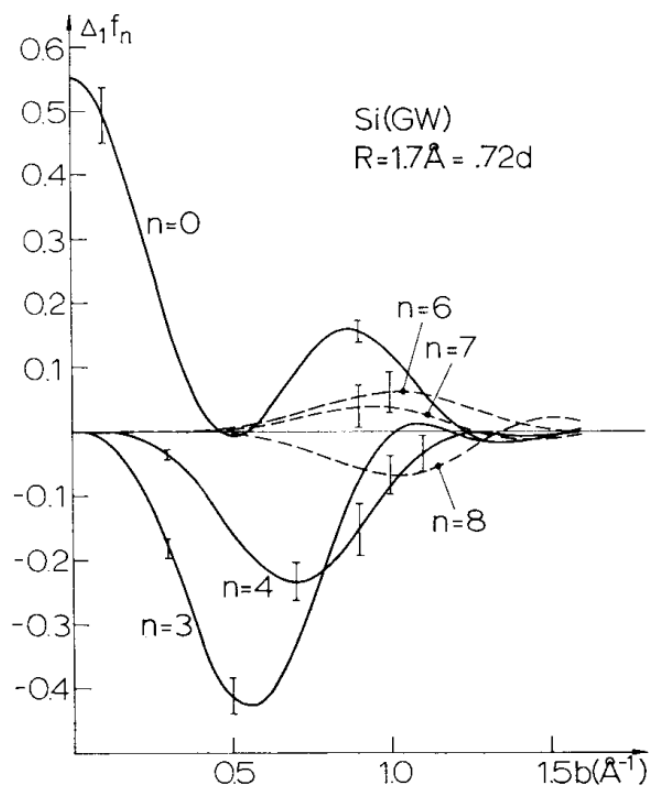


Figure 4. The radial scattering amplitudes $\Delta_1 f_n$ of a crystal atom of silicon calculated from the GW data with a sphere of radius $0.72d$.

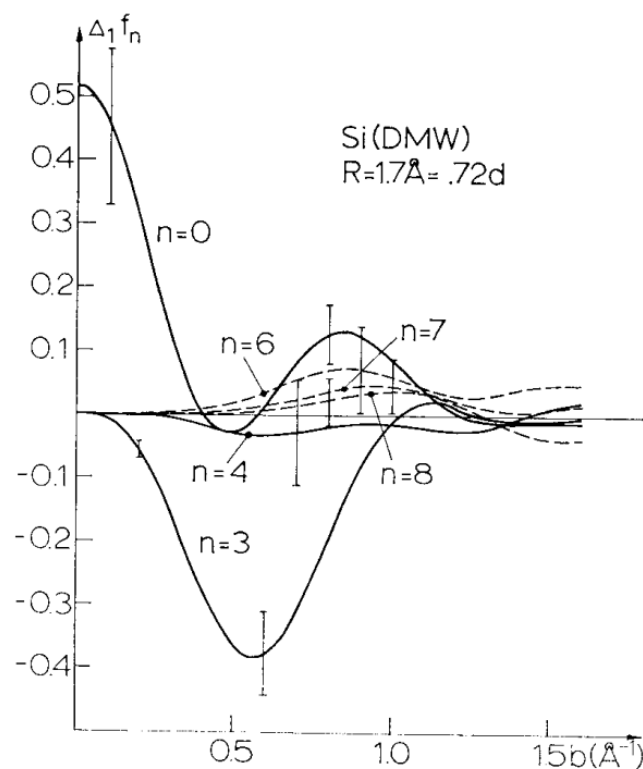


Figure 5. The radial scattering amplitudes $\Delta_1 f_n$ of a crystal atom of silicon calculated from the data of DeMarco & Weiss (1965) with a sphere of radius $0.72d$.

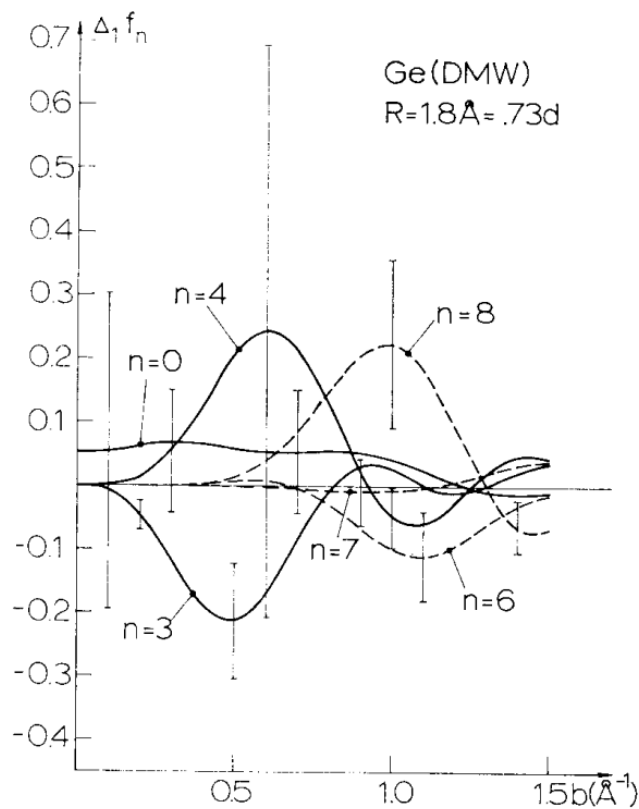


Figure 6. The radial scattering amplitudes $\Delta_1 f_n$ of a crystal atom of germanium calculated from the DMW data with a sphere of radius $0.73d$.

4. THE 'NONSPHERICAL STANDARD OF ADEQUACY'

To compare the quality of different data on silicon DAWSON introduced a «nonspherical standard of adequacy» [2]. The basic argument was that the deviations of the structure amplitudes from the model values must 'display the correct symmetry'. This statement was applied in a specific way equivalent to two assumptions: first, the lattice harmonic expansions (1) of the atoms do not contain significant higher order terms. Secondly, the radial atomic factors of the low order components are smooth functions of $\sin\theta/\lambda$.

Justification of these assumptions follows from the definition of the atoms as local objects [8]. Another argument is that wave functions with angular momentum l can give rise to components up to the order $n = 2l$ in the expansion (1), (*cf.* ref [6]), and it is reasonable to require that the states of high angular momenta are weakly occupied in the atoms. Thus, if the deviations from the spherical model are not equivalent to low order harmonic deformations of the atoms, the data cannot be expected to be accurate enough to contain information about the asphericities.

Furthermore, to apply this criterion it was necessary to require in ref. [2] that the model atoms already possess the correct spherical behaviour. If then the deviations from the model showed sufficient internal consistency according to the criterion, the nonspherical analysis was possible to carry through. The present method does not have these limitations, because the different components can be evaluated independently and for any data.

If spheres of appropriate size are used, the first step of the calculation will already show the order of magnitude of the different components. Occurrence of significant higher order components will indicate nonspherical inadequacy of the data. However, by using large spheres contributions from neighbouring atoms may cause higher components to appear. On the other hand, small spheres suppress them because of the more confined locality. Thus, for the criterion to be applicable we must take the spheres large enough for us to observe the possible occurrence of the higher components and small enough to get satisfactory evaluation of the components in one step. This kind of optimum choice is the real purpose of fig. 1.

In our examples we assume only the 3rd and the 4th order deformations to be present. Thus, from fig. 2 we immediately see the excellent nonspherical adequacy of GW(C). Fig. 3 proves similarly that a nonspherical analysis will be reasonable in the case of HKKK(Si), described also by DAWSON [2] as highly adequate; still, the components $n = 6, 7$ are clearly visible here.

Fig. 4 corresponds to GW(Si). Contrary to the conclusion in ref. [2] the nonspherical consistency seems to be good also here. The 3rd and the 4th orders dominate the nonspherical behaviour completely. There is,

however, a significant difference in the spherical component as compared with fig. 3. DMW(Si), fig. 5, shows a very similar spherical behaviour. Thus, there seems to be in these cases some systematic difference with a relatively smooth $\sin\theta/\lambda$ dependence between the Pendellösung method and the Bragg reflexion measurements. As to the nonspherical adequacy of DMW(Si), although the higher components are small, there is one alarming feature, the almost complete absence of the 4th order. If we assume that the nonsphericities are bound up with the angular momenta, the highest order ought to be even. A significant odd component, such as the 3rd in this case, corresponds to an antisymmetric density, and a corresponding even component is needed to cancel the negative electron density in the minimum directions of the odd harmonics. Thus, we conclude that the nonspherical behaviour is not completely adequate.

Finally, fig. 6 shows the corresponding results for DMW(Ge). This is a very obvious example of nonspherical inadequacy. Apart from the error bars due to experimental uncertainties, this is evident from the large values of the 8th and 6th components.

5. CONVERGENCE

Extensive calculations were performed to study the convergence properties of the iteration procedures K34 and K034. They were designed to give an idea of the effect of the following factors on convergence: the radius, the basic model, the quality of data — or, more specifically, their accuracy, the cut off value of $\sin\theta/\lambda$, coincident reflexions and absent reflexions of low $\sin\theta/\lambda$. As examples of the calculations, figures 7 to 10 show the progress of iteration, in particular its dependence on the radius R , in the case of HKKK(Si). Figures 7 and 8 were obtained from K34 using the radii $1.7 \text{ \AA} = 0.72d$ and $2.2 \text{ \AA} = 0.94d$, respectively. Similarly, figures 9 and 10 represent K034 iteration with the radii 1.7 \AA and $2.0 \text{ \AA} = 0.85d$, respectively. The starting model was the spherical model $F(0, 0)$ of ref. [2] and the curves represent the spherical corrections Δf_0 and the nonspherical components f_3 and f_4 of the prepared models in the successive steps of iteration.

In general, R/d seems to be the most important factor. For both procedures it has a limiting value, beyond which the procedure diverges. For K34 it is about 1.0 and for K034 about 0.85. As far as could be stated, these values depend only on the geometry of the problem and not on the other factors mentioned. For K34 convergence was still stated at $R = 0.94d$ (cf. fig. 8), but divergence at $R = 1.02d$. K034 converged at $R = 0.72d$ and diverged strongly at $R = 0.94d$, while at $R = 0.85d$ a more compli-

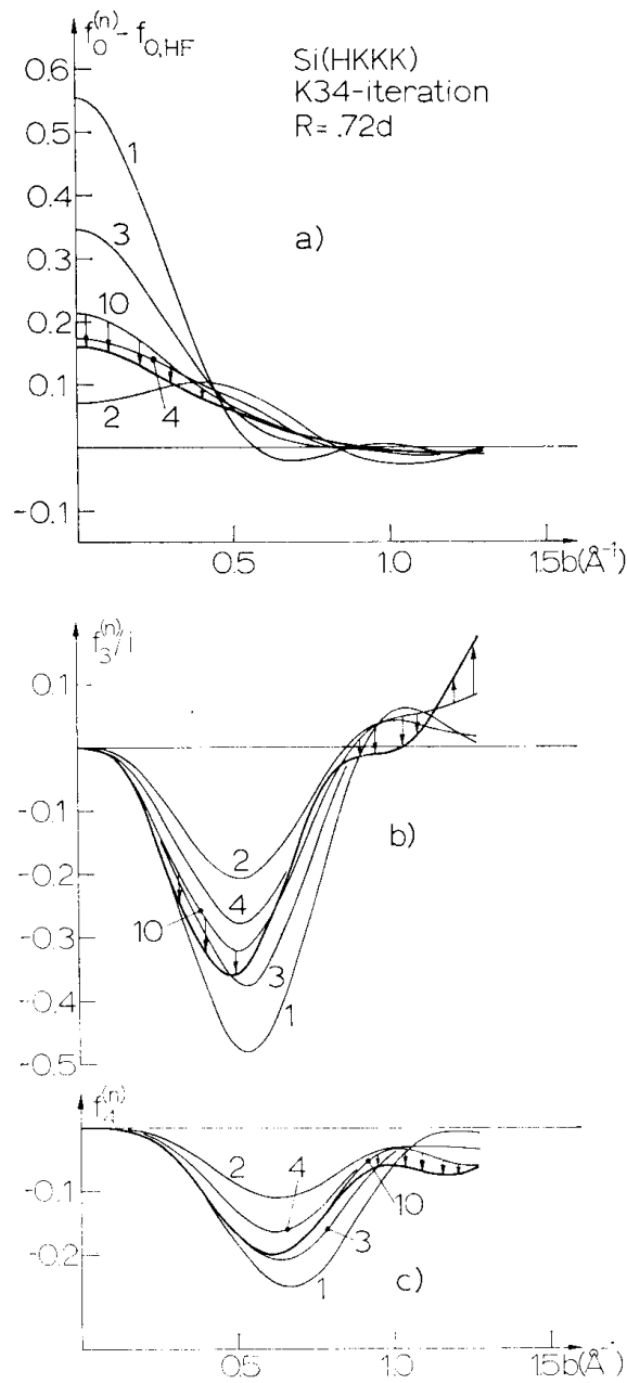


Figure 7. The radial scattering amplitudes a) Δf_0 b) f_3/i c) f_4 for successive prepared models in K34 iteration of HKKK data of silicon calculated with a sphere of radius $0.72d$.

cated situation occurred, (*cf.* fig. 10). The successive intermediate results showed neither convergence nor divergence, but an oscillation between two fixed curves.

The K34 iteration has a better convergence than K034. The reason is obvious. The coupling between components of different orders, especially that of the spherical component with the lowest order nonspherical ones,

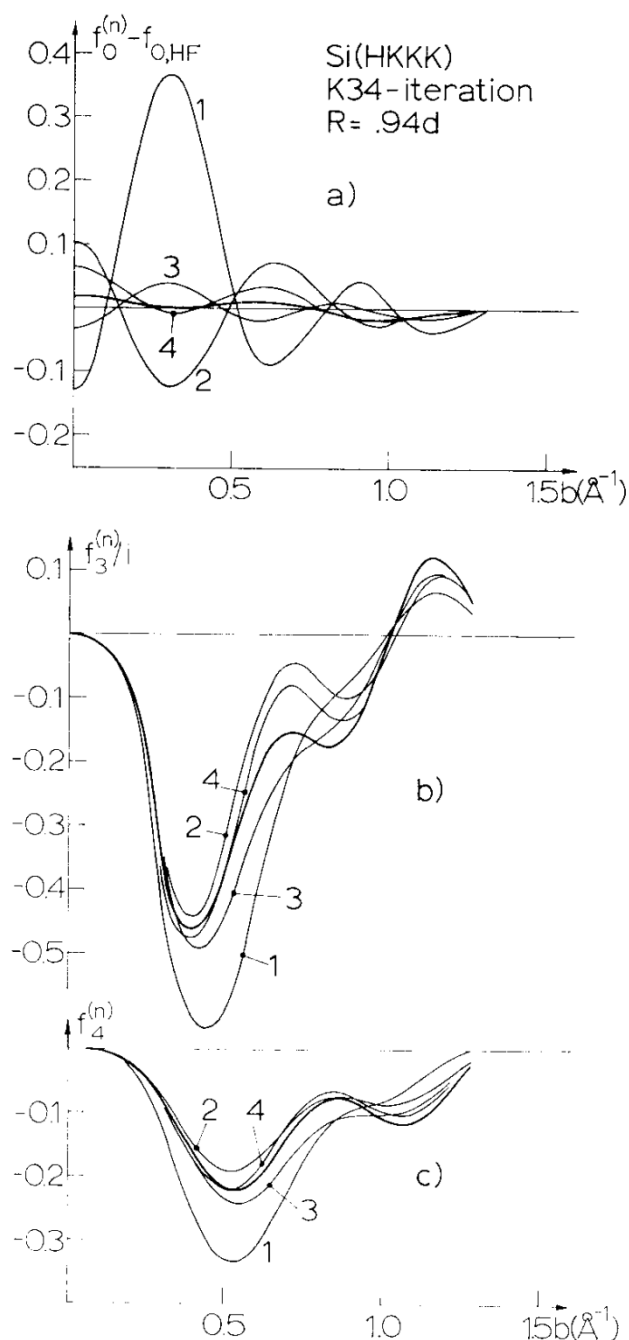


Figure 8. The radial scattering amplitudes a) Δf_0 b) f_3/i c) f_4 for successive prepared models in K34 iteration of HKKK data of silicon calculated with a sphere of radius $0.94d$.

is strong due to overlapping of spheres. This is clearly seen also in the behaviour of Δf_0 in K34 (figs. 7a, 8a) where the change in each step is merely due to corrections of the nonspherical components. The strengthening of the coupling with increasing radius appears as an increasingly oscillatory behaviour of the iteration which finally turns into a divergence. In K034 this coupling introduces at each step a large exaggeration of the correction to the preceding model, causing the strongly alternating nature

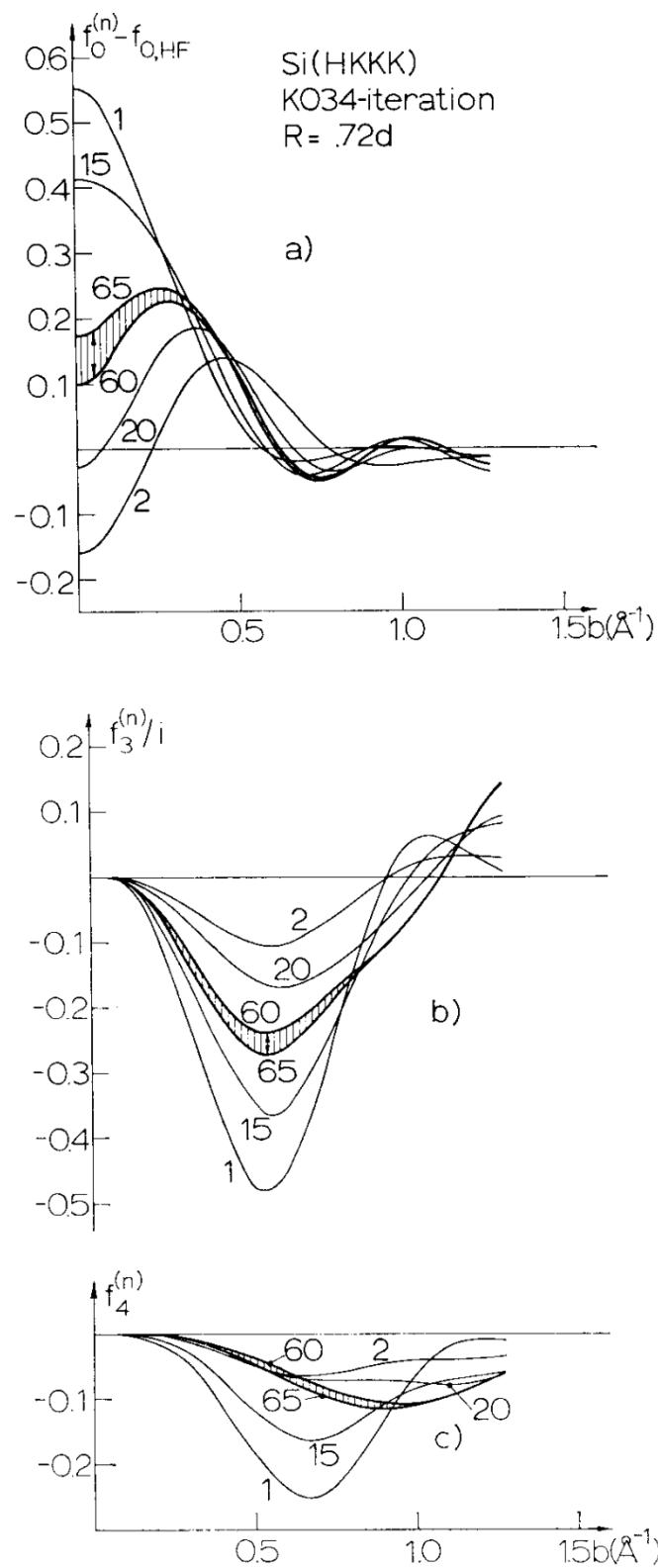


Figure 9. The radial scattering amplitudes a) Δf_0 b) f_3/i c) f_4 for successive prepared models in K034 iteration of HKKK data of silicon calculated with a sphere of radius $0.72d$. The shaded area shows the oscillation of the result at the limit.

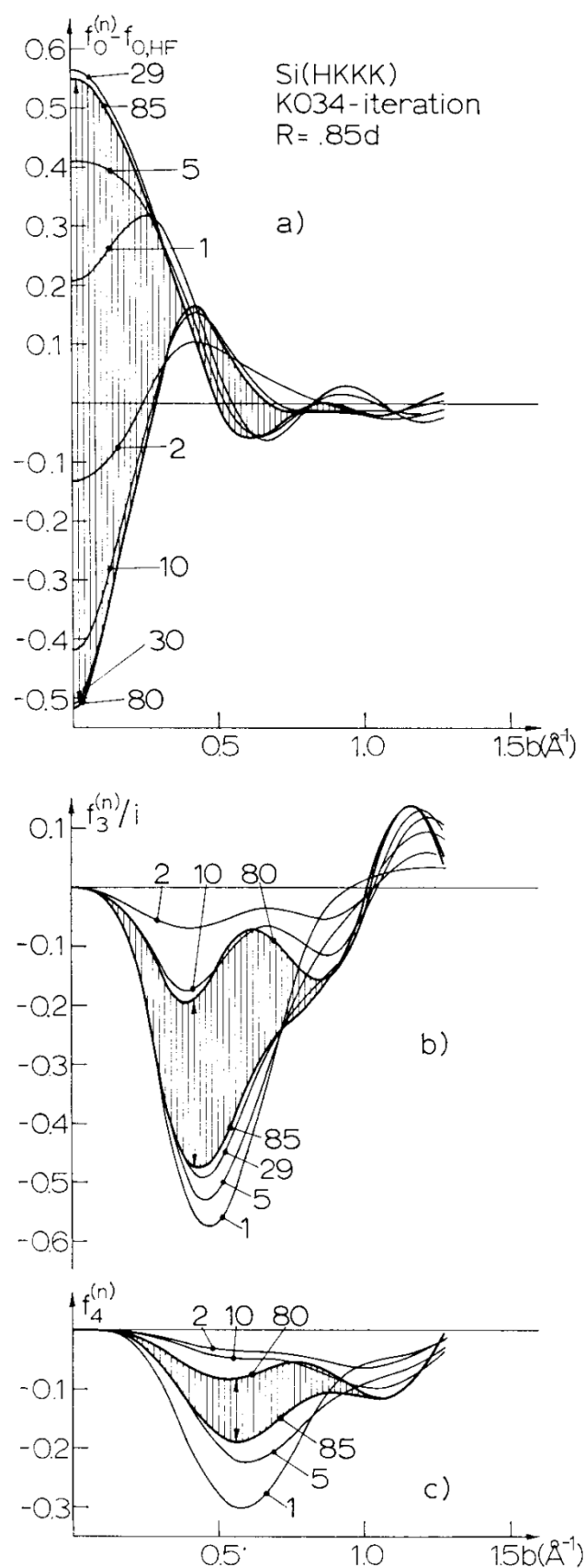


Figure 10. The radial scattering amplitudes a) Δf_0 b) f_3/i c) f_4 for successive prepared models in K034 iteration of HKKK data of silicon calculated with a sphere of radius $0.85d$. The shaded area shows the oscillation of the result at the limit.

of the convergence. This also makes the limiting radius smaller for K034. However, unexpectedly large radii are needed in both procedures to build up a divergence.

Starting from different models had little effect on the convergence. One might think that a good enough model would lead to a convergent procedure even with a somewhat larger R , but this seemed not to be the case. For instance, for HKKK(Si) the model obtained by K34 with $R = 2.2 \text{ \AA}$, fitting well with the data was used as the initial model for another K34 with $R = 2.4 \text{ \AA}$ and for K034 with $R = 2.2 \text{ \AA}$, but again the divergence was quite clear after a few loops. Moreover, when this model was used for K034 with $R = 2.0 \text{ \AA}$ the »stationary oscillation» appeared, this time, however, with a much smaller amplitude.

The quality of the data can be seen to effect the convergence in two different ways. The absence of one or several reflexions from the data tends to improve the convergence slightly, while changing the alternating nature of convergence to monotonic. This seems natural, since it should be easier to reach consistency of the prepared model with less complete data. On the other hand, inaccuracy or internal inconsistency of the data seems to make the convergence somewhat slower. All these effects have, however, little significance compared with the dominant role of the radius.

6. INDETERMINACY OF THE PREPARED MODEL

Each convergent iteration yields a prepared model defined in terms of radial atomic factor curves. For a given set of data these curves may depend on the number of components included in the iteration procedure, on the order in which the different components are treated, on the radius used and on the reference model. Thus, we have a multitude of different prepared models to deal with. Fig. 11 shows some examples corresponding to HKKK(Si). Certain general requirements will, however, restrict the range of models to be discussed.

First, the result must be consistent with the data simultaneously in all components assumed to be significant. These components must therefore be treated on an equal basis. In the present case this means that K034 must always be applied as the final refinement of the model. Variations in the order of treatment of the components are therefore equivalent to variations of the initial model in the K034 iteration. Use of K034 is, however, limited by its slower convergence. By $R = 0.72d$ there are no difficulties, but already at $R = 0.85d$ K034 gives no unique result, (*cf.* fig. 10). Still, when used as refinement of the K34-model it shows only very small »stationary oscillations» so that a definite prepared model is obtained.

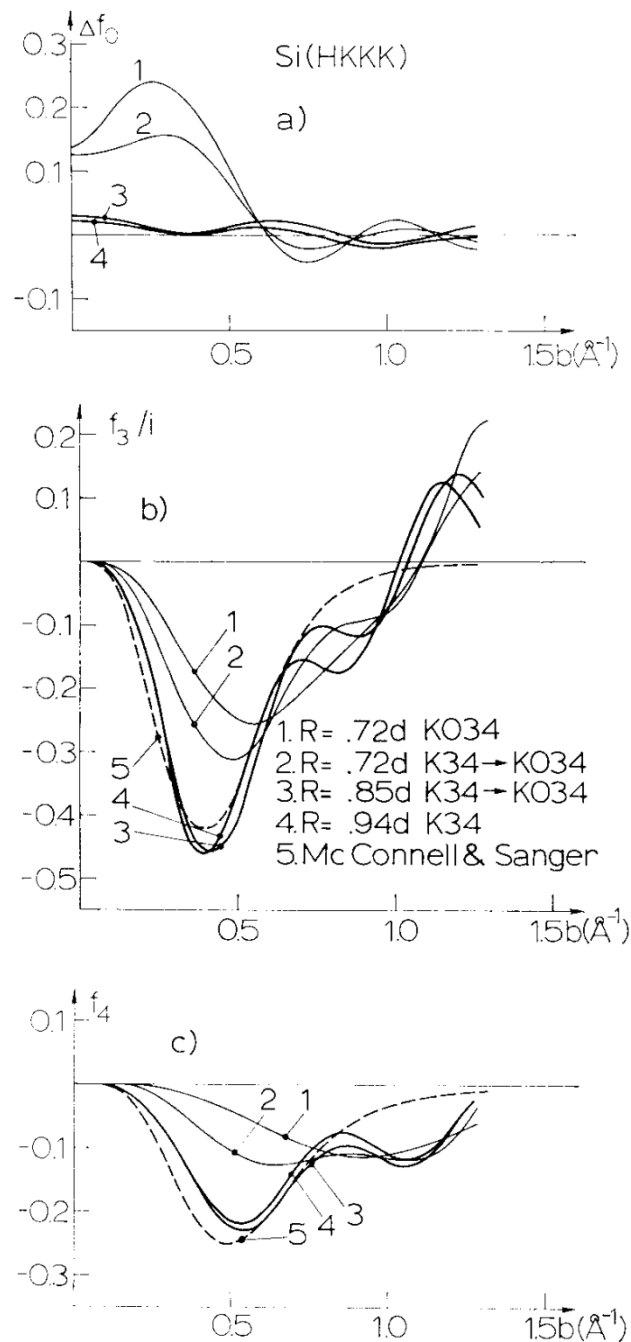


Figure 11. The radial scattering amplitudes a) Δf_0 b) f_3/i and c) f_4 of the final prepared models for the HKKK data of silicon obtained by iteration. Model 1 is obtained by K034 with $R = 0.72d$. Models 2 and 3 are refinements of the K34 result by K034 with $R = 0.72d$ and $R = 0.85d$, respectively and model 4 is a K34 result with $R = 0.94d$. Model 5 is the result of McConnell & Sanger (1969) obtained by a parametric approach.

Only if the K34-prepared model does not indicate any spherical corrections will completion with K034 be unnecessary. This is, in fact, the case with both HKKK(Si) and GW(C), when the larger radii are used, but not, for instance, with DMW(Si) and GW(Si). This justifies in the first two

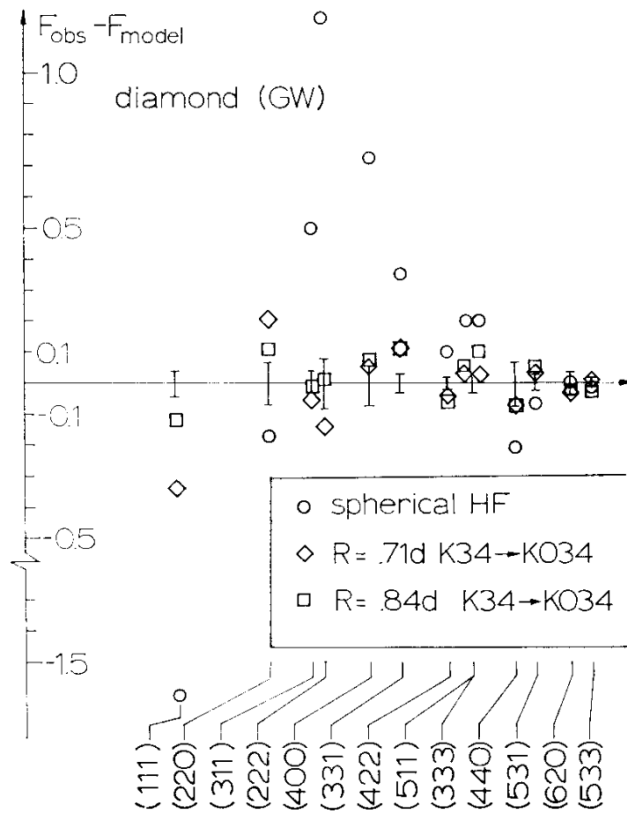


Figure 12. The differences between the GW structure amplitudes of diamond and those of the original theoretical model and those of two prepared models obtained with the radii $0.71d$ and $0.84d$, as compared with the experimental uncertainties reported.

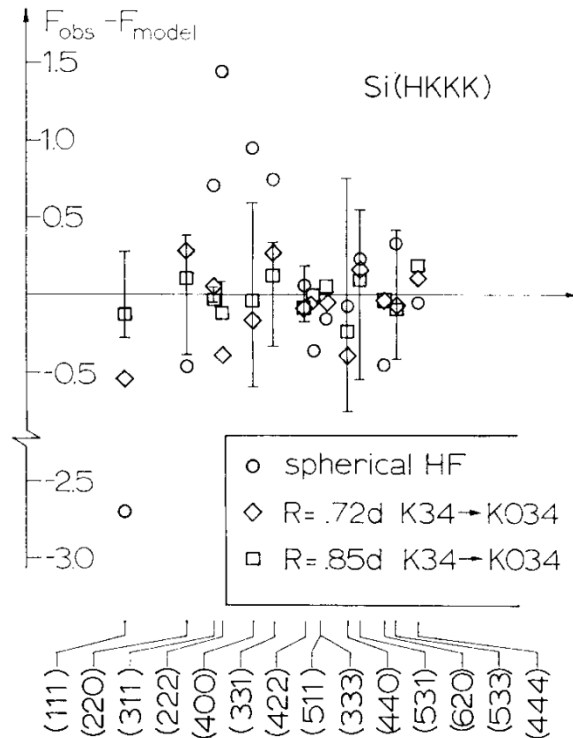


Figure 13. The differences between the HKKK structure amplitudes of silicon and those of the original theoretical model and those of two prepared models obtained with the radii $0.72d$ and $0.85d$, again compared with the experimental uncertainties reported.

cases the treatment of nonsphericities without paying attention to the possible spherical corrections, as done by DAWSON [1, 2] and McCONNELL and SANGER [5].

The dependence of the results on the radius is interesting, (*cf.* fig. 11), because in principle a larger sphere ought to give a more complete result, *i.e.* a model consistent with the data within a larger region of the unit cell. This is also seen from figs. 12 and 13 which show that larger spheres lead to a better fit. For HKKK(Si) and GW(Si) as well as for GW(C) each iteration with R smaller than about $0.85d$ yielded at least two structure factors with significant deviations from the experimental values, while for all of the data almost complete fit was obtained with $R = 0.85d$, or larger. Thus, for instance, curves 1 and 2 in fig. 11 do not explain the whole set of data, while curves 3 and 4 do. Therefore, only the results obtained by the larger spheres can be regarded as interpretations of the data. We can take, for instance, the K034-refined K34 results obtained by $R = 0.85d$ as the results of the iteration, figs. 14, 15, 16.

In principle the uncertainties of the analysis are of two different kinds, experimental and interpretational. The error bars in figures 2 to 6 show the order of magnitude of the experimental uncertainties of the prepared models. In this context the interpretational uncertainty is equal to the freedom we have in interpretation of a given set of structure amplitudes in terms of separate atoms, within the restrictive requirements of locality and low order harmonic behaviour of the atoms. It is coupled to the indeterminacy of the division of the charge density into atoms, but also incompleteness of the data is contributory. The variations of the possible prepared models give, at least, an idea of the uncertainty's magnitude.

Some of the results obtained using the smaller spheres differed considerably, *e.g.* curves 1 and 2 in fig. 11. However, once the minimum radius for obtaining an exhaustive model was exceeded, only small variations of the results were found when the procedure was varied. Especially in the case of HKKK(Si) this was studied carefully; curves 3 and 4 in fig. 11 are typical examples of the differences observed. For GW(C) such variations seemed to be even smaller.

The method may introduce specific limitations in the behaviour of the resulting curves, and the variations of the results therefore do not necessarily cover the whole range of interpretational uncertainty. Still, the foregoing observations indicate that in these cases the experimental uncertainty is important and probably dominant as compared with the interpretational one. Incompleteness of the data will, however, increase the latter uncertainty considerably simply due to lack of information. The importance of limitations attributable to the method can be discussed separately.

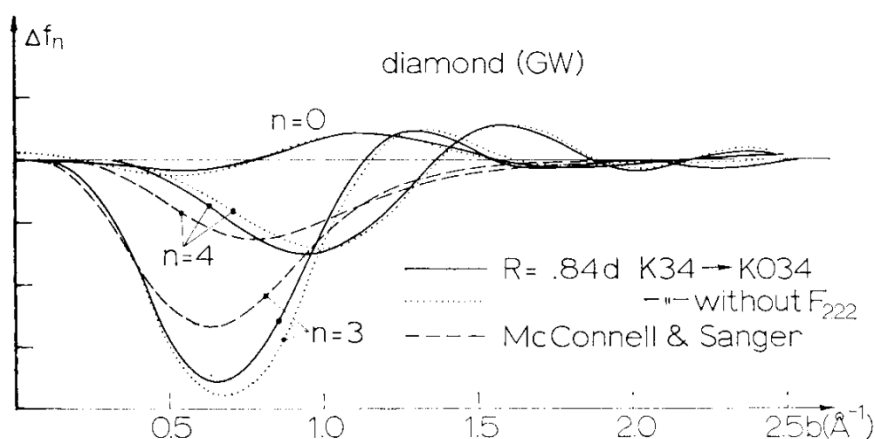


Figure 14. Radial scattering amplitudes Δf_0 , f_3/i and f_4 of an atom in diamond as calculated from the GW data by the present iterative method (solid lines) and by the parametric approach of McConnell & Sanger (broken lines). The dotted lines are obtained by iteration when F_{222} is omitted.

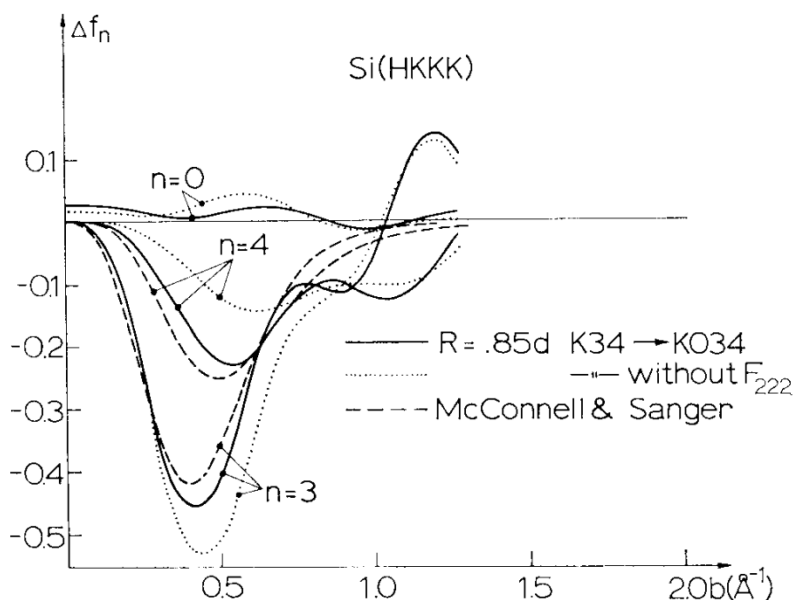


Figure 15. Radial scattering amplitudes Δf_0 , f_3/i and f_4 of an atom in silicon crystal as calculated from the HKKK data by the present iterative method (solid lines) and by the parametric approach of McConnell & Sanger (broken lines). The dotted lines are obtained by iteration when F_{222} is omitted.

7. CONSISTENCY AND F_{222}

To speak of internal consistency of the data implies that there are relationships between structure amplitudes, such that omission of one of them will not essentially reduce the information included in the data, provided the data are good enough. Also it ought to be possible to determine the value of one of the structure amplitudes on the basis of the others. The present method provides a straightforward check of these statements.

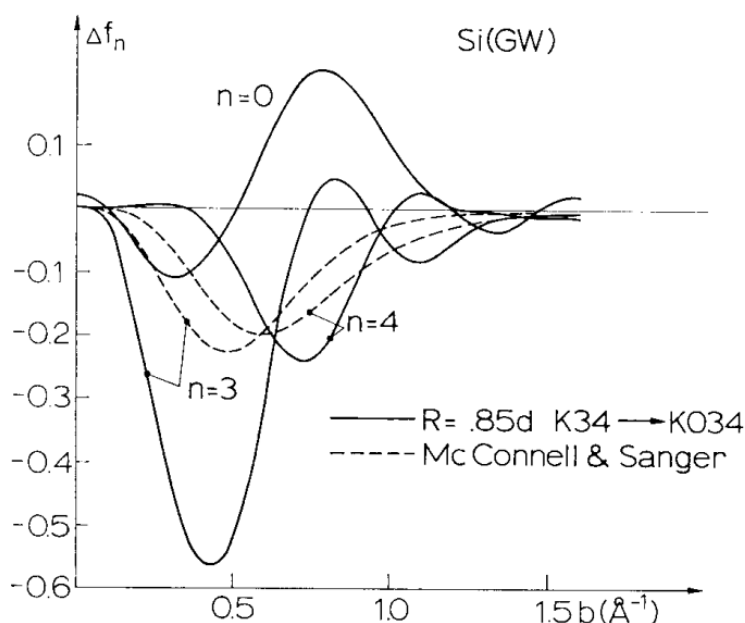


Figure 16. Radial scattering amplitudes Δf_0 , f_3/i and f_4 of an atom in silicon crystal as calculated from the GW data by the present iterative method (solid lines) and by the parametric approach of McConnell & Sanger (broken lines).

The check was made on the weak 222 reflexion because of the special interest in it. It was omitted from both GW(C) and HKKK(Si), and the analysis was then repeated using $R = 0.85d$ and K34-iteration completed by a final K034 refinement. As seen in fig. 14 the results with and without F_{222} are practically equal for diamond, in accordance with the first statement. In the case of Si, fig. 15, the differences are somewhat larger, indicating that the degree of nonspherical consistency is not as high. This is, however, natural because in Si the nonsphericities contribute a much smaller percentage to the structure amplitudes than in diamond, and observation of them is correspondingly more difficult. In any event, this shows that the main part of the information about the nonspherical components is contained already in the strong reflexions.

The values of F_{222} are also easily obtained, since $|F_{222}| = 8|f_3|$. From the f_3 curves of the figures 14 and 15 we get the values 1.35 and 2.25 for diamond and silicon respectively, while the prepared model obtained in the ordinary analysis, with F_{222} included, yields 1.15 and 1.56 and the experimental values used were 1.16 and 1.44.

The percentage differences of the various f_3 curves are, however, rather large at these values of b , and the prediction obtained on the basis of the other structure amplitudes can therefore not be very good even for diamond in spite of the smallness of the changes in the general behaviour of f_3 . Nevertheless it seems that the other reflexions require the values of $|F_{222}|$ to be somewhat larger than the experimental ones used. At least the value

0.90 reported by HEWAT, PRAGER, STEPHENSON and WAGENFELD [16] for Si is too small to fit in with the observed nonspherical systematics contained in the other reflexions.

8. SPECIAL PROPERTIES OF THE METHOD

Formally the method can be applied to any data regardless of their quality. In all of the present examples — DMW(Si) and DMW(Ge) included — it yields a prepared model with complete fit to the data. The impression is therefore that this is an efficient transformation of the experimental information into the form of atomic scattering amplitudes.

Such a transformation will, however, not be possible for an arbitrary set of structure amplitudes because of the restrictive requirements of locality and low order harmonic behaviour of the atoms inherent in the method. Yet, in some degree, the iteration seems to accommodate the radial atomic factors to fluctuations of the data. It introduces in the prepared model features which improve the fit artificially but which we should judge as inconsistencies according to our nonspherical standard of adequacy. This concerns particularly the analysis using large spheres, where the requirement of locality is weaker.

The infiltration of inconsistencies into the results is particularly clear in case of less complete data. Thus, in the case of DMW(Ge), with several low order reflexions missing, violent oscillations of the atomic factor curves of the prepared model were introduced, and the final result was clearly nonsense. In this way, however, a very good fit resulted even from the smallest sphere used ($R = 0.73d$) and obviously would have been obtained from still smaller ones. The situation was similar in the case of DMW(Si). Both of these cases were found earlier to be inadequate for the nonspherical analysis, and the good fit is certainly made possible only by the incompleteness of the data.

On the other hand, if the data are relatively complete up to the cut off in $\sin\theta/\lambda$, the iteration is not able to transfer single errors or obvious inconsistencies of the data into the results, or at least this will happen extremely slowly, thus effecting a rough separation of the internally consistent average behaviour of the data from more or less random deviations. Therefore in the cases of GW(C), GW(Si) and HKKK(Si) the final fit indicates good internal consistency of the data. In such cases considerably different values for one or two reflexions would appear in the analysis as deviations from the general pattern of consistency. This would particularly be the case, if for some reason relatively small spheres would be sufficient.

These statements imply that a good nonspherical consistency probably

indicates the existence of an exhaustive prepared model as the result of the iterative procedure, but that the reverse conclusion, in general, cannot be made, particularly not in case of defective data. This emphasizes the importance of the preliminary check of adequacy by a one-step calculation.

Also in cases of good data we get some artificial features in the results. For instance, the sinuosity of the curves at higher values of b is certainly unreal. This seems evident, because there are no significant deviations from experimental data even in the starting model $F(0, 0)$ in this region, (*cf.* figs. 12 and 13). It can therefore be regarded as an artifact produced by the iteration to extend the fit even to unessential fluctuations of the data. It may also be due to the method itself, which probably generates wavings, analogous to the termination effects in charge density, with a wavelength inversely proportional to the radius R .

9. COMPARISON WITH THE PARAMETRIC APPROACH

It is certainly an advantage of the present method, as compared to the parametric one, that it does not contain *a priori* assumptions about the behaviour of the radial atomic factor curves. We can thus understand the observed behaviour as a purely experimental result. It is worth noting that the three adequate data treated indicate relatively well-defined general behaviour of these curves. Once stated this can be used as a justification of parametric methods, provided that the functional form used has a behaviour of the proper type.

Figures 14, 15, 16 show for comparison also the results of McCONNELL and SANGER [5]. They are based on the parametrization suggested by DAWSON [1, 2]. According to these figures the functional form seems to be properly chosen. The shape follows the general behaviour of our results the differences being mainly due to oscillations of our curves.

In the case of HKKK(Si) the agreement is even quantitatively remarkably good. This agreement, however, is in a sense accidental, because it is possible only when the spherical deviation from the initial model turns out to be negligible. But since this is the case here, the results prove the equivalence of the methods. The disagreement between the two results for GW(Si) is clearly a failure of the parametric approach due to omission of the spherical correction indicated by the data — whatever its origin. The difference of the values obtained by McCONNELL and SANGER for the distortion parameters, when two different theoretical models were used for carbon in diamond, is a similar indication. Of course, it ought to be possible to include the spherical component also in the parametric approach. Once

a proper parametric representation is found the results ought again to be equivalent.

For diamond the results differ more than one would expect on account of the small spherical correction. The presence of the spherical component, though small, may cause part of the difference but probably not all of it. Another possible explanation is that the parametric approach is not similarly bound to the requirement of locality, and search for the best fit simply leads slightly beyond the limit to which this requirement can be weakened in the iterative method. The differences in the nonspherical components are, in any event, in that direction. It should be noted that in order to get a model with good fit we had to go almost to the limit in this respect, *i.e.* we had to use as large spheres as possible, both for Si and for diamond. Also fig. 12 gives a slight indication that further enlargement of the spheres — if it were possible — would still improve the fit at the two first reflexions, but the fit already obtained is a good one and there is not much to be gained in this way either. Definite statement of the reasons for the difference is not possible without a closer study of the properties of the parametric approach.

10. DISCUSSION OF THE RESULTS

The results show that it is possible to interpret the data GW(C), HKKK (Si) and GW(Si) in terms of separate atoms, which are local objects with low order harmonic deformations. This interpretation necessarily requires the atoms to possess significant components of third and fourth order. The function K_3 has tetrahedral character with four maxima, one in each of the bond directions, and minima in the opposite or antibond directions. The harmonic K_4 has a cubic nature with minima in the bond as well as in the antibond directions and maxima in the directions of the cubic crystal axes, (*cf.* ref. [1]). From the transformation rules of the radial functions (eqs. (6) and (7) in ref. [7]; *cf.* also eqs. (4) and (6) in ref. [8]), it follows that the radial density $\rho_3(r)$ corresponding to the $f_3(b)$ obtained will be mainly positive concentrated around one principal maximum, while $\rho_4(r)$ will have, like $f_4(b)$, one negative principal lobe. Thus, in the electron density the third order component is positive in the directions of the maxima of K_3 , while the fourth order component is negative in the maxima of K_4 . In this way their sum increases the electron density in the bond directions, while in the antibond directions the fourth order component partly cancels the reduction caused by the third order.

The large radius necessary to obtain a prepared model with good fit to the data shows that such an interpretation would not be possible in the

cases treated without allowance of a considerable overlapping of the atomic densities.

The interpretation obtained seems to be unique for a given set of data in the sense that the purely experimental uncertainty is dominant. This means that the radial scattering amplitudes f_3 and f_4 corresponding to the data treated are those given in figures 14, 15, and 16 within uncertainties of the order of the error bars in figs. 2, 3, and 4. They contain, however, some unessential and artificial details due to the method and only their general behaviour has any real significance.

On the basis of the spherical component f_0 we can also state definitely, that GW(C) and HKKK(Si) do not indicate spherical corrections to the initial HF model atoms, while the GW(Si) data do. However, since the general shape of the radial scattering amplitudes is largely determined by the requirement of locality, it can be attributed to the geometry of the crystal. The amount of actual experimental information included in it is therefore not very large. It can probably be expressed in terms of a couple of parameters, as is obvious from the comparison with the parametric approach. The problems connected with proper parametrization of the analysis will be discussed in detail in a subsequent paper.

Quantitative estimation of the real significance of the results is very difficult even if we could restrict the discussion to the experimental aspect of the problem only. Since the analysis is based exclusively on treatment of scattering amplitudes instead of charge densities, we need not worry about termination effects, *cf.* ref. [8]. The accuracy of the results is therefore mainly determined by the accuracy of the structure amplitudes measured. Estimation of the experimental accuracy, however, has turned out to be extremely difficult, (*cf. e.g.* [17]). We can also argue that most of the sources of systematic errors affecting the results have a relatively smooth dependence on $\sin\theta/\lambda$, *i.e.* on the absolute value of the scattering vector, rather than on its orientation. Therefore the nonspherical components are likely to be more reliable than the spherical correction. But this takes us no closer to a quantitative estimate of accuracy.

Our judgement of the quality of the data and the significance of the results is thus largely based on consistency criteria. The kind of consistency we are looking for in this connection is due to the requirements of locality and low order harmonic behaviour of the atoms. By the present method we can distinguish, to some extent, such a consistent average behaviour from inconsistent variations. This is an advantage of this analysis as compared with the earlier atomic factor calculation of KURKI-SUONIO [18, 19]. The fact that some of the data do fulfil the expectations in this respect confirms our confidence in these assumptions.

Consistency alone, however, is no guarantee of the accuracy of the data;

it is just a positive indication. The uncertainties discussed in the previous sections, and concluded to be something of the order of the experimental ones, constitute in a sense a minimum reasonable uncertainty. How much we should add to them depends just on the confidence we have in the consistency criteria. This question becomes particularly topical when we compare results obtained from different data on the same substance, *e.g.* figs. 15 and 16. For instance, we cannot find any essential difference between HKKK(Si) and GW(Si) merely on the basis of consistency arguments. The corresponding results, however, differ significantly if compared with the uncertainties treated, although there is qualitative agreement in non-spherical components. It should be noted that the fit of these results to the data is practically complete in both cases. The results themselves give no definite clue for judging which of them is more reliable, if we do not appreciate the agreement of the spherical behaviour of the HKKK result with the theoretical HF result as an argument. We are, thus, led back to the question of the reliability of the experimental methods, where the general opinion at present seems to be in favour of the Pendellösung method. If this is correct we must prefer the HKKK result.

Acknowledgement

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