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On the Crystal Structure of Potassium Nitrate in the High Temperature Phases I and III

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The crystal structure of the high temperature form of potassium nitrate has been redetermined on the basis of reported X-ray diffraction data obtained at 152°C. The nitrate groups are found to be statistically distributed between two-fold disordered aragonite type positions and two-fold disordered calcite type positions in the trigonal unit cell. The structure is similar to that of the high temperature form of sodium nitrate. A value of the configurational entropy derived on the basis of the statistical model is in reasonable agreement with the entropy change observed in the I, II transition.

In the ferroelectric phase III, the nitrate groups have previously been reported to occupy ordered aragonite type positions. It was found, however, that the crystal is probably built up of two kinds of domain, the structures of which are mutually related by centres of symmetry. The relative amount of the two kinds of domain was found to be close to the value predicted from the observed value of the spontaneous electric polarization. The apparent stability of the domain structure relative to an ordered structure is discussed. Finally, the structure is discussed in relation to the enthalpy changes observed in the transition I→III and III→II.

There are three known forms of solid potassium nitrate at ordinary pressure. Phase I is stable between 128°C and the melting point, 334°C, whereas phase II is stable below 128°C. Phase I transforms into III at 123°C on cooling under certain conditions,[1,2] the latter is reported to be metastable at ordinary pressure.[3,4] Phase III is stable at higher pressures at which other modifications also are formed.[5] At ordinary pressure phase III has been found to transform apparently irreversibly into II, starting at about 115°C.[1,2] Recent measurements have shown that phase III may be preserved in a metastable state at lower temperatures.[6]

Phase II has the orthorhombic aragonite structure.[7] The high temperature form I has been reported to have a rhombohedral structure with the nitrate groups orientationally disordered in calcite-type positions.[8] More recently a model, wherein the nitrate groups are distributed between twofold aragonite type positions, was proposed on the basis of an analysis of diffuse

X-ray scattering data.[9,10] Phase III is reported to have an ordered rhombohedral structure with the nitrate groups in aragonite type positions.[11] Structural properties of the solid nitrates have recently been reviewed and discussed in relation to thermodynamic quantities.[12]

The scope of the present work was to reconsider the distribution of molecules in phase I (and III) on the basis of Laue-Bragg diffraction data [8,11] and to compare particularly with thermodynamic data.

THE STRUCTURE OF PHASE I

The following analysis is based on the corrected X-ray diffraction data obtained by Tahvonen from a powder sample at 152°C.[8] The space group is $R\bar{3}m$[8] and the hexagonal unit cell dimensions are $a=b=5.420$ Å and $c=9.705$ Å [13] at 152°C, corresponding to three molecules of KNO_3 per unit cell. The number of independent reflections of nonzero intensity is 41, including 7 overlapping reflections, which are divided into three groups ($\sin\theta \leq 0.73$, Cu$K\alpha$ radiation).

Calculated structure factors based on the contribution from potassium in a three-fold position, notably at $(0,0,\frac{1}{2})$ etc., showed fairly good agreement with the experimental data, using an isotropic temperature factor of 5 Å^2 and the form factor for the neutral atom published by Hanson *et al.*[14]

A three-dimensional electron density map was worked out on the basis of the set of phases thus obtained and the normalized observed data. For the overlapping reflections the calculated values of the structure factors were employed. In the resulting electron density map the nitrogen atom appeared as a peak at the origin and the oxygen as distinct peaks in positions of the type $(x,x,0)$ (*i.e.* in calcite-type positions) and $(2x,x,z)$ (*i.e.* in aragonite-type positions), in a number of $2\times 6=12$ peaks per nitrogen atom peak. The heights of the peaks were reasonable compared with that of potassium, which appeared as expected.

The atoms were then weighted in accordance with the results of the electron density map and a new set of structure factors were computed incorporating all atoms in the calculation. The form factors of the neutral atoms were used [14] along with an isotropic temperature factor of 7 Å^2 for the light atoms. An R-value of nearly 10 % was thereby obtained. The sign of the (003) reflection, whose intensity is weak, was the only one that changed in the calculation. The calculated structure factors of the overlapping reflections to be used as observed amplitudes were then normalized to the observed data by equating the calculated mean values to the corresponding observed data *ect.* Another three-dimensional electron density map was subsequently worked out. It appeared to be very similar to that obtained previously. Parts of the result are shown in Fig. 1.

A total three dimensional difference electron density map was next worked out, excluding the overlapping reflections. The nitrogen atom was assumed to be at the origin, although it is actually situated outside the origin, when the nitrate group is in the aragonite-type position. Electron density minima appeared in the resulting map in positions corresponding to the positions of the nitrogen atoms and the potassium ions, respectively. The positions of the

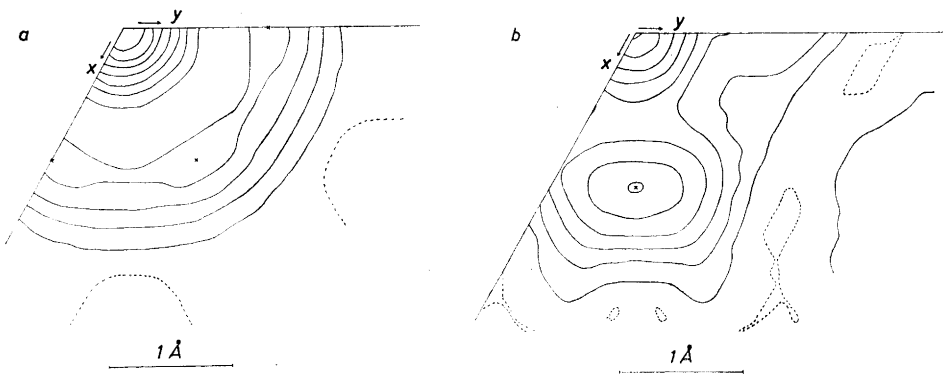

Fig. 1. Three dimensional electron density map showing the oxygen peaks. The nitrogen atom is at the origin. Contours at intervals of 0.5 el./Å^3. Zero contour dotted. a. $z=0$; b. $z=0.04$.

oxygen atoms, on the other hand, were found to lie in regions of positive electron density. Outside these regions the electron density was considerably closer to zero. The atomic weights were then adjusted corresponding to assigning small positive excess charges to nitrogen and potassium and small negative excess charges to oxygen and a second difference map was computed in which the peaks mentioned above appeared to be much reduced in magnitude. A series of difference maps were worked out in the course of the refinement. They showed all the same effect as described above. Also, the agreement between observed and calculated structure factors was somewhat better when weighted form factors were used. The following values (in electron units) were finally obtained for the excess charges: K: 0.8, N: 0.4, O: −0.4, which can only be expected to be correct to within an order of magnitude.

The structure was then refined, using least squares techniques. The positional parameters obtained from the Fourier map were kept fixed in this treatment. Thus the N atom was assumed to be at the origin. The coefficients of the temperature factors were computed from the formula

$$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$$

The symmetry restrictions applied to the coefficients are evident from Table 2.[15] Dependent parameters were reset after each L.S. cycle. The weights attached to the reflections were determined according to a standard weighting scheme. The structure factors were obtained by a linear combination of the structure factors representing the two individual structures, respectively. $F_{cal}=F_A\cdot X_1+F_C\cdot(1-X_1)$, where X_1 represents the fraction of the nitrate groups occupying aragonite-type positions and $1-X_1$ is the fraction of the nitrate groups in calcite-type positions. X_1 was kept fixed in the L.S. refinements. A series of computations were performed using different values of X_1. The overlapping reflections were excluded from the calculations, although calculated values were included in a final refinement. For $X_1=0.67$ an R-value of 5.2 % was obtained, excluding the overlapping reflections. Because

of the relatively great contribution to the structure factors from potassium, the R-factor was found, however, to vary rather slowly close to the minimum. Observed and calculated structure factors are listed in Table 1 and positional and thermal parameters in Table 2.

Table 1. Observed and calculated structure factors. Basic parameter values are those listed in Table 2. The calculated average values of the overlapping reflections are based on the formula

$$\left(\frac{\sum p(HKL) \cdot F_c^2(HKL)}{(1/N) \sum p(HKL)} \right)^{\frac{1}{2}}$$

where $p(HKL)$ denotes the multiplicity of the corresponding reflection, and N is the number of overlapping reflections over which the summation is taken.

$H\ K\ L$	$F_o(HKL)$	$F_c(HKL)$		$H\ K\ L$	$F_o(HKL)$	$F_c(HKL)$	
1 0 1	<6.0	3.61		1 0 7	14.2	14.63	
0 1 2	72.6	70.96		1 2 5	17.0	18.05	
0 0 3	7.3	8.15		1 3 1	9.5	10.06	
1 1 0	36.4	38.40		3 1 2	17.1	17.26	
0 2 1	37.7	39.44		2 2 3	9.8	9.00	
1 0 4	50.6	48.68		0 2 7	15.7	15.83	
2 0 2	35.5	35.07		0 1 8	11.6	11.19	
1 1 3	26.4	26.74		4 0 1	11.2	8.82	
0 1 5	22.2	20.64		1 3 4	12.3	11.75	
2 1 1	20.5	22.37		0 4 2	13.5	12.71	
0 2 4	12.8	12.92		3 0 6	15.9	16.20	18.23
1 2 2	15.6	17.10		0 3 6		9.13	
0 0 6	26.5	26.71		2 1 7	5.9	6.93	
3 0 0	17.8	18.48		0 0 9	16.4	13.09	19.02
2 0 5	9.4	9.42		3 1 5		6.44	
2 1 4	21.4	22.18		2 0 8		14.23	
3 0 3	23.6	10.00	24.29	3 2 1	4.7	4.13	
0 3 3		20.94		4 0 4	11.7	9.69	
1 1 6	17.2	19.12		2 3 2	12.6	12.22	
2 2 0	21.5	21.31		2 2 6	8.2	9.27	
				1 4 0	10.5	9.65	

In an alternative L.S. refinement the x-parameter of oxygen in $(x,x,0)$ and the x- and z-parameters of oxygen in $(x,\frac{1}{2}x,z)$ were treated as free parameters along with those of the previous analysis. The parameter values changed little compared with the previous values.

The z-parameter of the nitrogen atom referred to aragonite-type positions was next equated to the z-parameter of oxygen. The positional parameters were held constant in the corresponding L.S. refinement. Common values of the thermal parameters were assigned to the two nitrogen atoms. As a result very high values of the thermal parameters of oxygen in $(x,x,0)$ where thus obtained. Furthermore, the matrix of the thermal coefficients for this atom was no longer positive, definite. The thermal parameters of the remaining atoms, however, did not change much in this refinement. The apparently less satisfactory result obtained in the present treatment is possibly partly due to three-dimensional electron density overlap of the disordered nitrogen atom.

Table 2. Positional and thermal parameters. E.s.d. in parameters. Positional parameters are obtained from the electron density map, thermal parameters from the L.S. refinement. Hexagonal axes. The z-value of nitrogen referring to aragonite-type positions of the nitrate group is expected to be (practically) equal to the z-value of the corresponding oxygen atom (O1). See text.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0(ass.)	0(ass.)	0.5(ass.)	0.0542 (0.0058)	β_{11}	0.0100 (0.0018)	β_{11}	0	0
N	0(F)	0(F)	0(F)	0.0623 (0.0217)	β_{11}	0.0299 (0.0133)	β_{11}	0	0
O1	0.260(F)	$\frac{1}{2}x$	0.045(F)	0.0761 (0.0540)	0.0782 (0.0321)	0.0119 (0.0074)	β_{11}	0(ass.)	0(ass.)
O2	0.225(F)	x	0(F)	0.0899 (0.0908)	β_{11}	0.0381 (0.0191)	0.0573 (0.1589)	0(ass.)	0(ass.)

The values of β_{13} and β_{23} were put equal to zero in both cases in order to reduce the number of free parameters in the L.S.R. treatment, although this restriction is not a general requirement.[17]

For the sake of completeness the preceding treatment was extended, using free positional parameters for the oxygen atom. In this case, however, convergence could not be achieved.

Similar calculations were also performed, using individual isotropic temperature factors. R-factor values of 6.3 % and 6.1 % were thus obtained, respectively. The corresponding values of the temperature factors were reasonable.

RESULTS AND DISCUSSION

From the values of the positional parameters an apparent O—N bond length of nearly 1.22 Å is obtained. A correction of bond length due to librational motion [16] could be made on the basis of the approximation that the translational motion of the nitrate group be isotropic. As a result of the calculation an N—O bond length of 1.23_5 Å was obtained as an average value. This is not significantly different from the values quoted for sodium nitrate.[17]

Fig. 2 shows the disordered structure as obtained on the present basis. The structure is analogous to that recently obtained for the high temperature form of sodium nitrate.[18] Much of the general discussion given for that compound is therefore equally valid in this case.

Although the nitrate groups undergo hindered reorientations about the three-fold axes, the main time is spent in the equilibrium positions as obtained on the basis of the Laue-Bragg reflections. An approximate value for the root-mean-square amplitude of vibration of the oxygen atoms about the c-axis was obtained as an average of 6.5° from the two sets of thermal parameters

listed in Table 2. From the data for potassium listed in Table 2 values of the root mean square amplitudes of vibration along the three-fold axis and perpendicular to this direction were obtained as 0.22 Å and 0.35 Å, respectively. A similar anisotropic motion is also indicated for the sodium ions in sodium nitrate.[19,20] According to the values given in Table 2, this also applies to the motion of O1, whereas the results for O2 are more uncertain. The anisotropic movement may indicate that the motion of cations and anions is to some extent cooperative and/or that the quoted ionic positions actually are average values of a series of slightly displaced equilibrium positions originating in lattice interactions.

Table 3. Intermolecular distances. Hexagonal axes. O—N bond length=1.24 Å. 152°C.

	Distance (Å)
O1(x,$\frac{1}{2}x$,z)—K(2/3,1/3,—1/6)	2.79
O1(x,$\frac{1}{2}x$,z)—K(1/3,2/3,1/6)	2.97
O2(x,x,0) —K(2/3,1/3,—1/6)	2.69
O2(x,x,0) —K(1/3,2/3,1/6)	2.69
N1(0,0,z) —K(0,0,$\frac{1}{2}$)	4.42
O1(x,$\frac{1}{2}x$,z)—O1(2/3—x,1/3—$\frac{1}{2}x$,1/3—z)	2.45
O1(x,$\frac{1}{2}x$,z)—O1(1—$\frac{1}{2}x$,$\frac{1}{2}x$,z)	3.27
O1(x,$\frac{1}{2}x$,z)—O1(2/3—x,1/3+$\frac{1}{2}x$,1/3+z)	3.64
O1(x,$\frac{1}{2}x$,z)—O2(1—x,0,0)	3.20
O2(x,x,0)—O1(2/3—x,1/3—$\frac{1}{2}x$,1/3—z)	2.98
O2(x,x,0)—O2(1—x,1—x,0)	2.94
O2(x,x,0)—O2(2/3—x,1/3,1/3)	3.38

Values of intermolecular distances are presented in Table 3. The O—K separations obtained with nitrate in aragonite-type positions are rather closely related to distances found in the orthorhombic, aragonite structure.[7] The shortest O—K separation was calculated as 2.81 Å, using an O—N bond length of 1.24 Å and unit cell data reported for phase II.[13] In the present case, however, equilibrium is also associated with a considerably shorter O—K separation, 2.69 Å, which refers to calcite-type positions of the nitrate group.

It appears that one of the listed values of the intermolecular O—O distances is much shorter than twice the reported values of the van der Waals radius of oxygen, 2.8 Å.[21] The corresponding relative positions of the nitrate groups can therefore hardly represent accessible states of the system. In the following estimation of the configurational entropy of the present phase these positions were excluded. The remaining O—O intermolecular separations are well above 2.8 Å. The equation relating the configurational entropy to observable quantities was given in connection with the discussion of the crystal structure of sodium nitrate in the high temperature phase.[18] The basic microsystem used in the present case is shown in Fig. 3, where lines connecting two and two lattice sites represent forbidden relative O—O positions.

On the basis of $g_1=g_2=2$ and $X_1=2/3$, the configurational entropy was obtained as $\Delta Sc=(2.64-0.60)$ cal/mole K=2.04 cal/mole K. Assuming errors

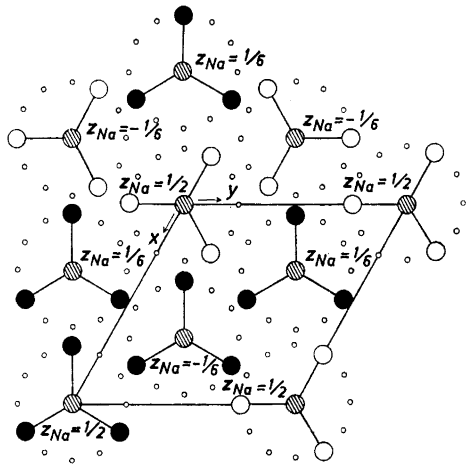

Fig. 2. Model of the statistical structure of potassium nitrate in phase I. Small circles represent staistical equilibrium positions of the oxygen atoms. An acceptable configuration of nitrate groups is shown. For neighbouring atoms on a common threefold axis: $z_K - z_N = \pm\frac{1}{2}$ (NO^-_3 in calcite type positions: white circles for the oxygen atoms) and $z_K - z_N \approx \pm\frac{1}{2}$ (NO_3^- in aragonite type positions: black circles for the oxygen atoms). Hexagonal axes.

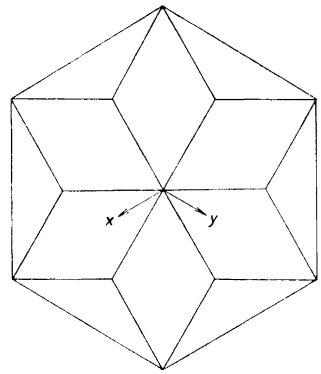

Fig. 3. Basic model used in the determination of the configurational entropy. The lines represent forbidden relative oxygen positions of the type $(x,\frac{1}{2}x,z)$. Hexagonal axes. Equivalent microsystems are centred at (1/3,2/3,2/3) and (1,2,0) etc.

in X_1 and $1-s$ equal to those used for sodium nitrate, we obtain $\Delta^2 S_C(\max)=0.13$ cal/mole K.

In the present approximation the maximum value of ΔS_C is nearly 2.51 cal/mole K, obtained for $X_1=0.40$. The reason why this value is not equal to the observed one must be ascribed to the "thermal" part of the entropy. Important in this connection is probably the relatively short O— K contact distance obtained with the nitrate group in a calcite-type position, compared with the other short O—K distances observed. This is further accentuated by the fact that the intermolecular distances between oxygen atoms in calcite-type positions are all well above 2.8 Å.

To compare the configurational entropy with the entropy of transition it is necessary to know the value of X_1 at the transition temperature, 128°C. Since this value was estimated on a thermodynamic basis to be only slightly greater than that given above, the difference may be ignored. The I—II transition entropy is observed to be (2.97 ± 0.03) cal/mole K [22], which is close to the average value of previously published data.[22] The difference between this value and the computed is considerably larger than the corresponding difference obtained for sodium nitrate.[18] However, the present transition involves a discontinuous change from one crystal structure to another, in contrast to that occurring in $NaNO_3$. The difference between the measured

and calculated value is to be ascribed to other factors such as changes in vibrational state etc. in the isothermal transition. A similar result was also obtained for potassium nitrite,[23] which exhibits an isothermal order-disorder transition at −14°C.[24] In the present case, however, the change in volume associated with the phase change is very small.

Because of the Coulomb repulsion, configurations involving long O—O distances may occur more frequently than others. This is supported by the observation that the molecules tend to form microdomains involving large O—O separations, especially at temperatures near the transition point.[9] Also, in the ordered structures of KNO_3[7] and $NaNO_3$,[17] for instance, the intermolecular O—O separations are found to be well above 3 Å.

THE STRUCTURE OF PHASE III

The hexagonal unit cell dimensions of phase III at 120°C are $a=b=5.43$ Å, and $c=9.11$ Å,[11] corresponding to three molecules per unit cell. The space group is $R3m$.[11] The molecular volume is 77.5 Å, which is about 5 % less than the molecular volume of phase I[13] (or[13,25] II) at 128°C. This indicates that the relative stability of phase III increases with pressure, as observed. Metastability of phase III at low pressures is indicated from kinetic studies at various temperatures and pressures.[4] Sawada *et al.*,[1] on the other hand, observed that the ferroelectric hysteresis loop did not change when the sample of phase III was kept for more than eight hours at 120°C.

Barth[11] carried out his structure factor calculations on the basis of space group $R3m$ and concluded that the structure is of the undisordered, aragonite-type. It may be noted that an O—K contact distance of 2.63 Å is obtained if the nitrate group is placed in a calcite-type position. Comparison with the corresponding value obtained for phase I indicates that any amount of calcite character must be expected to be small.

The ferroelectricity of phase III has been suggested to be of the order-disorder type[1] according to which the nitrate groups can inverte through the points, which become centres of symmetry in $R\bar{3}m$, under a strong hindrance due to the crystal field, and thus give rise to a hysteresis effect in an external electric field. In this respect phase III takes an intermediate state between those of the phases I and II.[1] The spontaneous polarization was observed to be 8 μ coul/cm^2.[1]

According to this, phase III may also be disordered. Therefore, a series of structure factor computations were made, using least squares methods. Basic X-ray data were those obtained by Barth from a powder sample of phase III at 120°C.[11] Values of the structure factors were computed from the formula $F^2\text{cal}=(1-s^2)F^2(R\bar{3}m)+s^2F^2(R3m)$, where s, the order parameter, is given by $s=X_+-X_-$. X_+ is the fraction of the nitrate groups in the position $(x,\frac{1}{2}x,z)$ and $X_-=1-X_+$ is the fraction of the nitrate groups in the position $(\frac{1}{2}x,x,-z)$ of space group $R3m$. Calcite-type positions of the nitrate groups were here excluded. s and x(O) were kept fixed in the L.S. refinements, the latter being computed on the basis of an apparent N—O bond length equal to 1.22 Å. z(O) (=z(N)) was allowed to vary along with the isotropic temperature factors. Two series of calculations were made. In the first one a single thermal parameter

for all atoms was allowed to vary. In the second B(K) and B(O) (=B(N)) were treated separately. The 012-reflection was excluded from the L.S. refinements since it suffers apparently from secondary extinction. (This is indicated irrespective of the value of s). The sample used was probably therefore not completely powdered. This introduces some doubt as to the accuracy of the experimental data. For this reason the "outer" reflections, 006 and 300, whose intensities are reported to be zero, were excluded from the L.S. refinement. The form factors used previously were also applied in the present calculations. The reflections were weighted according to a standard weighting scheme.

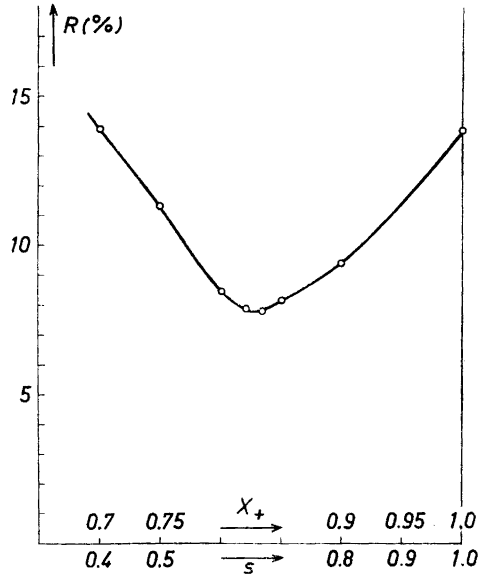

Fig. 4. R factor *versus* s and X_+. X_+=fraction of the nitrate groups having the oxygen atoms in the positions $(x,\frac{1}{2}x,z)$ etc. in space group $R3m$. X_-=fraction of the nitrate group having the oxygen atoms in the positions $(-x,-\frac{1}{2}x,-z)$ etc. in space group $R3m$.

Table 4. Observed and calculated structure factors. Basic parameter values are those of Table 5. N.O.=not observed. *=suffers from secondary extinction.

$H\,K\,L$	$F_o(HKL)$	$F_c(HKL)$	cos $A(HKL)$	sin $A(HKL)$
1 0 1	N.O.	5.22	−0.619	0.785
0 1 2	44.1 *	60.60	0.956	0.295
0 0 3	34.1	33.72	−0.304	0.953
1 1 0	36.9	36.10	1.000	0.000
0 2 1	39.4	39.35	−0.949	0.315
2 0 2	34.1	35.79	0.958	−0.286
1 0 4	31.2	30.92	0.928	0.372
1 1 3	19.7	21.45	−0.998	0.061
2 1 1	17.1	15.61	−0.938	−0.346
0 1 5	24.1	23.20	−0.952	0.307
1 2 2	13.9	10.33	0.944	0.330
0 2 4	N.O.	3.68	0.995	−0.098
3 0 0	N.O.	12.86	0.847	−0.532
0 0 6	N.O.	8.89	0.324	0.946

Fig. 4 shows the R-factor plotted against $s(X_+)$, as obtained from the second series. The agreement between observed and calculated structure factors is much better for $X_+=0.83$ than for $X_+=1$. Similarly, the temperature factor of the light atoms exhibits a well-defined minimum for $X_+=0.83$. Observed and calculated structure factors for $X_+=0.82$ are given in Table 4. The agreement between observed and calculated values is not so good for the 006- and the 300- reflections which were excluded in the L.S. refinement. However, the agreement is even worse for $X_+=1$. Positional and thermal parameters are listed in Table 5.

X_+ is related to the spontaneous polarization, μ_s, through the relation

$$X_+ - X_- = \mu_s / N \cdot \mu$$

where μ is the dipole moment of the ordered unit cell and N is the number of unit cells per unit volume. Using the values of the z-parameters listed in Table 5 and an excess charge of the nitrate group equal to one electron along with the unit cell dimensions quoted previously, we obtain $N\mu = 10.9\,\mu$ coul/cm^2. This leads to $X_+=0.87$ in reasonable agreement with the value obtained previously.

Intermolecular distances are listed in Table 6. The K—O contact distance in the present structure is seen to be close to the values obtained for phases I and II.[7] Intermolecular O—O separations in ordered regions are relatively

Table 5. Positional and thermal parameters. An apparent O—N bond length of 1.22 Å was assumed in the L.S. refinement. $X_+=0.82$.

	x	y	z	B Å^2
K	0(ass.)	0(ass.)	½(ass.)	8.54
O1	0.259(ass.)	½x(O1)	0.058	8.81
N1	0	0	z(O1)	B(O1)(ass.)
O2	−x(O1)	−½x(O1)	−z(O1)	B(O1)(ass.)
N2	0	0	−z(O1)	B(O1)(ass.)

Table 6. Intermolecular distances.

The O—N bond length was assumed equal to 1.24 Å. 120°C. Distances involving oxygen (O2) in calcite type positions (x,x,0) are included for comparison.

	Distance (Å)
O1(x,½x,z) —K(2/3,1/3,−1/6)	2.79
O1(x,½x,z) —K(1/3,2/3,1/6)	2.91
N1(0,0,z) —K(0,0,½)	4.03
O1(x,½x,z) —O1(2/3−x,1/3−½x,1/3−z)	2.09
O1(x,½x,z) —O1(1−½x,½x,z)	3.28
O1(x,½x,z) —O1(2/3−x,1/3+½x,1/3+z)	3.46
O1(x,½x,z) —O2(1−x,0,0)	3.22
O2(x,x,0) —O1(2/3−x,1/3−½x,1/3−z)	2.71
O2(x,x,0) —O1(2/3−x,1/3+½x,1/3+z)	3.87
O2(x,x,0) —O2(1−x,1−x,0)	2.95
O2(x,x,0) —O2(2/3−x,1/3,1/3)	3.19
O2(x,x,0) —K(2/3,1/3,−1/6)	2.63
O2(x,x,0) —K(1/3,2/3,1/6)	3.70

large, in accordance with observations generally made in ordered structures containing nitrate.[7,17] As in phase I an unacceptable O—O separation is obtained when two nearest anion neighbours are oriented in a "plus" and a "minus" position, respectively, so that two N—O bonds lie on a line joining the centres in the projection along the *c* axis. This gives rise to two kinds of ordered domains. Thus above a certain plane perpendicular to the *c* axis the nitrate groups are in "plus" positions, whereas they occupy "minus" positions below, or vice versa.

The present result introduces practically no disorder to explain the apparent stability of the system relative to a single domain structure, whose energy is expected to be a little lower. The actual domain structure may therefore originate in some other type of disorder which might compensate for the increase in energy.

As noted previously the calcite-type O—K distance in the present phase is 2.63 Å, which indicates that the calcite character must be small or zero. The introduction of a small amount of calcite character has no significant effect on the *R*-value. (At higher values the *R*-value increased.) However, inspection shows that a nitrate group may be placed in a two-fold disordered calcite-type position without producing unacceptable O—O distances, provided that none of the N—O bonds of the nearest neighbours point towards the centre of the nitrate group in the projection along the *c* axis. This corresponds to placing the nearest neighbours of a nitrate group in a calcite type position in "plus" and "minus" positions, alternately. As a consequence, a domain structure of the present kind will have to be established. Moreover, the establishment of a single domain could then be imagined in the absence of these restrictions.

Other sources such as ordinary lattice faults may possibly give rise to a similar result. However, the proposed domain structure as observed here, belongs to a coherent region of the lattice. This may seem to favour the alternative discussed above.

The change in enthalpy associated with the I, III transition has been measured to be 719($\pm$2) cal/mole at 123°C.[2] This corresponds to a transition entropy of 1.82($\pm$0.05) cal/mole K, assuming phase equilibrium to exist in the transition state. This figure is not much different from the value obtained for the configurational entropy of phase I. The difference may well be configurational in nature according to the previous discussion. However, the configurational entropy of phase III is evidently relatively small. Accordingly, this also applies to the "thermal" part of the entropy change associated with the III→I transition.

The enthalpy change ΔH(II—III) was observed to be 559($\pm$2) cal/mole at 113°C.[2] A part of this value will possibly have to be attributed to a positive change in Gibbs energy. The remaining part originates in the entropy change. Since the configurational entropy of phase III is small, this indicates that the thermal part of the entropy difference is not very different from that obtained for the II→I transition, and that the thermal part of the entropy change associated with the III→I is small, which agrees with the result obtained above.

The full matrix least squares computer program used is that written by Gantzel, Sparks and Trueblood (*IUCr World List* No. 384) and adapted for UNIVAC 1107 by Chr. Rømming, Chemistry Department, University of Oslo. The Fourier programme was written by Gantzel and Hope, Department of Chemistry, University of California, Los Angeles, California, U.S.A.

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