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On the Crystal Structure of the High-temperature Form of Silver Nitrate (AgNO₃-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 structure [1] which resembles neither the calcite- nor the aragonite-type structure.[2] It transforms (approximately isothermally) into a rhombohedral form I [3] 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 AgNO₃-I is similar to the disordered high-temperature varieties of sodium and potassium nitrate.[2] A metastable, rhombohedral phase III is formed on cooling AgNO₃-I,[6] analogous to the formation of the possibly isomorphous phase III of potassium nitrate.

The hexagonal unit cell axes of AgNO₃-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 detected [3] (as in the cases of NaNO₃-I and KNO₃-I [8]), an ordered (or partly ordered) structure of AgNO₃-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 $R3m$. "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 AgNO₃-I and is therefore in favour of $R\bar{3}m$, which is also in agreement with observations in NaNO₃-I [9] and KNO₃-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 NaNO₃-I [9] and KNO₃-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 AgNO₃-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 ($R3m$). Three of the referenced O—O separations are smaller than twice the van der Waals (ionic) radius. In NaNO₃-I [9] and KNO₃-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

Table 1. Intermolecular distances in $AgNO_3$-I. $d(N-O) = 1.25$ Å (ass). Hexagonal unit cell dimensions refer to 164°C,[3] space group $R\bar{3}m$. The uncertainty in values of interatomic distances involving calcite-type positions of the nitrate group is probably of the order of a few thousands of an Ångström. The remaining numbers are somewhat more uncertain. A = aragonite-type oxygen position. C = calcite-type oxygen position.

	Distance (Å)	Type of position
$N(0,0,0) - Ag(0,0,\frac{1}{2})$	4.261	
$N(0,0,z) - Ag(0,0,\frac{1}{2})$	3.94	
$O(x,x,0) - Ag(1/3,2/3,1/6)$	2.470	
$O(x/2,x,\bar{z}) - Ag(1/3,2/3,1/6)$	2.470 (ass.)	
$O(x,x,0) - O(2/3-x,1/3-x,1/3)$	3.215	CC
$O(x,x,0) - O(2/3-x,1/3,1/3)$	2.962	CC
$O(x,x,0) - O(1-x,1-x,0)$	2.703	CC
$O(x,x,0) - O(1,x,0)$	3.953	CC
$O(x,x,0) - O(1-x,0,0)$	3.500	CC
$O(x,x,0) - O(2/3-x/2,1/3+x/2,1/3+z)$	3.45	CA
$O(x,x,0) - O(2/3-x,1/3-x/2,1/3-z)$	2.68	CA
$O(x,x,0) - O(1-x/2,1-x,z)$	2.95	CA
$O(x,x,0) - O(1-x/2,x/2,z)$	3.54	CA
$O(x,x/2,z) - O(2/3-x/2,1/3+x/2,1/3+z)$	3.24	AA
$O(x,x/2,z) - O(2/3-x,1/3-x/2,1/3-z)$	2.26	AA
$O(x,x/2,z) - O(1-x/2,x/2,z)$	3.04	AA

aragonite-type positions (other types of positions being disregarded), a situation which is distinctly different from that of $NaNO_3$-I [9] or KNO_3-I.[10]

However, the magnitude of the transition entropy can thus hardly be accounted for since the transition is probably of the orientational order-disorder type. Some modification of the model seems therefore necessary and will be discussed subsequently.

Since two of the O−O distances are about 0.1 Å less than twice the van der Waals radius of oxygen, corresponding instantaneous equilibrium orientations may possibly deviate sufficiently from the average values to make the corresponding relative orientations accessible. However, it is necessary to assign a relatively low probability the these configurations, since otherwise the calculated entropy value should be comparable with those obtained for KNO_3-I [10] and $NaNO_3$-I [9] and thus considerably higher than the observed transition entropy of $1.30(\pm 0.01)$ cal/mole K.[5] In previous cases considered this has not been required as a first approximation. In these cases critical average O−O separations seem generally to exceed 2.8 Å. (Adjustment of the z-parameter of the aragonite-type oxygen (Table 1) to obtain

an O−O separation of 2.8 Å in this way, yields an unreasonably short O−Ag distance of 2.38 Å. The x-parameters of the oxygen atoms are furthermore considered to be rather accurate.)

Alternative types of accessible orientations, as indicated for $RbNO_3$-II,[11] may be thought of as a source of disorder. Inspection showed that a nitrate group can be placed at a normal contact distance from the silver ions in (1/3, 1/3, 1/6), (2/3, 1/3, −1/6) and (1/3, 2/3, 1/6), without giving rise to too short O−N, Ag−N, or Ag−O separations. Some of the orientations of the surrounding nitrate groups will, however, be blocked. Only a small fraction of the nitrate group is needed in this type of position to account for the main part of the transition entropy, since it comprises six statistically equivalent orientations per anion. Consideration of intermolecular distances is clearly in favour of this type of orientation as an additional equilibrium position. It is doubtful if an X-ray diffraction analysis will be of much help in this connection, considering the dominating effect of the cations on the structure factors.

The contribution to the configurational entropy from cation positional disorder is expected to be small.[11]

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On the Crystal Structure of Lithium Nitrate above Room Temperature

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Most univalent metal nitrates can exist in several distinctly different polymorphic forms at atmospheric pressure.[1] At ordinary temperature lithium and sodium nitrate have a rhombohedral crystal structure [2] of the (ordered) calcite-type [3,4] shown in Fig. 1. On heating, sodium nitrate transforms gradually into a rhombohedral, orientationally disordered structure stable above 276°C. The nitrate groups seem to occupy alternatively both disordered calcite- and aragonite-type positions in the high-temperature phase.[5]

A slight discontinuity in the ultra-violet spectrum of lithium nitrate was observed at 170°C [6] and ascribed to a previously undiscovered transition. Also, an anomaly in the electric resistivity has recently been detected at 230°C.[7] No phase change is, however, apparent from X-ray diffraction measurements [2,8] or thermal observations.[9]

This may not, however, exclude the possibility of orientational disorder in lithium nitrate at elevated temperatures, for example similar to that suggested for sodium nitrate at intermediate temperatures.[5] Accurate Cp-data are apparently not available. To be realistic a statistical model of a structure should give rise to instantaneous configurations which involve only acceptable intermolecular separations. It seemed reasonable for the present case to use the model recently put forward for $NaNO_3$-I [5] and KNO_3-I,[10] wherein the nitrate groups were shown to occupy disordered aragonite- and calcite-type positions, alternatively.

Values of interatomic distances calculated on this basis are listed in Table 1. The Li−O distance obtained assuming an oxygen atom in $(x,x,0)$ was used to estimate an approximate value of the z-parameter of oxygen (and nitrogen, assuming the anion to be planar) in an aragonite type position (O in $(x/2,x,z)$). The melting point of lithium nitrate is reported to be 253.1°C.[9] The short Li−O distance indicates a strong (electrostatic) attraction between the metal ion and the nearest oxygen atoms. The separation is, however, somewhat longer than the sum of the ionic and van der Waals radii.[11] The Li−N separations are relatively large, possibly in part due to the electrostatic repulsion between the cations and the nitrogen atoms. Similar results were also noted for sodium [5] and potassium nitrate.[10]

Of the twelve listed values for O−O separations at each temperature, only six exceed 2.8 Å, the generally accepted value of the O−O contact distance.[10] The remaining six values are seen to be considerably shorter than 2.8 Å and will therefore be assumed to be excluded at equilibrium. Inspection of Table 1 shows that two neighbouring anions cannot occupy disordered calcite-type positions (*i.e.* not equivalent according to space group $R\bar{3}c$), nor can they be situated in disordered aragonite-type positions (not equivalent according to $R\bar{3}c$). A nitrate group occupying a calcite-type position may, however, be located close to a nitrate ion in an aragonite-type position, *etc.* Thus apparently, disordered arrangements of the nitrate groups may occur. However, consideration of an assembly of molecules in the lattice shows that the structure must be of the ordered calcite-type (all anions equivalent according to $R\bar{3}c$; Fig. 1) at any temperature.