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NON-APPROXIMATE ANALYSIS OF EXPERIMENTAL STRUCTURE AMPLITUDES

II. The »Correct Model» for Sodium Nitrate

BY

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1. Introduction

The present paper is part of a larger work in which the aim has been set to elaborate a method for the accomplishment of a crystal analysis with the highest possible accuracy, starting from the experimental structure amplitudes. In the first part of the work [8] we presented the principles that will be employed, and outlined the programme of the analysis. The principles imply that the atomic scattering factor of each particular atom is considered separately, and this procedure will also make possible a critical treatment of the residual term. For this purpose we already have at our disposal a non-approximate method for the calculation of atomic scattering factors from experimental structure amplitudes [6, 7], which actually instigated us to undertake this work.

In this second part of the work we shall proceed to apply the method presented to the trigonal sodium-nitrate crystal, for which we have at our disposal the experimental structure amplitudes measured by INKINEN [5] at room temperature. Specifically, we intend to determine the »correct model», which plays a central part in our method, with the accuracy consistent with the existing experimental material.

As this is an account of the application of a new method, it would certainly be appropriate to give a detailed presentation of the calculations and considerations involved for the benefit of those who may contemplate application of the method. However, we shall here concentrate our attention mainly on the results concerning the crystal. Of the method itself only the details necessary to understand the results will be given, and the computing techniques will be described on a later occasion.

2. Data on the Parameters of Position and Motion

Sodium nitrate has a structure of calcite type at room temperature. The lattice constants of its trigonal unit cell are [12]

$$r = 6.3108 \pm 10^{-4}\ \text{Å}, \qquad \cos\alpha = 0.67859_1 \pm 10^{-5}.$$

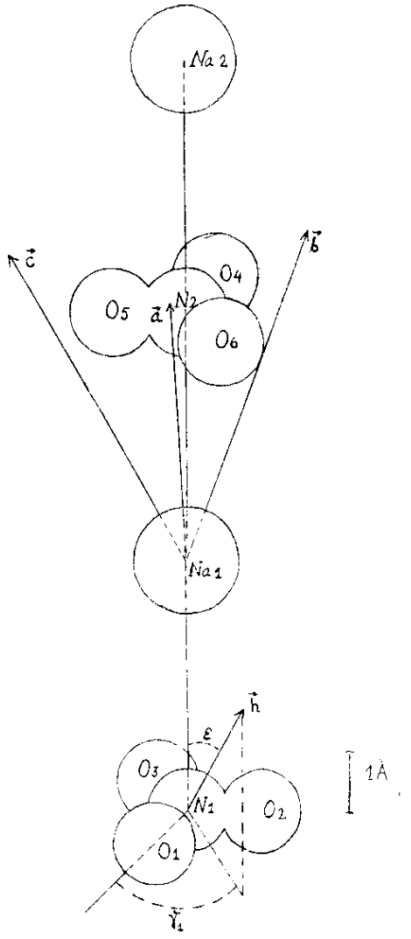

Fig. 1. The atoms in the unit cell, and the parameters employed in the treatment.

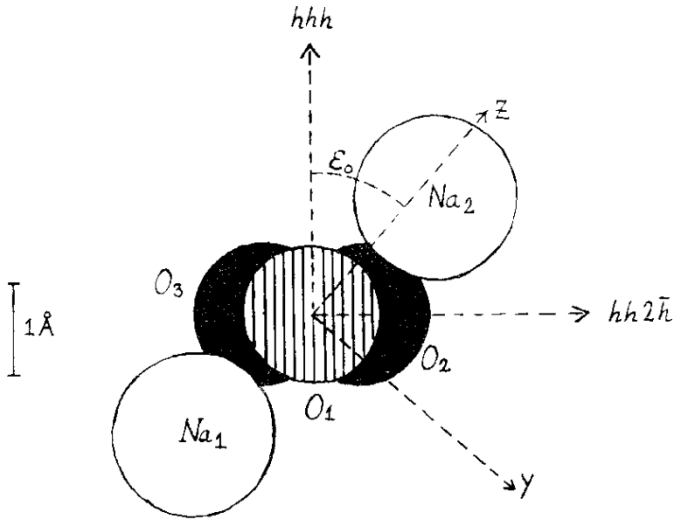

Fig. 2. The O_1 atom with its closest neighbours and the y and z axes of its motion. Projected on the normal plane of the N—O connecting line (x axis of the motion).

The cell contains two molecules, and the atoms have the following coordinates in it:

	Na_1 0, 0, 0	N_1 $-\frac{1}{4},-\frac{1}{4},-\frac{1}{4}$	O_1	$-\frac{1}{4}+u,-\frac{1}{4}-u,-\frac{1}{4}$	O_4	$\frac{1}{4}-u,\ \frac{1}{4}+u,\ \frac{1}{4}$
(1)	Na_2 $\frac{1}{2},\ \frac{1}{2},\ \frac{1}{2}$	N_2 $\frac{1}{4},\ \frac{1}{4},\ \frac{1}{4}$	O_2	$-\frac{1}{4},-\frac{1}{4}+u,-\frac{1}{4}-u$	O_5	$\frac{1}{4},\ \frac{1}{4}-u,\ \frac{1}{4}+u$
			O_3	$-\frac{1}{4}-u,-\frac{1}{4},-\frac{1}{4}+u$	O_6	$\frac{1}{4}+u,\ \frac{1}{4},\ \frac{1}{4}-u.$

The positions of the atoms are fully determined except for one parameter u, which defines the distance between the nitrogen and oxygen atoms. The following values for this parameter have previously been found:

WYCKOFF (1920)	[13]	$u = 0.24$ to 0.26	$d_{N-O} = 1.21$ to 1.23 Å
ELLIOT (1937)	[2]	0.2394 ± 0.0006	1.211 ± 0.003 Å
TAHVONEN (1947)	[11]	0.242 ± 0.003	1.22 ± 0.01 Å
SASS et al. (1957)	[10]	0.2402 ± 0.0008	1.218 ± 0.004 Å
INKINEN (1960)	[5]	0.242 ± 0.002	1.224 ± 0.010 Å .

The last of the values listed here is a preliminary estimate from the measured values under treatment in this work.

The crystal symmetry imposes a great restriction also on the form of motion of the atoms. The general harmonic, anisotropic thermal factor

$$10^{-c^2\varkappa^2}\ ;\ c^2 = c_1^2 \sin^2\Theta \cos^2\varphi + c_2^2 \sin^2\Theta \sin^2\varphi + c_3^2 \cos^2\Theta, \tag{2}$$

where the constants c_i indicate the amplitude of motion in its three principal directions, and Θ and φ are the directional angles in the axis system formed by these directions, reverts in the case of the sodium and nitrogen atoms to the form with rotational symmetry with respect to the trigonal axis,

$$c^2 = c_{\parallel}^2 \cos^2\varepsilon + c_{\perp}^2 \sin^2\varepsilon. \tag{3}$$

For the oxygen atoms, symmetry prescribes the N — O direction as one of the principal directions of the motion (i.e., as its x axis). If the angle between the z axis of the motion and the trigonal axis of the crystal is denoted ε_0 (see fig. 2), we may write

$$\begin{aligned} c_{O_i}^2 = {} & c_x^2 \sin^2\varepsilon \cos^2\gamma_i + (c_y^2 \sin^2\varepsilon_0 + c_z^2 \cos^2\varepsilon_0) \cos^2\varepsilon \\ & + (c_y^2 \cos^2\varepsilon_0 + c_z^2 \sin^2\varepsilon_0) \sin^2\varepsilon \sin^2\gamma_i \\ & + 2(c_z^2 - c_y^2) \sin\varepsilon_0 \cos\varepsilon_0 \sin\varepsilon \cos\varepsilon \cos\gamma_i \end{aligned} \tag{4}$$

(the significance of the directional angles ε and γ_i can be seen from fig. 1).

Making use of the formulae

$$(5)\qquad \varkappa^2 = \frac{(1+2\cos\alpha)(h^2+k^2+l^2)-\cos\alpha\,(h+k+l)^2}{4r^2(1-\cos\alpha)(1+2\cos\alpha)}$$

$$= 0.019531\,(h^2+k^2+l^2) - 0.005622\,(h+k+l)^2$$

$$\cos^2\varepsilon = \tfrac{1}{3}\,\frac{(1-\cos\alpha)(h+k+l)^2}{(1+2\cos\alpha)(h^2+k^2+l^2)-\cos\alpha\,(h+k+l)^2}$$

$$= \frac{(h+k+l)^2}{22.001\,(h^2+k^2+l^2) - 6.3337\,(h+k+l)^2}$$

$$\cos^2\gamma_1 = \tfrac{3}{2}\,\frac{(h-k)^2}{(h-k)^2+(k-l)^2+(l-h)^2}$$

(for $\cos^2\gamma_2$ and $\cos^2\gamma_3$ permute hkl),

we find for sodium and nitrogen

$$(6)\qquad \varkappa^2 c^2 = 0.00088768\,c_{\parallel}^2\,(h+k+l)^2 + 0.0065102\,c_{\perp}^2\,[(h-k)^2+(k-l)^2+(l-h)^2]$$

and for the oxygen atoms

$$(7)\qquad \varkappa^2 c_{O_1}^2 = a\,(h-k)^2 + b\,(h+k+l)^2 + c\,(h+k-2l)^2 + d\,(h+k+l)(h+k-2l),$$

$$a = 0.0097652\,c_x^2$$

$$b = 0.00088768\,(c_y^2\sin^2\varepsilon_0 + c_z^2\cos^2\varepsilon_0)$$

$$c = 0.0032551\,(c_y^2\cos^2\varepsilon_0 + c_z^2\sin^2\varepsilon_0)$$

$$d = 0.0033997\,(c_z^2 - c_y^2)\sin\varepsilon_0\cos\varepsilon_0.$$

The literature also contains some measurement results concerning the parameters of motion. Tahvonen [11] has used the mean isotropic parameters $\overline{c^2}$ and obtained the best fit with his experimental values when employing the parameters

$$\overline{c_{Na}^2} = 0.52\ \text{Å}^2;\quad \overline{c_N^2} = 0.61\ \text{Å}^2;\quad \overline{c_O^2} = 0.68 \pm 0.04\ \text{Å}^2.$$

Sass et al. [10] have only treated the oxygen atoms. Assuming the trigonal axis to be also a principal direction of motion, i.e., $\varepsilon_0 = 0$, they found a result corresponding to the parameter values

$$c_x^2 = 0.115\ \text{Å}^2;\quad c_y^2 = 0.40\ \text{Å}^2;\quad c_z^2 = 0.28\ \text{Å}^2;\ (\varepsilon_0 = 0).$$

Inkinen [5] estimated the mean isotropic motion parameters

$$\overline{c_{Na}^2} = 0.57\ \text{Å}^2;\quad \overline{c_N^2} = 0.45\ \text{Å}^2;\quad \overline{c_O^2} = 0.74\ \text{Å}^2,$$

but on closer study of the sodium atom his results appeared to indicate a slight anisotropy of motion:

$$c^2_{\mathrm{Na}_{||}} = 0.59 \text{ Å}^2; \qquad c^2_{\mathrm{Na}_{\perp}} = 0.55 \text{ Å}^2.$$

No estimate of a possible anisotropy in the motion of the nitrogen atom can be found anywhere, nor has any attention been paid to the possibility that the direction of the z axis for the motion of the oxygen atom might deviate from the trigonal axis ($\varepsilon_0 \neq 0$).

3. Structure Amplitudes

We calculate the theoretical structure amplitudes from the formula

$$F_{hkl} = \sum f_\nu(h\ k\ l) e^{2\pi i (hx_\nu + ky_\nu + lz_\nu)} \quad ; \quad f_\nu = 10^{-c^2_\nu \varkappa^2} f_{0,\nu} \ , \tag{8}$$

whence, considering the atom loci (1),

$$F_{hkl} = \begin{cases} 2f_{\mathrm{Na}} \pm 2\,[f_{\mathrm{N}} + f_{\mathrm{O}_1} \cos 2\pi(h-k)u + f_{\mathrm{O}_2} \cos 2\pi(k-l)u \\ \qquad + f_{\mathrm{O}_3} \cos 2\pi(l-h)u]; \ h+k+l = \begin{cases} 4n \\ 4n+2 \end{cases} \\ \pm 2\,[f_{\mathrm{O}_1} \sin 2\pi(h-k)u + f_{\mathrm{O}_2} \sin 2\pi(k-l)u \\ \qquad + f_{\mathrm{O}_3} \sin 2\pi(l-h)u]; \ h+k+l = \begin{cases} 4n+1 \\ 4n-1 \end{cases} \end{cases} \tag{9}$$

As previously done by INKINEN [5], we use for the scattering factors of the atoms at rest, $f_{0,\nu}$, the spherically symmetric theoretical values calculated by FREEMAN [3] for the Na^+ ion and by MCWEENY [9] for the neutral N and O atoms, with HÖNL's correction [4]. The motion parameters c^2 have the expressions (6) and (7). As our starting point we choose a model in which the parameters have the values employed by INKINEN:

$c^2_{\mathrm{Na}_{||}} = c^2_{\mathrm{Na}_{\perp}} = 0.57$ Å^2 ; $c^2_{\mathrm{N}_{||}} = c^2_{\mathrm{N}_{\perp}} = 0.45$ Å^2; $c_x^2 = c_y^2 = c_z^2 = 0.74$ Å^2 ;
$2\pi u = 87.0°$ ($u = 0.242$).

The structure amplitudes consistent with this model will be denoted F_I.

The measurement results of INKINEN will be used for the experimental structure amplitudes. They include all observed reflections in the range $\varkappa < 0.62$ Å^{-1}. There is no phase problem, as all structure amplitudes are real, and the calculated theoretical values F_I already establish unambiguously the signs of all measured structure amplitudes.

The experimental structure amplitudes and those consistent with the chosen model are listed in table I. The table contains all reflections predicted by the structure, with $\varkappa < 0.62$ Å^{-1}. In addition to the indices hkl,

Table I

Experimental structure amplitudes F_{exp} with their limits of error δF consistent with the measuring accuracy, theoretical structure amplitudes F_{theor} and differences $\Delta F = F_{exp} - F_{theor}$, calculated for the atom loci (1). The different theoretical values have been calculated with the parameters

	c^2_{Na} (Å²)	c^2_N (Å²)	c^2_x (Å²)	c^2_y (Å²)	c^2_z (Å²)	$\cos^2\varepsilon_0$	$2\pi u$
I	0.57	0.45	0.74	0.74	0.74	—	87.0°
II	0.57	0.45	0.42	1.30	0.65	0.55	87.0°
III	0.57	0.45	0.42	1.30	0.65	0.55	87.6° .

1 hkl	2 $\cos^2\varepsilon$	3 $\cos^2\gamma$	4 $\varkappa$[Å^{-1}]	5 $\lvert F_{exp}\rvert$	6 F_I	7 F_{II}	8 F_{III}	9 ΔF_I	10 ΔF_{II}	11 ΔF_{III}	12 δF
000	—	—	0	84.22	82.22	82.22	82.22	2.00	2.00	2.00	—
110	0.2143	0.75	0.1287	7.15	— 8.40	— 8.41	— 8.12	1.25	1.26	0.97	0.10
211	0.5217	0.75	1650	40.94	41.38	40.97	40.71	—0.44	—0.03	0.23	0.29
222	1	—	1788	29.02	—28.39	—27.86	—27.86	—0.63	—1.16	—1.16	0.29
$1\bar{1}0$	0	1	1976	14.38	15.52	15.20	14.95	—1.14	—0.82	—0.57	0.09
201	0.1698	1	2169	19.46	19.40	19.08	19.31	0.06	0.38	0.15	0.12
200	0.0638	0.75	2359	18.81	16.29	17.32	17.36	2.52	1.49	1.45	0.13
220	0.2143	0.75	2575	13.01	12.48	12.61	12.57	0.53	0.40	0.44	0.09
332	0.8136	0.75	2643	31.52	29.95	29.97	29.80	1.57	1.55	1.72	0.28
321	0.4500	1	2665	14.33	14.28	14.41	14.59	0.05	—0.08	—0.26	0.16
$\bar{2}01$	0.0096	0.9643	3034	14.91	14.90	14.98	14.86	0.01	—0.07	0.05	0.10
$21\bar{1}$	0.0375	0.9643	3077	13.47	14.12	14.02	13.87	—0.65	—0.55	—0.40	0.11
433	0.8721	0.75	3190	—	— 1.06	— 0.42	0.29	—	—	—	—
310	0.1348	0.9643	3246	10.21	9.79	9.49	9.63	0.42	0.72	0.58	0.08
422	0.5217	0.75	3300	9.70	10.33	9.08	9.05	—0.63	0.62	0.65	0.13
432	0.6480	1	3331	11.91	11.77	11.26	11.40	0.14	0.65	0.51	0.11
320	0.1958	0.9643	3367	12.82	12.78	13.04	12.95	0.04	—0.22	—0.13	0.10
$2\bar{1}\bar{1}$	0	0.75	3423	19.77	20.01	19.50	19.89	—0.24	0.27	—0.12	0.14
444	1	—	3575	31.19	31.73	30.76	30.76	—0.54	0.43	0.43	0.28
412	0.3231	0.9643	3669	10.46	11.13	10.73	10.64	—0.67	—0.27	—0.18	0.09
442	0.6303	0.75	3753	9.34	10.51	9.66	9.68	—1.17	—0.32	—0.34	0.09
431	0.3840	0.9643	3847	9.81*	8.37	8.87	8.97	1.19	0.59	0.58	0.10
411	0.2143	0.75	3862	—	1.96	2.88	2.55	—	—	—	—
330	0.2143	0.75	3862	—	1.96	1.92	1.62	—	—	—	—
$2\bar{2}0$	0	1	3953	9.97	8.52	9.48	9.50	1.45	0.49	0.47	0.10
$3\bar{1}1$	0.0486	1	4053	2.25	1.86	1.92	1.54	0.39	0.33	0.71	0.40
543	0.7660	1	4085	8.84	8.76	8.87	8.77	0.08	—0.03	0.07	0.08
$\bar{3}21$	0.0052	0.9231	4125	—	0.94	0.73	0.51	—	—	—	—
$3\bar{1}0$	0.0205	0.9231	4157	< 1.3	1.03	0.57	0.43	—	—	—	—
532	0.4934	0.9643	4242	9.38	9.07	9.38	9.29	0.31	0.00	0.09	0.10
$32\bar{1}$	0.0774	0.9231	4283	15.92	15.33	15.68	15.80	0.59	0.24	0.12	0.14
554	0.9304	0.75	4324	—	0.12	0.23	0.31	—	—	—	—
420	0.1698	1	4338	7.49*	8.40	7.58	7.56	—0.91	—0.09	—0.07	0.08
410	0.1159	0.9231	4376	—	0.84	0.02	— 0.18	—	—	—	—
524	0.5410	0.9643	4456	7.48	7.76	7.82	7.77	—0.28	—0.34	—0.29	0.08
$22\bar{2}$	0.0168	0.75	4603	6.88*	— 6.28	— 6.41	— 6.47	—0.50	—0.26	—0.26	0.12
403	0.2044	0.9231	4613	—	0.76	1.14	0.98	—	—	—	—
400	0.0638	0.75	4717	20.47	19.93	20.10	20.15	0.54	0.37	0.32	0.16

1 hkl	2 $\cos^2\varepsilon$	3 $\cos^2\gamma$	4 $\varkappa$[Å^{-1}]	5 $\lvert F_{exp}\rvert$	6 F_I	7 F_{II}	8 F_{III}	9 ΔF_I	10 ΔF_{II}	11 ΔF_{III}	12 δF
644	0.7969	0.75	0.4755	7.09*	6.94	7.63	7.75	0.15	−0.10	−0.17	0.06
521	0.2513	0.9231	4755	13.17*	12.90	13.22	13.34	0.27	−0.17	−0.31	0.12
531	0.3152	1	4776	1.70	1.33	1.36	1.09	0.37	0.34	0.61	0.34
645	0.8364	1	4887	5.29	5.68	5.26	5.32	−0.39	0.03	−0.03	0.21
655	0.9458	0.75	4902	12.52	12.92	12.36	12.30	−0.40	0.16	0.22	0.38
643	0.6221	0.9643	4911	5.53	6.36	5.72	5.66	−0.83	−0.19	−0.13	0.22
633	0.5217	0.75	4950	11.33*	11.47	10.58	10.78	−0.14	0.17	−0.01	0.12
552	0.5217	0.75	4950	11.33*	11.47	11.71	11.88	−0.14	0.18	−0.01	0.12
$\bar{3}20$	0.0036	0.9868	4983	6.42	5.44	5.98	6.09	0.98	0.44	0.33	0.12
$3\bar{2}1$	0.0142	0.9868	5016	5.92	5.96	5.61	5.71	−0.04	0.31	0.21	0.11
541	0.3440	0.9231	5080	—	0.82	0.71	0.64	—	—	—	—
$41\bar{1}$	0.0543	0.9868	5115	7.04	6.41	7.01	6.93	0.63	0.03	0.11	0.11
653	0.6563	0.9643	5149	5.60*	6.21	5.63	5.58	−0.61	−0.43	−0.43	0.06
440	0.2143	0.75	5149	15.25*	16.92	16.81	16.85	−1.67	−1.29	−1.29	0.15
$4\bar{1}2$	0.0823	0.9868	5192	5.50	4.99	5.10	5.21	0.51	0.40	0.29	0.10
$3\bar{2}\bar{1}$	0	0.8929	5230	11.45	11.98	12.19	12.03	−0.53	−0.74	−0.58	0.09
623	0.3882	0.9231	5260	—	0.58	−0.39	−0.53	—	—	—	—
664	0.8136	0.75	5285	6.87	5.81	6.66	6.66	1.06	0.21	0.21	0.15
$4\bar{1}0$	0.0284	0.8929	5305	—	0.45	1.52	1.44	—	—	—	—
$3\bar{2}2$	0.0284	0.8929	5305	—	0.45	1.03	0.96	—	—	—	—
642	0.4500	1	5330	6.07	5.65	6.22	6.23	0.42	−0.15	−0.16	0.08
666	1	—	5363	<5.9	−4.62	−3.67	−3.67	—	—	—	—
520	0.1495	0.9868	5393	5.53	4.60	5.30	5.39	0.93	0.23	0.14	0.09
622	0.2988	0.75	5451	5.38	−4.36	−4.34	−4.38	−1.02	−1.04	−1.00	0.16
530	0.1868	0.9868	5515	5.53*	5.61	5.67	5.59	−0.10	−0.18	−0.08	0.11
$43\bar{1}$	0.1046	0.8929	5526	—	−0.29	−0.21	−0.07	—	—	—	—
510	0.1046	0.8929	5526	—	−0.29	−0.68	−0.54	—	—	—	—
754	0.7138	0.9643	5643	5.01*	4.90	4.74	4.79	0.09	0.15	0.12	0.10
652	0.4699	0.9231	5651	—	0.49	1.08	0.98	—	—	—	—
765	0.8805	1	5716	4.66	4.46	4.27	4.41	0.20	0.39	0.25	0.09
$41\bar{1}$	0.0108	0.75	5732	—	−0.83	−0.53	−0.27	—	—	—	—
631	0.2641	0.9868	5798	4.35	4.32	3.64	3.70	0.03	0.71	0.65	0.12
$33\bar{2}$	0.0418	0.75	5828	10.01	10.11	9.97	9.74	−0.10	0.04	0.27	0.23
743	0.5069	0.9231	5859	—	0.54	0.41	0.34	—	—	—	—
504	0.2082	0.8929	5876	—	0.36	0.40	0.35	—	—	—	—
612	0.2082	0.8929	5876	—	0.36	1.54	1.47	—	—	—	—
764	0.7379	0.9643	5896	4.48	4.31	4.17	4.14	0.17	0.31	0.34	0.11
$3\bar{3}0$	0	1	5929	4.69	4.10	3.58	3.65	0.59	1.11	1.04	0.20
641	0.3027	0.9868	5956	4.00*	3.72	3.42	3.50	0.18	0.48	0.44	0.15
735	0.5611	1	5966	—	0.84	0.80	0.64	—	—	—	—
$41\bar{2}$	0.0222	1	5996	4.12	4.55	4.35	4.22	−0.43	−0.23	−0.10	0.14
$3\bar{3}1$	0.0024	0.9643	6045	—	0.80	0.99	0.79	—	—	—	—
776	0.9647	0.75	6067	8.10*	8.49	8.32	8.28	−0.39	−0.34	−0.33	0.23
$42\bar{0}$	0.0096	0.9643	6068	3.81*	3.99	4.10	4.13	−0.18	−0.17	−0.16	0.11
$42\bar{2}$	0.0375	0.9643	6154	3.94	4.34	3.86	3.83	−0.40	0.08	0.11	0.10
611	0.1486	0.75	6183	8.59*	8.90	8.47	8.24	−0.90	−0.42	−0.22	0.34
662	0.4551	0.75	6184	—	−3.48	−3.15	−3.17	—	—	—	—
$52\bar{1}$	0.0833	1	6192	4.69	4.33	4.76	4.70	0.36	−0.07	0.01	0.19

* cf. Table II.

the parameters $\varkappa$, $\cos^2\varepsilon$, $\cos^2\gamma$ (5) are given, γ denoting the smallest of the angles γ_1, γ_2, γ_3. For each group of hkl and $\bar{h}\bar{k}\bar{l}$ with all their permutations one representative has been taken. In this connection the following rule should be noted:

$$(10) \qquad F_{hkl} = F_{klh} = F_{\bar{h}\bar{k}\bar{l}} = \begin{cases} F_{khl} \\ -F_{khl} \end{cases} \text{ for } h + k + l = \begin{cases} 2n \\ 2n + 1 \end{cases}.$$

There were several instances in the experimental material where two or even three structure amplitudes had to be measured in combination. These cases were treated by dividing the experimentally found total intensity among the different reflections in the proportion of the component intensities consistent with the theoretical model. On the assumption that a new model is always better than the old one, also as regards these reflections, the division into components has been repeated with each new model. The values, F_{exp}, for these reflections, corresponding to the successive models, have been separately compiled in table II. However, all components that have to be considered weak reflections have been omitted on account of the great relative inaccuracy of their values as found in this manner.

Table II

Structure amplitudes F_{exp} of the coincident reflections, calculated by division of the combined intensity into components in the proportion of the theoretical intensities calculated from F_I, F_{II} and F_{III}.

1	2 (I)	3 (II)	4 (III)
hkl	F_{exp}	F_{exp}	F_{exp}
431	9.56	9.46	9.55
420	7.49	7.49	7.49
$22\bar{2}$	6.78	6.67	6.73
644	7.09	7.53	7.58
521	13.17	13.05	13.03
633	11.33	10.75	10.77
552	11.33	11.89	11.87
653	5.60	5.20	5.15
440	15.25	15.52	15.56
530	5.51	5.49	5.51
754	4.99	4.89	4.91
614	3.90	3.90	3.94
776	8.10	7.98	7.95
$4\bar{2}0$	3.81	3.93	3.97
611	8.00	8.05	8.02

4. Correction of the Model

To determine the motion parameters of the atoms, the differences between the experimental and theoretical scattering factors have to be calculated for the different atoms by means of the series

$$\Delta f_T(hkl) = \frac{1}{V_0} \sum_{h'k'l'} \Delta F_{h'k'l'}\, \sigma_T(h - h',\ k - k',\ l - l') \tag{11}$$

(this series may also be used for the N and O atoms because they are represented in the Fourier series by distinct distribution peaks, which contain the bulk of the distribution of the respective atoms; see fig. 10a). For the region T_{Na} we choose a sphere with radius R = 1.05 Å and with its centre in the origin, and for the regions T_{N} and T_{O} revolution ellipsoids with their axes of revolution parallel to the trigonal axis and with the half-axes $C = 1.066$ Å (in the direction of the trigonal axis) and $A = 0.521$ Å, the former ellipsoid having its centre in the centre of the nitrogen atom and the latter in the point $2\pi u = 87.2°$ on the N—O connecting line. We have also calculated the values of this series for the entire nitrate group, using the ellipsoid with $A = 2.20$ Å and $C = 1.50$ Å as region. In all these cases the shape transform σ_T has the form

$$\sigma_T(hkl) = 3V_T \frac{\sin 2\pi\sqrt{t} - 2\pi\sqrt{t}\cos 2\pi\sqrt{t}}{(2\pi\sqrt{t})^3};$$

$$t = a_1(h^2 + k^2 + l^2) + \tfrac{1}{3}(a_2 - a_1)(h + k + l)^2 \tag{12}$$

$$a_1 = \frac{A^2}{r^2(1 - \cos\alpha)} \qquad a_2 = \frac{C^2}{r^2(2\cos\alpha + 1)},$$

with the provision that the structure amplitudes F_{hkl} in the series (11) are always referred to the centre of the region T.

We have always computed the values of the series (11) by including only terms for which the corresponding experimental structure amplitudes occur in table I, that is, all terms corresponding to weak reflections have been omitted and lumped with the residual term.

The motion of each model atom has to be chosen such that Δf_T decreases to zero before the break-off point is reached. For the sodium atom the Δf_T values calculated by INKINEN [5] are available, and we adopt them here with some minor complementations (table III; fig. 3a). Inkinen has also made some suggestions concerning the interpretation of these results. We note that on an average the resulting curves seem to comply with our criterion. At this stage we shall not pay any attention to the slight difference between the values found for different directions, which Inkinen

Table III

The difference between the experimental and the theoretical scattering factor of the Na_1 atom, as calculated by means of models I and III. For some points the standard deviation δ calculated on the basis of the experimental errors is stated.

1 *hkl*	2 $\varkappa$[Å^{-1}]	3 $\Delta f_T^{(I)}$	4 $\Delta f_T^{(III)}$	5 δ
000	0	0.32	0.37	
111	0.0894	0.29	0.35	
222	1788	0.20	0.30	0.04
333	2682	0.11	0.22	
444	3575	0.03	0.14	
555	4469	−0.02	0.07	0.04
666	5363	−0.05	0.03	
$1\bar{1}0$	1976	0.22	0.20	
$2\bar{2}0$	3953	0.06	0.02	
$3\bar{3}0$	5929	0.03	0.05	
100	1179	0.28	0.31	
200	2359	0.18	0.16	
300	3538	0.09	0.04	0.02
400	4717	0.01	−0.01	
500	5897	−0.02	−0.03	
110	1287	0.27	0.30	
220	2575	0.15	0.14	
330	3862	0.02	0.02	
440	5149	−0.05	−0.05	

has shown to vanish if the motion of the model atom is made slightly anisotropic. The Δf_T for the nitrate group has still so high values close to the break-off point that one should be careful of the contribution of this group to the residual term even at the sodium atom, particularly when the model is yet uncorrected with respect to the N and O atoms (fig. 7a).

For the determination of the motion parameters of the nitrogen atoms, Δf_{T_N} values have been calculated in the directions *hhh*, $h\bar{h}0$ and *h*00 (table IV; fig. 4a). The values furnish no distinctly evident cause to alter the assumed state of motion.

Values of $\Delta f_{T_{O_1}}$ have been calculated in order to study the motion of the oxygen atoms, particularly in the $h\bar{h}0$ direction for the determination of c_x^2 and at numerous points *hhk* in order to find the undefined principal directions and to fix the parameters c_y^2 and c_z^2 (table V; fig. 5a). (We have only calculated the real part; the imaginary part is identically zero in the

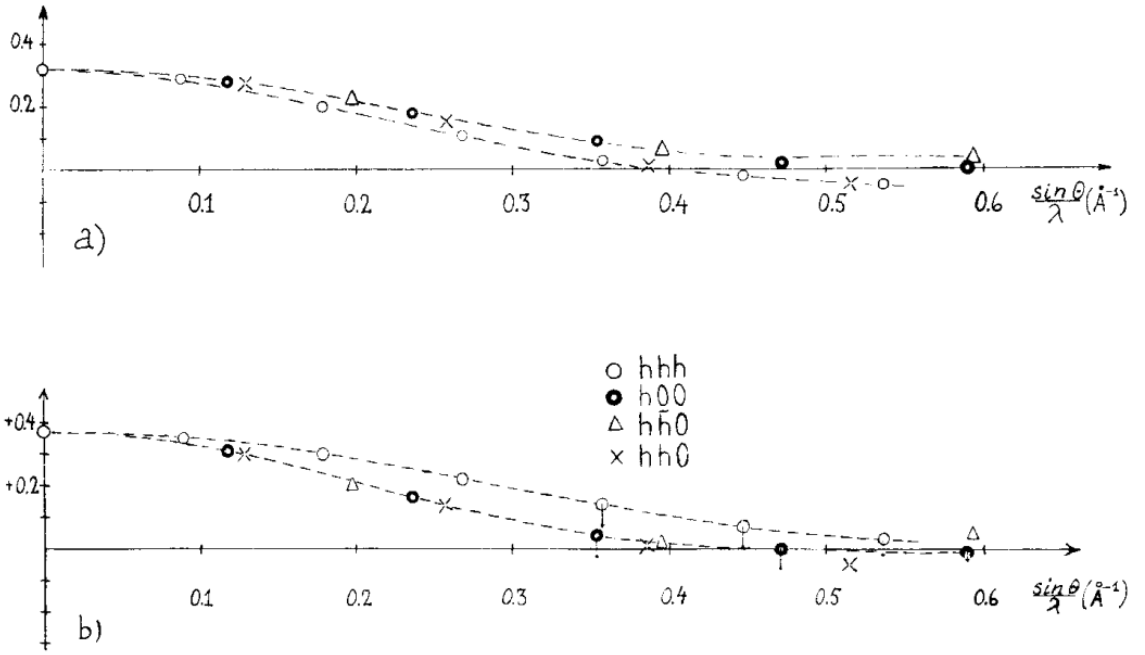

Fig. 3. The difference between the experimental and the theoretical scattering factor of the Na_1 atom in the directions $\cos^2\varepsilon = 1$ (hhh); $\cos^2\varepsilon = 0$, $\cos^2\gamma = 1$ $(h\bar{h}0)$; $\cos^2\varepsilon = 0.0638$, $\cos^2\gamma = 0.75$ $(h00)$; $\cos^2\varepsilon = 0.2143$, $\cos^2\gamma = 0.75$ $(hh0)$, as calculated by means of model I (a) and model III (b). In fig. 3b the shift produced by a $\Delta c^2_{Na} = -0.05$ Å^2 variation of the parameter of the model is marked for some points.

hhk directions, and on the whole it depends mainly on the possible error in the position parameter u and on the asymmetry of the distribution with respect to the centre of the O atom, so that it is obviously inessential in the determination of the motion parameters.) According to our criterion the results provide a clear reason for making a correction in the assumed motion of the oxygen atoms.

In order that it might be seen with the greatest possible clarity what the calculated values tell us about the directions of the y and z axes of the motion, we resorted to the following auxiliary construction. In all calculated *hhk* directions the value of Δf_T for the point $\varkappa = 0.5$ Å^{-1} was determined by graphical interpolation. In the zy plane we then traced the different *hhk* directions and marked off on these, from the origin, lengths corresponding to the residues found on subtraction of these Δf_T values from an arbitrarily fixed constant (fig. 6). The curve joining their end points obviously has the greatest distance from the origin in the direction in which the amplitude of motion is highest. It is evident from the diagram in fig. 6 that a strongly anisotropic temperature factor has to be chosen. The amplitude of motion must have its maximum in a direction forming an angle of about 45° with the trigonal axis and being approximately perpendicular to the connecting line of the two closest sodium atoms (cf. fig. 2); its minimum must obviously

Table IV

The difference between the experimental and the theoretical scattering factor of the N_1 atom, as calculated by means of models I and III. For some points the standard deviation δ calculated on the basis of the experimental errors is stated.

1 hkl	2 $\varkappa$[Å^{-1}]	3 $\Delta f_T^{(I)}$	4 $\Delta f_T^{(III)}$	5 δ
000	0	−0.014	0.043	
111	0.0894	0.005	0.056	0.021
222	1788	0.071	0.087	
333	2682	0.105	0.103	
444	3575	0.110	0.095	
555	4469	0.075	0.062	0.015
666	5363	0.026	0.021	
$1\bar{1}0$	1976	−0.012	0.033	
$2\bar{2}0$	3953	−0.006	0.013	
$3\bar{3}0$	5929	0.005	0.001	0.007
100	1179	−0.014	0.041	0.022
200	2359	−0.004	0.035	
300	3538	0.007	0.028	
400	4717	0.017	0.019	0.015
500	5897	0.019	0.010	

be in the N—O direction, which is in agreement with the result of SASS et al. (cf. section 2). After some trials we arrived at the parameter values

$$c_x^2 = 0.42 \text{ Å}^2, \quad c_y^2 = 1.30 \text{ Å}^2, \quad c_z^2 = 0.65 \text{ Å}^2, \quad \cos^2\varepsilon_0 = 0.55,$$

and with this choice our criterion is well satisfied (fig. 5b). The model obtained from model I by changing the state of motion of the oxygen atoms to one having the above-mentioned characteristics has been denoted by the index II. For the sake of comparison, fig. 6 also gives the result of another try with $c_x^2 = 0.41$ Å^2, $c_y^2 = 1.28$ Å^2, $c_z^2 = 0.70$ Å^2, and $\cos^2\varepsilon_0 = 0.5$ (inner curve); this result shows that the angle ε_0 should preferably be chosen slightly smaller than 45° in order that our criterion may be satisfied.

For the determination of the position parameter u of the oxygen atoms the values of the experimental Fourier series and of the truncated theoretical Fourier series $\varrho(xyz) = \Sigma\, F_{hkl}\, e^{-2\pi i(hx+ky+lz)}$ have been calculated in four points, s_1, s_2, s_3, s_4, on the N—O connecting line, nearly symmetrical about the centre of the oxygen atom. (In both series only the terms corresponding to measured reflections were taken into account.) The site of the maximum we determined by finding the location of the apices of the

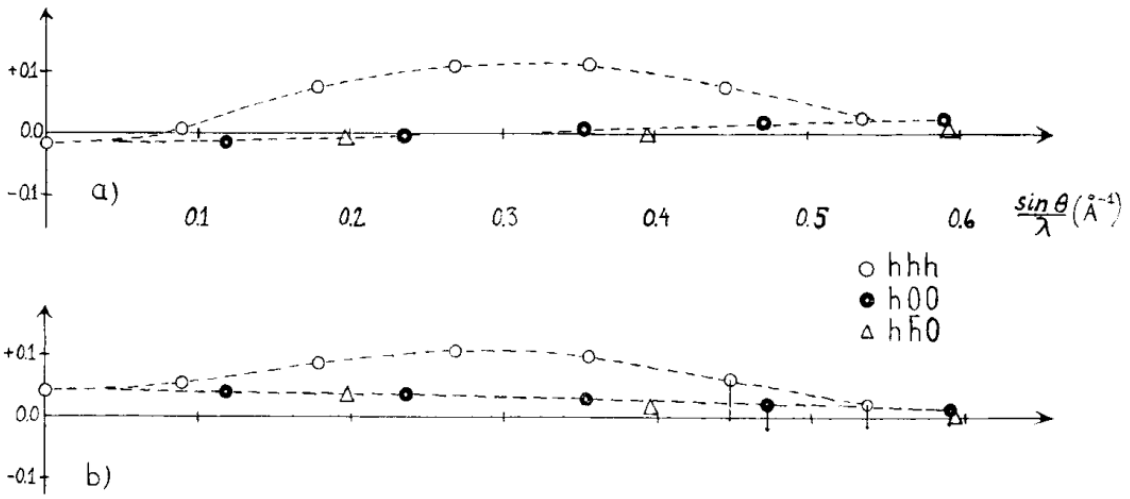

Fig. 4. The difference between the experimental and the theoretical scattering factor of the N_1 atom in the directions $\cos^2\varepsilon = 1$ (hhh); $\cos^2\varepsilon = 0$, $\cos^2\gamma = 1$ $(h\bar{h}0)$; $\cos^2\varepsilon = 0.0638$, $\cos^2\gamma = 0.75$ $(h00)$, as calculated by means of model I (a) and model III (b). In fig. 4b the shift produced by a $\Delta c_N^2 = -0.05$ Å² variation of the parameter of the model is marked for some points.

two parabolas opening downward and passing through the points s_1, s_2, s_3 and s_2, s_3, s_4 respectively, and taking their mean. The parameter value employed in the theoretical model was then corrected so that the maximum calculated according to the model coincided with that of the experimental series. (The first to suggest this procedure for elimination of the break-off error, which is identical with the use of the difference series, was BOOTH [1].) The results of these calculations are shown in table VI. In this manner the value $2\pi u = 87.6°$, or $u = 0.2433$, was found for the parameter. This value falls within the limits of error stated by TAHVONEN and by INKINEN, but is clearly outside those of ELLIOT and of SASS et al. (cf. section 2), who apparently did not take into account the principally approximate character of the performed calculations. The model derived from model II by giving u this value has been denoted by the index III.

Employing model III, we now recalculated Δf_T for the different atoms, tables III to V, figs. 3b, 4b, 5b (with respect to the O atom the values calculated by means of models II and III coincide so closely that fig. 5b represents both of them equally well), and as a check we calculated the Fourier difference series along four different straight lines:

(a) the trigonal axis: $x : y : z = 1 : 1 : 1$; table VIII, fig. 8
(b) a line parallel to (c), passing through the Na atom: $x : y : z = 1 : -1 : 0$; table IX, fig. 9
(c) the N—O connecting line: $x : y : z = 1 : -1 : 0$; table X, fig. 10
(d) the Na-O connecting line (through the point $u = 0.25$): $x : y : z = 1 : 0 : -2$; table XI, fig. 11.

Table V

The difference between the experimental and the theoretical scattering factor of the O_1 atom, as calculated by means of models I, II and III. For some points the standard deviation δ calculated on the basis of the experimental errors is stated.

1 hkl	2 $\cos^2\varepsilon$	3 $\varkappa$[Å^{-1}]	4 $\Delta f_T^{(I)}$	5 $\Delta f_T^{(II)}$	6 $\Delta f_T^{(III)}$	7 δ
000	—	0	0.023	0.021	0.024	
$1\bar{1}0$	0	0.1976	0.056	0.010	0.018	
$2\bar{2}0$	0	3953	0.073	0.003	0.008	
$3\bar{3}0$	0	5929	0.075	−0.005	−0.003	
001	0.0638	1179	0.027	0.021	0.020	
002	0.0638	2359	−0.006	0.015	0.011	
003	0.0638	3538	−0.047	0.007	0.005	0.008
004	0.0638	4717	−0.079	0.001	0.003	
005	0.0638	5897	−0.090	−0.002	−0.001	
$\frac{4}{3}\ \frac{4}{3}\ \frac{16}{3}$	0.2143	5149	−0.120	0.007	0.006	
226	0.2988	5451	−0.115	0.010	0.007	
336	0.5217	4950	−0.128	0.013	0.010	
446	0.7696	4755	−0.100	0.013	0.010	
556	0.9454	4902	−0.074	0.010	0.007	
111	1	0894	0.026	0.024	0.026	
222	1	1788	−0.011	0.026	0.025	0.010
333	1	2682	−0.047	0.023	0.019	
444	1	3575	−0.072	0.018	0.012	
555	1	4469	−0.068	0.011	0.007	0.010
666	1	5363	−0.044	0.005	0.003	
664	0.8136	5285	−0.025	0.011	0.008	
$\frac{16}{3}\ \frac{16}{3}\ \frac{8}{3}$	0.6303	5004	−0.016	0.015		
663	0.6303	5630	−0.030	0.011	0.009	0.009
440	0.2143	5149	0.021	0.012	0.011	

Attention is particularly drawn to the fact that the differences obtained on calculation by means of model I between the Δf_T curves of Na in the different directions have changed their character and no longer absolutely require an anisotropic motion parameter. Even otherwise the results show that we cannot make any further essential improvement of our model on the basis of our criterion. However, it seems, from a scrutiny of the Δf_T curves as well as the $\Delta\varrho$ curves, as if the mean motion parameters of the Na and N atoms were at the upper limits of the values permitted by the criterion. At some points of the Δf_T curve we have indicated the shift that would be produced by a correction of the parameter by $\Delta c^2_{Na} = -0.05$ Å^2,

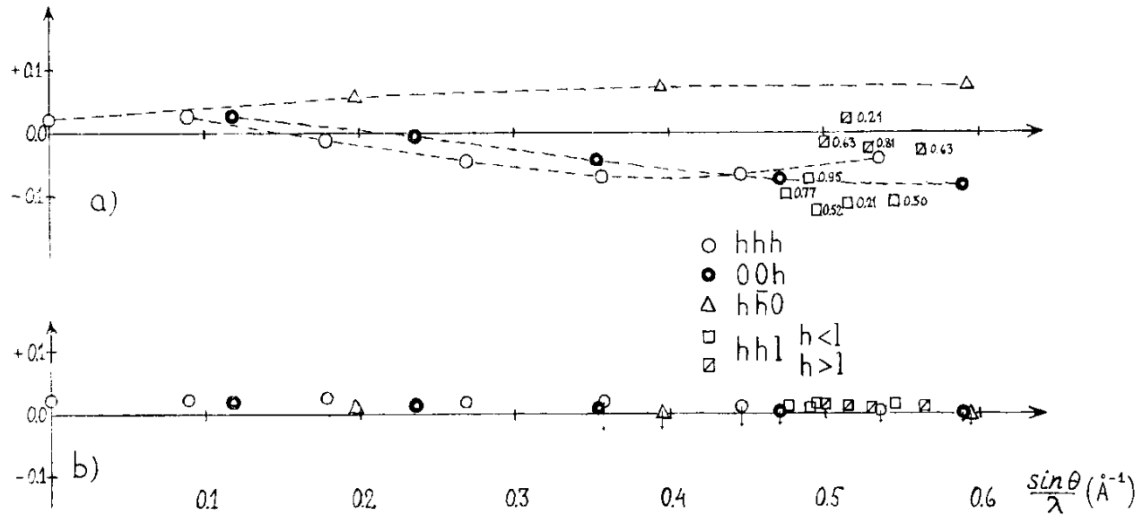

Fig. 5. The difference between the experimental and the theoretical scattering factor of the O_I atom in the directions $\cos^2\varepsilon = 0$, $\cos^2\gamma_1 = 1$ $(hh\bar{0})$ and some different directions with $\cos^2\gamma_1 = 0$ (hhl), as calculated by means of model I (a) and model II (or III) (b). In fig. 5b the shift produced by a $\Delta c_O^2 = -0.05$ Å² variation of the parameter of the model is marked for some points (the values entered beside the points are values of $\cos^2\varepsilon$).

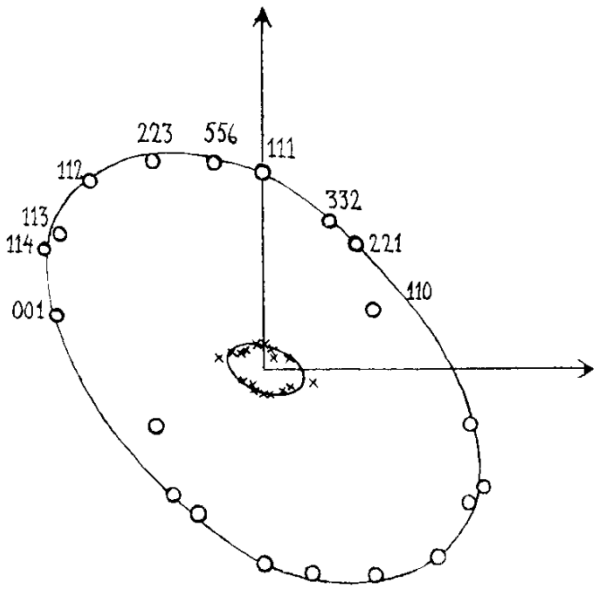

Fig. 6. Auxiliary plot for the determination of the principal directions of the motion of the O atom. The outer curve has been obtained by means of model 1, the inner curve by means of a model with $c_x^2 = 0.41$ Å², $c_y^2 = 1.28$ Å², $c_z^2 = 0.70$ Å², $\cos^2\varepsilon_0 = 0.5$ (cf. fig. 2).

for the N and O atoms respectively. Likewise we have indicated on some of the plotted $\Delta\varrho$ curves at the site of the atom the effect of a -0.05 Å² correction of its own motion parameter. On the strength of these indications we consider it appropriate to choose for the parameters consistent with the measured values the parameters of model III with the corrections $\Delta c_{Na}^2 = -0.02$ Å² and $\Delta c_N^2 = -0.03$ Å².

Table VI

Determination of the position parameter u of the O atoms: The experimental and theoretical electron density values according to the truncated Fourier series for four points on the N—O connecting line; the distances s and s_{max} of these points and of the calculated maximum point from the centre of the N atom; the resulting distance d_{N-O} between the N and O atoms and the corresponding parameter $2\pi u$ in the different cases.

s[Å]	ϱ_I		ϱ_{II}		ϱ_{III}	
	Theor	Exp	Theor	Exp	Theor	Exp
1.1244	15.1956	14.9856	14.9993	14.9889	14.9250	14.9882
1.1947	15.8414	15.7030	15.6648	15.7085	15.6417	15.7097
1.2650	15.7455	15.6626	15.5672	15.6694	15.5976	15.6720
1.3352	14.9436	14.8941	14.7423	14.9010	14.8233	14.9041
s_{max}[Å]	1.2205	1.2260	1.2206	1.2261	1.2257	1.2262
d_{N-O}[Å]	1.2228	1.2283	1.2228	1.2283	1.2312	1.2317
$2\pi u$	87.0°	87.39°	87.0°	87.39°	87.6°	87.63°

5. Discussion of the Model

The calculations have brought us to a model with the parameter values

Na: $c_{||}^2 = c_{\perp}^2 = 0.55$ Å^2

N: $c_{||}^2 = c_{\perp}^2 = 0.42$ Å^2

O: $c_x^2 = 0.42$ Å^2, $c_y^2 = 1.30$ Å^2, $c_z^2 = 0.65$ Å^2, $\cos^2\varepsilon_0 = 0.55$ ($\varepsilon_0 \approx 42°$)
$2\pi u = 87.6°$ ($u = 0.2433$, $d_{N-O} = 1.231$ Å).

A question still unclarified is that of the accuracy with which this model represents the correct model.

As a preliminary observation we may say that the corrections that have been performed appear rather expedient. In the first place it is natural from a physical point of view that the greatest motion of the oxygen atoms should be oriented in the direction in which their freedom of motion is greatest (cf. fig. 2) and the least motion in the direction where their mobility is most restricted.

Qualitative corroboration is further lent to the corrections made in the course of our calculations by the fact that, owing to their effect, the model has distinctly come closer to the experimental values. A general idea of the effect of the corrections can be obtained by studying the differences between experimental and theoretical structure amplitudes (table I). We can see at once that the correction made to the state of motion has brought a very essential improvement, particularly if one disregards the great dif-

ferences near $x = 0$, which are caused by the fact that in the models the number of electrons per unit cell is too small by two. The sum of the squares of the deviations*, $R = \Sigma (F_{exp} - F_{theor})^2$, has the following magnitudes in the different instances: model I, 32.79; model II, 18.72; model III, 17.16. Looking at the individual structure amplitudes, we may note that, except for the very first reflections, the greatest differences have been essentially rectified (e.g. 442, 431, $2\bar{2}0$, 420, $\bar{3}20$, 664, 520) with very few exceptions (440, 622, $3\bar{3}0$) without any disturbance being caused in the fit at other points.

The circumstance that the z and y axes of the motion of O-atoms are set at oblique angles to the trigonal axis obviously has its essential significance too. We have tried to find the best possible model with $\cos^2\varepsilon_0 = 1$ (cf. [10]), but not by far as good a fit could be obtained. In the best case we had $R = 26.52$, and it proved impossible in particular to reduce the great differences in the reflections 442 and 664; the 622 reflection got even worse than in any of our models. On the whole there are few other reflections on which oblique orientation of the motion would have a strong effect. The most distinct indication of this might be obtained by measuring separately the reflections 633 and 552, here measured in combination, for which all other possible models yield structure amplitudes equal in magnitude.

The improvement of the model is also evident in the Fourier difference series (figs. 8 to 11). It is obvious (fig. 10) that also the correction of the parameter u is fully justified, seeing that the asymmetry in the vicinity of the centre of the O atom disappears entirely on account of it. It is further noted that also in the interior parts of all atoms good fit obtains, particularly if the small correction made to model III is taken into account. The improvement of the model will also be seen from $\Delta f_{T_{NO_3}}$ (table VII, fig. 7).

However, these observations in themselves say nothing about the quantitative reliability of the parameters. This question can only be answered by a detailed, critical consideration of all factors affecting the accuracy.

6. The Accuracy of the Parameter Determination

In accordance with the considerations presented in the first part of this work [8] the accuracy of the model is mainly determined by the accuracy with which the criteria for determination of the state of motion can

* In this sum one term corresponds to each of the structure amplitudes listed in table I, that is, the index permutations have been omitted in order that each measured value might have the same weight.

be applied. This latter accuracy is in turn primarily dependent on how heavy the deformations of the different atoms can be. Of course, this is partly a matter of opinion, but it is also possible to fall back upon the information furnished by the Δf_T curves of the atoms, which approximately represent the deformations.

It is to be expected that the sodium ion is only slightly deformed. The fairly insignificant differences between the Δf_T curves for different directions also make this probable. On the other hand, the deformation may be rather heavier in the N atom, which is surrounded by O atoms. Of this, too, we can detect signs in the differences between the Δf_T curves calculated for the nitrogen atom in different directions, which appear fairly great considering the small size of the atom and of the region employed in the calculation relating to it. Also, the O atoms could be imagined to be deformed rather than the Na atom, but as there is not the least sign of such conditions in the Δf_T curves of these atoms, we can hazard the estimate that their deformations are quite small in the inner part, which is included in T_0.

If we study the effect of a small change in the state of motion of each model atom on its Δf_T curves (figs. 3b, 4b, 5b; see also table XII) and on the $\Delta\varrho$ curves at the site of the atom itself (figs. 8c, 10d), we may reasonably conclude that the determination of the mean motion parameters is burdened with the inaccuracies $\overline{c^2_{\mathrm{Na}}} \pm 0.02$ Å^2, $\overline{c^2_{\mathrm{N}}} \pm 0.03$ Å^2, $\overline{c^2_{\mathrm{O}}} \pm 0.03$ Å^2 from this cause. A similar scrutiny of the effect that would be produced in the $\Delta f_{T_{\mathrm{Na}}}$ curves by a slight anisotropy of the state of motion of the Na atom (cf. [5: figs. 5a, b] and table XII) has led us to the following conclusion: $|c^2_{\mathrm{Na}\parallel} - \overline{c^2_{\mathrm{Na}}}|$ and $|c^2_{\mathrm{Na}\perp} - \overline{c^2_{\mathrm{Na}}}| < 0.01$ Å^2. In like manner we may reason, on the strength of the experience gained in the course of our determination of the state of motion of the oxygen atoms (cf. fig. 6), that the motion parameters of this atom type can be varied independently of each other within the limits

$$c_x^2 \pm 0.01 \text{ Å}^2,\ c_y^2 \pm 0.02 \text{ Å}^2,\ c_z^2 \pm 0.02 \text{ Å}^2,$$
$$0.58 > \cos^2\varepsilon_0 > 0.52 \quad (\varepsilon_0 \approx 42^\circ \pm 2^\circ).$$

The deformation of the N atom impedes the observation of a potential anisotropy of its motion and compels us to give its estimated limits a wider range: $|c^2_{\mathrm{N}\parallel} - \overline{c^2_{\mathrm{N}}}|$ and $|c^2_{\mathrm{N}\perp} - \overline{c^2_{\mathrm{N}}}| < 0.04$ Å^2.

On the strength of what has been said in the first part of this work [8], we may confidently believe that these limits cover almost completely the effects of the inaccuracy in the residual term on the parameter values. For, in the estimation of the parameter limits for each atom the inaccuracy due to the contribution of that atom to the residual term has automatically been taken into account. Further, it is obvious, by virtue of the property

Table VII

The difference between the experimental and the theoretical structure amplitude of the nitrate group $(NO_3)_1$, as calculated by means of models I and III. For some points the standard deviation δ calculated on the basis of the experimental errors is stated.

1 hkl	2 $\varkappa$[Å^{-1}]	3 $\Delta f_T^{(I)}$	4 $\Delta f_T^{(III)}$	5 δ
000	0	0.31	0.40	
111	0.0894	0.50	0.56	0.08
222	1788	0.68	0.86	
333	2682	0.42	0.68	
444	3575	−0.12	0.22	
555	4469	−0.37	−0.03	0.10
666	5363	−0.22	0.02	
100	1179	−0.61	−0.35	
200	2359	−0.97	−0.46	
300	3538	−0.19	0.00	
400	4717	0.16	0.15	0.05
500	5897	−0.13	0.03	
110	1287	−0.35	−0.21	
220	2575	−0.14	0.06	
330	3862	0.10	0.03	
440	5149	−0.44	−0.31	
$\frac{1}{2}\bar{\frac{1}{2}}0$	0988	−0.44 +0.01i	−0.24 −0.02i	
$1\bar{1}0$	1976	−0.75 +0.00i	−0.46 −0.04i	0.04 0.07
$\frac{3}{2}\bar{\frac{3}{2}}0$	2965	0.33 −0.11i	0.28 −0.08i	
$2\bar{2}0$	3953	0.69 +0.03i	0.27 −0.19i	0.15
$\frac{5}{2}\bar{\frac{5}{2}}0$	4941	0.19 +0.32i	0.09 +0.01i	
$3\bar{3}0$	5929	0.13 +0.01i	0.32 +0.08i	0.06 0.06

Tables VIII—XI

The values ϱ_{exp}, $\Delta\varrho_I$, $\Delta\varrho_{II}$, $\Delta\varrho_{III}$ (in Å^{-3}), as calculated by means of the Fourier series with the coefficients F_{exp}, ΔF_I, ΔF_{II}, and ΔF_{III} respectively:

Table VIII

along the trigonal axis, $x : y : z = 1 : 1 : 1$, at intervals $\Delta = 0.2331$Å,

1		2	3	4	5
	n	ϱ_{exp}	$\Delta\varrho_I$	$\Delta\varrho_{III}$	δ
(N)	0	15.125	0.362	0.251	0.023
	1	12.026	0.262	0.203	
	2	5.838	0.016	0.062	
	3	1.424	−0.199	−0.089	
	4	−0.204	−0.215	−0.132	0.017
	5	−0.531	−0.119	−0.112	
	6	−0.389	−0.115	−0.173	
	7	−0.117	−0.181	−0.254	
	8	0.068	−0.141	−0.184	
	9	0.340	−0.034	−0.012	0.020
	10	0.400	−0.033	0.044	
	11	−0.196	−0.106	−0.039	
	12	−0.599	−0.088	−0.089	
	13	−0.270	0.027	−0.034	
	14	−0.148	0.115	0.047	0.017
	15	1.556	0.146	0.108	
	16	9.812	0.162	0.169	
	17	23.104	0.177	0.227	
(Na)	18	29.992	0.181	0.251	0.023

Table IX

along the line with $x : y : z = 1 : -1 : 0$ passing through the Na atom, at intervals $\Delta = 0.1406$ Å,

1		2	3	4
	n	ϱ_{exp}	$\Delta\varrho_I$	$\Delta\varrho_{III}$
(Na)	0	29.992	0.181	0.251
	1	27.213	0.185	0.239
	2	20.109	0.188	0.209
	3	11.632	0.172	0.177
	4	4.728	0.123	0.152
	5	0.852	0.037	0.125
	6	−0.364	−0.070	0.076
	7	−0.279	−0.163	0.006
	8	−0.086	−0.210	−0.065
	9	−0.171	−0.193	−0.098
	10	−0.283	−0.119	−0.063
	11	−0.119	−0.022	0.025
	12	0.302	0.061	0.128
	13	0.692	0.099	0.192
	14	0.806	0.083	0.184
	15	0.636	0.028	0.113
	16	0.352	−0.043	0.016
	17	0.128	−0.100	−0.060
	18	0.048	−0.121	−0.083

of local convergence of the Fourier series, that the inaccuracy in the other parameters has no effect on the determination of the parameters of a given atom. This is also seen from table XII, which contains some information on how the values that determine the different parameters are affected by the variation of a given parameter within the permissible limits.

Of factors that may have on the residual term a slight effect exceeding the limits determined by the possible variations of the model, there remain only heavy deformations and interatomic distributions. To the parameter determination this effect does not, however, cause any other inaccuracy than that due to the fact that the deformations determine the accuracy with which our criteria can be applied. (We have not paid any attention to the circumstance that we have approximated the motions by a harmonic oscillation. Its effect is difficult to assess, but we place our confidence in

Table X

along the N—O connecting line,
$x : y : z = 1 : -1 : 0$, at intervals
$\Delta = 0.1406$ Å,

1	2	3	4	5	6
n	ϱ_{exp}	$\Delta\varrho_{I}$	$\Delta\varrho_{II}$	$\Delta\varrho_{III}$	δ
−18	0.359	0.130	0.081	0.068	
−17	0.643	0.008	−0.027	0.002	
−16	0.951	−0.071	−0.115	−0.044	
−15	1.087	−0.071	−0.117	−0.027	
−14	0.915	−0.027	−0.025	0.054	
−13	0.525	0.022	0.098	0.144	
−12	0.152	0.028	0.163	0.175	
−11	0.025	−0.015	0.124	0.116	
−10	0.185	−0.082	0.009	0.000	
− 9	0.464	−0.137	−0.104	−0.105	
− 8	0.625	−0.158	−0.147	−0.141	
− 7	0.605	−0.140	−0.104	−0.101	
− 6	0.673	−0.091	−0.012	−0.019	
− 5	1.384	−0.021	0.074	0.061	
− 4	3.290	0.065	0.127	0.119	
− 3	6.514	0.160	0.153	0.161	
− 2	10.439	0.253	0.170	0.200	
− 1	13.782	0.330	0.188	0.235	
(N) 0	15.125	0.362	0.198	0.251	
1	13.721	0.321	0.184	0.234	
2	10.088	0.192	0.140	0.190	
3	5.953	−0.010	0.074	0.139	
4	3.441	−0.231	−0.001	0.100	0.024
5	3.925	−0.395	−0.067	0.077	
6	7.218	−0.440	−0.101	0.065	
7	11.648	−0.358	−0.085	0.060	
8	14.986	−0.210	−0.010	0.063	0.021
(O) 9	15.663	−0.083	0.102	0.074	
10	13.512	−0.041	0.206	0.085	
11	9.643	−0.079	0.253	0.082	
12	5.634	−0.131	0.228	0.059	0.024
13	2.644	−0.123	0.162	0.031	
14	0.993	−0.026	0.111	0.023	
15	0.338	0.111	0.109	0.047	
16	0.180	0.216	0.137	0.085	0.023
17	0.205	0.220	0.141	0.101	
18	0.359	0.130	0.081	0.068	

Table XI

along the Na—O connecting line,
$x : y : z = 1 : 0 - 2$, at intervals
$\Delta = 0.1325$ Å.

1	2	3	4
n	ϱ_{exp}	$\Delta\varrho_{I}$	$\Delta\varrho_{III}$
(Na) 0	29.992	0.181	0.251
1	27.531	0.183	0.241
2	21.032	0.184	0.212
3	12.729	0.172	0.169
4	5.201	0.142	0.117
5	0.282	0.101	0.066
6	−1.560	0.052	0.023
7	−1.127	0.009	−0.003
8	0.151	−0.022	−0.009
9	1.028	−0.046	0.004
10	0.998	−0.068	0.027
11	0.389	−0.091	0.049
12	0.047	−0.110	0.062
13	0.828	−0.115	0.064
14	3.151	−0.101	0.062
15	6.767	−0.073	0.063
16	10.816	−0.050	0.068
17	14.129	−0.050	0.074
(O) 18	15.663	−0.083	0.074
19	14.917	−0.134	0.061
20	12.147	−0.180	0.044
21	8.268	−0.193	0.030
22	4.470	−0.168	0.030
23	1.718	−0.120	0.039
24	0.390	−0.076	0.043
25	0.219	−0.059	0.025
26	0.563	−0.074	−0.022
27	0.808	−0.102	−0.081
28	0.670	−0.115	−0.124
29	0.239	−0.094	−0.129
30	−0.206	−0.045	−0.092
31	−0.436	0.008	−0.035
32	−0.411	0.032	0.006
33	−0.246	0.011	0.009
34	−0.079	−0.043	−0.023
35	0.019	−0.098	−0.065
36	0.048	−0.121	−0.083

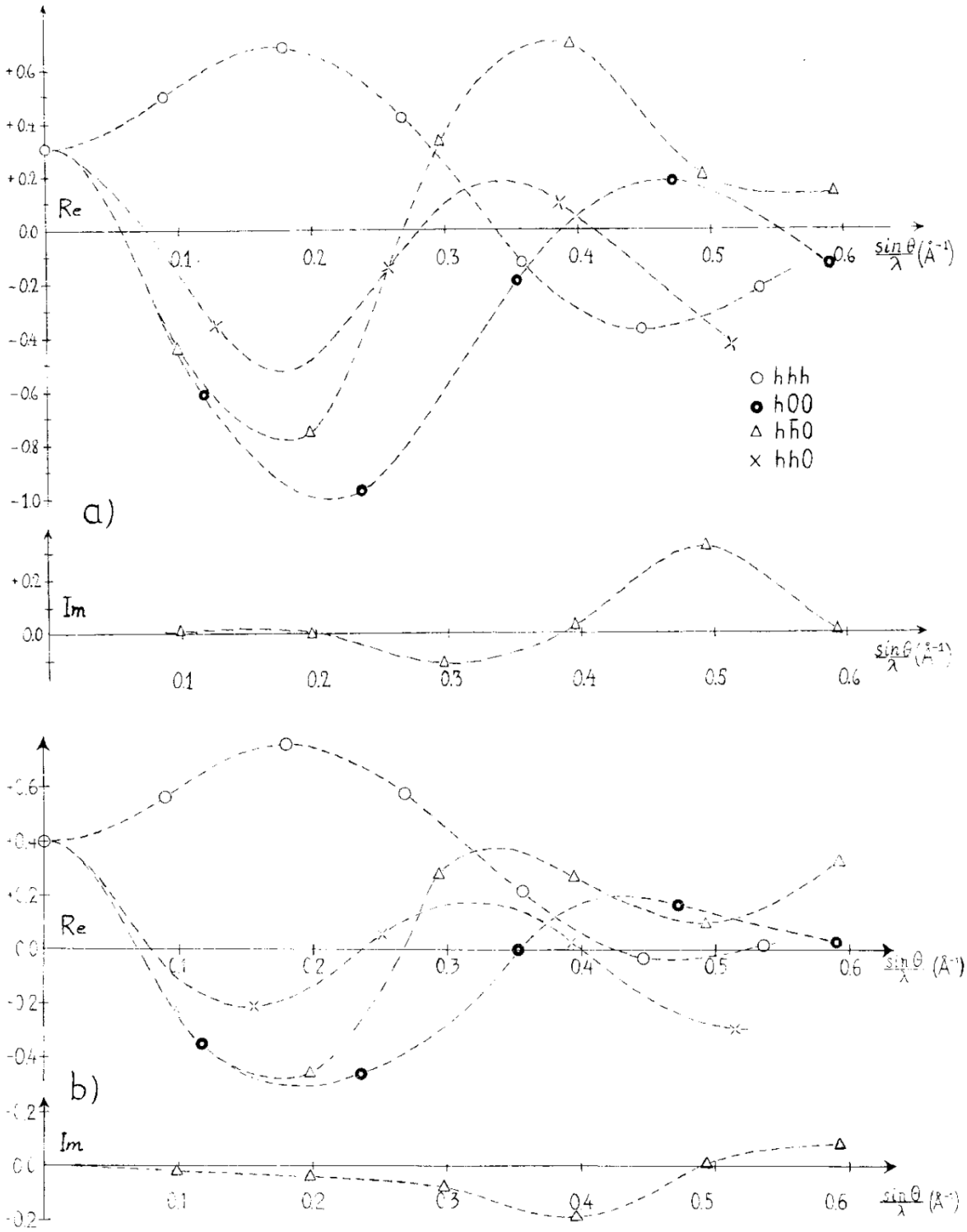

Fig. 7. The difference between the experimental and the theoretical structure amplitude of the $(NO_3)_1$ group in the directions $\cos^2\varepsilon = 1$ (hhh); $\cos^2\varepsilon = 0$, $\cos^2\gamma = 1$ $(h\bar{h}0)$; $\cos^2\varepsilon = 0.0638$, $\cos^2\gamma = 0.75$ $(h00)$; $\cos^2\varepsilon = 0.2143$, $\cos^2\gamma = 0.75$ $(hh0)$, as calculated by means of model I (a) and model III (b). (Re = real part, Im = imaginary part.)

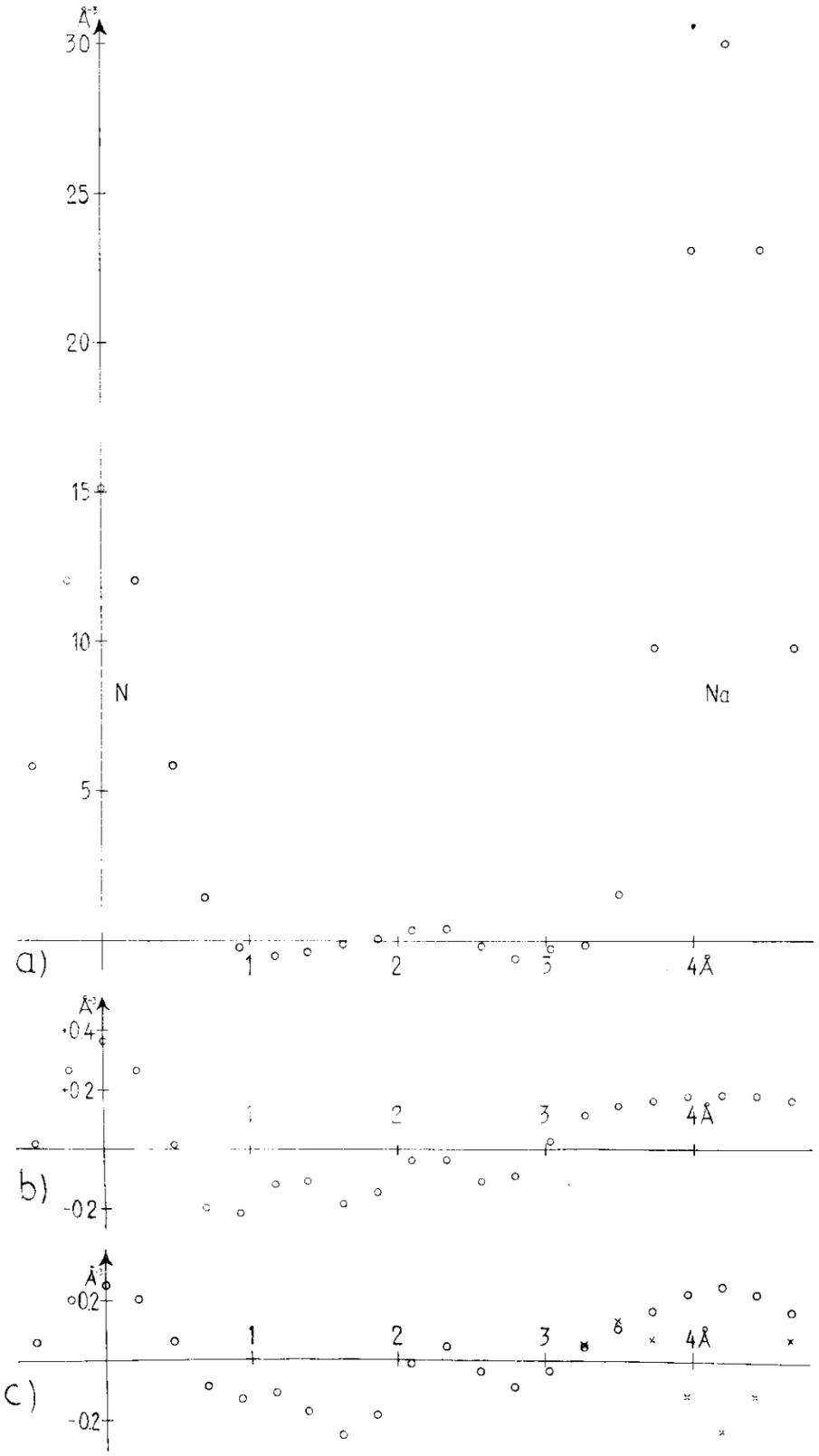

Fig. 8. ϱ_{exp}, $\Delta\varrho_{I}$ and $\Delta\varrho_{III}$ (a, b and c respectively) as calculated along the trigonal axis, $x : y : z = 1 : 1 : 1$. In fig. 8c also the effect of the correction $\Delta c^2_{Na} = -0.05$ Å^2 is shown (×).

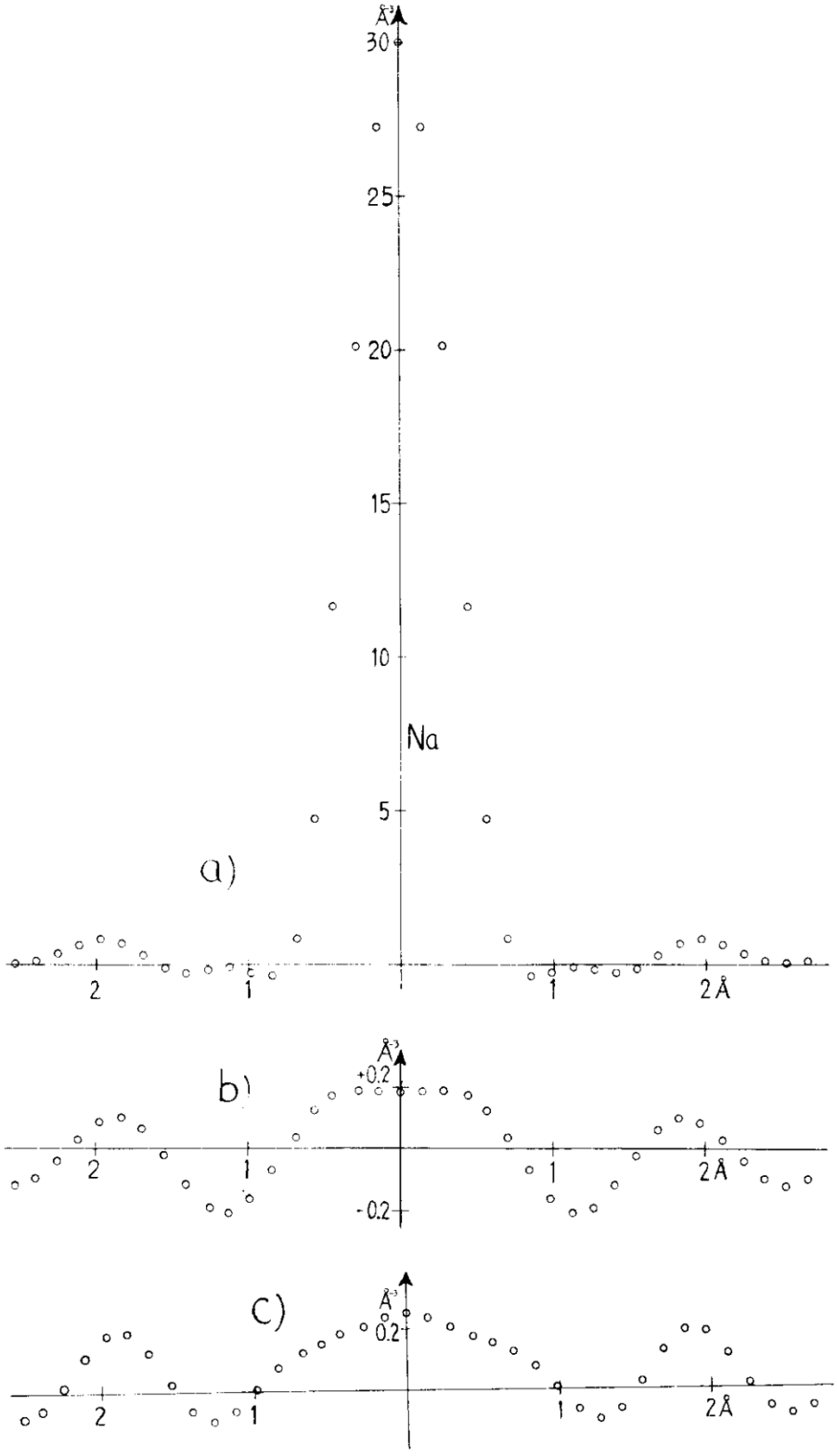

Fig. 9. ϱ_{exp}, $\Delta\varrho_{I}$ and $\Delta\varrho_{III}$ (a, b and c respectively) as calculated along the line with $x : y : z = 1 : -1 : 0$ passing through the Na atom.

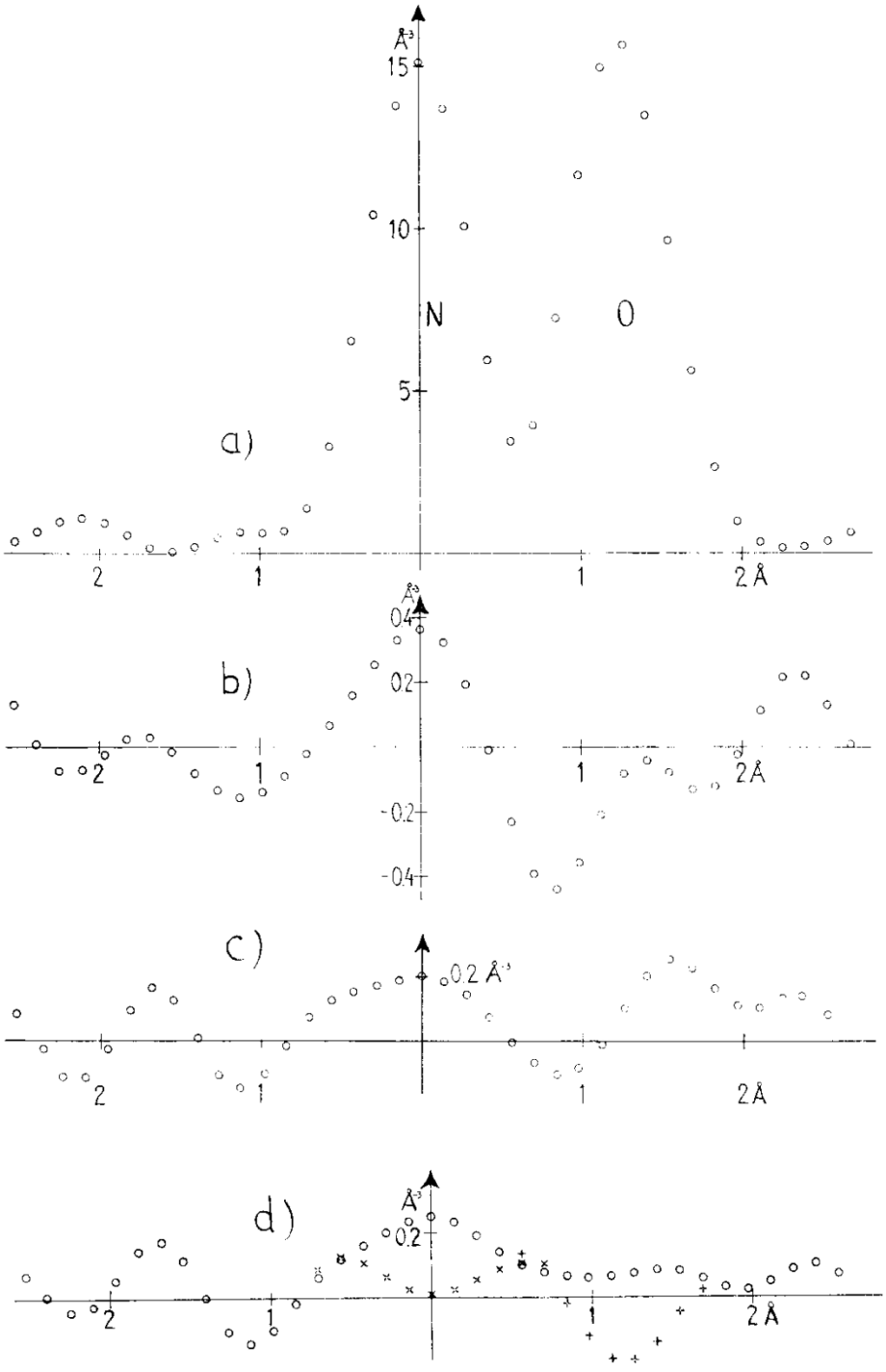

Fig. 10. ϱ_{exp}, $\Delta\varrho_{I}$, $\Delta\varrho_{II}$, and $\Delta\varrho_{III}$ (a, b, c, and d respectively) as calculated along the N—O connecting line, $x : y : z = 1 : -1 : 0$. In fig. 10d also the effect of the correction $\Delta c_N^2 = -0.05$ Å² (×) and that of $\Delta c_O^2 = -0.05$ Å² (+) are shown.

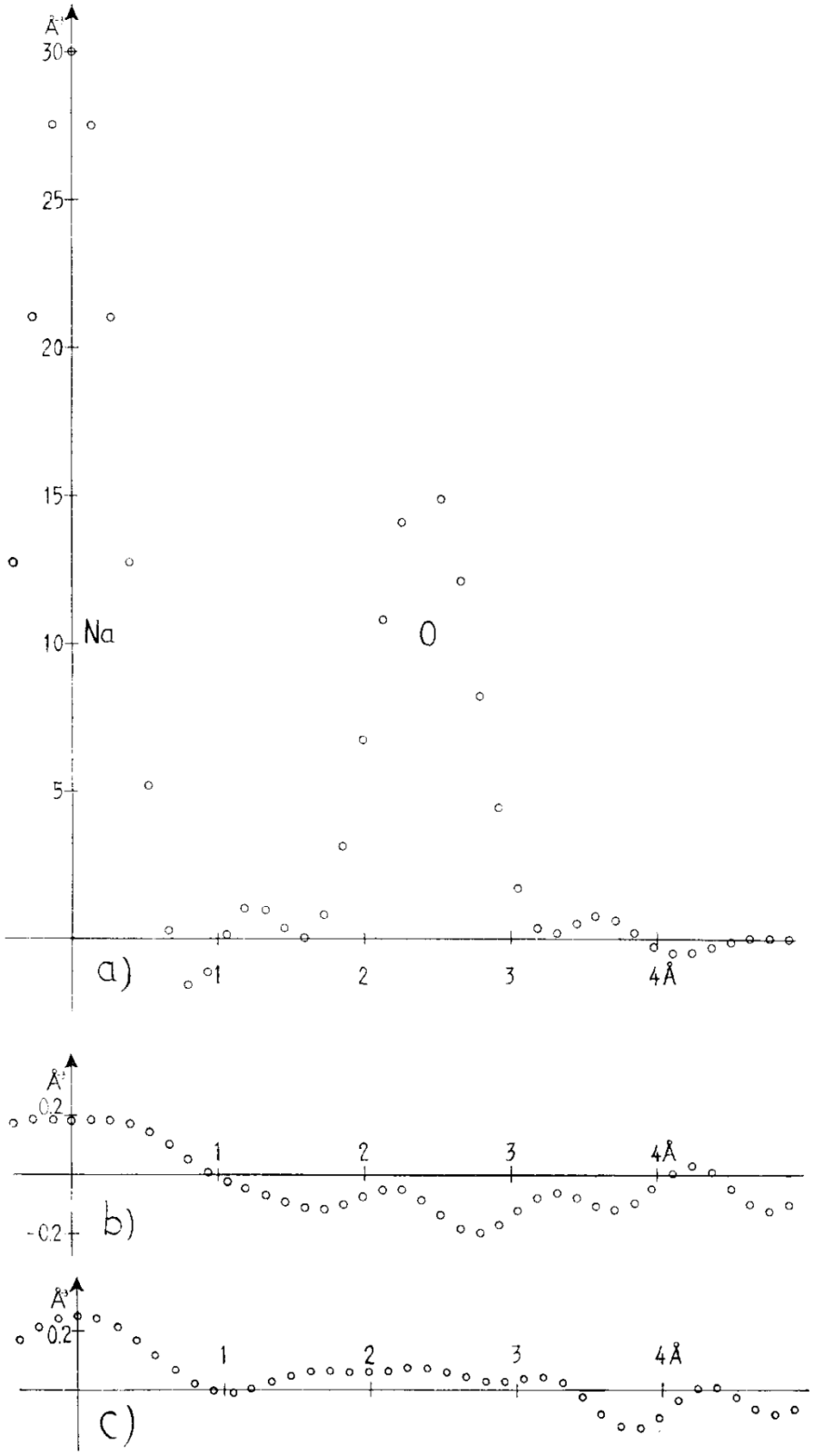

Fig. 11. ϱ_{exp}, $\Delta\varrho_{I}$ and $\Delta\varrho_{III}$ (a, b and c respectively) as calculated along the Na—O connecting line, $x : y : z = 1 : 0 : -2$.

the belief that it will not produce in the results any errors exceeding the limits found by our other considerations. Obviously this question would arise primarily in the case of the oxygen atoms.)

The foregoing considerations have as yet had no relation at all to the position parameter u, the determination of which contains no corresponding component of interpretation. We can also see from table XII that the effect exerted by the other parameters on its determination is nil. Therefore this is the only parameter in respect of which the contributions of the deformations and of the interatomic distributions to the residual term may carry some significance. Although we cannot yet present a complete treatment of these factors, it is obvious that all that is essential in this respect is included in the NO_3 group. The calculated $\Delta f_{T_{NO_3}}$ (table VII, fig. 7) is of considerable magnitude in the vicinity of the break-off point, even when calculated according to the best model, and it is therefore certain to make a contribution to the residual term. Preliminary studies show that its effect on the parameter $2\pi u$ is within the limits $\pm 0.15°$. It is also clearly observable that the weak and coincident reflections in the measured range, the treatment of which has been included in that of the residual term for practical reasons, have a strong share in this contribution.

7. The Influence of Experimental Errors

In the preceding treatment no attention at all has been paid to the inaccuracies of the experimental values constituting the basis of the calculations; consequently their effect has to be added to the error limits found in the foregoing. The experimental errors can be classified into random and systematic errors, and their treatment can be based mainly on the data given by INKINEN [5] concerning accuracy in experiment.

Inkinen has stated the error limits δF consistent with the experimental accuracy separately for each F_{exp} (table I). Considering the structure amplitudes as mutually independent statistical variables with the standard deviation δF, we may compute the standard deviation of the Δf_T and $\Delta \varrho$ series. This was done in some points for the different series; the results have been incorporated in the respective tables. Variations in the Δf curves of the magnitude found here would be equivalent to the following standard deviations in the values found for the mean motion parameters:

$$\delta(\overline{c^2_{Na}}) = 0.015 \text{ Å}^2,\ \delta(\overline{c^2_N}) = 0.017 \text{ Å}^2,\ \delta(\overline{c^2_O}) = 0.017 \text{ Å}^2 \text{ (cf. table XII)}.$$

It should be noted that the values of the different series and especially the values of one and the same series in closely adjacent points are not

mutually independent. In order that we might see the effect of these errors on the shape of the $\Delta\varrho$ and Δf_T functions, we should therefore also compute the standard deviations of the differences $\Delta\varrho(\mathbf{r}_1) - \Delta\varrho(\mathbf{r}_2)$ and $\Delta f_T(\mathbf{h}_1) - \Delta f_T(\mathbf{h}_2)$. It is already evident from the values stated above that they will be small. It can be submitted that the standard deviation of the differences is of the same order of magnitude as that of either value individually, provided that the distance between the points under consideration is large enough, which roughly implies that we should have $|\mathbf{r}_1 - \mathbf{r}_2| > 0.3$ Å, and $|\mathbf{h}_1 - \mathbf{h}_2| > 0.4$ Å^{-1} for Na, > 0.5 Å^{-1} for N, and > 0.2 Å^{-1} for NO_3 (note: $\varkappa = \frac{1}{2}|\mathbf{h}|$). It follows that the effect of the random errors on the difference between the values of a thermal factor as calculated in the principal directions equals their effect on the mean thermal factor.

Apart from this we may note that if for the points $\mathbf{r}_1$ and $\mathbf{r}_2$ the points s_1 and s_4 employed in our determination of the parameter u are chosen, we find $\delta(\varrho(s_1) - \varrho(s_4)) = 0.0166$, which corresponds to the inaccuracy $\delta(2\pi u) = 0.04°$.

However, it should be pointed out that the error limits stated by INKINEN have been assessed in consideration of the standard deviation found in the intensity measurements as well as the numerous possibilities of systematic errors. Taking into account the high number and small magnitude of the different systematic errors, one can advocate the inclusion of their effects in the standard deviations calculated in the foregoing. But on the strength of Inkinen's considerations special attention should be paid to two factors that may exert an influence even markedly exceeding that of the others, namely, specific orientation and the possible error committed in the determination of the absolute level.

Inkinen states the effect of specific orientation on the structure amplitudes as not exceeding 0.5 %, which would produce a difference of 1 % between the absolute levels of the structure amplitudes in the extreme directions $\cos^2\varepsilon = 1$ and $\cos^2\varepsilon = 0$. In the first order, the effect of the said specific orientation is to give the experimental values $[1 + 0.01\,(\cos^2\varepsilon - \frac{1}{3})]F$ instead of the values F, provided that the average level is correct. Its significance can be seen from the curves in fig. 12, which have been obtained by calculating values of the series $\Delta f_{T_{Na}}$ with the coefficients $0.01(\cos^2\varepsilon - \frac{1}{3})\,F_{III}$. In the Δf_{T_N} and Δf_{T_O} series the effect of orientation was so small that the difference between the outermost curves ($\cos^2\varepsilon = 1$ and $\cos^2\varepsilon = 0$) was only 0.013 at its highest and would not have been visible in the scale of the figure. It can be seen that the orientation does not affect the choice of motion parameters, as its effect on the Δf_T values is small and decreases on approach of the break-off point so that it causes no deviations from our criterion. We also note that the difference between the Δf_T curves in the extreme directions for the sodium ion resembles that produced by

Table XII

The effect of parameter changes in model III on the basis for determination of the parameters.

Change	$\Delta(\Delta f_{T_{Na}})$		$\Delta(\Delta f_{T_N})$		$\Delta(\Delta f_{T_O})$		Δd_{N-O}
$\overline{\Delta c^2_{Na}} =$ 0.02 Å²	444	0.029	555	0.005	444	0.002	−0.00007 Å
	555	0.029	666	0.003	555	0.002	
	666	0.023	400	0.004	003	0.002	
	300	0.029	500	0.002	004	0.002	
	400	0.026			663	0.001	
	500	0.012			220	0.001	
$\overline{\Delta c^2_N} =$ 0.03 Å²	444	0.007	555	0.035	$1\bar{1}0$	0.001	−0.00004 Å
	555	0.007	666	0.024	$2\bar{2}0$	0.001	
	666	0.006	400	0.026	$3\bar{3}0$	0.001	
			500	0.017			
$\overline{\Delta c^2_O} =$ 0.03 Å²	333	0.005	555	0.009	444	0.023	−0.00002 Å
	555	0.017	666	0.006	555	0.017	
	666	0.016	400	0.003	004	0.014	
	300	−0.002	500	0.001	005	0.009	
	400	0.005			$2\bar{2}0$	0.017	
	500	0.008			$3\bar{3}0$	0.010	
Na: $\Delta c^2_{\parallel} =$ $-\Delta c^2_{\perp} =$ 0.01 Å²	444	0.012					
	555	0.013					
	300	−0.012					
	400	−0.011					
N: $\Delta c^2_{\parallel} =$ $-\Delta c^2_{\perp} =$ 0.04 Å²			444	0.009			
			555	0.013			
			666	0.009			
			300	−0.019			
			400	−0.014			
			500	−0.010			

the effect of orientation; but it cannot be due exclusively to the orientation, which would have to be twice as strong to account for the difference.

INKINEN has not given any separate estimate of the accuracy of the absolute level of the experimental structure amplitudes. He was induced to study it mainly by the circumstance that $\Delta f_{T_{Na}}$ has remarkably high values for small values of $\varkappa$. If this is considered to be reality, it implies that the total of the electron distribution belonging to the sodium atom is clearly in excess of ten electrons, as would be consistent with a completely ionized

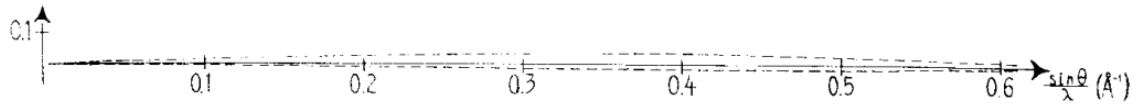

Fig. 12. The potential effect of specific orientation on the $\Delta f_{T_{Na}}$ curves in the extreme directions $\cos^2\varepsilon = 1$ (upper curve) and $\cos^2\varepsilon = 0$ (lower curve).

atom; according to fig. 3b it would be about 10.4. INKINEN observes that this could also be attributed to an excessively high level. In this connection he concedes that an error of 3 % in the level can be considered possible, although it would clearly surpass all other possible experimental errors. This would have an effect greater than that of the other sources of error in a degree that makes it worth while to investigate whether it might be possible to use the results for a check on the magnitude of the potential absolute error (however, this question leads to considerations too extensive in scope to be presented in this connection, and we have therefore postponed its treatment). If this should prove to be the case, it would result in slight corrections of the parameter values found for the »correct model». The magnitude of the effect is easy to ascertain by application of an appropriate percentage correction to the experimental values and adjustment of the theoretical model to fit these values. It is found in this manner that a — 1 % correction of the level would produce the following corrections in the mean values found for the different parameters:

$$\Delta\overline{c^2_{Na}} = + 0.02 \text{ Å}^2, \Delta\overline{c^2_N} = + 0.02 \text{ Å}^2, \Delta\overline{c^2_O} = + 0.03 \text{ Å}^2.$$

The effect on the determination of the anisotropicity of the motion would be very slight and that on the parameter u practically nil.

Combining all the preceding considerations, we may write:

Na: $\overline{c^2} = 0.55 \pm 0.035$ Å^2; $|c^2_{||} - \overline{c^2}|$ and $|c^2_{\perp} - \overline{c^2}| < 0.02$ Å^2;

N: independent of each other, $c^2_{||}$ and $c^2_{\perp} = 0.42 \pm 0.05$ Å^2;

O: $c^2_x = 0.42 \pm 0.045$ Å^2, $c^2_y = 1.30 \pm 0.045$ Å^2, $c^2_z = 0.65 \pm 0.045$ Å^2, however so that $|c^2_x - \overline{c^2}| < 0.02$ Å^2, $|c^2_y - \overline{c^2}|$ and $|c^2_z - \overline{c^2}| < 0.03$ Å^2, $\cos^2\varepsilon_0 = 0.55 \pm 0.03$ and $2\pi u = 87.6° \pm 0.2°$ ($u = 0.2433 \pm 0.0006$, $d_{N-O} = 1.231 \pm 0.003$ Å) .

However, these limits of accuracy do not contain the effect of the potential error in the absolute level (see above). Later treatment may possibly further alter and render more precise our opinion on the contribution of the deformations and interatomic distributions to the residual term, and this would primarily concern the parameter u.

Summary

In accordance with the programme of analysis presented in the first part of the work [8], the »correct model» for the $NaNO_3$ crystal at room temperature is determined on the basis of INKINEN's values of measurement [5].

It is found that

— the measurements do not indicate anisotropy in the motion of the sodium and nitrogen atoms, but slight anisotropy remains a possibility, particularly in the case of the nitrogen atom;

— the motion of the oxygen atoms is strongly anisotropic, the smallest amplitude occurring in the direction of the N—O connecting line and the greatest amplitude nearly perpendicularly to the line connecting the two closest Na atoms;

— the distance d_{N-O} is slightly greater than previous estimates (cf. section 2).

The results are expressed in greater detail by the values found for the parameters of the model, which are:

Na: $\overline{c^2} = 0.55 \pm 0.035$ Å^2, $|c_{||}^2 - \overline{c^2}|$ and $|c_{\perp}^2 - \overline{c^2}| < 0.02$ Å^2;

N: independent of each other, $c_{||}^2$ and $c_{\perp}^2 = 0.42 \pm 0.05$ Å^2;

O: $c_x^2 = 0.42 \pm 0.045$ Å^2, $c_y^2 = 1.30 \pm 0.045$ Å^2, $c_z^2 = 0.65 \pm 0.045$ Å^2, however so that $|c_x^2 - \overline{c^2}| < 0.02$ Å^2, $|c_y^2 - \overline{c^2}|$ and $|c_z^2 - \overline{c^2}| < 0.03$ Å^2, $\cos^2\varepsilon_0 = 0.55 \pm 0.03$ and $2\pi u = 87.6^\circ \pm 0.2^\circ$ ($u = 0.2433 \pm 0.0006$, $d_{N-O} = 1.231 \pm 0.003$ Å),

where c^2 is the parameter occurring in the harmonic thermal factor $10^{-c^2\varkappa^2}$ (2), (3), (4). The effect of the potential error in the absolute level is not included in the limits stated. Correction of the level by -1 % would result in a change of the values by $\Delta\overline{c_{Na}^2} = +0.02$ Å^2, $\Delta\overline{c_N^2} = +0.02$ Å^2, $\Delta\overline{c_O^2} = +0.03$ Å^2. A more detailed study of the deformations and interatomic distributions may perhaps furthermore slightly affect the parameter u. According to a preliminary estimate their effect is within $2\pi u \pm 0.15^\circ$, which has been included in the limits stated above.

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