

## The Atomic Scattering Factors of the Potassium Ion in Trigonal Potassium Nitrate

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(Received 20 August 1956 and in revised form 4 February 1957)

The writer has previously developed a method for the determination of the atomic scattering factor of an ion in a crystal of which the structure factors are known. Applying this procedure to trigonal  $\text{KNO}_3$ , he has determined the atomic scattering factor values of the K ion for the reflexions  $(hhh)$ ,  $(h00)$ ,  $(hh0)$  and  $(h\bar{h}0)$ . When the atomic scattering factor values obtained in this way are presented graphically against  $\sin \theta/\lambda$ , it is found that the values calculated for the different reflexions differ systematically. This difference is rotationally symmetrical with regard to the trigonal axis and increases at small  $\sin \theta/\lambda$  values, attains its largest value at  $\sin \theta/\lambda = 0.24$ , decreases thereafter and has wholly vanished by  $\sin \theta/\lambda = 0.46$ . This cannot be explained solely by the heat motion but requires that an electronic anisotropy of the K ion be taken into account. A critical error analysis shows that this phenomenon cannot be due to the errors arising from the method of calculation; moreover, the experimental values used in the calculations seem to be reliable.

### Introduction

The writer has shown (Korhonen, 1953, 1955) that if the structure factors  $F_{(hkl)}$  of a crystal are known, the atomic scattering factors  $f_{1,(hkl)}$  of an ion 1, belonging to this crystal and having the position coordinates  $(x_1, y_1, z_1)$ , can be calculated as follows:

$$\left. \begin{aligned} f_{1,(hkl)} &= \frac{4\pi R^3}{V} \left\{ \frac{1}{3} F_{(hkl)}^1 \right. \\ &\quad \left. + \sum_{h'k'l'} F_{(h'k'l')}^1 \frac{1}{\alpha^2} \left( \frac{\sin \alpha}{\alpha} - \cos \alpha \right) \right\}, \\ F_{(hkl)}^1 &= F_{(hkl)} \cdot \exp \left[ -2\pi i (h(x_1/a) \right. \\ &\quad \left. + k(y_1/b) + l(z_1/c)) \right], \\ \alpha &= 2\pi R/d_{(h-h', k-k', l-l')}. \end{aligned} \right\} \quad (1)$$

Here  $d_{(h-h', k-k', l-l')}$  denotes the spacing of the lattice planes  $(h-h', k-k', l-l')$ .  $F_{(hkl)}^1$  is the structure factor for the reflexion  $(hkl)$  when the point  $(x_1, y_1, z_1)$  is taken as the origin.  $V$  is the volume of the unit cell and  $R$  the ionic radius of ion 1.

The writer has also shown (Korhonen, 1956a) that, using series (1) to determine the atomic scattering factors from the always limited number of structure factors experimentally measured, the error due to the breaking-off can be removed as far as possible by using the 'difference series method'. Artificial structure factors  $F_{\text{art.},(hkl)}$  for the crystal under consideration are constructed by the aid of the theoretical atomic scattering factors and of the appropriate values for the heat motion to correspond as nearly as possible to the real structure factors  $F_{(hkl)}$  at those values of  $\sin \theta/\lambda$  at which the last structure factors have been measured. The difference,  $\Delta f_{1,(hkl)}$ , between  $f_{1,(hkl)}$  and  $f_{1,\text{art.},(hkl)}$  is then calculated by the aid of series

(1') and by using the structure factor differences

$$\left. \begin{aligned} \Delta F_{(hkl)}^1 &= F_{(hkl)}^1 - F_{\text{art.},(hkl)}^1: \\ \Delta f_{1,(hkl)} &= \frac{4\pi R^3}{V} \left\{ \frac{1}{3} \Delta F_{(hkl)}^1 \right. \\ &\quad \left. + \sum_{h'k'l'} \Delta F_{(h'k'l')}^1 \frac{1}{\alpha^2} \left( \frac{\sin \alpha}{\alpha} - \cos \alpha \right) \right\}, \\ \Delta F_{(hkl)}^1 &= F_{(hkl)}^1 - F_{\text{art.},(hkl)}^1, \\ \alpha &= 2\pi R/d_{(h-h', k-k', l-l')}. \end{aligned} \right\} \quad (1')$$

### Procedure

The trigonal unit cell with dimensions  $r = 7.181 \text{ \AA}$  and  $\alpha = 44^\circ 8.5'$  is used in the following calculations. Table 1, column (3), shows the  $F_{(hkl)}$  values measured experimentally by Tahvonen (1947a).

For the K ion the atomic scattering factors calculated by Hartree's method, and for the atoms N and O those measured experimentally by Tahvonen (1947b), were used as the artificial atomic scattering factors. The heat motion of the atoms was taken into consideration by multiplying the atomic scattering factors by the Debye factor  $D$ :

$$D = 10^{-c^2 \sin^2 \theta/\lambda^2}. \quad (2)$$

For the K ion the value  $c_K^2 = 2.054 \text{ \AA}^2$  and for N and O the value  $c_{N,O}^2 = 3.640 \text{ \AA}^2$ , found by trial and error, were used. The position of the  $\text{NO}_3$  group in the lattice is not known accurately; the group has been supposed to rotate (Kracek, Barth & Ksanda, 1932). By using the method of trial and error it was found convenient to divide each group into two positions in the lattice so that the crystal symmetry

Table 1

( <i>hkl</i> )	sin $\theta/\lambda$ ( $\text{\AA}^{-1}$ )	$F_{(hkl)}$	$F_{\text{art.}, (hkl)}$	$\Delta F_{(hkl)}$
(1)	(2)	(3)	(4)	(5)
000	0.0000	(100.66)	100.66	0.00
110	0.1188	3.65	2.03	+1.62
211	0.1485	44.31	47.28	-2.97
222	0.1546	(-14.47)	-5.99	+1.52
$\bar{1}10$	0.1853	22.22	26.36	-4.14
200	0.2201	23.03	26.52	-3.49
332	0.2322	30.90	30.84	+0.06
220	0.2375	21.71	23.43	-1.72
321	0.2413	16.12	16.17	-0.05
433	0.2789	13.55	13.84	-0.29
2 $\bar{1}1$	0.2877	12.55	14.22	-1.67
422	0.2971	7.79	7.54	+0.25
310	0.3012	9.53	12.02	-2.49
444	0.3091	16.16	16.66	-0.50
$\bar{2}11$	0.3210	10.88	11.59	-0.71
442	0.3349	5.77	7.27	-1.50
431	0.3501	13.08	15.29	-2.21
411	0.3562	10.18	15.02	-4.84
330	0.3562	10.18	8.72	+1.46
543	0.3604	10.53	10.82	-0.29
220	0.3706	13.15	14.63	-1.48
554	0.3762	8.70	9.03	-0.33
532	0.3827	10.35	11.80	-1.45
310	0.3892	5.81	7.77	-1.96
32 $\bar{1}$	0.3993	10.45	10.59	-0.14
420	0.4016	6.00	6.05	-0.05
644	0.4193	9.58	10.42	-0.84
655	0.4258	7.09	7.16	-0.07
222	0.4311	6.83	7.65	-0.82
521	0.4374	7.52	7.18	+0.34
400	0.4402	8.26	7.04	+1.22
633	0.4456	6.88	4.65	+2.23
552	0.4456	6.88	8.76	-1.88
653	0.4585	5.03	5.16	-0.13
666	0.4637	5.87	7.52	-1.65
541	0.4639	5.87	5.30	+0.57
664	0.4644	5.87	7.57	-1.70
321	0.4692	2.88	3.58	-0.70
440	0.4750	7.12	5.59	+1.53
4 $\bar{1}1$	0.4776	7.67	7.72	-0.05
642	0.4826	5.03	5.84	-0.81
321	0.4903	6.46	5.78	+0.68

$$F_{\text{art.}, (hkl)} = 2f_{\text{K art.}, (hkl)} \pm 2f_{\text{N art.}, (hkl)} \cos 2\pi(h+k+l)\alpha \\ \pm 2f_{\text{O art.}, (hkl)} \{ \cos 2\pi[(h+k+l)\alpha + (h+k-2l)\beta] \\ + \cos 2\pi[(h+k+l)\alpha + (h-2k+l)\beta] \\ + \cos 2\pi[(h+k+l)\alpha + (-2h+k+l)\beta] \}. \quad (4)$$

The plus signs are valid when  $(h+k+l)$  is divisible by 4 and the minus signs when it is divisible by 2.

For the parameters  $\alpha$  and  $\beta$  the following values were used:

$$2\pi\alpha = 6^\circ 30', \quad 2\pi\beta = 47^\circ. \quad (5)$$

The artificial structure factors obtained in this way are seen in Table 1, column (4); they have been calculated for Cu  $K\alpha$  radiation (Hönl, 1933*a, b*). The differences  $\Delta F_{(hkl)} = F_{(hkl)} - F_{\text{art.}, (hkl)}$  are given in column (5).

We see that the differences  $\Delta F_{(hkl)}$  are rather small, and when calculated for one molecule only they must, in addition, be divided by 2. The method we have used in the above calculations seems to apply well to the crystal—at least as well as the rotation coupled with vibration (Tahvonen, 1947*a*). Also, the electron distribution of the  $\text{NO}_3$  group on the plane ( $\bar{1}\bar{1}0$ ) obtained here corresponds very well with the experimental electron distribution given by Tahvonen (1947*a*). All this may mean that the  $\text{NO}_3$  group has two positions of equal value in this crystal and that the crystal symmetry corresponds to the statistical average.

Having now available the values  $\Delta F_{(hkl)}$ , we need only know the value for the ionic radius  $R$  in order to use series (1'). The value 1.33  $\text{\AA}$  was used for  $R$ . The values of  $\alpha$  can be obtained by calculating the spacings  $d_{(h-k, k-k', l-l')}$  from the dimensions of the unit cell.

## Results

Table 2, column (3), presents the differences  $\Delta f_{\text{K}, (hkl)}$  obtained by calculations. In column (4) there are the values of the artificial atomic scattering factors of the

Table 2

( <i>hkl</i> )	sin $\theta/\lambda$ ( $\text{\AA}^{-1}$ )	$\Delta f_{\text{K}, (hkl)}$	$f_{\text{K art.}, (hkl)}$	$f_{\text{K}, (hkl)}$
(1)	(2)	(3)	(4)	(5)
111	0.0773	+0.00	16.98	16.98
100	0.1100	-0.49	15.65	15.16
110	0.1188	-0.45	15.28	14.83
222	0.1546	+0.14	13.62	13.76
$\bar{1}10$	0.1853	-1.01	12.00	10.99
200	0.2201	-1.08	10.36	9.28
333	0.2319	+0.20	9.83	10.03
220	0.2375	-0.93	9.62	8.69
444	0.3091	+0.15	6.95	7.10
300	0.3301	-0.87	6.26	5.39
330	0.3562	-0.65	5.49	4.84
220	0.3706	-0.73	5.09	4.36
555	0.3864	+0.03	4.68	4.71
400	0.4402	-0.17	3.48	3.31
666	0.4637	-0.05	3.07	3.02
440	0.4750	-0.04	2.89	2.85

was fulfilled at the same time. Thus, the following coordinates for the atoms were used:

$$2 \text{ K: } (0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}). \\ 4 (\frac{1}{2} \text{ N}): (\frac{1}{4}-\alpha, \frac{1}{4}-\alpha, \frac{1}{4}-\alpha; \frac{1}{4}+\alpha, \frac{1}{4}+\alpha, \frac{1}{4}+\alpha; \\ \frac{3}{4}-\alpha, \frac{3}{4}-\alpha, \frac{3}{4}-\alpha; \frac{3}{4}+\alpha, \frac{3}{4}+\alpha, \frac{3}{4}+\alpha). \\ 12 (\frac{1}{2} \text{ O}): (\frac{1}{4}-\alpha-\beta, \frac{1}{4}-\alpha-\beta, \frac{1}{4}-\alpha+2\beta; \\ \frac{1}{4}+\alpha+\beta, \frac{1}{4}+\alpha+\beta, \frac{1}{4}+\alpha-2\beta; \\ \frac{1}{4}-\alpha-\beta, \frac{1}{4}-\alpha+2\beta, \frac{1}{4}-\alpha-\beta; \\ \frac{1}{4}+\alpha+\beta, \frac{1}{4}+\alpha-2\beta, \frac{1}{4}+\alpha+\beta; \\ \frac{1}{4}-\alpha+2\beta, \frac{1}{4}-\alpha-\beta, \frac{1}{4}-\alpha-\beta; \\ \frac{1}{4}+\alpha-2\beta, \frac{1}{4}+\alpha+\beta, \frac{1}{4}+\alpha+(\beta),$$

and, in addition, six positions which can be obtained by adding  $\frac{1}{2}$  to the above coordinates. (3)

The structure factors  $F_{\text{art.}, (hkl)}$  could then be calculated by the formula:

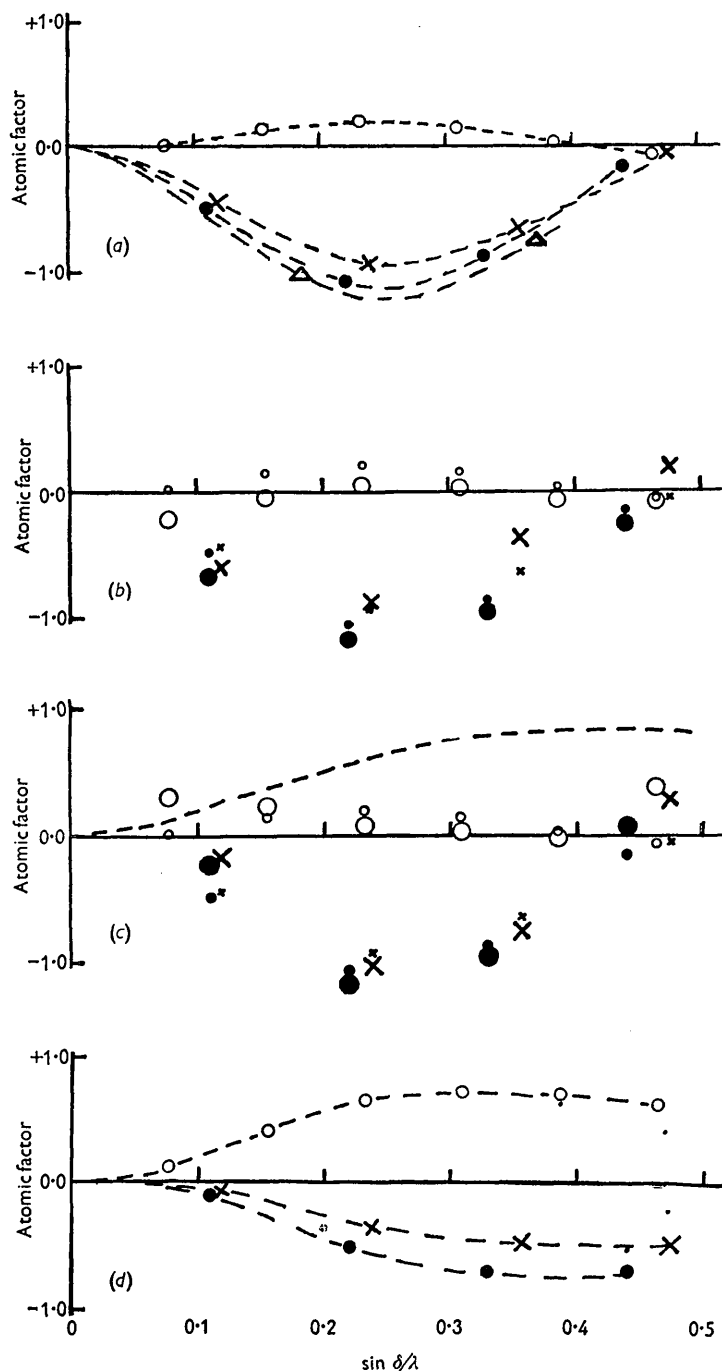


Fig. 1. (a) Differences between the experimental and theoretical atomic scattering factors of the K ion in the trigonal  $\text{KNO}_3$  crystal. The circles stand for reflexions  $(hhh)$ , the solid circles for  $(h00)$ , the crosses for  $(hh0)$ , and the triangles for  $(\bar{h}h0)$ . The broken curves show the corresponding atomic scattering factor curves. (b) Differences between the experimental and theoretical atomic scattering factors of the K ion in the trigonal  $\text{KNO}_3$  crystal. The small symbols are the same as in (a). The large symbols stand for the differences when the artificial crystal needed in the calculations contains only two K ions in the positions  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . (c) Differences between the experimental and theoretical atomic scattering factors of the K ion in the trigonal  $\text{KNO}_3$  crystal. The small symbols are the same as in (a). The large symbols stand for the differences obtained from series (1') when the value  $1.575 \text{ \AA}^2$  is used in the Debye factor for the K ions in the artificial crystal. The broken line stands for the theoretical atomic scattering factors of the K ion in the artificial crystal. (d) The circles  $(hhh)$ , solid circles  $(h00)$ , and crosses  $(hh0)$  stand for the atomic scattering factors of the K ion having ellipsoidal heat motion. The horizontal axis stands for those of the K ion having spherically symmetrical heat motion. The values calculated back from series (1') have been denoted by small points when they deviate from the corresponding initial values.

K ion,  $f_{K \text{ art.}, (hkl)}$ , and in column (5) the final atomic scattering factor values  $f_{K, (hkl)}$  for Cu  $K\alpha$  radiation.

The differences  $\Delta f_{K, (hkl)}$  are presented also graphically against  $\sin \theta/\lambda$  in Fig. 1(a).

### Examination of the results

The accuracy of the results will be discussed first. Errors may arise both from calculations and from the errors in the experimental structure factors used in the calculations.

The writer has shown earlier (Korhonen, 1955) that the value used for  $R$  has only a slight influence on the results, and therefore no noticeable errors can arise from this source.

The artificial structure factors needed in the calculations are used only as temporary approximate values (cf. Korhonen, 1956a, p. 7) and therefore they also have only a slight influence on the results. In order to show this more clearly the author calculated the new structure factor differences for the  $\text{KNO}_3$  crystal from the measured structure factors by using as the artificial crystal, this time, a crystal containing only the K ions in the positions  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ .

Table 3

(hkl)	$\Delta F_{\text{new}}$	$\Delta F_{\text{old}}$	(hkl)	$\Delta F_{\text{new}}$	$\Delta F_{\text{old}}$
000	64.00	0.00	554	-1.16	-0.33
110	-26.91	+1.62	532	+0.81	-1.45
211	+16.51	-2.97	$\bar{3}10$	-3.41	-1.96
222	-31.71	+1.52	$3\bar{2}\bar{1}$	+1.73	-0.14
$\bar{1}10$	-1.78	-4.14	420	-2.60	-0.05
200	+2.31	-3.49	644	+1.76	-0.84
332	+11.26	+0.06	655	-0.74	-0.07
220	+2.47	-1.72	$\bar{2}22$	-0.51	-0.82
321	-2.78	-0.05	521	+0.44	+0.34
433	-2.45	-0.29	400	+1.30	+1.22
$2\bar{1}\bar{1}$	-2.83	-1.67	633	+0.08	-0.13
422	-6.91	+0.25	552	+0.08	-0.13
310	-4.93	-2.49	653	-1.29	-0.13
444	+2.26	-0.50	666	-0.27	-0.43
$\bar{2}11$	-2.24	-0.71	541	-0.27	-0.43
442	-6.47	-1.50	664	-0.23	-0.43
431	+1.78	-2.21	$3\bar{2}\bar{1}$	-3.10	-0.70
411	-0.80	-2.08	440	+1.34	+1.53
330	-0.80	-2.08	411	+1.97	-0.05
543	-0.17	-0.29	642	-0.51	-0.81
$\bar{2}20$	+2.97	-1.48	321	+1.14	+0.68

Table 3 shows the new  $\Delta F_{\text{new}}$  values, which are quite different from the old values  $\Delta F_{\text{old}}$ . The new results calculated by the aid of series (1'), however, differ only very slightly from the old ones, as seen from Fig. 1(b). It is, therefore, sure that the coordinates and the temperature factors of the  $\text{NO}_3$  group have no profound influence upon the obtained results. Their influence on the results is so small because the  $\text{NO}_3$  group is situated outside the sphere ( $x^2 + y^2 + z^2 = R^2$ ) used at integration.

The temperature factor of the K ion has a little greater influence on the results. In order to show the influence of this factor the author calculated once

more the new structure factor differences for the  $\text{KNO}_3$  crystal by using, this time, the value  $1.575 \text{ \AA}^2$  instead of  $2.054 \text{ \AA}^2$  for  $c_K^2$  in the Debye factor (cf. formula (2)). Using these structure factor differences in series (1') he obtained the results seen in Fig. 1(c) (the large points). They deviate a little from the old results (the small points), but the deviations are large only at the beginning and end points, as one can expect (cf. Korhonen, 1956b, p. 18). The broken line in Fig. 1(c) shows the values of the atomic scattering factors for the K ion when the value  $1.575 \text{ \AA}^2$  is used in its Debye factor.

We see clearly from Fig. 1(c) that we can expect better values for the beginning and end points if we lower the artificial atomic scattering factor values from the broken line towards the horizontal axis. This is due to the fact that the  $\Delta f_{(hkl)}$  differences calculated this last time by the aid of series (1') are differences between the large points and the broken line and therefore the last points are bent towards the broken line (the so-called 'Gibbs phenomenon').

We see, however, that the temperature-factor value of the K ion also has no profound influence on the results and that the temperature-factor value  $2.054 \text{ \AA}^2$  is a proper choice.

$\Delta F_{(hkl)}$  values are unknown beyond  $\sin \theta/\lambda = 0.5$ . This causes errors to the results, as seen, for instance, from Fig. 1(c), where the last points are bent towards the broken line. Here it is important to know how much error can arise from this source. The only way to determine this question is to take a known case where we can expect a greater termination error than in our actual crystal, and to determine the termination error in that case.

The author has earlier (Korhonen, 1956a) treated an artificial crystal having the same dimensions as our trigonal  $\text{KNO}_3$  crystal and having only the theoretical K ions in the positions  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . He made these K ions vibrate so that the mean square of the displacement formed a flattened rotational ellipsoid with the trigonal axis as its rotational axis. Then he calculated the structure factors for this crystal up to the reflexion ( $\bar{3}21$ ), i.e. to the same limit as in Table 1. After this he calculated anew the structure factors for this crystal, now letting the K ions vibrate with spherical symmetry, and formed the structure factor differences by subtracting the latter from the former values. By the aid of these structure factor differences, and using series (1'), he calculated back the corresponding atomic scattering factor differences for the K ion. The results of these calculations are seen in Fig. 1(d). We see that only the three last values show large deviations. These three last points, however, differ clearly from each other in the correct directions (towards the corresponding correct values) and they also differ clearly from the horizontal axis.

When we now return to Fig. 1(a) we see that in this case all these last three points have nearly the same value, falling nearly on the horizontal axis. This

phenomenon cannot be due solely to the termination error: a great part, at least, comes from the experimental structure factors. Thus we can conclude that the termination error in Fig. 1(a) is even smaller than in Fig. 1(d) because the discontinuity produced by equating all  $\Delta F_{(hkl)}$  values to zero at  $\sin \theta/\lambda > 0.5$  is greater in the latter case.

The errors due to the experimental values are more difficult to estimate. However, no known error in experimental values leads to a dependence on the crystallographic directions like that seen in Fig. 1(a), so we have no particular reason to suspect the experimental values. When, in addition, we consider the smooth course of the curves in Fig. 1(a), compared with each other, and the fact that they all begin at zero level, indicating thus the right electron number, it must be admitted that the experimental values used in the calculations seem accurate enough. These conclusions cannot of course prove that the experimental values are certainly correct, but they show we have reasons to think so.

Consequently, the only remaining possibility seems to be to interpret the curves in Fig. 1(a) as due to the K ion itself. Let us first try to find such a heat motion of the K ion, which, according to the formula

$$f_{K, (hkl)} = f_{K \text{ theor., } (hkl)} \exp [-8\pi^2 \overline{u_{(hkl)}^2} \sin^2 \theta/\lambda^2], \quad (6)$$

should lead back to our results when  $f_{K \text{ theor., } (hkl)}$  is the atomic scattering factor of the K ion calculated theoretically and  $\overline{u_{(hkl)}^2}$  is the mean square of the displacement perpendicular to the lattice plane  $(hkl)$ . This, however, is impossible, as can be seen from Fig. 1(a), where the differences between the atomic scattering factor curves for different reflexions increase at first but then decrease and finally vanish (cf. Fig. 1(a) with Fig. 1(d), where the atomic scattering factor curves obey the formula (6)).

We arrive, therefore, at the result that we must, in addition, take a possible electronic anisotropy of the K ion into account (cf. Korhonen, 1956b, where the author also obtained results like this). It may be that the last experimental structure factors have greater experimental errors than the first structure factors and that this phenomenon causes the vanishing of the differences between the different atomic scattering factor curves at large  $\sin \theta/\lambda$  values. This assumption, however, is not very likely, for the experimental accuracy is essentially the same for all reflexions in the method used by Tahvonen.

With the aid of the differences between the atomic scattering factor values seen in Table 2 the differences between the electron distributions of the same ions also can be calculated. Fig. 2 presents the difference

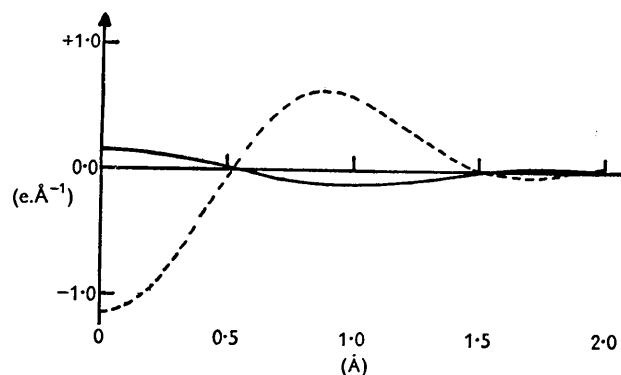


Fig. 2. Differences between the electron distribution of the K ion in the trigonal  $\text{KNO}_3$  crystal and that of the theoretical K ion projected on the trigonal axis (solid line) and on the direction perpendicular to the trigonal axis (broken line).

between the electron distribution of the K ion in the trigonal  $\text{KNO}_3$  crystal and that of our artificial K ion projected on the trigonal axis (solid line) and on the direction perpendicular to the trigonal axis (broken line). The former difference is slight all the way, while the latter is much greater and shows that electrons have moved from the centre outwards in the directions perpendicular to the trigonal axis.

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