

Series A

VI. PHYSICA

135

NON-APPROXIMATE ANALYSIS OF
EXPERIMENTAL STRUCTURE
AMPLITUDES

III. The Scale

BY

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1. Introduction

In part I [7]* of this work we outlined a method for analysing experimental crystal structure amplitudes determined with high accuracy. In part II [8]* we described the first phase of applying this method to sodium nitrate, using experimental values measured by INKINEN [6]. According to a remark made by INKINEN, there is some doubt concerning the absolute scale of these measurements, producing an additional uncertainty in the derived results. Although the experiments would seem to indicate extremely high accuracy in the measured structure amplitudes, there is still a relatively large difference between the experimental and theoretical structure-amplitude of the sodium ion at small values of \varkappa ($= \sin \Theta/\lambda$), which may be an indication of too high a scale.

Here we want to make a closer study of the scale problem, which is here a question of striving for extreme accuracy. We are already beyond the accuracy of any least-squares or reliability-index method. Moreover, such a method would mislead us, especially in the present case where we have one electron missing in the theoretical model. Consequently, some true differences exist and they ought to be excluded from the minimization procedure. A detailed analysis of the results obtained evidently provides the only way of observing errors of the order we are concerned with. Our program will therefore be, first, to study in detail what kind of effects a scale error will cause in the results, and secondly to see if such features are present in our application and to consider their significance.

2. Effects of a scale error

The results of our analysis are values of the Fourier series

$$(1) \quad \varrho(x, y, z) = \frac{1}{V_0} \sum_{hkl} F_{hkl} e^{-2\pi i(hx+ky+lz)}$$

or of the series

$$(2) \quad f_T(h, k, l) = \frac{1}{V_0} \sum_{h'k'l'} F_{h'k'l'} \sigma_T(h - h', k - k', l - l').$$

*) References [7] and [8] will be henceforth referred to as I and II.

When inspecting the effects of an error of scale, we can separate three parts in them.

First, F_{000} is the total number of electrons in the unit cell, and thus the corresponding term in both series is known exactly and does not depend on the scale. In the Fourier series this quantity is just the average density of electrons, while in the series (2) it represents the scattering amplitude of a region T filled with this average density, which for $h = k = l = 0$ is equal to the number of electrons in T due to the average density.

Secondly, there is the experimental part with the experimental coefficients F_{hkl} , and the scale error means that all terms of this part are multiplied by a common factor $k \neq 1$.

The third part includes all other terms, i.e. the residual term and those corresponding to weak reflections, which are not determined experimentally. In our analysis we use a theoretical residual term, which gives a reasonable continuation to the experimental atomic factors. Because of this requirement it will depend on the scale in a definite manner.

We now see, that the results of this analysis have a unique scale dependence. If we omit the residual term, it will be very simple. The scale factor k will just multiply all deviations from the average, and in this simplified case the error in ρ or f_T caused by k is therefore linear in the difference between the true value and the value obtained with a uniform average distribution. The residual term will somewhat confuse the situation, but we still expect to observe the strongest dependence in regions where the electron density possesses the greatest deviations from its average value, i.e. at the atomic positions and in the »empty space».

We can see the effects in detail if we produce artificial experimental values by multiplying the theoretical ones by a scale factor and analyse them. We must take into account only those reflections for which the

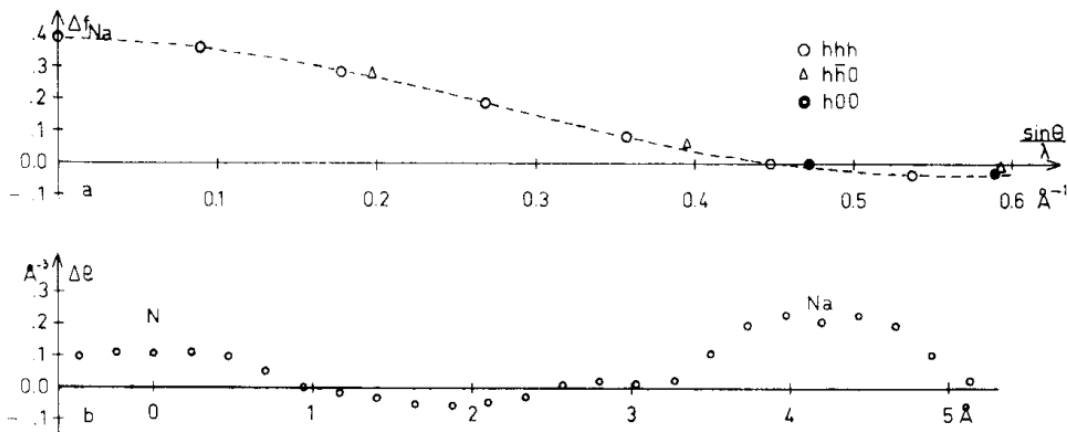


Fig. 1. The effect of increasing the scale by 5% a) on the difference series Δf_T for T_{Na} and b) on the Fourier difference series along the trigonal axis.

experimental structure amplitudes exist and determine the temperature factors in the theoretical values anew according to the »correct model» principles. The difference series shown in fig. 1 are found when the theoretical values F_{III} given in II are used as the starting point and a scale factor of 1.05 is chosen.

It is seen that the effect of the residual term is to cancel partly the deviations caused by the wrong scale and thus to diminish strongly the sensitivity of the results to variations of scale. There are still effects remaining which will certainly lead to anomalies if they are strong enough, and which will, if detected in experimental results, reveal an error in scale. We classify them into three forbidden features:

- deformation of atoms,
- negative (or too high) electron density between atoms,
- wrong electron number of atoms.

The deformation appears most clearly in the Fourier difference series. In the present application, for instance, the curve in fig. 1b tends to rise and sink with the scale in the inner region, of about 0.7 Å radius, of the Na atom, while in the outer region it tends to stay where it is. If in addition we take into account the fact that it in the innermost region, of a radius of about 0.4 Å, is very sensitive to the choice of the temperature factor (cf. fig. 8c in II), we see that the deformation of interest in the Na atom is just the height difference between the outer and inner parts of its difference Fourier picture, which is entirely formed in the region between 0.4 and 0.9 Å from the middle point. Obviously this phenomenon will have a similar character in any other case.

We have already in I discussed the question of acceptable deformations, which is largely a matter of judgement. We could of course define a criterion of least deformation, thinking any deformation to be unlikely, and let k be determined by it. But it is by no means clear that this principle would be strictly correct, since »deformation» here means merely deviations of an atom's electron distribution from the theoretical one used for calculation. However, this is actually a widely used principle. The difference-map methods of COCHRAN [2], CRUICKSHANK [3] and LEUNG et al. [9] are just analytical formulations of this principle. If we instead look how that deformation appears in atomic factor curves, we get a method much like the one used by DAWSON [4] for finding scaling errors. This principle is perhaps somewhat better justified, in view of the fact that we are looking for a known, particular type of deformation.

The second feature, too high or too low a density of electrons in inter-atomic space, gives rise to the requirement that the minimum density must be chosen zero, which has sometimes been used [10]. This criterion gives the scale only roughly. In principle it is certainly correct, if applied to cases

like this where very low densities are known to exist. However, the deviation from the average density will always be very small here. At exactly zero density it just equals the average (0.677 \AA^{-3} in NaNO_3). Therefore very accurate values indeed, also for the residual term, are necessary before any reasonable accuracy can be gained. We see in fig. 1 b that a 5% error in scale will cause in empty space a maximum error of only about 0.05 \AA^{-3} .

The situation would get much more favourable if whole regions of zero density could be assumed. Series (2) gives us $f_T(0)$, which is the total number of electrons in the region T . (The effect of scale error on electron numbers in some empty regions, calculated in this way, are given in table VI in a later context.) Because the convergence here is substantially better (if not too small regions are used), we can get an appreciably better accuracy. The crucial question is now whether the correct number of electrons can be known. If we make it exactly zero in any empty region, we certainly get too high a scale. In this way the unavoidable element of arbitrariness is again introduced into the analysis.

The third effect, the deviation of an atom's electron number from its correct value, can also be observed by computing $f_T(0)$ for a suitable region T (cf. table VI). It may well provide the most accurate criterion since we have here the strongest deviations from the average, and, on the other hand, the series has good convergence properties (cf. fig. 5). The task is just to choose the scale factor so as to make $f_T(0)$ equal to the correct value of electron number. However, it is not immediately clear how the region T must be chosen, since a small part of the distribution of the atom can be spread into a wide region. That makes also this criterion to a certain extent a matter of judgement.

In this type of study our treatment seems to offer two advantages. First, series (2) makes possible a direct numerical calculation of numbers of electrons in different regions. Secondly, it permits the evaluation of errors in the residual terms (cf. sec. 4), which is badly needed when we try to estimate the significance of the features discovered.

3. Remarks on the structure amplitudes

Our task is to see whether any of the anomalies described above appear in the present application. To that end, we shall examine separately the results obtained by using the difference series, the Fourier series and by the calculation of $f_T(0)$ from series (2). Some remarks on the structure amplitudes are, however, necessary before presenting the calculations.

The experimental structure amplitudes will be those given by INKINEN [6], and as theoretical values we shall use those obtained from model III in

II. In order to have the correct total number of electrons, we must subtract the Hönl correction from the experimental values instead of adding it to the theoretical ones as usual. (In the difference series, of course, this makes no difference.)

For calculating the residual terms, we sought analytic approximations for the theoretical atomic factors in the region of high \varkappa . We used functions of the type

$$(3) \quad f_{\text{analytic}} = \sum_i A_i e^{-a_i \varkappa^2},$$

where a method of LÖWDIN and APPEL [11] for finding the parameters A_i and a_i could be used. Numerous functions given in the literature for approximating atomic factors could not be used here, since we are mostly interested in the residual-term region.

Table I

The parameters for analytic approximation of the theoretical atomic factors.

Na		N		O	
A	a	A	a	A	a
1.804	0.138	1.721	0.308	1.713	0.232
4.723	3.140	1.080	6.570	13.890	11.410
3.424	8.880				

Table II

Accuracy of the analytic approximations of the theoretical atomic factors.

atom	interval	$ f_{\text{anal}} - f_{\text{theor}} $
Na	$0.01 < \varkappa^2 < 0.7$	< 0.03
	$0.7 < \varkappa^2 < 2.5$	< 0.02
N	$0.3 < \varkappa^2 < 0.7$	< 0.010
	$0.7 < \varkappa^2 < 2.3$	< 0.008
O	$0.3 < \varkappa^2 < 2.3$	< 0.008

We arrived at the parameter values given in table I. They constitute a representation for the atomic factors f_{Na} , f_{N} , f_{O} at zero temperature in limited regions of κ . The resulting maximum deviations from the theoretical values of FREEMAN [5] and MCWEENY [12] are given in table II.

In the course of the calculation some minor errors were observed in the theoretical atomic factor values given by INKINEN [6], which we have used as the starting point in calculating theoretical structure amplitudes. They obviously arise from inaccuracies in the graphical interpolation procedure used in their evaluation. They have no essential effect on any of the previously derived results. For exactness they are corrected here. They were observed by a semi-analytical interpolation procedure, which proved reliable in all calculated examples. An approximate analytic representation of type (3) was formed and the remaining differences interpolated graphically. It was also found that the temperature factor B_{N} given by INKINEN did not agree with the given numerical values, which, however, may be due to a misprint. The correct value corresponding to his f_{N} values seems to be $B_{\text{N}} = 1.140 \text{ \AA}^2$ instead of the given 1.040 \AA^2 . Our result in II must therefore also be corrected to $c_{\text{N}}^2 = 0.465 \pm 0.05 \text{ \AA}^2$.

The revised theoretical values F'_{III} for model III without the Hönl correction as well as the corresponding experimental values F'_{exp} and differences $\Delta F'_{\text{III}}$ are given in table III.

4. Evaluation of the corrections

The features searched for appear as such fine details in the results that no conclusions at all can be made before all important corrections and errors have been evaluated. In I we classified them into experimental errors, possible variations of the »correct model» and »heavy deformations and interatomic distributions».

We assume that the standard deviations given in II express the correct order of magnitude of all experimental errors (except those resulting from the scale, of course). The limits given for the parameters define the variations of the »correct model». Thus the main trouble is caused by the »heavy deformations and interatomic distributions». In practice this means that we have to evaluate errors caused by the use of theoretical values for the weak reflections and for the reflections just above the cut-off limit; the variations of the »correct model» will take care of reflections lying farther away.

The error due to weak reflections will no doubt be a most important one. We see from the calculated Δf_{Na} (fig. 3 a) and Δf_{NO_3} (fig. 7 b in II) that the structure amplitudes of the Na ion and the NO_3 group deviate from the theoretical ones in the measured κ region. Therefore the theoretical values

Table III

F'_{exp} = experimental structure amplitudes with the Hönl correction

F'_{III} = the corresponding revised theoretical values

$\Delta F'$ = $F'_{\text{exp}} - F'_{\text{III}}$

F_{q} = quasi-experimental structure amplitudes for the weak and coincident reflections

F_{corr} = theoretical structure amplitudes with corrections due to f_{Na} and f_{NO_3} .

hkl	F'_{exp}	F'_{III}	$\Delta F'$	F_{q}	F_{corr}
000	84.00	82.00	2.00		83.54
110	7.37	8.12	0.75		7.10
211	40.73	40.12	0.61		40.74
222	-29.23	-27.81	-1.42		-28.91
$\bar{1}\bar{1}0$	14.17	14.67	-0.50		14.17
201	19.46	19.35	0.11		
200	18.61	17.29	1.32		18.53
220	12.80	12.43	0.37		12.79
332	31.32	29.70	1.62		31.08
321	14.13	14.38	-0.25		14.34
$\bar{2}01$	14.91	14.92	-0.01		
$2\bar{1}\bar{1}$	13.28	13.72	-0.44		13.34
433	-	-0.39		-0.75	
310	10.02	9.34	0.68		9.80
422	9.51	8.76	0.75		9.04
432	11.91	11.40	0.51		
320	12.82	12.97	-0.15		
$2\bar{1}\bar{1}$	19.58	19.60	-0.02		19.68
444	31.00	30.50	0.50		31.20
412	10.46	10.63	-0.17		
442	9.16	9.56	-0.40		9.08
431	9.36	8.74	0.62	9.40	9.50
411	-	2.40		2.35	
330	-	1.47		1.43	
$\bar{2}\bar{2}0$	9.79	9.30	0.49		9.88
$3\bar{1}\bar{1}$	2.25	1.54	0.71		
543	8.66	8.57	0.09		8.97
$\bar{2}\bar{2}\bar{1}$	-	0.51		0.47	
$\bar{3}\bar{1}0$	-	0.29		0.17	
532	9.21	9.16	0.05		9.06
$3\bar{2}\bar{1}$	15.75	15.60	0.15		15.60
554	-	0.19		0.39	
420	7.32	7.42	-0.10	7.31	7.34
410	-	0.18		-0.24	
524	7.48	7.74	-0.26		
222	-6.89	-6.56	-0.33	-6.88	-6.52
403	-	0.98		1.06	
400	20.31	19.99	0.32		19.97
644	7.46	7.64	-0.18	7.57	7.66
521	12.87	13.18	-0.31	12.83	12.98

Table III (continued)

hkl	F'_{exp}	F'_{III}	$\Delta F'$	F'_{q}	F'_{corr}
531	1.70	1.08	0.62		
645	5.29	5.31	— 0.02		
655	12.36	12.15	0.21		12.09
643	5.53	5.65	— 0.12		
633	{ 10.62	10.62	0.00	10.70	10.74
552	{ 11.71	11.71	0.00	11.73	11.67
320	6.42	6.10	0.32		
321	5.76	5.61	0.15		5.51
541	—	0.51		0.63	
411	6.88	6.76	0.12		6.48
653	{ 5.02	5.46	— 0.44	5.01	5.20
440	{ 15.37	16.68	— 1.31	15.38	15.94
412	5.50	5.21	0.29		
321	11.30	11.87	— 0.57		11.63
623	—	— 0.53		— 0.55	
664	6.72	6.48	0.24		6.46
401	{ —	1.44		1.32	
322	{ —	0.96		0.86	
642	5.92	6.06	— 0.14		5.88
666	—	— 3.83		— 3.71	
520	5.53	5.41	0.12		
622	— 5.53	— 4.54	— 0.99		— 5.14
530	{ 5.36	5.42	— 0.06	5.37	5.28
431	{ —	— 0.23		— 0.09	
510	{ —	— 0.70		— 0.63	
754	{ 4.76	4.64	0.12	4.74	4.64
652	{ —	0.99		1.07	
765	4.52	4.21	0.31		4.31
411	—	— 0.39		— 0.43	
631	4.21	3.59	0.62		4.07
332	9.87	9.61	0.26		9.71
743	—	0.20		0.30	
504	{ —	0.35		0.27	
612	{ —	1.47		1.45	
764	4.48	4.15	0.33		
330	4.55	3.52	1.03		4.22
641	{ 3.94	3.51	0.43	3.94	3.37
735	{ —	0.64		0.70	
412	4.12	4.21	— 0.09		
331	—	0.79		0.73	
776	{ 7.80	8.16	— 0.36	7.88	8.06
420	{ 3.84	4.02	— 0.18	3.75	3.84
422	3.81	3.72	0.09		3.78
611	{ 8.06	8.15	— 0.09	8.27	8.21
662	{ —	— 3.30		— 3.08	
521	4.54	4.59	— 0.05	4.42	4.39

certainly are poor approximations for many of the weak reflections in this region.

It is evident that the deviations of the experimental structure amplitudes from the theoretical ones, except for statistical errors, are chiefly caused by the differences between the true and the theoretical atoms inside the regions T_{Na} and T_{NO_3} used in the calculation. (It was also seen that choosing larger regions did not cause essential changes in the Δf curves). If this is accepted, we can construct estimates for the weak reflections by correcting theoretical values with corrections corresponding to the calculated Δf_{Na} and Δf_{NO_3} . The regular behaviour permits a reliable interpolation of Δf_{Na} , but no simpler way was found for getting the Δf_{NO_3} values than just to calculate series (2) separately for each (hkl) in question. We call the structure amplitudes reached in this way quasi-experimental, and give their values F_q in table III.

Quasi-experimental values are evaluated also for the coincident reflections. In this case the experimental total intensities are divided in the ratio of the component intensities corresponding to the corrected theoretical values.

The corrections due to weak and coincident reflections can now be estimated just by calculating their contribution to the series with use of the F_q values.

We can get an idea of the reliability of the quasi-experimental values by making the same corrections in the theoretical values of the measured reflections. Comparison of the corrected values F_{corr} (table III) with the experimental ones shows that all significant differences have been essentially corrected. This correction causes the sum $R = \Sigma(F_{\text{exp}} - F)^2$, calculated for the terms considered (odd reflections omitted), to drop from its value $R = 15.58$ down to 2.65, which is already near the value $\Sigma\delta^2 = 1.22$ calculated from statistical errors. This makes us believe that the evaluated contributions of weak reflections will also be more than just qualitatively correct.

There will obviously also arise significant errors from the fact that the theoretical structure amplitudes in the residual-term region differ from the true ones in a manner that cannot be represented by variation of parameters. This is true at least for the contribution of the nitrate group, as is clearly seen from the wavy end of the calculated Δf_{NO_3} (fig. 7 b in II). For the sodium ion this seems to be less important.

We can explain this error by saying that it is a consequence of too poor a model for the nitrate group. However, we know how its structure amplitudes can be improved in the low z region up to the cut-off limit. The correction is just expressed by the calculated Δf_{NO_3} . Neither do we need anything else as long as we are interested only in effects outside T_{NO_3} . The reason is that

we can take any model for NO_3 , and no changes in the resulting experimental distribution outside T_{NO_3} will occur unless we choose a bad model which gives a discontinuous continuation to the experimental f_{NO_3} . A discontinuity in the structure amplitude will always cause extended oscillations in the distribution. Now we do not know what the improved model actually is, except for just the corrected F values below the cut-off limit, but we do know that it must be essentially better than the old one, and the oscillations, certainly present in the original Fourier picture, must be largely eliminated. Outside T_{NO_3} the result therefore is the same as if we had corrected the residual term of the theoretical model to give a more reasonable continuation to the experimental f_{NO_3} . Because the improvement of the model concerns only the region T_{NO_3} , the corrections obtained are valid in the outside region for the difference series as well as for the total series.

In this way we get an estimate for the contribution of the NO_3 group to this cut-off error everywhere outside the region of the ion itself, for instance in f_{Na} , by taking the corrections to the F_{hkl} values corresponding to the calculated Δf_{NO_3} , and calculating the change caused by them in f_{Na} . Of course we can equally well ask about the correction to the distribution density at the Na ion or between the atoms. The only thing we cannot do in this way is to evaluate this correction in the NO_3 group itself or in its immediate neighbourhood, where it unfortunately is the largest. To do this we in fact ought to guess the continuation of Δf_{NO_3} in the residual-term region.

5. Calculations and discussion of results

The difference series will be examined first. Of the three anomalies we are searching for the only one that can be seen in the difference series is the deformation of atoms. Here the Na ion is a much more rewarding object of study than the atoms of the nitrate group. It is more compact and separate from its surroundings, and we can therefore expect it to be less deformable and at the same time more sensitive to scale changes. Thus it seems reasonable to concentrate in this connection on the study of the Na ion alone.

The Fourier difference series at the Na atom along the trigonal axis, as well as Δf_{Na} , have been calculated; with the results shown in figs. 2 and 3. In order to make the significance of scale more pronounced, we present in adjacent figures results where a 5% lower scale is used for the experimental structure amplitudes and a corresponding adjustment of the theoretical model according to the »correct model» principles is made. The contributions of weak reflections in both series, δ_{weak} , have been calculated with use of the coefficients $F_{\text{q}} - F'_{\text{III}}$ ($F_{\text{q}} - F'_{\text{exp}}$ for strong coincident reflections) as

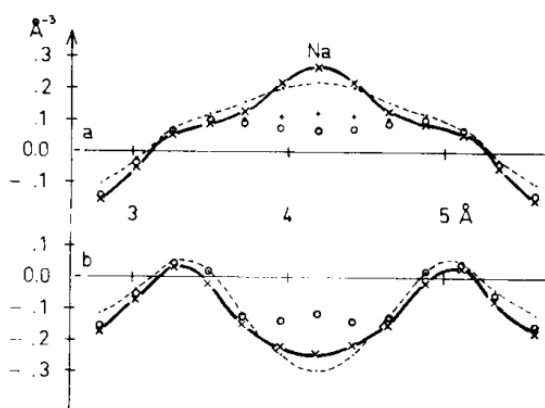


Fig. 2. Fourier difference series at the Na ion along the trigonal axis a) with the original scale, b) with the scale reduced by 5%. The result is given without corrections ($\cdot - \cdot$), corrected for the weak reflections and the cut-off error ($\times - \times$) and with a slight change of the temperature factor c_{Na}^2 in addition to the corrections ($+$). The circles stand for the result when the theoretical atomic factor of Boys is used.

well as the correction of the cut-off error due to the nitrate group, as explained in sec. 4. The numerical values of these corrections as well as the uncorrected values are given in tables IV and V.

The same corrections have also been made in the case of the lower scale. Actually, we ought to compute new Δf 's by using experimental values with the lower scale and the corresponding theoretical values, and to evaluate these corrections all over again. We also calculated some values of Δf_{NO_3} , enough to get an idea of its behaviour. Together with the new Δf_{Na} (fig. 3 b) they gave clear evidence that the corrections will be only slightly different. Therefore we found it justified to take the corrections numerically equal. It must be borne in mind that that they are of a rather approximate character in any event.

The effect of experimental errors was seen in II to be of the order of 0.02 \AA^{-3} in the Fourier series and 0.04 in Δf_{Na} . The effect of parameter variation is also studied in II (cf. figs. 3 b and 8 c in II). In the Fourier picture only the innermost region, not beyond 0.4 \AA from the middle point, is sensitive to the temperature factor c_{Na}^2 , and will depend on the particular choice of it within the limits of the »correct model». The other parameters have no significance here. The numerical values of δ_{param} in table IV were found when c_{Na}^2 , c_{N}^2 and c_{O}^2 were given maximum variations within these limits (0.035 , 0.05 and 0.045 \AA^2 respectively).

Let us now look in $\Delta \rho$ for the particular type of deformation discussed in sec. 3. Taking into account the possibility of varying c_{Na}^2 , we see that in the original scale (fig. 2 a) we have no height change in the critical region, in contrast to the reduced scale (fig. 2 b), where a slope is clearly seen. This

Table IV

Fourier difference series along the trigonal axis at intervals 0.2331 Å, uncorrected (Δq) and corrected (Δq_{corr}), with the estimated contribution of the weak reflections (δ_{weak}), the correction of the cut-off error due to the NO_3 group (δ_{resNO_3}), that due to both the Na ion and the NO_3 group (δ_{res}), and the effect of possible changes of the parameters (δ_{param}).

n	Δq	δ_{weak}	δ_{resNO_3}	δ_{res}	Δq_{corr}	δ_{param}	
T_{NO_3}	4	-0.090	-0.004	0.150	0.152	-0.092	∓ 0.014
	5	-0.064	-0.013	0.123	0.115	-0.085	∓ 0.014
	6	-0.136	0.010	0.074	0.060	-0.140	∓ 0.006
	7	-0.258	0.036	0.057	0.047	-0.175	± 0.011
	8	-0.221	0.029	0.036	0.032	-0.160	± 0.015
	9	-0.052	0.001	-0.017	-0.016	-0.067	± 0.010
	10	0.013	-0.015	-0.062	-0.060	-0.062	± 0.006
	11	-0.064	-0.016	-0.063	-0.060	-0.140	∓ 0.011
	12	-0.101	-0.014	-0.032	-0.033	-0.148	∓ 0.023
	13	-0.023	0.013	-0.004	-0.010	-0.046	∓ 0.010
T_{Na}	14	0.071	-0.020	0.005		0.056	∓ 0.011
	15	0.120	-0.035	0.001		0.086	∓ 0.020
	16	0.158	-0.033	0.006		0.131	± 0.088
	17	0.202	-0.007	0.026		0.221	± 0.325
Na	18	0.222	0.011	0.040		0.273	± 0.460

situation does not suggest any change of scale from the original one. If we take the criterion strictly, we can say that only changes below 2% could be allowed, an increase equally well as a decrease, and here we already have included the uncertainties in evaluating the corrections.

Of course we have no guarantee of the correctness of this principle itself. Only a knowledge of the goodness of the theoretical atomic factor of the Na ion could give more assurance to this reasoning. To get some idea of the order of magnitude of possible changes in the model, we took the theoretical atomic factor of BOYS [1] for Na^+ , which no doubt is the best one available, and calculated new Δq values. Also this result is given in fig. 2, and it does not give any reason for changing the conclusions.

We are not able to make any accurate quantitative conclusions from the Δf_{Na} curves. The uncorrected results (fig. 3a) show very clearly the reason for suspecting too high a scale: the average trend of these curves is strikingly similar to fig. 1a, which gives the isolated effect of a 5% increase of scale. In the corrected results (fig. 3c) this similarity is not so evident any more, although the beginning still is equally high. The high values near $\kappa = 0$

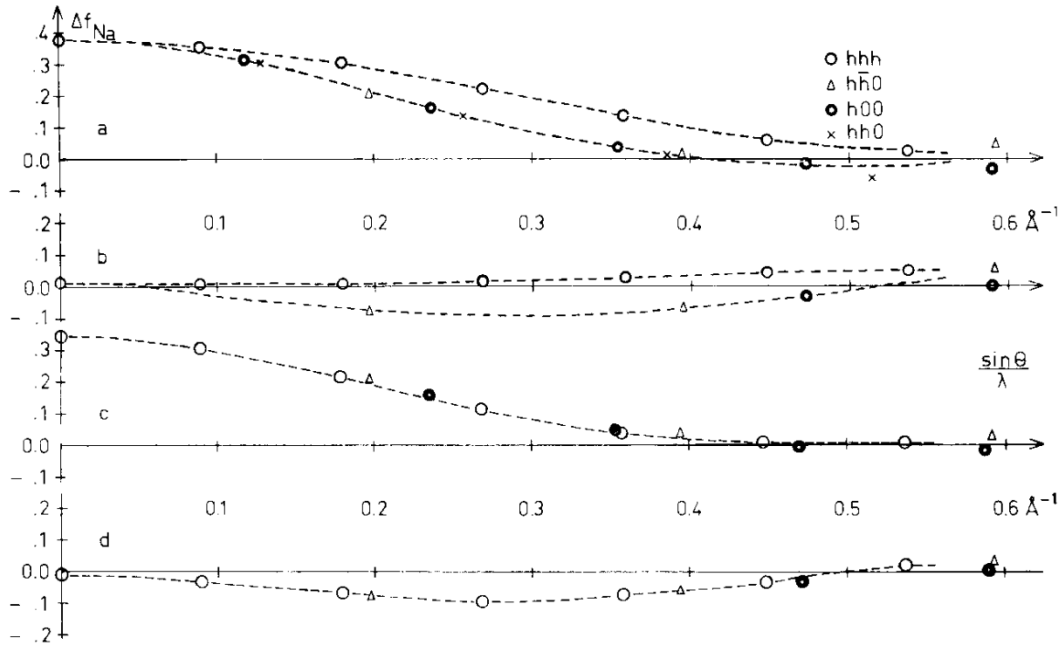


Fig. 3. The difference series Δf_T for T_{Na} , a) uncorrected and with the original scale, b) uncorrected but with the scale reduced by 5%, c) corrected for weak reflections and the cut-off error due to the NO_3 group and with the original scale, and d) the same as c) but with the scale reduced.

Table V

The difference between the experimental and the theoretical scattering factor of the Na ion, uncorrected (Δf_{Na}) and corrected ($\Delta f_{Na, corr}$), with the estimated contribution of the weak reflections (δ_{weak}) and the correction of the cut-off error due to the NO_3 group (δ_{resNO_3}).

hkl	Δf_{Na}	δ_{weak}	δ_{resNO_3}	$\Delta f_{Na, corr}$
000	0.367	-0.002	-0.022	0.343
111	0.346	-0.010	-0.030	0.306
222	0.291	-0.028	-0.048	0.215
333	0.217	-0.044	-0.061	0.112
444	0.144	-0.048	-0.057	0.039
555	0.082	-0.037	-0.038	0.007
666	0.036	-0.017	-0.012	0.007
$\bar{1}\bar{1}0$	0.206	0.000	-0.001	0.205
$2\bar{2}0$	0.027	-0.008	0.013	0.032
$3\bar{3}0$	0.044	-0.017	-0.002	0.025
200	0.164	-0.003	0.000	0.161
300	0.045	-0.005	0.009	0.049
400	-0.009	-0.005	0.007	-0.007
500	-0.023	0.000	0.004	-0.019

mean just that the experimental values give about 0.4 electrons more in the region T_{Na} than the theoretical ones. A more extensive study of the numbers of electrons in different parts of the unit cell is necessary before we can decide whether there is anything unnatural in this result.

There is, however, another feature which must be noted. After the corrections, the differences between the principal directions, $\cos^2\varepsilon = 1$ and $\cos^2\varepsilon = 0$, in the Na ion have completely vanished. This says that the experimental values show no sign of ellipsoidal deviations from spherical symmetry in the Na ion.

As an attempt to use the empty space criterion, we have calculated values of the Fourier series on the trigonal axis between the ions. The values of the Fourier difference series were calculated at distances $n \cdot 0.233 \text{ \AA}$ from the middle point of the nitrate group. The points $n = 7, \dots, 13$ lie outside both T_{NO_3} and T_{Na} and will be studied more closely.

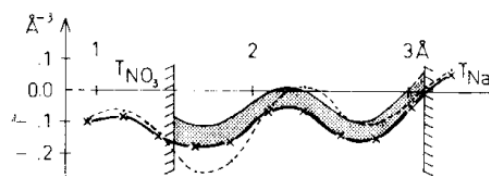


Fig. 4. Electron density in the interatomic space along the trigonal axis. ($\cdot - \cdot$) = the uncorrected $\Delta\rho$, ($\times - \times$) = $\Delta\rho$ corrected for the weak reflections and for the cut-off error, (—) = the estimated upper limit for the experimental electron density.

The contribution of weak reflections was evaluated as before. The cut-off error can now be estimated for both ions because we are outside both regions. The effect of experimental errors was given in II as of the order of 0.02 \AA^{-3} . The effect of possible variations of the temperature parameters was also calculated as before.

The electron density of our model in this empty region has small positive values. A closer examination shows that it lies below 0.06 \AA^{-3} at all points considered, being in the middle part of the region considerably less. This gives us an upper limit for the experimental electron density, when added to the corrected values, as shown in fig. 4. The numerical values of the results and corrections are given in table IV.

We see that even the upper limit, which in fact is taken rather high, has negative values, which certainly is wrong. If we compare this curve to fig. 1 b, which gives the effect of a 5% error in scale, we see that only a negligible part of this feature could arise from too high a scale. In particular, it seems impossible to explain the valley on the right side of the curve in this way. We also believe that the evaluated corrections cannot be so much in error.

So the only possible explanation seems to be that there are some isolated errors in the experimental values, and we can only take the situation as a warning example of the serious effect such errors can have on the details of the Fourier picture. This circumstance makes it impossible to draw any conclusions about the effect of the scale in such a calculation. It also shows that caution is needed in using the deformation criterion.

As a last attempt to find new arguments concerning the scale, we calculated the number of electrons in different regions of the unit cell, viz. for both ions separately and for their surroundings, and finally for the whole »empty space». We therefore calculated $f_T(0)$ for the following regions: spheres containing the sodium ion with radii 1.05, 1.20, 1.30 Å and ellipsoids containing the nitrate group with $A = 2.20$, $B = 1.50$ Å, which was used in II, and with $A = 2.20$, $B = 1.87$ Å. The surroundings of the ions were then obtained as the differences between the largest and smallest sphere or ellipsoid, respectively. The whole empty space is represented by the rest of half a unit cell, when both T_{Na} and T_{NO_3} are subtracted, and in this particular case we chose regions that are tangent to each other. This condition of tangency is achieved if we choose the larger one of the two T_{NO_3} regions together with a T_{Na} whose radius is 1.11 Å, or the smaller one of them together with a T_{Na} of 1.20 Å radius.

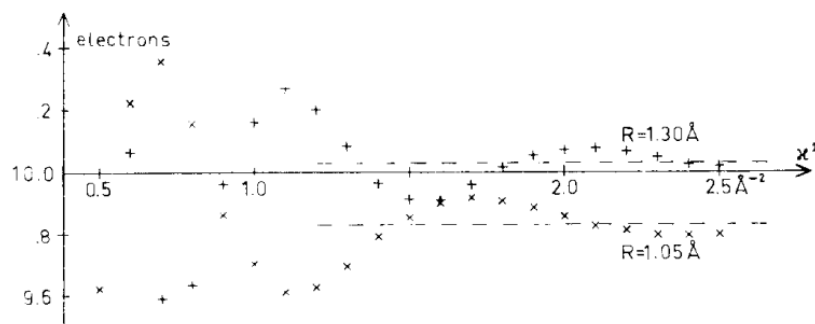


Fig. 5. Progress of convergence of the series $f_T(0)$ for T_{Na} with two different radii.

The residual terms were calculated with the aid of the analytic representations (3). In order to follow the progress of convergence, we plot the theoretical partial sum as a function of the cut-off limit x^2 . Two of these curves are shown in fig. 5. All of them show a similar, very regular behaviour with smooth damped oscillations, which allows us to determine the limits of these series rather accurately. In any event, the errors here are negligible compared to other inaccuracies in evaluating the experimental sum.

The experimental results are obtained by adding the difference series to the theoretical values. The contributions of weak reflections are evaluated

as before. The largest contribution to the cut-off corrections, that of the nitrate group δ_{resNO_3} , can be estimated directly only for the Na and empty space regions, but not for the NO_3 regions, as explained in sec. 3. However, in this particular case of calculating electron numbers, we can make use of the known exact result for the whole unit cell, which must remain unchanged in every calculation. Also, the cut-off correction to $f_T(0)$ must be zero for the whole cell, and in T_{NO_3} it is therefore the negative of its value in the complementary region, where a direct calculation is possible. The standard deviation δ_{exp} is again understood to express limits on experimental errors and the effect of varying the parameters (δ_{param} calculated as before) to give limits for the residual term. Numerical results are listed in table VI. For comparison, the isolated effect of a 2% increase in scale is also given here calculated in the same way as fig. 1.

Table VI

Number of electrons in different regions (columns 1, 2 and 3), the contribution of weak reflections (δ_{weak}), the cut-off error due to the NO_3 group (δ_{resNO_3}) and the Na ion (δ_{resNa}), the standard deviation (δ_{exp}), the effect of possible variations of the parameters (δ_{param}), and the effect of raising the scale by 2 per cent ($\delta_{2\%}$).

region	Theor.	Exp.	cor- rected	δ_{weak}	δ_{resNO_3}	δ_{resNa}	δ_{exp}	δ_{param}	$\delta_{2\%}$
Na sphere:									
1. $R = 1.05 \text{ \AA}$	9.83	10.20	10.19	-.002	-.022	.01	.065	$\mp .041$.145
2. $R = 1.20 \text{ \AA}$	9.95	10.29	10.31	.022	.019	-.02	.062	$\mp .009$.103
3. $R = 1.30 \text{ \AA}$	10.03	10.33	10.39	.034	.041	-.02	.060	$\pm .024$.070
shell between Na spheres 1 and 3									
	0.20	0.13	0.20	.036	.063	-.025	.069	$\pm .065$	-.073
NO_3 ellipsoid:									
$A = 2.20, B = 1.50 \text{ \AA}$	30.35	30.94	30.86	-.027	-.05	$\sim .00$	$\sim .10$	$\mp .016$.209
$A = 2.20, B = 1.87 \text{ \AA}$	30.55	31.12	31.09	.003	-.03	$\sim .00$	$\sim .10$	$\mp .012$.119
shell between the two NO_3 ellipsoids									
	0.20	0.18	0.23	.030	.022		$\sim .06$	$\pm .004$	-.085
half unit cell less ($T_{\text{Na}} + T_{\text{NO}_3}$):									
$R = 1.20;$ $A = 2.20$ $B = 1.50$	0.70	0.64	0.69	.005	.05		$\sim .10$	$\pm .025$	-.31
$R = 1.11;$ $A = 2.20$ $B = 1.87$	0.58	0.77	0.80	-.011	.04		$\sim .10$	$\pm .042$	-.25

At first it should be noted that the errors and corrections are noticeably smaller compared to the effect of the scale error than in the electron density calculations. Thus, if we knew beforehand the number of electrons in any of the regions, we should get a reliable criterion for correct scale.

The Na ion is known to have 10 electrons. The experimental results for different T_{Na} are: 10.19, 10.31, 10.39 electrons for radii of 1.05, 1.20, 1.30 Å respectively, provided the original scale is correct. They show a steady increase with growing radius. The number of electrons in the shell between the first and third sphere is 0.2, which means that the increase is significant if the scale is not too low more than about 3%.

In these circumstances the starting point of our considerations, the high value of $\Delta f_{\text{Na}}(0)$, loses its significance as an argument about the scale. The idea behind the original doubt is certainly that the number of electrons in T_{Na} ought to be exactly 10 (which however does not mean that $\Delta f_{\text{Na}}(0)$ ought to be zero). A rough extrapolation shows that the radius of a sphere containing 10 electrons is about 0.93 Å, if the original scale is correct, and only about a 1% reduction of scale is necessary to change it into 0.98 Å, which is the commonly used value for the ionic radius of Na^+ . Thus the original requirement is actually very easily satisfied with such a smaller sphere. However, this does not provide any argument concerning the scale since the electron cloud spreads out farther, and one choice of boundary seems no more justified than another within the limits considered. Only the choice of a scale at least 3% higher would make the electron number of the Na ion well defined. However, the electron number then comes out about 10.5, so that the criterion is not applicable.

The nitrate group is again a less favourable object for making conclusions about the scale. A nitrate ion has 32 electrons (in our model only 31), but the outer ones are known to be rather widely distributed in space. The results for the two ellipsoids, 30.86 and 31.09 seem therefore quite reasonable.

The electron numbers in the empty space regions are of course not known beforehand. We can only be sure that they are slightly greater than zero. Such regions, however, have been examined here since the Fourier analysis of empty space gave negative densities. We see that a considerable part of the negative regions found there lie inside the shell regions between the smallest and largest sphere or ellipsoid. In both cases, however, we get clearly positive results, which confirms that the negative density is only a rather local feature and shows that the calculation of f_T is rather insensitive to single errors in the structure amplitudes. Even a raise of scale would be allowed, with an upper limit of 5%, the limit being set by the requirement that both values be positive.

The number of electrons in the whole empty space is found to be 0.7 and 0.8 in the two calculated cases. Again a 5% increase in scale is needed before

it vanishes, and before we can be sure of too high a scale having been reached.

The occurrence of anomalies in all these cases is rather insensitive to scale errors. The calculation of electron numbers would in principle be the most accurate one. The limits of accuracy in the results would allow accuracies of scale up to $\pm 1\%$, if the correct result could be known for any T . But none of them is known exactly, and we can only resort to arguments of what is reasonable, which seem to include uncertainties of at least 3 or 4%. The criterion of least deformation, when understood literally, reaches also a 1.5–2% accuracy, but it is somewhat questionable in principle. The examination of electron density in empty space for this purpose is completely spoiled by isolated errors in the experimental values, and would even in principle scarcely go beyond 5% in accuracy.

The qualitative statements of the different criteria obviously hold generally. The numerical limits of their accuracy are valid only for this particular case. In different crystals the possibilities for scale control may be quite different, and also more extensive (greater cut-off limit) experimental material will certainly make possible a more accurate treatment.

One additional remark can still be made. In the measurements of Inkinen the scale is fixed relative to the structure amplitudes of NaCl observed by VIHINEN [13]. These are, however, also relative measurements where the scale is determined afterwards. The criterion used is only shortly mentioned in ref. [13] (page 19) and no attention is paid to the reliability of the principle or to the accuracy of the result. The present work gives rise to some criticism of VIHINEN's method, although at the same time it shows that no major errors can exist. The scale of the measurements of VIHINEN ought to be controllable with a much better accuracy than that of the present case, since they give an appreciably longer and more complete series of structure amplitudes. Actually, we have made such an analysis and found that the accuracy fortunately happens to be rather good, only an error of the order of 1% being possible.

From all our considerations we draw the conclusion that the original scale of the experimental structure amplitudes considered is correct to within $\pm 2\%$. This is not quite indisputable if the analysis of these values alone is considered, since the only argument that reaches such limits is the somewhat questionable deformation criterion. Such limits would, however, have been quite reasonable on the basis of the experimental work described by Inkinen, where the fixing of the scale relative to the basic scale is actually rather accurate. The unfortunate suspicion of too high a scale turned out to be quite groundless. There does not even exist a preferable direction for correcting the scale in any of our considerations; instead, an increase in the original scale looks just as possible as a decrease.

Now that the limits of scale are fixed, we can immediately find the corresponding limits for parameter values given in II because the effect of changing the scale has already been studied there for each of them. We can now also understand the values given in table VI to be experimental results concerning the distribution of electrons in NaNO_3 .

Summary

The effects of scale errors in crystal structure analysis are studied in detail in the case of the NaNO_3 crystal. A critical analysis of the experimental structure amplitudes, measured by INKINEN [6], is made in order to find such effects. No significant anomalies could be seen, and the original suspicion of too high a scale was shown to be groundless.

The accuracy of such control methods turned out to be rather poor, hardly better than some 3–4% in this case. However, in this particular case one has reason to believe that the error in the original scale lies below 2%.

It is shown that our method of analysis [7] makes possible an evaluation of the contribution of weak, unmeasured reflections in the results, as well as a reasonable estimation of cut-off errors. Both of them were taken into account in all considerations. The slight difference between the main crystallographic directions in f_{Na} was seen to arise only from these errors.

Numerical values are given for the electron number in different regions of the unit cell. They show, for instance, that there is a somewhat higher concentration of electrons around the peak corresponding to the Na ion than what is indicated by the theoretical values.

In the course of the work some minor errors in the previously used values are rectified.

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Printed November 1963