

rather than being planar, that exists as a dimer, that packs in layers to resemble charge-transfer compounds, and forms a clathrate with benzene as a guest molecule.

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The Crystal Structures of γ - and β -KNO₃ and the $\alpha \leftarrow \gamma \leftarrow \beta$ Phase Transformations

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On heating KNO₃ at atmospheric pressure, a solid-state phase transformation occurs from α -KNO₃ to β -KNO₃ at $\sim 128^\circ\text{C}$. On cooling from $\sim 200^\circ\text{C}$, β -KNO₃ transforms at $\sim 124^\circ\text{C}$ to γ -KNO₃, which reverts to α -KNO₃ at $\sim 100^\circ\text{C}$. The precise temperature range in which the various phases occur depends on the previous treatment of the sample. X-ray powder diffractometer data have been used to determine the structures of γ - and β -KNO₃, and the hitherto ambiguous situation concerning the NO₃ orientation and disorder has been resolved. For γ -KNO₃ the space group is $R3m$ with hexagonal axes $a = 5.487$ (1), $c = 9.156$ (3) Å (91°C), $Z = 3$, while for β -KNO₃ the corresponding data are $R\bar{3}m$, $a = 5.425$ (1), $c = 9.836$ (4) Å (151°C), $Z = 3$. In γ -KNO₃, there are two equivalent types of NO₃ positions, but within each cell the NO₃ groups all belong to one type. With β -KNO₃, each NO₃ is in disorder between the two types of position. Relationships between the structures of the α -, β - and γ -phases are given.

Introduction

At atmospheric pressure, KNO₃ can exist in several different phases depending on the temperature. When heated from room temperature through the transition at $\sim 128^\circ\text{C}$, KNO₃ transforms from an orthorhombic structure (α -KNO₃) to a trigonal structure (β -KNO₃). On cooling the β -phase from $\sim 200^\circ\text{C}$, KNO₃ passes through another trigonal phase (γ -KNO₃) between $\sim 124^\circ\text{C}$ and $\sim 100^\circ\text{C}$ before reverting to the α -phase. γ -KNO₃ exhibits ferroelectric properties (Sawada, Nomura & Fujii, 1958).

The structure of α -KNO₃ has been studied by Edwards (1931) and more recently by Nimmo & Lucas (1972, 1973), the latter using single-crystal neutron diffraction data; the Nimmo & Lucas structure has been confirmed by Holden & Dickinson (1975) with single-crystal X-ray data. The unit cell is orthorhombic with $a = 5.414$ (2), $b = 9.166$ (9), $c = 6.431$ (9) Å (25°C),

$Z = 4$; the space group is $Pm\bar{c}n$ and the structure is of the aragonite type. β -KNO₃ has been investigated by Tahvonen (1947), Shinnaka (1962) and Strømme (1969), and γ -KNO₃ by Barth (1939) and Strømme (1969). In these phases, the NO₃ conformation and orientation is uncertain. Ordered models have been considered for γ -KNO₃, static and dynamic disordered models for β - and γ -KNO₃, and free rotation models for β -KNO₃. The γ -KNO₃ space group has been taken as $R3m$, but both $R\bar{3}m$ and $R\bar{3}c$ have been suggested for β -KNO₃. All β - and γ -KNO₃ structural studies have used the X-ray powder diffraction photographic data of Tahvonen (1947) and Barth (1939), respectively. The latter data contained only ten observed reflexions. Shinnaka (1962) also made X-ray diffuse scattering photographic studies.

The aim of the present study was to determine the β - and γ -KNO₃ structures, and to relate the α -, β - and γ -KNO₃ structures.

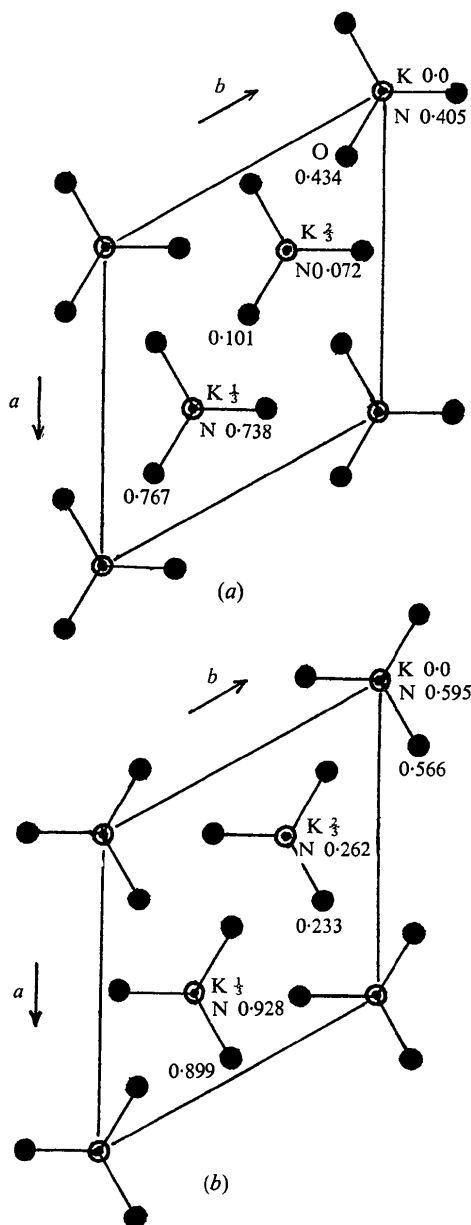


Fig. 1. (a) The structure of γ -KNO₃ (91 °C) and (b) its equivalent (with alternative NO₃ orientation and position).

Experimental

β - and γ -KNO₃ data were collected on an X-ray powder diffractometer incorporating a small electrical sample furnace. The briquet sample of analytical grade KNO₃ was continuously rotated about the diffraction vector. ω - 2θ scans were made with $\Delta(2\theta)=0.05^\circ$ steps and a step-time of 100 s. Filtered Cu $K\alpha$ radiation was used throughout.

The β -KNO₃ data were collected at 151 °C. The sample was then heated to 200 °C and held at that temperature for ~0.5 h before slowly cooling to 91 °C at which temperature the γ -phase was isolated. The temperature region in which γ -KNO₃ is obtained depends on the previous treatment of the sample, and in the present study was lower than that generally reported. In fact, it was found that γ -KNO₃ could be cooled to room temperature and would continue to exist for ~0.5 h before reverting to α -KNO₃.

Analysis

Both β - and γ -KNO₃ unit cells were found to be trigonal and the reflexions were indexed on hexagonal axes:

$$\begin{aligned} \gamma\text{-KNO}_3(91^\circ\text{C}) \quad a &= 5.487 (1), \quad c = 9.156 (3) \text{ \AA} \\ \beta\text{-KNO}_3(151^\circ\text{C}) \quad a &= 5.425 (1), \quad c = 9.836 (4) \text{ \AA}. \end{aligned}$$

In both phases the systematic absences were $-h+k+l \neq 3n$, which implied that the possible space groups were $R3$, $R\bar{3}$, $R32$, $R3m$, $R\bar{3}m$.

γ -KNO₃ is ferroelectric which reduces the possible space groups to $R3$ and $R3m$ for this phase. For $R3$, the NO₃ group would be in an asymmetric orientation relative to the matrix of K atoms, which is considered unlikely, and thus $R3m$ was favoured. Further it was expected that the higher-temperature β -phase would possess higher symmetry than the γ -phase and therefore that its space group would be $R\bar{3}m$. These choices for the γ - and β -KNO₃ space groups were confirmed by subsequent satisfactory structure determinations. Reflexions such as $1\bar{1}2$, $2\bar{2}1$ occur in the β -phase indicating the space group cannot be $R\bar{3}c$. In both the γ - and β -phases, there are three formula units in the hexagonal unit cell. The background was measured on both sides

Table 1. Atomic parameters of γ -KNO₃ (91 °C) and β -KNO₃ (151 °C) determined by least-squares refinement

Standard deviations are in parentheses and parameters without standard deviations were fixed in refinement by space-group requirements. Temperature factor = $\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \}$.

		<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
γ -KNO ₃	K	0	0	0	0.038 (6)	β_{11}	0.030 (5)	$\beta_{11}/2$	0	0
	N	0	0	0.405 (6)	0.09 (3)	β_{11}	0.00 (1)	$\beta_{11}/2$	0	0
	O	0.131 (2)	\bar{x}	0.434 (3)	0.05 (2)	β_{11}	0.007 (4)	0.03 (2)	-0.001 (3)	$-\beta_{13}$
Number of independent reflexions = 43, number of variables = 12, $R_w = 0.09$, $R = 0.18$										
β -KNO ₃	K	0	0	0	0.109 (7)	β_{11}	0.029 (3)	$\beta_{11}/2$	0	0
	N	0	0	$\frac{1}{2}$	0.03 (2)	β_{11}	0.06 (1)	$\beta_{11}/2$	0	0
	O	0.130 (2)	\bar{x}	0.475 (5)	0.05 (2)	β_{11}	0.10 (1)	0.04 (2)	0.008 (8)	$-\beta_{13}$
Number of independent reflexions = 33, number of variables = 11, $R_w = 0.06$, $R = 0.13$										

of each peak and the integrated intensity I and $\sigma(I)$ were determined from $I = P - SB$ and $\sigma^2(I) = I + SB(1 + S)$, where P = total counts in peak, B = total background counts (both sides), S = number of steps in peak scan/number of steps in background scans.

I and $\sigma(I)$ were corrected for Lorentz-polarization-cones effects giving $Y_o^2 = m|F_o|^2$, except for superposed non-equivalent reflexions (e.g. 033, 303), where $Y_o^2 = \sum m|F_o|^2$; m is the multiplicity factor. (For the type of diffractometer geometry used, the absorption correction is constant for all reflexions.)

The least-squares refinement program was a version of *ORFLS* modified by Taylor & Cox (1973) so that the refinement is made by minimizing $R_w = [\sum w(Y_o^2 - Y_c^2)^2 / \sum w(Y_o^2)^2]^{1/2}$, $w = [\sigma^2(Y_o^2)]^{-1}$; R is given by $\sum |Y_o^2 - Y_c^2| / \sum Y_o^2$.

With this program, superposed non-equivalent reflexions are retained in the data set.*

γ -KNO₃ structure and ferroelectric properties

With the structure proposed by Barth (1939) as an initial model, a least-squares refinement varying a scale factor, atomic coordinates and anisotropic temperature factors converged to the parameters given in Table 1; interatomic distances and angles are listed in Table 2. A Fourier map, calculated with $|F_o|$ and phase angles from the above refinement, confirmed the structure and in particular the NO₃ conformation and orientation; there was no evidence for any NO₃ disorder as proposed, for example, by Strømme (1969). The structure and its equivalent (with alternative NO₃ orientation and position) are illustrated in Fig. 1(a) and (b) respectively. In both cases, each NO₃ layer is between two K layers and the distances from any O atom to the nearest K atoms above and below are approximately equal [2.87 (2), 2.91 (1) Å]. However the NO₃ layer is not half-way between the K layers. In Fig. 1(a) the NO₃ layer is closer to the lower rather than the upper K layer, and *vice versa* in Fig. 1(b). In each case, therefore, there is a resultant dipole moment and hence γ -KNO₃ is ferroelectric. With no external electric field, domains

* Tables of Y^2 values for γ - and β -KNO₃ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31596 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester, CH1 1NZ, England.

Table 2. *Interatomic distances and angles for γ -KNO₃ (91 °C) and β -KNO₃ (151 °C)*

Appropriate bond length and angle corrections are less than the relevant parameter errors and are not included.

	γ -KNO ₃	β -KNO ₃
Interatomic distances (Å)		
K...O	2.87 (2)	2.68 (4)
	2.91 (1)	3.07 (2)
N-O	1.28 (2)	1.25 (2)
Interatomic angles (°)		
O-N-O	116 (2)	116 (1)

exist in the crystal such that some would have one type of unit cell predominating, the remainder the other type.

The spontaneous polarization, with the NO₃ layers

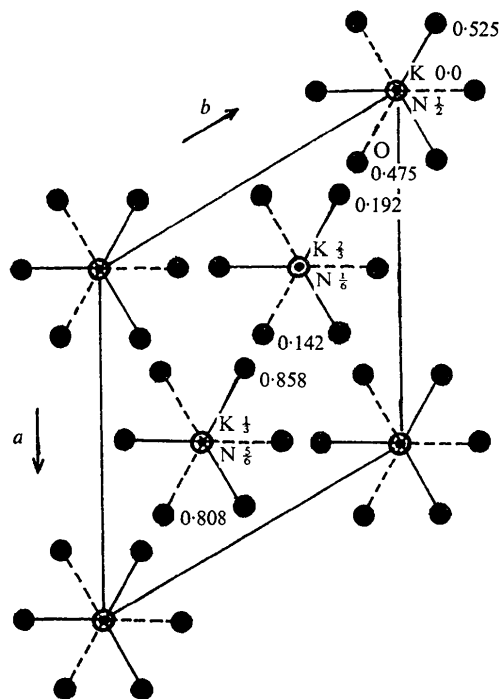


Fig. 2. The structure of β -KNO₃ (151 °C). The NO₃ on each site is in dynamic disorder between two orientations.

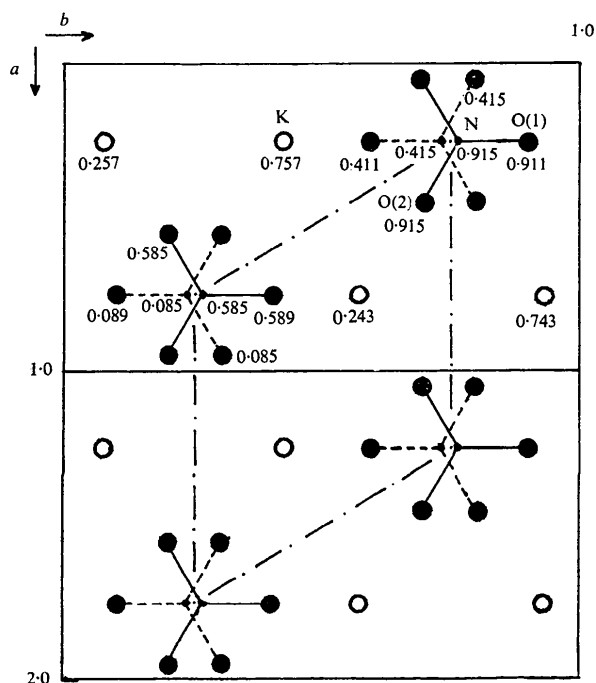


Fig. 3. The structure of α -KNO₃ (25 °C) as determined by Nimmo & Lucas (1973). The pseudo-hexagonal cell shown ($c_{\text{hex}} = \frac{2}{3}c$, origin at height $\frac{1}{2}c$) is simply related to the γ - and β -KNO₃ cells.

0.60 Å from the half-way position between K layers, was calculated as 0.12 Cm^{-2} . This is comparable with the experimental result of 0.08 to 0.10 Cm^{-2} (Sawada, Nomura & Asao, 1961), which may well be lower than the calculated value due to incomplete ferroelectric domain alignment.

β -KNO₃ structure

In the paraelectric β -phase there were several structural models to be considered, the most obvious of which was a static disorder between the two NO₃ orientations of the γ -phase. Accordingly, this was refined by least squares starting with the γ -KNO₃ coordinates but now with a centrosymmetric unit cell. The refinement converged with atomic parameters for K and O as given in Table 1, and for N as follows: $z = 0.46$ (1), $\beta_{11} = 0.03$ (2), $\beta_{33} = 0.02$ (4); the residuals were $R_w = 0.06$, $R = 0.14$. A Fourier map, calculated with $|F_o|$ and phases from the above refinement, confirmed the K and O positions but clearly indicated $z(\text{N}) = \frac{1}{2}$. Consequently, a least-squares refinement was made as above, but with N fixed in the special position $(0, 0, \frac{1}{2})$. The results are given in Table 1. Only $z(\text{N})$ and $\beta_{33}(\text{N})$ are different from the previous β -KNO₃ refinement, and the residuals are essentially the same although there is now one less variable. Further, no phases changed as a result of fixing $z(\text{N}) = \frac{1}{2}$ and so the Fourier map is unchanged, thus confirming the atomic coordinates of Table 1 and in particular the NO₃ locations; the O positions were quite sharp with no indication of any additional disorder. The structure is illustrated in Fig. 2, and the interatomic distances and angles are given in Table 2.

The distances from any possible O position to the nearest K atoms in the layers above and below are not equal [2.68 (4), 3.07 (2) Å]. The centre of the six O positions around each N atom is coincident with that atom, which lies half-way between K layers. These facts suggest that the NO₃ groups may be in dynamic (as opposed to static) disorder between the two equilibrium positions.

An alternative model with O atoms in $(x, 0, \frac{1}{2})$ positions was tried, but least-squares refinements failed to converge.

KNO₃ phase transformations

The structure of α -KNO₃ has been determined by Nimmo & Lucas (1972, 1973), and it was shown that the NO₃ groups are slightly non-planar [confirmed by Holden & Dickinson (1975)]. This is also the case for both γ - and β -KNO₃. The α -KNO₃ structure is illustrated in Fig. 3; the pseudo-hexagonal cell shown transforms to the hexagonal unit cells in the γ - and β -phases. In α - and β -KNO₃, the NO₃ groups have essentially the same two possible orientations, and lie slightly above and below the planes $z_{\text{hex}} = \frac{1}{6}, \frac{5}{6}$. The K atoms are slightly on either side of the planes $z_{\text{hex}} = 0, \frac{1}{3}, \frac{2}{3}, 1$ in α -KNO₃, but lie in these planes for β -KNO₃. During the $\alpha \rightarrow \beta$ transition, layers of K atoms and

NO₃ groups must translate in the ab plane and *repack* in a manner quite similar to that which occurs perpendicular to the threefold axis in a h.c.p. \rightarrow f.c.c. transition.

On cooling β -KNO₃, c contracts rapidly and at the $\beta \rightarrow \gamma$ transition undergoes a 5.4% discontinuous decrease [from the data of Kawabe, Yanagi & Sawada (1965)]. It seems likely that space limitations between K layers cause the NO₃ groups to occupy only one of the two orientations possible on each site in β -KNO₃, with a consequent adjustment of their position between K layers. (In a given γ -KNO₃ unit cell, the NO₃ groups all have one orientation.)

Whereas the γ -KNO₃ structure is a simple modification of the β -KNO₃ structure, β -KNO₃ is only obtained from α -KNO₃ after a considerable amount of *repacking* in which the volume per molecule increases. If γ -KNO₃ was to form directly on heating α -KNO₃, the *repacking* that would have to occur would be very similar to that of the $\alpha \rightarrow \beta$ transition. However, both the volume per molecule and the distance between successive K planes are smaller in γ -KNO₃ than in α - and β -KNO₃, and it is suggested that under these circumstances the potential barriers are too high for the *repacking* to occur, and hence for γ -KNO₃ to form directly on heating α -KNO₃.

Conclusion

The γ - and β -KNO₃ structures have been determined. For γ -KNO₃ the structure is essentially in agreement with that proposed by Barth (1939), while for β -KNO₃ the previously suggested structures are incorrect. However, the β -KNO₃ structure closely resembles that of high-temperature phase NaNO₃ (Siegel, 1949).

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