X-ray Diffraction Study of the Orientational Relation between the IV and III Phases of Ammonium Nitrate

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A unique orientational relationship between phases IV and III of ammonium nitrate, NH_4NO_3, was observed. Powdered ammonium nitrate contained in a glass capillary was repeatedly put through the IV–III–II or IV–II phase transitions by thermal cycling between 20 and 100 °C. This led to the development of an X-ray diffraction texture which was different for every specimen but constant during repeated cycling. Analysis of the XRD patterns showed that all observed textures arose from one orientational relationship between phase III and the phases IV and II. Except for the spread of the textures this relationship was maintained for all observed transitions. A matrix for the transformation of planes and directions was calculated. The orientational relationship could be described by the following three sets of parallel directions in the crystal structures of phases IV and III: $[100]_{IV}//[01\bar{1}]_{III}$, $[\bar{1}01]_{IV}//[3\bar{1}4]_{III}$ and $[\bar{1}\bar{1}2]_{IV}//[3\bar{1}1]_{III}$. The formation of the texture was explained by a nucleation and growth mechanism which does not allow the complete dissolution of phase IV in water before phase III is formed. On the basis of the observed transformation matrix between phases IV and III, a mechanism for the IV–III transition was proposed.

Introduction

In extensive previous research[1,2] on the structure and phases of the industrially important material ammonium nitrate NH_4NO_3 (AN), at least five phases have been characterized. The phases of particular interest in this study are those occurring between 20 and 100 °C, *i.e.*, phases II–IV. It is in this temperature range that serious problems are experienced by users and producers of AN, such as caking and physical breakdown of prills to fine particles. Both phenomena are said to be due to phase changes involving phase III, in which water plays a key role as a catalyst. Many investigations of the IV–III–II phase transitions have been reported, but the precise mechanism and possible structural relationships between phases (especially phase III) is still not known. The space groups, average transition temperatures, and unit cell dimensions (in Å), of the phases I–V are now generally accepted to be as follows:

Phase I:[3,4]
cubic; $Pm3m$; $Z = 1$; (above 125 °C); $a = 4.3655(2)$

Phase II:[5,6] tetragonal; $P42_1m$; $Z = 2$; (84 °C); $a = 5.7193(1)$; $c = 4.9326(1)$

Phase III:[7,8]
orthorhombic; $Pnma$; $Z = 4$; (32 °C); $a = 7.7184(3)$; $b = 5.8447(1)$; $c = 7.1624(1)$

Phase IV:[6,9]
orthorhombic; $Pmmn$; $Z = 2$; (−17 °C); $a = 5.7574(1)$; $b = 5.4394(1)$, $c = 4.9298(1)$

Phase V:[10,11]
orthorhombic; $Pccn$; $Z = 8$; (below −17 °C); $a = 7.9804(1)$; $b = 8.0027(1)$; $c = 9.8099(1)$

Phase IV transforms directly to II at an average temperature of 51 °C under "dry" conditions.[12] Phases I, II, IV, and V go through a simple chain of structural transformations which involve reorientation of the ions together with small shifts in their positions. This similarity between the II, IV, and V phases is clearly demonstrated in Figure 1 where suitably oriented projections of the structure are shown. Phase III on the other hand, has an orthorhombic structure which does not appear to fit in with the above simple scheme.[7,8] This phase is stable between 32 and 84 °C and reportedly[2,3,13–15] grows only in the presence of moisture.

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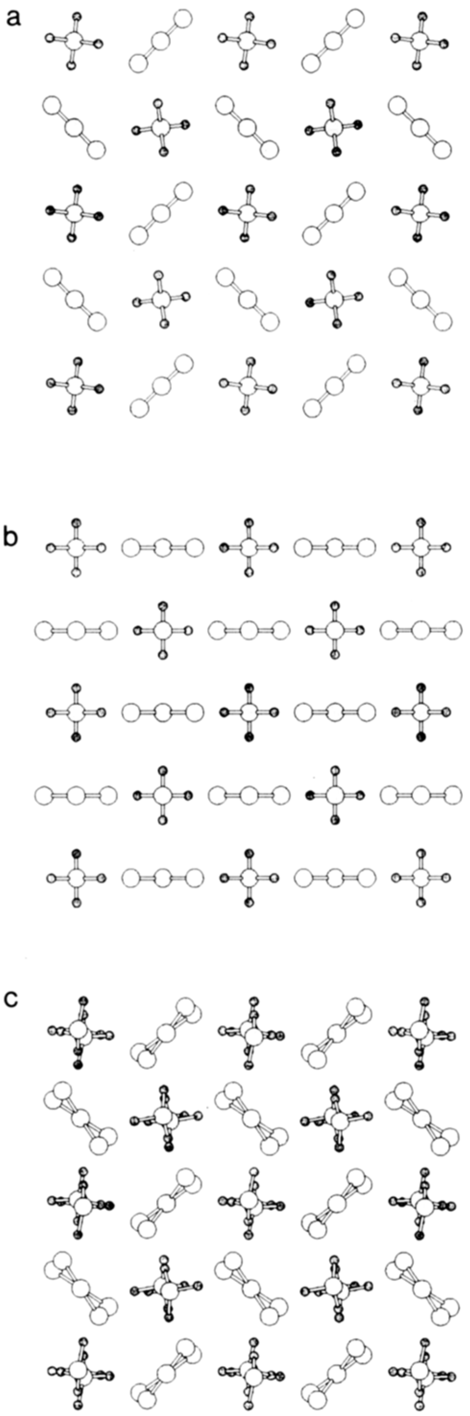

Figure 1. Projections of the AN phases II (a), IV(b) and V(c) (axes omitted) showing the structural similarity between the phases.

The occurrence of phase III and the structural transitions between this and other phases of AN has been found by several researchers[2,13–15] to depend on a number of factors, including humidity, thermal history of the sample, and sample preparations. In earlier diffraction studies by the present authors[2] a modified Weissenberg camera was used to follow the IV–II–IV and IV–III–II–III–IV phase transitions as a function of temperature, relative humidity, and sample preparation. A wide fluctuation of transition temperatures was observed in agreement with the findings by others.[1,13] Also, AN samples only transformed consistently to phase III when ground under "wet" conditions.[12] This corroborates the proposed surface catalytic role of water and the importance of hydrogen bonding.[2,3,13,14] A mechanism often proposed for the IV–III–IV transition[3,14] involves the dissolution of phase IV on one side of a water–AN interface and the growth of phase III on the other. This mechanism does not require any structural relationship between the phases. It should also be noted that in recent work on the solvent mediation of the phase change[14] the experiments were carried out on single crystals suspended in oil. In the course of the X-ray powder diffraction (XRPD) study of AN by the present authors[2] (in which finely ground powder was used) it was found that a crystallographic texture, preferred orientation of the powder grains, developed when the sample was cycled several times through the phase transitions IV–(III)–II–(III)–IV. Every individual powder sample assumed its own individual set of texture axes, one axis for IV, one for III, and one for II. Now it was found that these sample dependent sets of texture axes were very simply related to each other. There was only one unique orientational relationship between the IV, III, and II phases, the different sets of texture axes being merely a consequence of viewing this unique relationship in different directions. This paper deals with the experiments, the results and their crystallographic interpretation which have led to the determination of the crystallographic relation between III and the other phases. The IV–III transition is considered in detail, the III–II transition being almost the reverse of the former.

Experimental Section

XRPD Observations. Finely ground (fine enough to give continuous rings on the XRPD photographs) AN powder (Merck AR grade) was put into Lindeman glass tubes of 0.5-mm i.d. at various humidities and cycled several times between room temperature and 100 °C each cycle taking about 2 h. XRPD photos were taken without removing the sample from the camera, at room temperature (phase IV), at 50 °C (phase III) and at 100 °C (phase II). Invariably preferred orientation textures as shown in Figure 2 were observed, although the starting sample always gave uniform diffraction rings indicating random orientation of the grains. During the exposure of the XRPD photos the specimen tube was rotating, like in a Debye–Scherrer camera, about its long axis. The appearance of the photos varied from uniform diffraction rings for the starting material to arcs typical for fibre textures and in exceptional cases to patterns typical of single-crystal rotation diagrams.

For a particular specimen the textures of the phases remained the same during cycling except for the degree of preferred orientation. When phase III was formed, the texture deteriorated somewhat but never disappeared completely. In the transition from the tetragonal II to the orthorhombic IV the directions of the *a* and *b* axes interchanged in some cases. For different specimens, however, the textures were different, showing quite clearly that the orientation of the texture was not due to external influences such as the narrowness of the glass tube or the curvature of the walls of the tube. When during thermal cycling the texture of IV changed into that of III and then into that of II, it was found that the IV and II textures were almost identical except for minor differences caused by the slight changes of the axial lengths. The axial systems of IV and II remained parallel although the phase transitions had not gone from IV to II directly but first from IV to III and thereafter from III to II. Hence III must have transmitted the knowledge of the axial orientation of IV to II which indicated that there existed a crystallographic relation between IV and III and between III and II. Detailed interpretations of the texture photos confirmed this and gave the required orientational relationship.

An increase in the spottiness of the diffraction rings showed that the texture formation was accompanied by a coarsening of the grains. When in a separate experiment the AN grains were surrounded by ground Lindeman glass powder (about 20% AN

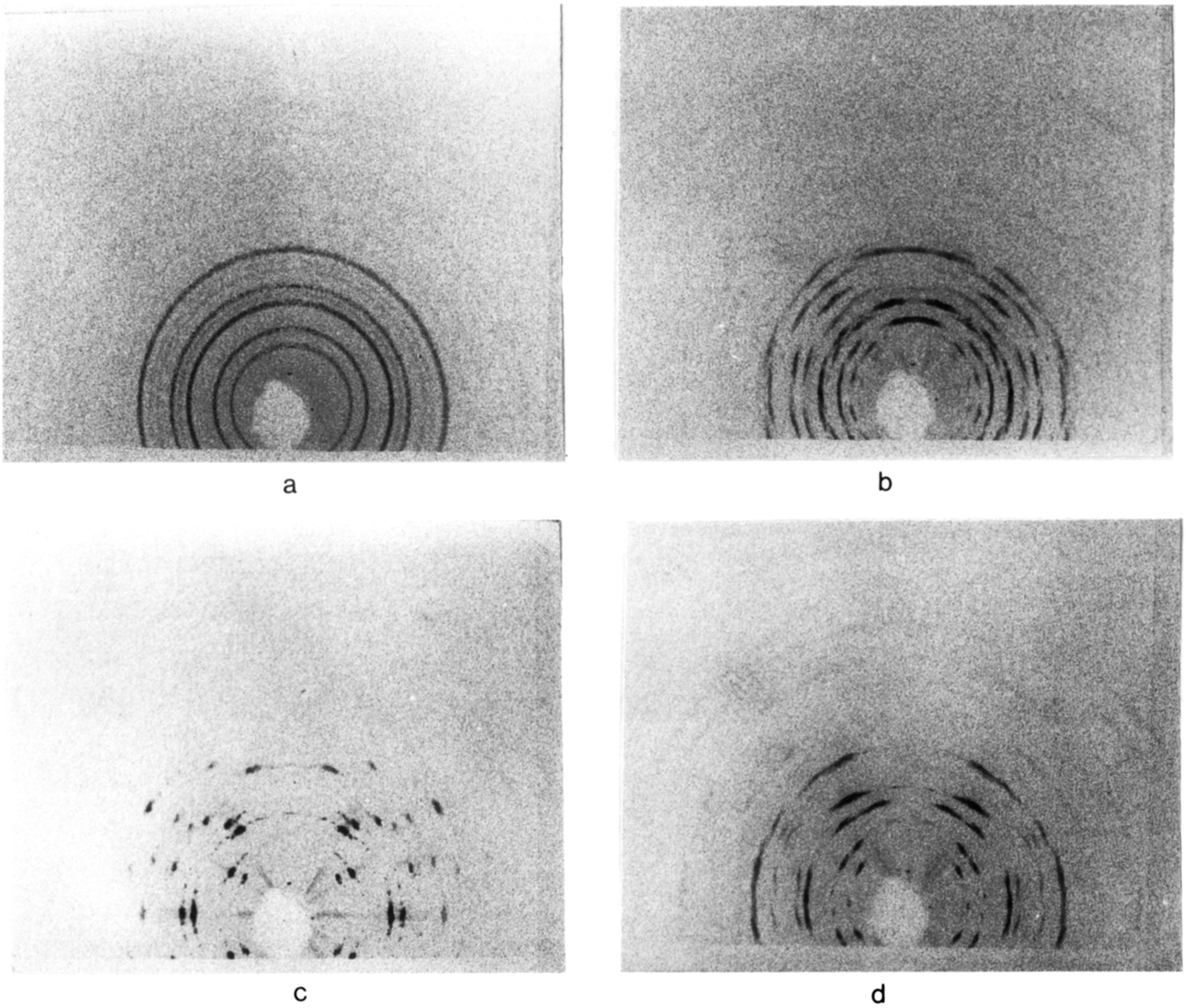

Figure 2. XRPD photographs of the same powdered AN sample showing (a) phase IV at room temperature before cycling, (b) texture development in phase III at 50 °C, (c) texture development in phase II at 100 °C, and (d) texture development in phase IV at room temperature after cycling.

in glass), no texture and no coarsening of the grains were observed. Contact between grains was therefore essential not only for grain coarsening but also for texture formation.

When samples were heated from room temperature to 40 °C grain growth and texture were observed for "wet" samples,[12] i.e., for samples showing phase III at 40 °C. No growth and no texture were observed for "dry" samples, i.e., for samples still in phase IV at 40 °C. When samples were heated from room temperature to 100 °C grain growth and texture were observed for "wet" and for "dry" specimens. The finding that "dry" samples also showed growth and texture during their IV–II–IV transitions indicated clearly that growth and texture were caused by the phase transitions and not by the presence of water vapor.

The texture extended over several millimeters along the specimen tube axis when the experiment was done in the modified Weissenberg camera described previously.[2] In this camera there was a small temperature gradient along the specimen tube because one end of the tube was freely exposed to the air stream used to heat or cool the specimen while the other end was connected to a relatively massive goniometer head. Because of this gradient the phase transition started at one end of the tube and spread to the other end carrying the texture along. This process is reminiscent of the moving heater technique used for growing single crystals and for zone refining, except that in the present case the material did not melt (mp = 169.6 °C) and did not cool down again after the passing of the "hot zone". In a separate experiment the specimen tube was heated in stationary warm air outside the camera. Texture was also observed, but it changed from one end to the other end, thereby confirming that the orientation of the texture was not caused by external influences but rather by a nucleation and growth phenomenon involving the AN grains.

Evaluation of the XRPD Patterns. The usual method for the interpretation of fibre textures required standard (111) pole diagrams for the phases IV, III, and II. These have been calculated and are shown in Figures S1, S2, and S3 (supplementary material; see paragraph at end of paper). After indexing the patterns according to systems of axes proposed by Lucas et al.,[6,8] the centers of the *hkl* arcs were replotted as (*hkl*) poles on the reflection circles (for details see standard textbooks, e.g., ref 18). With a Wulff net of 5-in.-diameter the angles between several (*hkl*) poles and the fiber axis (rotation axis of the specimen tube) were measured. Next, circles which corresponded to these angles were drawn around the (*hkl*) poles on standard (111) projections. The circles intersected within the experimental accuracy and the spread of the texture in a point which was the fiber axis, i.e., it was the pole of the plane normal to the fiber axis.[19] The poles of the fiber axes for all textured samples were determined accordingly.

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[18] Barrett, C. S.; Massalsky, T. B. *Structure of Metals*; McGraw-Hill: New York, 1966.

[19] In a noncubic crystal the [*hkl*] direction and the pole of the (*hkl*) plane do not coincide, except that in the orthorhombic system the [h00], [0k0], and [00l] directions are parallel to the (*h*00), (0*k*0), and (00*l*) poles.

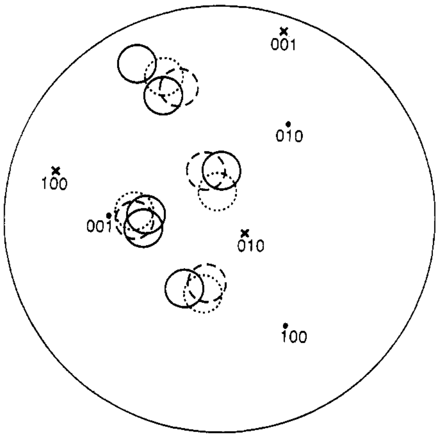


Figure 3. Stereographic positions of the poles of the textures of four different specimens as shown by four groups of circles. The size of the circles representing the average spread of the textures, dotted circles phase IV, dashed circles phase II, full circles phase III. The center of the stereogram being the (111) poles of phases IV and II and being near the (130) pole of phase III. Labeled dots and crosses giving the axial directions of phases IV and III, respectively, and allowing the calculation of the transformation matrix.

Results

Consider a run with sample one, say, for which the IV texture transformed into a III texture and later into II. The IV photo gave the IV fiber axis for sample one with the indices $H_1^{\mathrm{IV}} = (h_1^{\mathrm{IV}}k_1^{\mathrm{IV}}l_1^{\mathrm{IV}})$ referred to the IV system of axes. After the transformations to III and II the fiber axes became H_1^{III} and H_1^{II}, respectively. Hence the H_1^{IV} pole of IV transformed into the H_1^{III} pole in III and then into the H_1^{II} pole in II. For this particular specimen, therefore, the H_1^{IV} plane in IV was parallel to the H_1^{III} plane in III and parallel to the H_1^{II} plane in II. This, however, was not sufficient to fix the IV system of crystallographic axes to the III system of axes and to the II system of axes. At least three independent sets of parallel planes were required. In the present investigation four sets were measured. The independent sets came from different specimens, two and three say, which had different textures. Now the following relations had to be satisfied simultaneously: $H_1^{\mathrm{IV}}//H_1^{\mathrm{III}}//H_1^{\mathrm{II}}$, $H_2^{\mathrm{IV}}//H_2^{\mathrm{III}}//H_2^{\mathrm{II}}$, and $H_3^{\mathrm{IV}}//H_3^{\mathrm{III}}//H_3^{\mathrm{II}}$.

The solution was obtained by plotting the $H_{1,2,3}^{\mathrm{IV}}$ poles on the IV standard projection, the $H_{1,2,3}^{\mathrm{III}}$ poles on the III standard projection, and the $H_{1,2,3}^{\mathrm{II}}$ poles on the II standard projection. The III projection was then rotated by means of a Wulff net until the $H_{1,2,3}^{\mathrm{III}}$ poles on III coincided with (superimposed on) the $H_{1,2,3}^{\mathrm{IV}}$ poles on IV within the accuracy of the experiment and the spread of the textures. Figure 3 shows that the fit for the four sets of parallel planes is quite remarkable if it is realized that such a fit is extremely unlikely for random orientations of the axial systems. It was therefore concluded that, subject to the spread of the textures, a definite crystallographic relation existed between the phases IV and III when they were undergoing the phase transitions. Because II was always parallel to IV, the same could be said for the III–II transition.

IV–III Axial Transformation. From the superimposed standard projections in Figure 3 the direction cosines for the transformation between IV and III were obtained by graphical means and a rotation matrix was calculated. However, a structurally more meaningful description was derived from the observation that certain prominent poles in IV coincided with other prominent poles in III. This is shown in Figure 4 where the following pairing has been possible, $(010)_{\mathrm{IV}}//(\bar{1}11)_{\mathrm{III}}$, $(111)_{\mathrm{IV}}//(130)_{\mathrm{III}}$, and $(021)_{\mathrm{IV}}//(011)_{\mathrm{III}}$. Here // should be interpreted as very nearly parallel. From these three pairs of parallel planes follow, as shown in Figure 5 three sets of parallel directions: $[100]_{\mathrm{IV}}//[01\bar{1}]_{\mathrm{III}}$, $[\bar{1}01]_{\mathrm{IV}}//[3\bar{1}4]_{\mathrm{III}}$, and $[\bar{1}\bar{1}2]_{\mathrm{IV}}//[3\bar{1}1]_{\mathrm{III}}$.

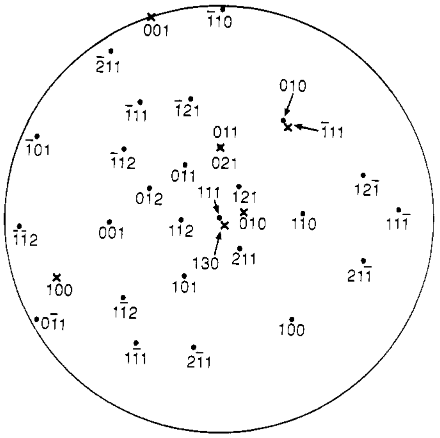


Figure 4. Superposition of the stereographic projections of the phases IV (dots) and III (crosses).

It was attempted to calculate a proper transformation matrix from these three sets of parallel planes by identifying the (*hkl*) poles with *hkl* points in the reciprocal lattice. All pole indices were multiplied by an integer (order of reflection) with the aim of equating $1/d_{hkl}^{\mathrm{IV}}$ and $1/d_{hkl}^{\mathrm{III}}$ as closely as possible. However, because the equality could not be satisfied exactly the resulting transformation matrix was restricted to the transformation of poles, planes and directions for which only the ratio of the indices was significant. The best possible match was 040 of IV with 333 of III, 333 of IV with 260 of III and 021 of IV with 022 of III.

The transformation matrix **P** which was defined by

$$(h,k,l)_{\mathrm{IV}} = (h,k,l)_{\mathrm{III}}\cdot\mathbf{P}$$

became

$$\mathbf{P} = \begin{bmatrix} 0 & -1/3 & 1/2 \\ 1/2 & 11/18 & 1/3 \\ -1/2 & 7/18 & 1/6 \end{bmatrix}$$

The transformation of the directions showed that during the IV–III transition [100], [010], and [001] of IV became $[01\bar{1}]$, $[\bar{6}\ 11\ 7]$, and [321] of III, respectively. Owing to graphical limitations and the approximate nature of the texture the transformed axes [011], [6 11 7], and [321] were not quite orthogonal anymore, the angles being

$$[01\bar{1}],\ [\bar{6}\ 11\ 7] = 88.9°$$

$$[01\bar{1}],\ [3\ 2\ 1] = 86.1°$$

$$[\bar{6}\ 11\ 7],\ [321] = 89.1°$$

It should be emphasized that the existence of above sets of parallel planes and directions of which many more are possible, does not necessarily imply that these particular sets play any critical role in the chemical processes which occur during the phase transition.

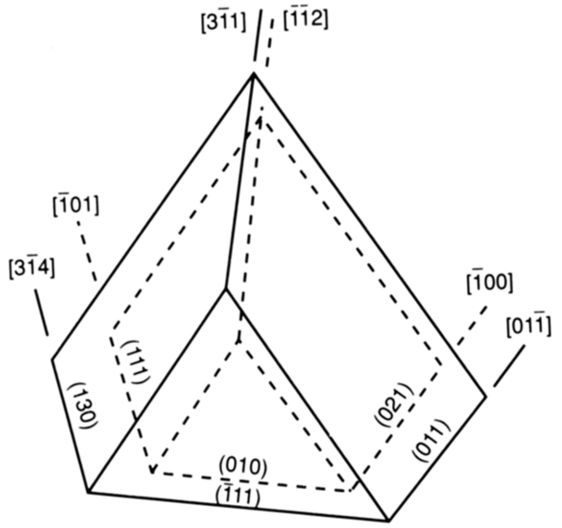
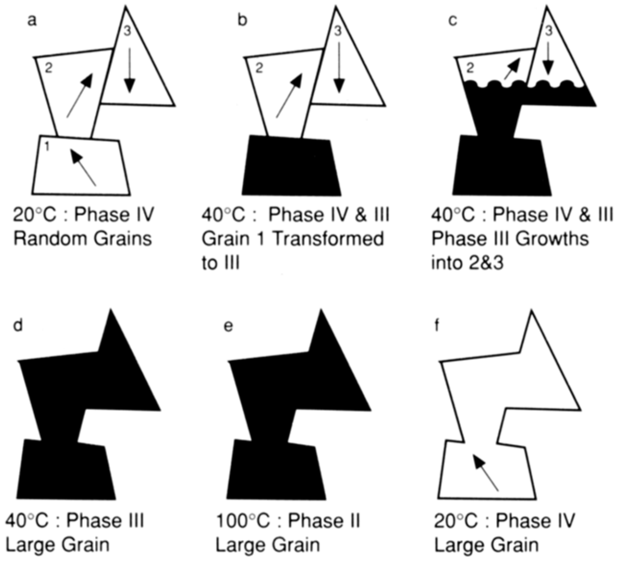


Figure 5. Schematic diagram showing parallel planes and directions for phase IV (dotted lines) and phase III (solid lines), not to scale.



20°C : Phase IV Random Grains

40°C : Phase IV & III Grain 1 Transformed to III

40°C : Phase IV & III Phase III Growths into 2&3

40°C : Phase III Large Grain

100°C : Phase II Large Grain

20°C : Phase IV Large Grain

Figure 6. Schematic diagram showing the development of texture in AN grains, under "wet" conditions, during the phase transitions from IV–III–II–III–IV, arrows representing crystallographic orientations.

Discussion

Three distinct processes are involved in the present observations, the first two are grain growth and texture formation which are closely linked, and the third is the establishment of a definite crystallographic relation between the phases. Grain growth manifested itself by a coarsening of the diffraction rings and texture formation by the breakup of the rings into arcs, in both cases the limit being a single-crystal pattern. From the simultaneous occurrence of grain growth and texture formation it was concluded that the formation of the texture was really a consequence of the growing together in the narrow space of the sample tube, of many small AN grains into one large grain of one orientation. With this in mind the development of the texture can be described as follows.

Consider a sample with a random orientation of grains as shown in Figure 6a. In humid conditions and in the presence of a small temperature gradient a certain IV grain in the hot end of the sample tube transforms into a III grain (Figure 6b). This grain becomes the seed grain for the growth of an enlarged grain with an axial orientation parallel to that of the first III grain (Figure 6c,d). In two dimensions this growth is terminated soon by the walls of the capillary, in the third dimension, along the capillary axis, the growth can continue unchecked. Ideally, as has been observed in a few cases, a single crystal can be grown in this way, but in general only preferred orientation of the grains along the tube axis has been observed. The crystallographic orientation of the fiber axis will therefore depend on the orientation of the first phase III seed grain and will be different for different specimens.

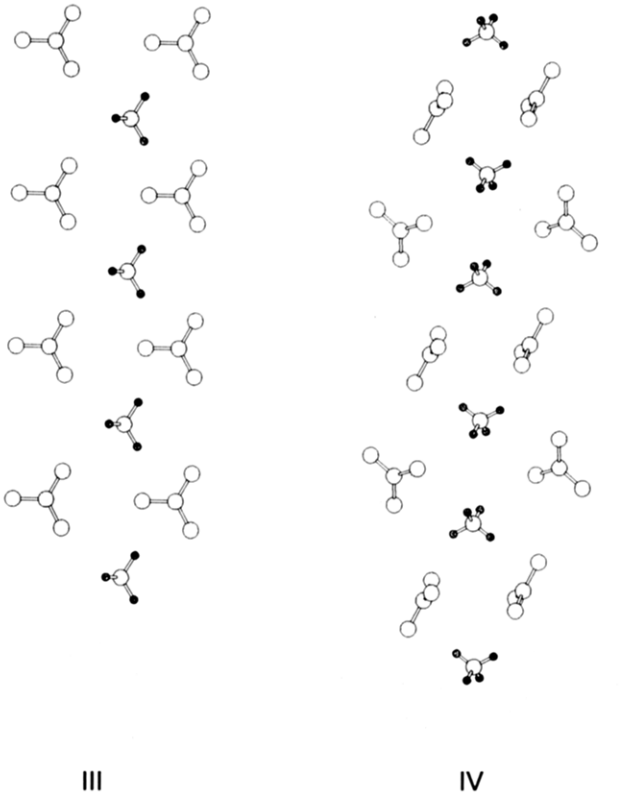


Figure 7. Strips of ions parallel to the (010) and $(\bar{1}11)$ planes in phase IV and III, respectively, and aligned according to the results presented here.

On further heating the oriented III grains transform to oriented II grains (Figure 6e), which on cooling become again oriented III grains (as in Figure 6d) and eventually oriented IV grains (Figure 6f). Hence, for every specimen there is a unique IV fiber axis which originated from a III axis and/or II axis. As shown above, these sets of three fiber axes, one set for every specimen, are in a definite relation to each other which requires that a IV crystal transforms into a III crystal and then into II crystal according to a unique crystallographic operation. However, the driving force for this operation cannot be very strong because in the process of the growing together of the grains (during the initial stages of texture formation) the seed grain imposes its orientation on the neighboring grains regardless of their individual orientations.

The proposed explanation for the observed crystallographic relation between the phases follows from a symmetry argument. The point groups of IV and III have 2-fold rotation axes along their respective *a*, *b*, and *c* axes. However, the axes of IV are rotated with respect to those of III as expressed in the relations below which have been calculated using the transformation matrix **P**:

$$(100)_{\mathrm{IV}} // (\bar{1}\ 9\ \overline{15})_{\mathrm{III}}$$

$$(010)_{\mathrm{IV}} // (\bar{1}11)_{\mathrm{III}}$$

$$(001)_{\mathrm{IV}} // (311)_{\mathrm{III}}$$

$$(100)_{\mathrm{III}} // (0\bar{2}3)_{\mathrm{IV}}$$

$$(010)_{\mathrm{III}} // (9\ 11\ 6)_{\mathrm{IV}}$$

$$(001)_{\mathrm{III}} // (\bar{9}73)_{\mathrm{IV}}$$

It was thought that a plane on the right might have noncrystallographic, local 2-fold axes which would match the crystallographic axes of the plane on the left. The pair $(010)_{\mathrm{IV}}//(\bar{1}11)_{\mathrm{III}}$ was selected for a detailed study because of the low order and hence dense packing of the $(\bar{1}11)$ plane.

One *d*-spacing thick slices parallel to $(010)_{\mathrm{IV}}$ and $(\bar{1}11)_{\mathrm{III}}$ were computed[20] and aligned as required by the above analysis, i.e., $[100]_{\mathrm{IV}}//[0\bar{1}1]_{\mathrm{III}}$. The positions of the A and N ions were found to be related by rows of 2-fold axes which were parallel in the two phases and which outlined similar but not identical strips of A and N ions. In Figure 7 it may be seen that the ions in the strips have different orientations and that the A–A separations are not the same, five A–A units in III corresponding to four units in IV. Therefore, in the transformation from IV to III the surface pattern of IV will have to contract by $^1/_5$ along the A–A direction [100] in order to match a similar pattern in III. It is suggested that the adsorption of water could achieve such contraction accompanied by a rotation of the ions.

A simple model for the IV–III transition may now be proposed. In dry conditions a IV crystal warmed to about 40 °C, the temperature at which III is the stable phase, does not transform because of the lack of nucleation of phase III. It will transform to II at a higher temperature (the IV–II transition is not considered to be a nucleation–growth phenomena). In wet conditions and at room temperature water will adsorb chemically on exposed (010) faces of IV grains and change above mentioned strips of ions to resemble similar strips in the $(\bar{1}11)$ face of III. Around 40 °C the so created III "phase" will then grow into the existing IV phase with an orientation given by the strips, i.e., $(010)\ [100]_{\mathrm{IV}}//(\bar{1}11)\ [01\bar{1}]_{\mathrm{III}}$.

Davey *et al.*[14] have recently proposed a novel solvent-mediated mechanism for the IV to III transition. In their proposed model a microscopic liquid layer of AN dissolved in water (or a water ethylene glycol mixture) is propagating through the crystal, dissolving phase IV on one boundary and depositing phase III on the other. This liquid interfacial layer between the phases is said to be a fully disordered, saturated solution of AN in the solvent. While their mechanism could produce a texture for a particular transition, from IV to III say, it would result in different textures, at random, for all subsequent transitions: III–II–III–IV–III, etc. The orientation of II would not be parallel to that of IV and the texture would change with every thermal cycle. Also, different specimens would give completely unrelated results. All of this is contrary to observations made in the present work.

The model proposed in this paper requires that there is at least a partially ordered transitional zone, allowing the transmission of crystallographic information from the disappearing phase to the growing phase. Whether this transitional zone is in the form of a liquid crystal, in which case water molecules would travel with the transition front, or in the form of a solid diffusion layer, in which case water would only be required for the initiation of the new phase, cannot be decided from the current experiments. Previous observations[14] that AN contaning 2% KNO_3 in solid solution transforms readily from phase IV to phase III without the help of water, suggest that the transitional zone is of the solid diffusion layer type.

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Supplementary Material Available: Standard (111) pole diagrams for ammonium nitrate using the unit cell parameters given in the text (1 page). Ordering information is given on any current masthead page.

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[20] ATOMS 2.1 by Shape Software was used.