AN ANALYSIS OF THE STRUCTURE AMPLITUDES OF NaCl MEASURED BY VIHINEN

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Abstract

The experimental structure amplitudes of NaCl measured by VIHINEN are analyzed. The original criterion for fixing the scale has been incorrect in principle. A more careful evaluation gives a correction factor 1.015 ± 0.01. The determination of the temperature parameters is sensitive to the scale, the values $B_{Na} = 1.28 \pm 0.02$ Å^2, $B_{Cl} = 1.11 \pm 0.02$ Å^2 corresponding to our result. From the numbers of electrons in different regions, the ionic radii could be determined as $R_{Na} = 1.15 \pm 0.06$ Å, $R_{Cl} = 1.67 \pm 0.06$ Å. Results concerning the deviations of the ions from spherical symmetry are not sensitive to the scale, but for the Cl ion they are naturally dependent on the choice of its ionic radius. The results concerning the average compression or enlargement of the ions are strongly dependent on the scale but not on the ionic radii. The Na ion cannot be observed to have any kind of deformation. In the Cl ion both the compression and the deviations from spherical symmetry are clearly significant.

Introduction

In connection with our analysis of NaNO$_3$, ref. [9], we were led to fix attention on the structure amplitudes of NaCl measured by VIHINEN [11], because they form the basis for fixing the scale in NaNO$_3$. The experiments of VIHINEN give a very accurate and complete set of structure amplitudes including all reflections up to $\varkappa \, (= \sin \Theta/\lambda) = 1.07$ Å^{-1} except the weak coincident pair 9 7 3, 11 3 3. However, the scale is no more absolute than in the work of INKINEN [4]. The measurements themselves are relative, and the absolute scale is determined afterwards »so that, when the method of KORHONEN was used for calculations of atomic structure factors, the sum of the atomic scattering factors of Na$^+$ and Cl$^-$ became equal to 28 at $\sin \Theta/\lambda = 0$.»

The »method of KORHONEN» [5] is just the way we use in calculating atomic factors with the series

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

if a sphere is chosen for the region T, as is pointed out in ref. [8]. There are no details given in the original work of VIHINEN, but in ref. [6] we can see that the spheres used have the traditional ionic radii 0.98 Å for Na and
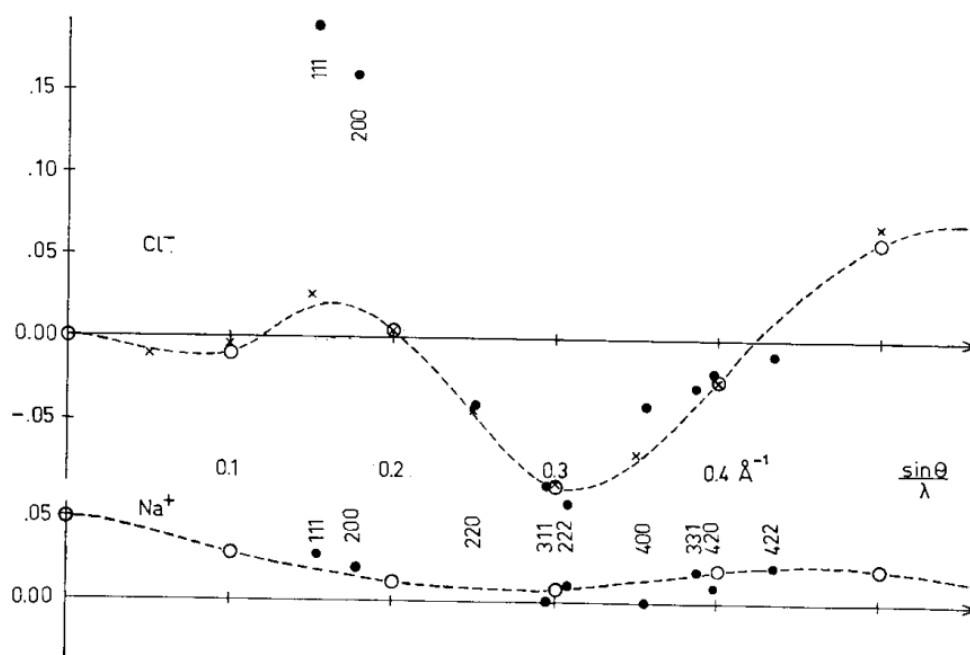
Figure 1. The differences between the theoretical atomic factors and their analytic approximations. The circles stand for the values of FREEMAN, the cross for those of BERGHUIS et al., and the solid circles correspond to the values given by VIHINEN.

1.84 Å for Cl. Making the sum of the numbers of electrons equal to 28 means that the rest of the unit cell is made completely empty. As stated in ref. [9], such a procedure will always make the scale too high. For instance, in the studied case of $NaNO_3$ an error of a few per cent would arise. It seems, however, that we must not take quite literally the explanation quoted above. Rather the differences Δf_T between the experimental and theoretical structure amplitudes of the regions T_{Na} and T_{Cl} seem to have been made zero at $\varkappa = 0$, as is seen in fig. 1 of ref. [6]. Interpreted in this way the criterion may give a nearly correct scale, although its justification is questionable.

In order to reduce the uncertainty of the scale we shall here carry through an analysis similar to the one made in ref. [9]. The more extensive experimental material will certainly make more accurate conclusions possible than in the case of $NaNO_3$, and, if succesful, the analysis will yield a firmer basis for fixing the scale in experimental work.

We shall also pay attention to other questions closely connected with this analysis, such as the determination of the most suitable radii for the spheres used in the calculation of the atomic scattering factors, i.e. the ionic radii, and the dependence of results concerning ionic deformations (like those of ref. [6]) on the scale and on the choice of the ionic radii.

The determination of the scale

In ref. [9] we saw that the shape of the Fourier difference series at the atomic positions and the numbers of electrons in suitable regions of the unit cell are those results which are most sensitive to changes of the scale. The latter, however, cannot be used effectively as a criterion for the scale determination, because the correct value of the electron number in any part of the unit cell cannot be known exactly. The control of the scale will therefore be primarily a comparison of the Fourier difference series with an artificially produced pure effect of a scale error.

We use the experimental values as given by VIHINEN, with the Hönl-correction included, so that the correct value for the number of electrons in the whole unit cell will result. In constructing the theoretical structure amplitudes we used the theoretical atomic factors of FREEMAN [3]. For comparison we also made some calculations with the values of BOYS [2].

To get the values of the theoretical atomic factors at each hkl, an interpolation must be performed, and at the first few reflections particular care is necessary to gain the reliability needed for a detailed analysis. During the preliminary calculations we found it desirable to check the values given by VIHINEN. For this purpose we took the approximate analytic representations

$$f_{Na^+} = 1.804\ e^{-0.138\,\varkappa^2} + 4.723\ e^{-3.140\,\varkappa^2} + 3.424\ e^{-8.880\,\varkappa^2}$$

(2) $\quad f_{Cl^-} = 8.350\ e^{-0.710\,\varkappa^2} + 5.012\ e^{-12.119\,\varkappa^2} + 4.638\ e^{-45.104\,\varkappa^2}\quad (\varkappa < 1.0\ \text{Å}^{-1})$

$\quad f_{Cl^-} = 2.823\ e^{-0.164\,\varkappa^2} + 7.561\ e^{-1.551\,\varkappa^2}\quad (0.9\ \text{Å}^{-1} < \varkappa < 2.0\ \text{Å}^{-1})$

for the theoretical atomic factors at zero temperature, and then found the deviations of the theoretical values from the analytic ones through a graphical interpolation. We also made use of the values given by BERGHUIS et al. [1], which almost completely coincide with those of FREEMAN, but which have been calculated at shorter intervals. Through this semianalytic procedure, which proved very reliable, the theoretical structure amplitudes were reproduced. The values given by VIHINEN were confirmed except for the first two reflections and some less significant deviations, as shown in fig. 1 and table I.

At first we calculated the Fourier difference series along the edge of the unit cell (fig. 2a). The effect on this curve of increasing the scale (fig. 3b) was found by calculating the difference series using the differences between the theoretical structure amplitudes multiplied by 1.02 and the theoretical values obtained by adjusting the temperature parameters to fit the multiplied values. To separate the effects from different sources we compared this with the deviation caused by a change of the temperature parameters (fig. 3a).

Table I

The theoretical structure amplitudes F of NaCl found through a semianalytic interpolation of Freeman's atomic factors, using $B_{Na} = 1.29$ Å^2 and $B_{Cl} = 1.15$ Å^2, compared with the values F_V given by Vihinen.

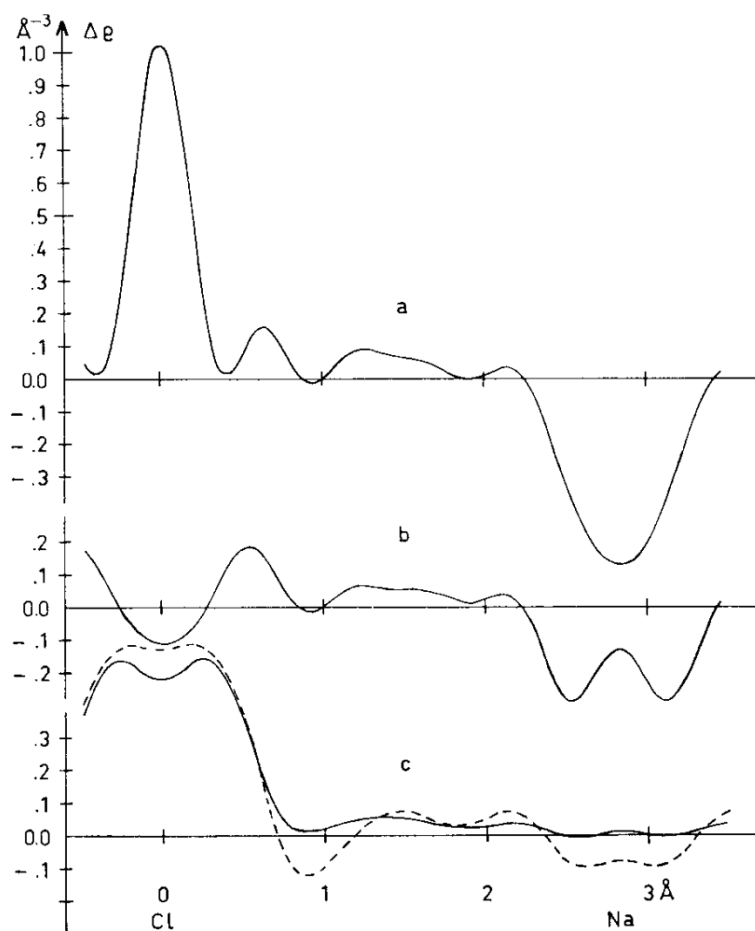| hkl	F_V	F	hkl	F_V	F
111	4.68	4.53	333, 511	2.36	2.37
200	20.75	20.61	440	8.54	8.55
220	16.82	16.86	531	2.34	2.35
311	2.48	2.46	442, 600	7.85	7.87
222	14.42	14.43	620	7.26	7.27
400	12.71	12.69	533	2.27	2.27
331	2.34	2.33	622	6.72	6.72
420	11.34	11.34	444	6.23	6.23
422	10.23	10.25			

Figure 2. Fourier difference series along the edge of the unit cell, (a) with the original scale and $B_{Na} = 1.29$ Å^2, $B_{Cl} = 1.15$ Å^2, (b) with the original scale and $B_{Na} = 1.31$ Å^2 $B_{Cl} = 1.13$ Å^2, (c) with the scale factor 1.02 and $B_{Na} = 1.27$ Å^2, $B_{Cl} = 1.10$ Å^2. For the dotted line in (c) the theoretical values of Boys are used with $B_{Na} = 1.28$ Å^2, $B_{Cl} = 1.105$ Å^2.
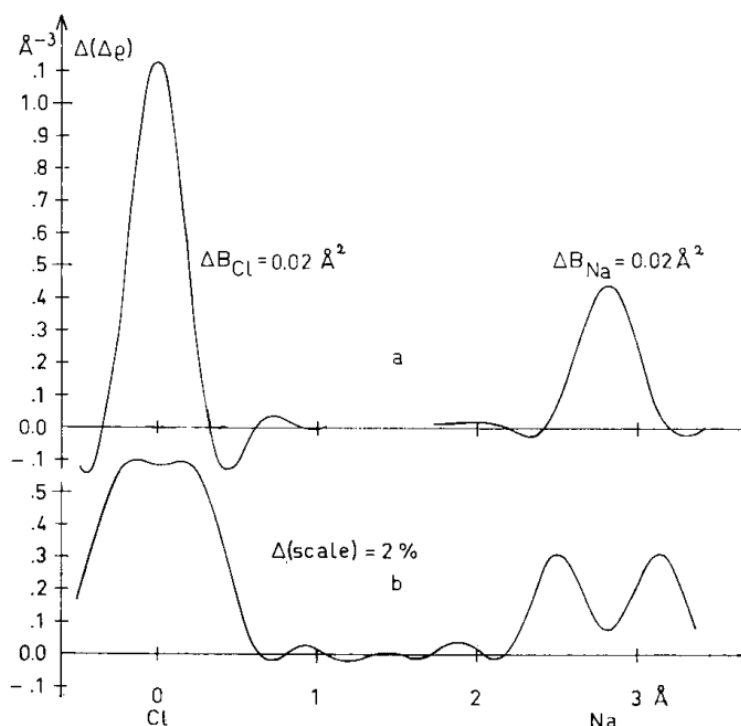
Figure 3. The effect on $\Delta\varrho$ caused by (a) increasing the temperature parameters by $\Delta B = 0.02$ Å², (b) increasing the scale by 2%.

The results apparantly suggest slightly different values for the temperature parameters, and another curve is shown in fig. 2b, where the values $B_{Na} = 1.31$ Å², $B_{Cl} = 1.13$ Å² have been used. A comparison with fig. 3b giving the effect of a scaling error shows a striking similarity at the Na ion. If this alone would do as a criterion, we should have the answer: The original scale is too low by 2%. In fig. 2c this correction of the scale has been made with the corresponding adjustment of the temperature parameters to $B_{Na} = 1.27$ Å², $B_{Cl} = 1.10$ Å². The curve is now quite flat at the Na ion but has got somewhat worse at the Cl ion. The deviations must, of course, be balanced by a greater weight at the Na ion because it is the smaller one and will therefore have the better theoretical atomic factor. Therefore we propose the following conclusion: The most probable scale is reached by increasing the original one by 1.5%, and a choice differing by more than 1% from that one would be in disagreement with the measurements.

As an immediate consequence of this correction of the scale we have to rectify all scale-dependent results found before. At first we notice the slight change of the temperature parameters, the new values being $B_{Na} = 1.28$ Å², $B_{Cl} = 1.11$ Å² with the limits ± 0.02 Å² due to the 1% uncertainty of the scale. The shapes of the Δf curves shown in fig. 1 of ref. [6] will also change and the conclusions made from these must be correspondingly modified

(see p. 10). Further we have to correct the scale of all measurements where these values have been used as the basis for fixing the scale. This applies at least to the structure amplitudes of $NaNO_3$ measured by INKINEN [4], and leads to a revision of the results of our analysis in ref. [9].

Remarks on the reliability

The situation here seems to be more favourable for the scale determination than it was in the case of $NaNO_3$, ref. [9]. The shape of the $\Delta\varrho$ curves is here about twice as sensitive to the scale (as well as to the temperature factors), clearly due to the much higher cut-off limit of the series. In addition, the sources of error are far less significant. Because of the higher cut-off limit there is practically no contribution in the residual term due to the deformations of the ions or to the electron distribution between the ions. The errors in the residual term are therefore included in the possible variations of the temperature factors. Errors coming from the coincident and weak reflections are also negligible. Only in the first two pairs of coincident reflections will the deformation of the Cl ion (fig. 1b of ref. [6]) make the components differ perceptibly, and the only weak reflection (9 7 3, 11 3 3) is completely harmless.

Only the effect of the experimental errors will be important and must be evaluated. The best we can do is to handle them as statistical errors with the standard deviations δ given in table IX of ref. [11]. In this way we get for $\Delta\varrho$ standard deviations of about 0.15 $Å^{-3}$, which roughly means an additional uncertainty of 0.5% in the scale.

One might also think that by calculating $\Delta\varrho$ for some other direction we could have come to a different result. At least at the Cl ion a different shape of the $\Delta\varrho$ curve is to be expected according to the result of ref. [6], which clearly shows deviations from spherical symmetry in the Cl ion. The $\Delta\varrho$ curves along the diagonal of the unit cell as well as along the face diagonal through a Cl ion are shown in fig. 4. Here the same quantities ΔF have been used as for fig. 2c. No reason to change the conclusion can be seen.

The most obvious objection to this analysis is that it is to a certain extent based on the reliability of the theoretical atomic factors at large values of $\varkappa$. As long as we do not know how good they really are, the only justification can be found by taking different theoretical atomic factors based on a different quantal approximation and by looking whether the results are changed. As a comparison we used the atomic factors of BOYS [2] to calculate $\Delta\varrho$ along the edge of the unit cell (dotted line in fig. 2c). Here the scale was 1.02 times the original one and $B_{Na} = 1.28$ $Å^2$, $B_{Cl} =$

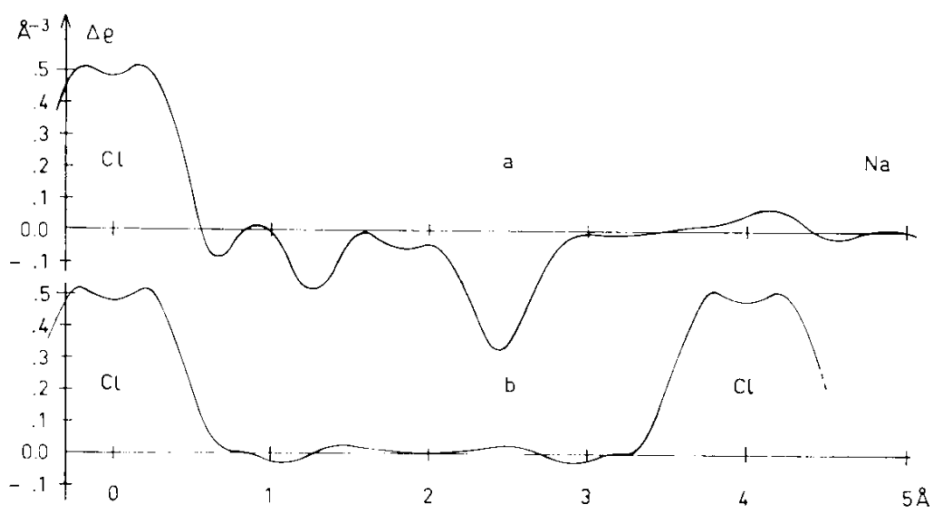Figure 4. Fourier difference series with a scale factor 1.02 and $B_{Na} = 1.27$ Å², $B_{Cl} = 1.10$ Å², (a) along the diagonal, (b) along the face diagonal of the unit cell.

1.105 Å². The evidence for the original scale being too low is somewhat more pronounced here, though not enough to make us change our conclusion.

The deformations and the ionic radii

The nature of the deformations of the ions is easily seen from the differences between the experimental and the theoretical atomic factors, which can be calculated with the difference series (1). Figs. 5a, b
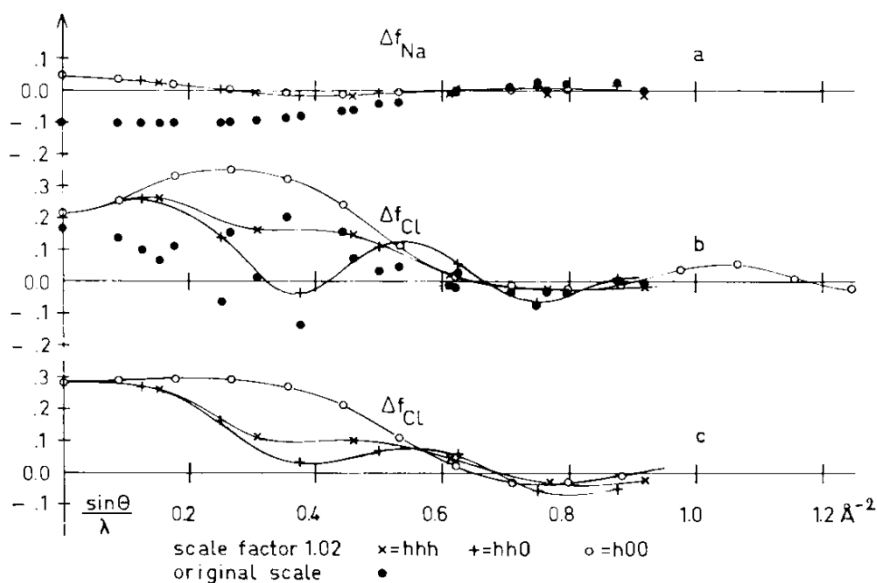

Figure 5. The difference series Δf_T, (a) for T_{Na} with $R = 0.98$ Å, (b) for T_{Cl} with $R = 1.84$ Å and (c) for T_{Cl} with $R = 1.67$ Å. The curves are drawn through points corresponding to the scale factor 1.02 and $B_{Na} = 1.27$ Å², $B_{Cl} = 1.10$ Å², the points calculated with the original scale and $B_{Na} = 1.31$ Å², $B_{Cl} = 1.13$ Å², are marked with solid circles.

give these results with both the corrected scale and the original one, in order to show the sensitivity to the scale. (At small values of $\varkappa$ the latter results deviate from those given in ref. [6] due to the rectified interpolation errors in the theoretical structure amplitudes.)

The dependence on crystallographic directions, i.e. the deviations from spherical symmetry, is not affected by the change of the scale. The curve for Δf_{Na} still shows complete spherical symmetry, and also the relative differences of the curves for Δf_{Cl} remain unchanged. Instead, the conclusions of ref. [6] concerning the average spherical deformations must be modified. On comparison with the free ions (represented by the theoretical values) there can be seen neither any enlargement nor compression of the Na ion. The Cl ion seems to be compressed in all directions, most strongly in the direction towards the neighbouring Na ion and least towards the nearest Cl ion. The 1 to 1.5% uncertainty of the scale still causes an appreciable inaccuracy in our knowledge about the strength of this compression.

In order to find the numbers of electrons in both ions, we have to calculate series (1) at $\varkappa = 0$ for T_{Na} and T_{Cl}. As we have stated before, the theoretical residual term can be used. The possible errors, supposed to be included in the variations of the temperature parameters, were found to be negligible compared to the experimental errors. For the calculation of the residual terms we made use of the analytic representations (2), which made the computing task much simpler. Table II gives the numbers of electrons found in this way for different regions with both the original scale and the corrected one, in order to see the sensitivity to the scale, and with the standard deviations δ. The radii of the Na- and Cl-centered spheres used here are chosen pairwise, the sum of each pair being equal to the ionic distance 2.280 Å.

For the empty space outside of the ionic spheres the first three pairs give an equal average electron density, with almost insignificant mutual differences, but the fourth one gives clearly more. In this respect any choice of the ionic radii between the first and the third pair would be equally suitable. In the spherical shells the average density decreases outwards in both ions. The large value in the innermost shell around the Na ion shows that the traditional ionic radius 0.98 Å must be too small. A natural way of fixing the radii on the basis of these values is to seek the point where the average densities in thin shells through that point are equal for Na- and Cl-centered shells. This point is about 1.15 Å from the center of the Na ion. The original scale gives 1.10 Å, and the standard deviations will cause an uncertainty of about $\pm$ 0.03 Å, which results in the estimates R_{Na^+} = 1.15$\pm$0.06 Å, R_{Cl^-} = 1.67$\pm$0.06 Å for the ionic radii, in good agreement with the values R_{Na^+} = 1.17 Å, R_{Cl^-} = 1.65 Å found by WITTE *et al.* [7] and R_{Na^+} = 1.18 Å, R_{Cl^-} = 1.64 Å by SCHOKNECHT [10].

Table II

Number of electrons $f_T(000)$ with its standard deviation $\delta(f_T)$ and the average electron density ϱ_{av} in different regions, with the scale factor 1.015 and with the original scale.

Region	Scale factor 1.015		Original scale		$\delta(f_T)$
	$f_T(000)$	$\varrho_{av}\text{Å}^{-3}$	$f_T(000)$	$\varrho_{av}\text{Å}^{-3}$	
Na sphere					
1. $R = 0.98$ Å	9.83		9.72		0.035
2. $R = 1.05$ Å	9.93		9.82		0.035
3. $R = 1.20$ Å	10.08		10.00		0.04
4. $R = 1.32$ Å	10.17		10.11		0.045
Cl sphere					
1. $R = 1.84$ Å	17.80		17.77		0.06
2. $R = 1.77$ Å	17.68		17.64		0.06
3. $R = 1.62$ Å	17.41		17.31		0.05
4. $R = 1.50$ Å	17.13		17.00		0.05
Na-centered shell					
2.—1.	0.101	0.112	0.104	0.115	0.015
3.—2.	0.151	0.063	0.175	0.073	0.03
4.—3.	0.091	0.038	0.115	0.048	0.03
Cl-centered shell					
3.—4.	0.273	0.074	0.307	0.084	0.035
2.—3.	0.277	0.051	0.330	0.061	0.045
1.—2.	0.115	0.040	0.135	0.047	0.025
¼ unit cell less a pair of spheres					
pair 1.	0.38	0.026	0.51	0.035	0.05
pair 2.	0.39	0.023	0.54	0.032	0.05
pair 3.	0.52	0.026	0.70	0.035	0.06
pair 4.	0.70	0.033	0.89	0.042	0.065

It is interesting to observe that with these radii we have in the Na ion 10.02 ± 0.05, i.e. essentially 10, electrons but only 17.50 ± 0.11 electrons in the Cl ion, 0.5 electrons being spread wider.

The new choice of the ionic radii will also have some effect on the Δf curves from which the conclusions about the ionic deformations were made. A calculation shows that the effect on Δf_{Na} is completely negligible and cannot be seen in the scale of fig. 5a. In Δf_{Cl} (fig. 5c), however, we find a considerable reduction in the differences between the curves for different

crystallographic directions, which means that the deviations from spherical symmetry were partly caused by regions not belonging to the Cl ion. Still a significant deformation is present inside the more realistic region, so that our previous conclusions remain qualitatively valid.

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