

Evidence of Additional Disorder in the Rhombohedral Form of Potassium Nitrite (KNO₂-II)

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In a previous article¹ models of the disordered structures of the cubic (I) and rhombohedral form (II) of potassium nitrite were deduced on the basis of an X-ray diffraction study.

The heat of the II-I transition, reported to be continuous,² has been estimated to (120 ± 30) cal/mole from DTA measurements at about 40°C,³ corresponding to an entropy change of approximately (0.4 ± 0.1) cal/mole K. Since the importance of disorder is expected to increase with temperature, the II-I transition is thought to reflect mainly a change in orientational disorder associated with the nitrite ions. However, the magnitude of the change is evidently only moderate.

Taking sterical effects into account, a value of the orientational entropy of KNO₂-I may be evaluated on the basis of the model described earlier for RbNO₃.⁴ In Table 1 are listed calculated statistical intermolecular O-O separations less than the corresponding van der Waals contact distance, 2.8 Å, in KNO₂-I. Table 2 contains the corresponding number of forbidden nitrite-group positions relatively to a chosen anion orientation associated with

Table 1. Statistical, intermolecular O-O separations less than 2.8 Å in KNO₂-I.

$a=6.66$ Å; space group = $Fm\bar{3}m$;
 $x_O=y_O=0.120$, $z_O=0.076$, $x_N=y_N=z_N=0.1$

Atoms involved	Distance (Å)
$(x_O, x_O, z_O) - (\frac{1}{2}-x_O, \frac{1}{2}-x_O, z_O)$	2.45
$(x_O, x_O, z_O) - (\frac{1}{2}-x_O, \frac{1}{2}-x_O, -z_O)$	2.65
$(x_O, x_O, z_O) - (\frac{1}{2}-z_O, \frac{1}{2}-x_O, x_O)$	2.68
$(x_O, x_O, z_O) - (\frac{1}{2}-x_O, \frac{1}{2}-z_O, x_O)$	2.68

the origin. Using these data, the orientational entropy of the system was computed as

$$S(\text{orient.}) = R \sum_{i=1}^2 x_i \ln(g_i/x_i) + R/2 \ln(1-s) = (6.89 * -1.91) \text{ cal/mole K} = 4.98 \text{ cal/mole K, taking } g_1=g_2=16 \text{ and } x_1=x_2=0.5.$$

The latter figure seems reasonable since the two types of orientation are apparently very similar.¹ An approximately correct formula representing the quantity $s(=s(g_1, g_2, x_1, x_2))$ has been given elsewhere.⁴

The corresponding value for KNO₂-II was obtained as 3.56 cal/mole K on the basis of a model wherein the nitrite group was taken to occupy statistically only one crystallographic set of orientation.¹ The difference in computed orientational en-

* This figure was erroneously quoted as 7.44 cal/mole K in Ref. 1.

Table 2. Number of forbidden orientations of neighbouring nitrite groups (L) relatively to a chosen orientation of the nitrite group associated with the origin (S).

A. Fixed position of the nitrite group at the origin as quoted in Table 5a, Ref. 1.

Type or orient. involved	Lattice sites associated with L-nitrite groups					
	$(\frac{1}{2}, -\frac{1}{2}, 0)$	$(0, -\frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, 0, \frac{1}{2})$	$(0, \frac{1}{2}, \frac{1}{2})$	$(-\frac{1}{2}, 0, \frac{1}{2})$	$(-\frac{1}{2}, \frac{1}{2}, 0)$
$a(S)-a(L)$	8	2	2	8	2	2
$a(S)-b(L)$	8	2	2	8	2	2

Number of forbidden orientations of L-type anions

B. Fixed position of the nitrite group at the origin as quoted in Table 5b, Ref. 1.

Type of orient. involved	Lattice sites associated with L-nitrite groups.					
	$(\frac{1}{2}, -\frac{1}{2}, 0)$	$(0, -\frac{1}{2}, -\frac{1}{2})$	$(\frac{1}{2}, 0, -\frac{1}{2})$	$(0, \frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, 0, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{2}, 0)$
$b(S)-a(L)$	8	2	2	8	2	2
$b(S)-b(L)$	8	2	2	8	2	2

Number of forbidden orientations of L-type anions.

entropy for these two phases is much larger than the II—I transition entropy. Provided that the model of KNO_2 -I is essentially correct, this indicates the orientational disorder of KNO_2 -II to be more pronounced than implied by our previous model. Thus the figures correspond to an additional orientational entropy of about 1 cal/mole K of KNO_2 -II at elevated temperatures. (The entropy change observed in the III—II transition at about -13°C ⁶ is approximately 1 cal/mole K higher than the quoted orientational entropy of KNO_2 -II, so that even at low temperatures there may in principle be room for a small additional disorder in KNO_2 -II.)

An equilibrium orientation of the nitrite group is expected to yield O—K contact distances of approximately 2.7 Å and relatively large N—K separations.¹ The latter has been observed in univalent metal nitrates and seems on the whole to be in accordance with recent results of other studies.⁶⁻⁹ The only kind of orientation of the anion which was found to satisfy these requirements, apart from that proposed previously,¹ is shown in Fig. 1.

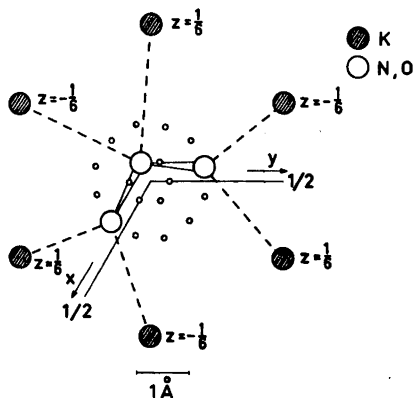


Fig. 1. Possible additional equilibrium positions of the nitrite group in KNO_2 -II. The twofold symmetry axis of the nitrite group shown coincides with the [110]-direction (*i.e.* a twofold symmetry axis of the space group). The angle between the plane of the anion and the x,y -plane is 13° . Small circles indicate statistically equivalent equilibrium positions of oxygen and nitrogen, respectively.

The twofold symmetry axis of the nitrite group coincides with one of the twofold axes of the space group. The corresponding positional parameters were computed on the basis of the unit cell dimensions and structural parameters of the anion given in Ref. 1. The result is $x_{\text{O}}=0.1723$, $y_{\text{O}}=-0.0625$, $z_{\text{O}}=-0.0228$, $x_{\text{N}}=y_{\text{N}}=-0.0780$ and $z_{\text{N}}=0$.

Each oxygen atom makes contact with two potassium ions at a distance of 2.70 Å. The shortest N—K separation (of twofold multiplicity) is 3.07 Å, which is somewhat shorter than the corresponding N—K distances of 3.15 and 3.17 Å obtained for the alternative orientation of the nitrite group.¹ From the preceding discussion only a minor fraction of the molecules is expected to occupy this type of orientation.

There are six statistically equivalent anion positions of the present kind. Inspection shows that all intermolecular O—O separations involving both sets of position are greater than 2.8 Å. In accordance with basic assumptions⁴ the orientational entropy of the system is then simply given by the first term in the right-hand side of the $S(\text{orient})$ -equation quoted above. Here $g_1=g_2=6$ so that if the fraction of molecules occupying the present kind of orientation, x_1 , is assumed equal to 0.20, the orientational entropy of KNO_2 -II becomes 4.56 cal/mole K. Adding the observed II—I entropy change (0.4 cal/mole K) leads to $S(\text{orient.})=4.96$ cal/mole K for KNO_2 -I (at temperatures near the transition point), which is close to the value computed directly from the structural model¹ suggested for KNO_2 -I (4.98 cal/mole K). (The same numerical result is obtained with $x_1=0.80$. However, in accordance with previous discussion the distribution is considered less likely than the former one.)

The shortest distance between two (statistically occupied) nonequivalent oxygen positions is only 0.06 Å. Any resolution of the two sets of position in the electron density map is thus impossible. This is also expected for the positions of the nitrogen atom.

From the results obtained above the present model of disorder, wherein the nitrite groups are taken to occupy statistically two nonequivalent sets of orientation in KNO_2 -II as indicated, appears to be more likely than the previous one¹ involving only one specific set of orientation of the nitrite group.

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On the Crystal Structure of the High-temperature Form of Silver Nitrate ($\text{AgNO}_3\text{-I}$)

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Three solid forms of silver nitrate are observed at atmospheric pressure. Phase II, stable at room-temperature, has an ordered, orthorhombic and centrosymmetric structure¹ which resembles neither the calcite- nor the aragonite-type structure.² It transforms (approximately isothermally) into a rhombohedral form I³ at about 159.5°C. Experimental values of the heat of transformation are 593 ± 9 ⁴ and 561 ± 4 cal/mole K.⁵ It has been stated that there seems to be no reason to doubt that $\text{AgNO}_3\text{-I}$ is similar to the disordered high-temperature varieties of sodium and potassium nitrate.² A metastable, rhombohedral phase III is formed on cooling $\text{AgNO}_3\text{-I}$,⁶ analogous to the formation of the possibly isomorphous phase III of potassium nitrate.

The hexagonal unit cell axes of $\text{AgNO}_3\text{-I}$ have been determined as $a = 5.203 \pm 0.005$ Å and $c = 8.522 \pm 0.005$ Å at 164°C,³ corresponding to three molecules per unit cell. Since intensities of intermediate re-

flections, corresponding to a *c*-axis equal to twice the quoted value, could not be detected³ (as in the cases of $\text{NaNO}_3\text{-I}$ and $\text{KNO}_3\text{-I}$ ⁹), an ordered (or partly ordered) structure of $\text{AgNO}_3\text{-I}$ according to either the centrosymmetric space group $R\bar{3}c$ or the noncentrosymmetric $R3c$ is most likely ruled out in favour of either a completely disordered structure belonging to the centrosymmetric space group $R\bar{3}m$ or an ordered (or partly ordered) structure of the noncentrosymmetric $R\bar{3}m$. "Completely ordered" corresponds to a statistical distribution of nitrate groups over several equivalent orientations, incorporating distribution over several nonequivalent sets of orientation, provided that statistically centrosymmetric point group symmetry of the nitrate groups is established.

The magnitude of the transition entropy indicates considerable disorder in $\text{AgNO}_3\text{-I}$ and is therefore in favour of $R\bar{3}m$, which is also in agreement with observations in $\text{NaNO}_3\text{-I}$ ⁹ and $\text{KNO}_3\text{-I}$.¹⁰ It may be noted that either of the four space groups mentioned above yields the same, ordered configuration of the cations.

The equilibrium orientations of a single nitrate group surrounded by anions of this configuration are expected to incorporate aragonite-type and/or calcite-type positions as in $\text{NaNO}_3\text{-I}$ ⁹ and $\text{KNO}_3\text{-I}$,¹⁰ depending on the relative dimensions of this system. There are two equivalent orientations of each kind ($R\bar{3}m$).

Table 1 contains corresponding intermolecular distances referred to the $\text{AgNO}_3\text{-I}$ lattice. An approximately correct value of the *z*-parameter of the nitrate group (assumed to be planar) in the aragonite-type position was determined on the supposition that the Ag—O (aragonite) separation is equal to the Ag—O (calcite) distance.

The Ag—O distance is found to be somewhat smaller than the sum of the ionic radii (2.52 Å). The Ag—N separations are considerably larger than the sum of the ionic radii. This applies also to the O—O separations referring to ordered calcite- ($R\bar{3}c$) (= $R3c$ for special positions in question) or the ordered aragonite-type structure ($R\bar{3}m$). Three of the referenced O—O separations are smaller than twice the van der Waals (ionic) radius. In $\text{NaNO}_3\text{-I}$ ⁹ and $\text{KNO}_3\text{-I}$ ¹⁰ this number is two and one, respectively. If these distances be inaccessible at equilibrium, inspection shows that the structure will consist of ordered domains with nitrate groups in either calcite- or