Thus, for $\mathbf{K}=\mathbf{0}$,

$$\langle \mathbf{p}'|U^\dagger\delta\hat{T}U|\mathbf{p}\rangle=-i4\pi\, e^2\, p\hbar\omega c I(p) \times f(p^2-2m_0\hbar\omega,\mathbf{0})\delta(\mathbf{p}'-\mathbf{p})\,, \qquad (C.20)$$

where

$$I(\mathbf{p})=\int \mathrm{d}^3k k^{-2}(p-k_z)^{-1}\delta[\varepsilon(\mathbf{p})-\varepsilon(\mathbf{p}-\mathbf{k})-\hbar\omega]$$

$$=m_0(4\pi p^2)^{-1}\int_{k_0}^{k_c}\mathrm{d}k k^{-1}(2p^2-k^2-2m_0\hbar\omega)^{-1} \qquad (C.21)$$

with

$$k_0=p-(p^2-2m_0\hbar\omega)^{1/2} \qquad (C.22)$$

and, for p large,

$$I(p)\simeq m_0(2\pi p^2)^{-1}\log\{k_c p(m_0\hbar\omega)^{-1}\}\,, \qquad (C.23)$$

it following that

$$\langle \mathbf{p}'|U^\dagger\delta\hat{T}U|\mathbf{p}\rangle=iA(p)f(p^2-2m_0\hbar\omega,\mathbf{0})\delta(\mathbf{p}'-\mathbf{p}) \qquad (C.24)$$

for $\mathbf{K}=\mathbf{0}$.

The contribution from $U^\dagger\Delta^\dagger\hat{T}^\dagger\delta U$ may be computed similarly.

References

Boyce, J. F. & Roberts, S. A. (1974). *Acta Cryst.* A**30**, 543–548.

Pines, D. (1963). *Elementary Excitations in Solids.* New York, Amsterdam: Benjamin.

Shevchik, N. J. (1974). *J. Phys. C*, **7**, 3930–3936.

Acta Cryst. (1976). A**32**, 499

A Probable Crystallographic Path for Phase Transformations in Single Crystals of Ammonium Nitrate

By S. Swaminathan

Physics Department, I.I.T., Madras, India

(*Received* 13 *May* 1975; *accepted* 17 *November* 1975)

Assuming that the shuffles of a solid-state single-crystal phase transformation are least-motion processes consistent with the symmetry of the phases and with the accepted interatomic distances, it follows that the structure of the higher-symmetry phase will be predictable solely from its space-group symmetry and unit-cell dimensions if the complete crystal structure of the low-symmetry phase has already been determined [Swaminathan & Srinivasan, *Acta Cryst.* (1975). A**31**, 628–634]. The possibility has been here verified successfully in the sequence V → IV → II of the phase transformations in ammonium nitrate.

Introduction

At the end of a paper on the thermal cycle of phase transformations in potassium nitrate (Swaminathan & Srinivasan, 1975) is the following statement: 'Crystallographically an important point also emerges. If the crystal structure of the lower-symmetry phase is known, the crystal structure of the higher-symmetry phase may be predicted from only a knowledge of the unit-cell dimensions and the space-group symmetry of the higher-symmetry phase'.

Many transformations in crystals of inorganic substances show the important characteristics of martensitic transformations in metals and alloys. The underlying idea of the paper on the KNO_3 transformations is that the 'shuffles' of solid-state phase transformations must be least-motion processes consistent with the symmetry of the phases and subject to acceptable interatomic van der Waals contact distances between chemically non-bonded atoms, and that therefore the structure of the higher-symmetry phase of a transformation must be predictable from the structure of the low-symmetry phase.

Martensitic transformations

Martensitic transformations generally involve lattice deformations which lead to macroscopic shape changes in crystals undergoing transitions from one phase to another. Between the phases of a transformation exists a strong orientation relationship. Often the lattice deformations will not produce the correct atomic or molecular positions within the unit-cell, and additional displacements (shuffles) which produce no macroscopic effects are then required. They may arise, for example, if the atomic positions in the parent deformed cell do not have the observed space-group symmetry of the daughter phase (Christian, 1965; Wayman, 1964).

The polymorphs of ammonium nitrate

Below its fusion temperature of 165°C ammonium nitrate exists in five distinct phases with reversible transitions between them in the sequence V → IV → III → II → I (Hendricks, Posnjak & Kracek, 1932; Cleaver, Rhodes & Ubbelohde, 1963). In dry crystals without occluded water phase IV goes directly over to phase II and the sequence becomes:

$$\begin{array}{ccccc} \mathrm{V} & \xrightarrow{-18\,^{\circ}\mathrm{C}} & \mathrm{IV} & \xrightarrow{50\,^{\circ}\mathrm{C}} & \mathrm{II} \\ \text{tetragonal} & & \text{orthorhombic} & & \text{tetragonal} \\ P4_2 & & Pmmn & & P\bar{4}2_1m \end{array}$$

(Brown & McLaren, 1962). The crystal remains single through the sequence of transformations, and a two-fold symmetry axis (parallel to the *c* axis of phase IV) transforms into the unique axis of the tetragonal phases.

We attempt below to explain the sequence V → IV → II of transitions in ammonium nitrate along lines similar to those used for potassium nitrate (Swaminathan & Srinivasan, 1975). Only, unlike the spherical K^+ ion, the ammonium ion is a complex tetrahedral cation and takes part in a network of hydrogen bonds in all phases of ammonium nitrate.

N–H···O distances are very close to or in excess of the sum of the van der Waals radii (Kitaigorodsky, 1955; Pauling, 1960) of the oxygen and nitrogen atoms (Baur, 1972). A hydrogen bond in ammonium nitrate is signified only by the two important characteristics: (i) H···O distance and (ii) ∠N–H···O. The averages of these two characteristics over a list of fifteen unbifurcated bonds (Hamilton & Ibers, 1968) are given below:

	Average	Maximum	Minimum
N–H···O	2·96 Å	3·07 Å	2·87 Å
H···O	1·96	2·38	1·82
∠N–H–O	162°	174°	119°

The crystal structures of all three phases have been reported (Amoros, Arrese & Canut, 1962; Choi, Mapes & Prince, 1972). The crystallographic data are in Table 1, but the atomic coordinates of the phase V structure only are given in Table 2.

The low-symmetry phase V structure

Fig. 1 shows the phase V structure in the (001) projection down the unique axis. The origin is chosen so that the cation centres are at $z=0{\cdot}25$ and $z=0{\cdot}75$ on the 4_2 and 2 symmetry axes parallel to *c* (here assumed vertical). The cations or the anions are not all equivalent by symmetry. The asymmetric unit in the primitive cell has two anions and (because they occupy rather particular positions) four cations. The mirrors of the $\bar{4}2m$ point-group symmetry of the cations coincide with the (220) and the symmetry-equivalent ($\bar{2}20$) planes of phase V.

Table 2. *Atomic coordinates of phase* V NH_4NO_3 (*Amoros et al.*, 1962)

Ion	Atom	*x*	*y*	*z*
NO_3	N	0·250	0·250	0·518
	O(1)	0·120	0·270	0·456
	O(2)	0·380	0·230	0·456
	O(3)	0·250	0·250	0·642
NO_3'	N′	0·250	0·250	0·018
	O(1)′	0·120	0·230	0·956
	O(2)′	0·380	0·270	0·956
	O(3)′	0·250	0·250	0·143
NH_4	N	0·000	0·000	0·250
	H(1)	0·076	0·076	0·190
	H(2)	0·076	−0·076	0·310
NH_4'	N′	0·500	0·000	0·250
	H(1)′	0·576	0·076	0·190
	H(2)′	0·424	0·076	0·310
NH_4''	N″	0·500	0·500	0·250
	H(1)″	0·424	0·424	0·310
	H(2)″	0·424	0·576	0·190
NH_4'''	N‴	0·000	0·500	0·250
	H(1)‴	−0·076	0·424	0·310
	H(2)‴	−0·076	0·576	0·190

The σ_h planes of the D_{3h} point-group symmetry of the anions are vertical and do not coincide with the (220) or ($\bar{2}20$) planes, but intersect with them along vertical lines passing through (±0·250, ±0·250, 0·0) in the base plane. On each such line there lie pointing vertically upwards, N–O bonds of two anions one above another in a unit cell. The two anions do not eclipse each other along the vertical, for their σ_h planes are turned about the common line of their vertical bonds, in the same sense but through unequal angles of 36° and 54° from the (220) planes. (Alternatively, they may be described as turned in opposite senses through the same angle of 9° from the (400) or (040) planes.) All the anions in phase V have the same inverted-Y orientation with an N–O(3) bond pointing vertically upwards. Were it not for the O(1) and O(2) atoms (see Fig. 1 and Table 2), the (220) and ($\bar{2}20$) planes of almost mirror symmetry would be planes of real crystallographic mirror symmetry in this phase. Structures such as these are liable to phase transformations in which the elements of pseudo-symmetry in the parent phase become elements of true symmetry in the daughter phase.

Phase V → phase IV transformation

(i) *Lattice deformation and lattice correspondence*

The dimensions of the orthorhombic phase IV unit cell are: $a=5{\cdot}745$, $b=5{\cdot}438$ and $c=4{\cdot}942$ Å. Then $\mathbf{a}'=$

Table 1. *Crystallographic data of the phases of ammonium nitrate*

Phase	Symmetry	*a* (Å)	*b* (Å)	*c* (Å)	*Z* (Å³)	Reference
V	tetragonal $P4_2$	7·98	7·98	9·78	8	Amoros *et al.* (1962)
IV	orthorhombic *Pmmn*	5·745	5·438	4·942	2	Choi *et al.* (1972)
II	tetragonal $P\bar{4}2_1m$	5·74	5·74	4·95	2	Choi *et al.* (1972)

$\mathbf{a}+\mathbf{b}$, $\mathbf{b}'=\mathbf{a}-\mathbf{b}$ and $\mathbf{c}'=2\mathbf{c}$ are respectively 7·911, 7·911 and 9·884 Å long, and $\angle(\mathbf{a}',\mathbf{b}')=86°52'$. Compared with the phase V tetragonal axes, $a=b=7{\cdot}98$ and $c=9{\cdot}78$ Å, the above values show that the phase V primitive tetragonal cell is deformed into a non-primitive monoclinic unit cell of nearly the same dimensions, but the tetragonal lattice is deformed into a lattice of orthorhombic symmetry as reflected in the phase IV unit cell (see Table 1). If the phase V unit cell is sheared by 3°8′ on the A (or B) faces the square base is changed into a rhombus whose semi-diagonals are 5·795 and 5·486 Å. Thus the inner square, $A'B'C'D'$, of Fig. 1 becomes the (a,b) base plane of the phase IV unit cell. The c axis has the same direction but is actually halved in the transformation. The columns of cations at A', B', C' and D' have indeed vertically a period of 0·5 c_V. But at A, B, C, D and E in Fig. 1 the period is the true translation c_V.

The phase V (220) and $(\bar{2}20)$ planes of near-mirror symmetry are thus to be transformed into the true (100) and (010) crystallographic mirror planes of phase IV according to the least-motion hypothesis.

(ii) *Reorientation of the ions*

For all except the O(1) and O(2) atoms the (220) and $(\bar{2}20)$ are pseudo-mirror planes in phase V. It is only necessary for every anion to turn about its vertical N–O bond and align its σ_h plane with the $(220)_V$ or $(\bar{2}20)_V$ planes to make them truly mirror planes for the whole assembly of ions in the structure. If σ_h is aligned with (220) a σ_v is aligned with $(\bar{2}20)$ and *vice versa.*

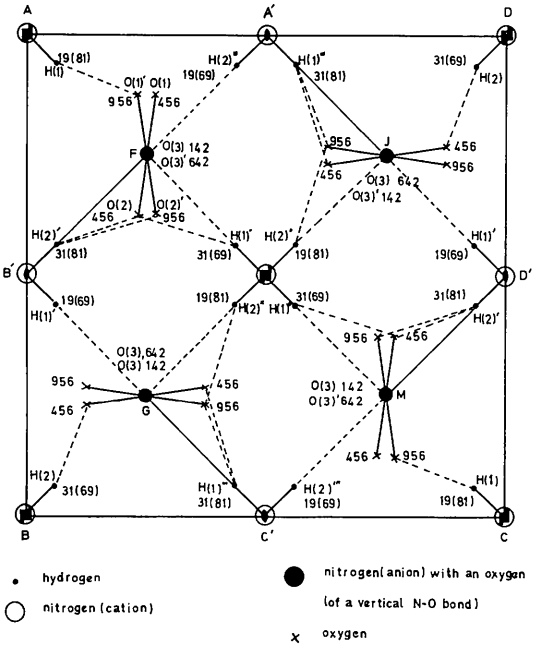

Fig. 1. Phase V structure. Unique-axis projection. Numbers are z coordinates ($\times 10^3$). The hydrogen bonds are shown by dashed lines.

The centres of the anions are $0{\cdot}5c_V$ apart vertically. To halve the unit-cell vertical translation, the anions with N–O bonds on the same vertical line must both have the same orientation after realignment, *i.e.*, both σ_h planes must be on the (220) plane, or both on $(\bar{2}20)$.

The σ_h planes of the anions are vertical. If they are to be related by a horizontal plane of n-glide symmetry in phase IV, the σ_h planes of all anions must be parallel to each other. This demands that the realignment of the anions must be such that all σ_h planes lie on the (220) planes, or all on $(\bar{2}20)$.

The dimensions of a NO_3^- ion are 2·32 Å in its own plane, and 2·20 Å along its principal axis (Ubbelohde, 1965). If all σ_h planes are aligned on the (220), there must be a distension of the lattice along $A'B'$, and (relatively) a contraction along $A'D'$ (Fig. 1). Thus the shear deformation of the phase V lattice (as discussed above) by 3°8′ is a consequence of the cooperative pattern of realignment of the NO_3^- ions during the phase V → phase IV transformation. To assume the shear as the primary cause rather than the result of the transformation can be useful in deducing the course of the phase change. When atoms bonded together even by feeble hydrogen bonds are separated further than the equilibrium distance between them, there must arise on each of them a feeble restoring force. If atoms come closer than the equilibrium distance repulsive forces arise between them. As energy rises more steeply for steric hindrance, repulsive forces are generally much stronger than attractive forces for the same displacements from the equilibrium configuration. Even if the mutual action and reaction forces be equal, the turning moments on the respective ions about the axes of rotation may well be different. It must be assumed that the phase V structure at the temperature of transformation represents a configuration of near-unstable equilibrium for the ions. Such details may be easy or difficult to deduce, but they are hardly necessary for the present purpose, namely to show that the structures of the higher-symmetry phases IV and II may be deduced from the low-symmetry phase V structure.

Let the anions at F with O(1) and O(1′) at $z=0{\cdot}456$ and 0·956 respectively (Fig. 1) turn to lie along $A'B'$. After realignment the distance between O(1) and the nitrogen atom at $z=0{\cdot}250$ at A' becomes 2·680 Å. During and after the realignment the distance of O(1) from H(2)‴ (inside the unit cell at A' in Fig. 1) is greater than 2·468 Å. No steric hindrance develops between the advancing oxygen atoms of the anions at F and the hydrogen atoms of the cations at A', and so the cations at A' are not forced to change orientation. There is however, after the realignment, steric hindrance between these oxygen atoms and the nitrogen atoms at the centres of the cations at A', – the distance is 2·682 Å – and this must force the ions bodily apart. (The orientations necessary for phase IV being assumed, the ions cannot turn.) We take this into calculation a little later below. Steric hindrance between the advancing oxygens and the hydrogens at B' (on the other side of F in Fig. 1) force both the cations at B' to swivel around, thus bringing them into translational equivalence in phase IV with the cations at A'.

The stretching hydrogen bonds between a cation at A' and the anions at J (Fig. 1) turning into the (220) plane cannot drag the cations at A' into changing their phase V orientation. For if they did, there would be severe steric hindrance between the hydrogens of the cations at A' and the oxygen atoms of the anions at F now realigned on the (220) plane along $A'B'$.

Phase IV symmetry requires that the anions at J (Fig. 1) be in the erect-Y orientation if the anions at F retained the phase V inverted-Y orientation. (Driven by the turning anions at F the anions at J move on perhaps rather well anchored cations at E, and so are turned into the new orientation.) The anion at J must rotate in its own plane about its principal axis into the erect-Y orientation even as it aligns itself on the (220) plane.

In complex ionic crystals (Pauling, 1960) the distances between coordinating ligand atoms change only insignificantly if the coordination number remains the same in a transformation. In phase V the minimum distance between two coordinating oxygen atoms that belong to different anions is 3·038 Å. If the anions at F and J, after realignment on the (220) planes, were in the same inverted-Y orientation the closest distance between a pair of oxygen atoms (not from the same NO_3^- ion) would be 2·827 Å. The two atoms would require to be separated along the vertical by 0·114 c_V to make the distance between them at least 3·038 Å. This is achieved with least motion if instead of bodily vertical displacement of the ions, those at J merely turned into the erect-Y orientation on the (220) plane. By mere rotation about the principal axis through 60° into the new orientation, the vertical separation between the previously too close oxygen atoms becomes 0·124c_V. Other steric repulsions (see below) force them together. If the minimum separation must be 3·038 Å they can draw vertically nearer to one another by only just 0·005 c_V. Thus the nitrogen atoms of the two anions must come to $z=0·523$ (at F) and 0·513 (at J); at F the two atoms O(1) and O(2) come to the new common level, $z=0·461$, and O(3) to 0·647; O(3) at J goes to 0·389, and O(1) and O(2) to 0·575. From each of these atoms after realignment, 0·5 c_V away along the vertical, is another atom of the same kind. This will satisfy the requirement that c_{IV} must be equal to 0·5 c_V.

The oxygen atom, O(2), of the anion at J and at $z=0·075$ would be too close to the hydrogen at $z=0·190$ of the cation at E. This cation with its centre at $z=0·250$ at E is forced to turn around the vertical by 90°. This brings the two cations at E into proper orientation for the phase IV n-glide and c-translation symmetry (compare Figs. 1 and 2).

The hydrogen atom at $z=0·190$ (on the line $A'F$) between the nitrogen at A' at $z=0·250$ and O(1) at F (now after realignment) at $z=0·461$ is not situated favourably for a hydrogen bond. Between the two heavier atoms now at only 2·682 Å from each other there must inevitably be steric hindrance and mutual repulsion. The minimum they must be apart is 2·90 Å, the sum of their van der Waals radii. The further vertical separation necessary is 0·021 c_V. The oxygen at 0·461 cannot move any further up, as this would make the O–O edge of the coordination polyhedron less than the minimum assumed 3·038 Å. The nitrogen at the cation centre thus moves from $z=0·250$ to 0·229 below. This same vertical separation of 0·232 c_V (*i.e.* 0·461–0·229) is similarly necessary between O(2) at 0·575 and the nitrogen of the cation at E; this nitrogen moves up to $z=0·807$. This same reason causes the cation at E with centre at $z=0·25$ to shift upwards to $z=0·307$, away from a too close oxygen at $z=0·075$ of an anion at J after realignment on the (220) plane. The translational symmetry of c_{IV} is thus also satisfied.

The structure after the reorientations and shuffles of the ions is shown in Fig. 2. The planes at $z=0·018$, 0·268, 0·518 and 0·768 (in terms of c_V) each individually possess n-glide symmetry. Shifting the origin to the plane at $z=0·018$, the coordinates of the atoms in terms of the phase IV unit cell are given in Table 3, where for comparison the experimental values from a determination of the structure by single-crystal neutron diffraction (Choi *et al.*, 1972) are also given.

The justification for the implicit assumption that the ions are rigid groups has been set out in detail before in the paper on KNO_3 transformations (Swaminathan & Srinivasan, 1975) and is omitted here.

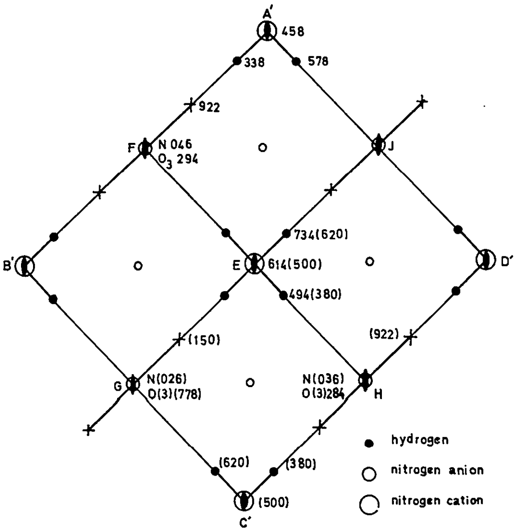

Fig. 2. Reorientations and shuffles of the ions to produce phase IV (*Pmmn*) symmetry. The z coordinates ($\times 10^3$) correspond to the origin at the same vertical level as it was in phase V. The n-glide plane containing the centres of symmetry is 0·036 c_{IV} above the level of the origin. (The values corresponding to the conventional origin at a centre of symmetry are in Table 3.)

Table 3. *Atomic coordinates in phase* IV

Ion	Atom	(This work) x	y	z	(Choi *et al.*) x	y	z
NO_3^-	N	0·500	0·000	0·010	0·500	0·000	0·007
	O(1)	0·318	0·000	−0·114	0·316	0·000	−0·117
	O(2)	0·500	0·000	0·258	0·500	0·000	0·263
NH_4^+	N	0·000	0·000	0·422	0·000	0·000	0·414
	H(1)	0·147	0·000	0·308	0·145	0·000	0·29
	H(2)	0·000	0·148	0·542	0·000	0·148	0·53

Phase IV → phase II transformation

The dimensions of the rectangular unit cells of phases IV and II (see Table 1) obviously show the lattice correspondence (Brown & McLaren, 1962): the *a*, *b* and *c* axes of phase IV transform into the corresponding axes of phase II. The phase II space-group symmetry, $P\bar{4}2_1m$, is shown in the unique-axis projection in Fig. 3. The orientations of the cations in Fig. 2 are already compatible with the mirror and glide planes of symmetry in Fig. 3. These planes of symmetry, especially the vertical glide planes, demand however that the cations related by them should have their centres at the same *z* level. The cations concerned are those that in phase IV are related by the horizontal *n*-glide symmetry. There can be no reason why one of them must move to the level of the other, either vertically up or down. It is more reasonable, in virtue of their symmetry equivalence, that they move towards each other by the same amount to equalize the levels of their centres. For example, the cations with centres at $z=0·422$ [in Fig. 2, (0·458) at A'] and at $z=0·578$ [marked (0·614) at *E*] move together the same amount in opposite directions to bring their centres to the same common level at $z=0·500$. In phase IV they were also related by a centre of inversion.

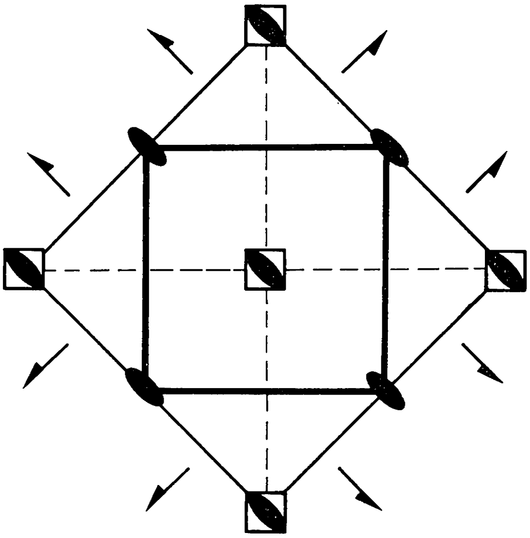

Fig. 3. Symmetry of phase II, $P\bar{4}2_1m$, shown in the unique-axis projection.

The anions in phase IV have their σ_h planes at 45° to the new phase II mirror planes in Fig. 3. The reorientation required (so that they avoid steric hindrance with their own images in the new mirror planes) is that they should realign themselves with the σ_h on the new mirrors by turning about their vertical N–O bonds through 45°. It is also necessary in order to avoid steric hindrance with the cations now in their new positions to suit phase II symmetry (see previous paragraph). Thus the cations at *F* and *J* (Fig. 2), related by inversion symmetry in phase IV, turn in opposite senses through 45° to lie on the new mirror planes of phase II. The $\bar{4}$ symmetry of phase II requires them to retain their respective opposite orientations. No adjustment of the anion levels is dictated by the new symmetry, for unlike the cations the anions that are related by glide symmetry in phase II are already at the same *z*-level in phase IV (they are translation equivalent, *e.g.* the anions at *F* and *H* in Fig. 2). Where hydrogen bonds are not possible, the distances between nitrogen and oxygen atoms are equal to or greater than 2·90 Å. H···O distances where the hydrogens are favourably located for hydrogen bonds are well inside the allowed or observed range. There seems no reason to adjust the positions and orientations of the ions any more than required above for reasons of symmetry.

The reorientations of the anions and the levelling of the cations are implicit in the structure proposed for phase II by Choi *et al.* (1972). We have shown here that both phase IV and phase II structures can be derived from the low-symmetry phase V structure solely on considerations of symmetry and the least-motion hypothesis. The atomic coordinates of phase II NH_4NO_3 are in Table 4.

Table 4. *Atomic coordinates in phase* II

Ion	Atom	x	y	z
NO_3^-	N	0·500	0·000	0·010
	O(1)	0·371	−0·129	−0·114
	O(2)	0·629	0·129	−0·114
	O(3)	0·500	0·000	0·258
NH_4^+	N	0·000	0·000	0·500
	H(1)	0·147	0·000	0·380
	H(2)	0·000	0·147	0·620

Twinning

Twinning can occur as a result of phase transformations if alternative symmetry-equivalent paths are available for the phase transformations. In the IV → II transformation in NH_4NO_3 the anions at *F* could have aligned their σ_h planes on the mirrors parallel to *FJ* rather than the mirror perpendicular to it along *FG* (see Figs. 2 and 3). The result would have been a phase II end structure that is a mirror image of the other by reflexion in the $(010)_{II}$ plane which is not a crystallographic mirror plane in phase II.

Similarly in the phase V → phase IV transformation the anions at *F* could have aligned themselves on the $(\bar{2}20)_V$ planes rather than the $(220)_V$ planes. The result would then be a structure for phase IV in which the *c* axis being the same as before, the *a* and *b* axes are interchanged. It is possible that with nucleation of the transformation in different parts of the crystal, both kinds of phase IV domains are present at the end of the transformation. The two domains would be related by an element of non-crystallographic symmetry parallel to *A′C′* in Fig. 1.

Conclusion

An attempt has been made to consider the sequence of transformations, V → IV → II, in ammonium nitrate crystals on the basis of the ideas of martensitic transformations in metals. A similar attempt on the thermal cycle of phase transformations in potassium nitrate was recently published. In particular the aim here was to show that on a least-motion hypothesis (*i.e.* the shuffles are least-motion processes consistent with symmetry and accepted interatomic distances) the higher-symmetry phase structure may be predictable solely from its unit-cell dimensions and space-group symmetry if the low-symmetry phase of the transformation has a completely determined crystal structure. These considerations yield an adequate explanation of twinning observed in the transitions. The ions are treated here as rigid groups. It would be interesting indeed if a structure with high pseudo-symmetry is solved and the structure of the result of a possible phase transformation were predicted and later succesfully verified.

¶ The author wishes to thank the Deutsche Akademische Austauchdienst for a visiting fellowship in Frankfurt, where this work was done.

References

Amoros, J. L., Arrese, C. & Canut, M. (1962). *Z. Kristallogr.* **117**, 92–107.

Baur, W. H. (1972). *Acta Cryst.* B**28**, 1456–1465.

Brown, R. N. & McLaren, A. C. (1962). *Proc. Roy. Soc.* A**266**, 329–343.

Choi, G. S., Mapes, J. E. & Prince, E. (1972). *Acta Cryst.* B**28**, 1357–1361.

Christian, J. W. (1965). *The Theory of Phase Transformations in Metals and Alloys.* Oxford: Pergamon Press.

Cleaver, B., Rhodes, E. & Ubbelohde, A. R. (1963). *Proc. Roy. Soc.* A**276**, 453–460.

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids.* New York: W. A. Benjamin.

Hendricks, S. B., Posnjak, E. & Kracek, F. C. (1932). *J. Amer. Chem. Soc.* **54**, 2766–2786.

Kitaigorodsky, A. I. (1955). *Organischeskaya Kristalloximiya.* U.S.S.R: Izdatelstvo Akademii Nauk.

Pauling, L. (1960). *Nature of the Chemical Bond.* Ithaca: Cornell University Press.

Swaminathan, S. & Srinivasan, S. (1975). *Acta Cryst.* A**31**, 628–634.

Ubbelohde, A. R. (1965). *Melting and Crystal Structures.* Oxford Univ. Press.

Wayman, C. N. (1964). *Introduction to the Crystallography of Martensitic Transformations.* New York: Macmillan.

Acta Cryst. (1976). A**32**, 504

The Squared Power Method to Fit a Plane to a Set of Points*

By Lawrence C. Andrews and Herbert J. Bernstein

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, *U.S.A.*

(*Received* 16 *June* 1975; *accepted* 14 *October* 1975)

The ‘power method’ provides a computationally easy method for the determination of the best plane through a set of points. By repeatedly taking squares, one rapidly obtains the maximum eigenvalue and corresponding eigenvector of the inertia tensor. The result is the least-squares result when the points have independent, isotropic weights.

Introduction

We present a simple alternative to the use of least-squares techniques (Scheringer, 1971) for the determination of the best plane through a set of points. Though the basic method presented is old (National Physical Laboratory, 1957) (NPL) and the power method has been discovered by crystallographers more than once (Schomaker, Waser, Marsh & Bergman, 1959), its advantages seem not to have been fully exploited to date. This may well be due to some problems which arise from the particular formulations of the technique chosen in the past. In particular, the method can be subject to slow convergence and capture by the wrong eigenvector. When applied in other eigenvalue searches where negative eigenvalues arise, it can suffer

---

* Research performed under the auspices of the U.S. Energy Research and Development Administration, supported by NSF contract AG-370.