

An optical study of the phase transitions of ammonium nitrate and its properties in the range 15-90°C (phase IV, III, II' and II)

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An Optical Study of the Phase Transitions of Ammonium Nitrate and its Properties in the Range 15–90°C (Phase IV, III, II' and II)

By *I. Michaelis de Sáenz, J. C. Tessore and R. Leone* (Montevideo)*)

With 6 figures and 2 tables in the text

Abstract

Phase transitions of NH_4NO_3 occurring between 15 and 90°C, were revised by optical methods. Special attention was paid to the II'–IV transition. The transition temperature of this transformation is $T_{\text{II}'\text{--IV}} = 45.3^\circ\text{C}$, $T_{\text{IV--II}'} = 47.8^\circ\text{C}$. An intermediate phase II' of tetragonal or lower (rhombohedral?) symmetry was observed as samples were annealed for long periods of time in the stability range of NH_4NO_3 III. The influence of humidity and the thermal history of the samples on the transition was studied and related to the multiple transformation twinning, ease of transformation and thermodynamic stability.

Some optical properties of NH_4NO_3 III were revised, the result being a positive optic sign and $2V_\gamma = 86 \pm 1^\circ$. The orientation relations in the different phase transitions were studied. The addition of KNO_3 produces a lowering of the II'–IV transition temperature and decreases the $2V$ values.

Zusammenfassung

Die Phasenumwandlungen des Ammoniumnitrats wurden zwischen 15 und 90°C untersucht, mit besonderer Berücksichtigung der II'–IV-Umwandlung. Die pseudo-metastabile Umwandlungstemperatur ist 45,3° bei fallender Temperatur und 47,8°C bei steigender. Intermediäre tetragonale oder symmetrisch niedrigere (rhomboische?) Kristalle wurden durch längeres Erhitzen der Modifikation II, im Stabilitätsbereich der Phase III, erhalten. Der Einfluss des Feuchtigkeitsgehaltes und der Umwandlungsbereitwilligkeit (ease of transformation) wurden mit der Verzwillingung und der thermodynamischen Stabilität der Kristalle verglichen.

Die optischen Eigenschaften der im Untersuchungsbereich auftretenden Phasen wurden nachgeprüft. (Modifikation II hat $2V_\gamma = 86 \pm 1^\circ$ und ist optisch positiv). Ebenfalls wurden die Orientierungsverhältnisse bei den verschiedenen Phasenumwandlungen unter-

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sucht. Der Einfluss eines steigenden KNO_3 -Gehalts äussert sich durch Erniedrigung der Umwandlungstemperatur II'-IV und durch einen abnehmenden Wert des optischen Achsenwinkels bei der Phase III.

INTRODUCTION AND NOMENCLATURE

The following names are used in this paper for the modifications of NH_4NO_3 occurring between 15 and 90°C :

- IV Orthorhombic modification stable below $T_c = 32,3^\circ\text{C}$ (M. DE SÁENZ, AMONINI and PRESA [1964]).
- III Orthorhombic modification, stable above 32.3 up to 84.2°C (HOVI, PÖYHÖNEN and PAALASSALO (1960).
- II Tetragonal modification, stable between 84.1 and 125°C (HOVI, PÖYHÖNEN and PAALASSALO (1960), SHINNAKA (1956), AMOROS, ALONSO and CANUT (1958).
- II' is an intermediate phase of tetragonal or lower (orthorhombic?) symmetry (TESSORE 1965).

The information about the metastable phase-transition is rather poor, it is generally admitted to occur at about 50°C but the results of the different authors in many aspects disagree with each other and with our own observations. The fact that NH_4NO_3 can directly transform from modification IV into II or II' was already noted by WALLERANT (1905). In the description of the phase diagram NH_4NO_3 - KNO_3 , this author however simply marks the transition point at about 50°C and makes no comment on the metastable transition. At that time metastable transitions were hardly admitted at all, so that this is not so surprising. BRIDGMAN (1916) observes that at higher pressures the transition IV-II occurs directly in equilibrium. The extension of Bridgman's P-T curve indicates a transition point of 50.5 at atmospheric pressure (BOWEN 1926). HENDRICKS, POSNJAK and KRACEK (1932) point out that the metastable transition apparently occurs between phases II and IV, but "the character of these phases depends upon the previous thermal history of the salt, such that II' and IV', closely similar to, but not identical with II and IV, are formed under suitable conditions." SHINNAKA (1956, 1959) supposes that in phase II as well as in the metastable phase II, hindered rotation of the nitrate groups occurs. AMOROS, ALONSO and CANUT (1958), AMOROS and BANERJEE (1960) and AMOROS and CANUT (1962) refer to a "metastable phase" called II'. This form was obtained heating directly a crystal of form IV above 55°C by AMOROS, ALONSO and CANUT (1958) who state that "the structure" (of phase II') "differs only little from that corresponding to form II and accounts for the

natural path from one form to the other.” (Translation from the original Spanish text.) The authors have attempted to identify this phase by single X-ray diagrams. II' would be metastably disordered and would definitely turn into II if sufficient energy were available.

We do not quite agree with this nomenclature: If the intermediate phase II' forms during the transition occurring at about 45°C, two possibilities exist. The phase, being different from II, may either be unstable under all conditions or it may be a metastable phase with a so far unknown range of stability. The term “metastable phase” as used by AMOROS and coworkers should, for the moment, be avoided, as it is certainly not identical with II (metastable II) and for the present it is not clear whether or not II' has any stability range at all.

The designation IV' given by HENDRICKS, POSNJAK and KRACKER to phase IV above its stability range is not necessary as, to our knowledge, no difference between IV and IV' has been described. A special denomination is not justified and the phase should be simply called metastable phase IV when found outside its stability range.

Phases occurring below 15° and above 90°C, are not considered in this paper.

EXPERIMENTAL RESULTS

Microscopic determinations were made using the Leitz thermostatic heating stage and the universal stage with Emmon's heating segments. The relative positions of the crystals were either determined on the Universal Stage or by using the method of quantitative conoscopy as described by M. de SÁENZ and TESSORE (1969). Annealing of the samples was carried out either in thermostats or stoves. The rapid transfer from the thermostat to the heating stage does not alter the results. The data determined by these methods are given in tables I and II.

Table 1. Optical properties of ammonium nitrate in the range 15—90°C

Modification II	Tetragonal. Uniaxial (+)
Intermediate states II'	Tetragonal or lower (Orthorhombic?) 2V _γ =0–62° or higher after long periods of annealing (+)
Modification III	Orthorhombic. 2V _γ =86°15' (115 det.) (+) X // b, Y // a, Z // c
Modification IV	Orthorhombic. 2V _α =36°30' (50 det.) (–) X // b, Y // c, Z // a

For refractive index determinations see HENDRICKS, DEMING and JEFFERSON (1933). Birefringence of these modifications is extremely high. That of modification III being somewhat lower than that of the others.

Table 2. Heating and cooling experiments*)

Dry Samples

<i>Treatment</i>	<i>Modifications obtained</i>
1. NH_4NO_3 crystallized at 15–25°C Dried over SiO_2 and P_2O_5	IV
2. Heated for some hours at 70°C	(IV) **) or III
3. Heated for a few minutes at 86°C	II
4. Cooled below 50° but above 35°C	IV
5. Heated above 50° but below 84°C	II'
6. Cooled as 4	IV

On repeated cooling and heating as in 4–5–6, III does not appear again. II' and IV are alternatively obtained.

Dry Samples initially fused

1. NH_4NO_3 heated on slides rapidly up to 175°C	Melt
2. Cooled below 174° above 125°C	I
3. Cooled below 125° above 84°C	II
4. Cooled below 84°C	II' (uniaxial) + III
5. Further cooling in the range 50–84°C	(II') + (III) + III formed from II'
6. Cooled below 50°C	IV twinned + (III)
7. Cooled below 32°C	IV patchy + (IV twinned)
8. Heated above 50°C	II' uniaxial
9. Cooled below 50°C	IV twinned + IV patchy
10. Annealed between 32 and 50°C	III recrystallizing to large idiomorphic cryst.

Alternative:

9'. Annealed for months between 60 and 82°C	II' uniax. + II', biax. + III
10'. Cooled at room temperature	as above or IV
11'. Heated between 60 and 82°C	II' uniax. + II' biax. + III
12'. Heated above 85°C	(II' uniax.) + (II' biax.) + II
13'. Heated above 125°C	I
14'. Cooled below 125° above 84°C	II uniaxial

Wet Samples

These samples are maintained in the presence of humid gelatine saturated with ammonium nitrate.

1. NH_4NO_3 cryst. between 15 and 25°C	IV large single cryst.
2. Heated above 50°C	II' single cryst.
3. Cooled and annealed somewhat above 50°C	III
4. Cooled below 30°C	IV single cryst. or mosaic
5. Heated above 35°C	III single cryst. or aggregates

Transformations 4 and 5 were repeated up to 40 times with the same crystal. II' was not met again. The orientation after the successive transformations varied, but is not random. Frequently the same initial orientation was approximately repeated or single crystals after transforming into an aggregate would suddenly yield again a single crystal of similar orientation. By microscopic study it is impossible to distinguish whether the aggregate may be a multiple twin with irregular contact faces as the individuals are very small and irregular. It is impossible to obtain thin sections without causing transformation of the crystals.

*) Comments on the results obtained with these samples as summarized in this table, are given below.

**) Modifications mentioned in parenthesis; e.g. (III) means that the same phase was maintained in spite of heating or cooling.

DISCUSSION OF THE EXPERIMENTAL RESULTS

a) *Optical properties*

Phase IV: There is no agreement in the literature on the optical orientation of phase IV. Our results agree with those of HENDRICKS, POSNJAK and KRAČEK (1932). Accurate measurements of the optic axial angle were made: $2V_\alpha = 36.5 \pm 15'$ (50 det.). The optical properties of modification III proved somewhat different from those given in the literature. The optic axial angle has so far been said to be about 90° and the optic sign negative. (Compare data calculated from the refractive index determinations of HENDRICKS, DEMING and JEFFERSON (1933), revision by GOODWIN and WHETSTONE (1947), and by AMOROS and CANUT (1962) who have even drawn structural conclusions from the optic sign, until now regarded as negative.)

In the present study, crystals were prepared crystallizing NH_4NO_3 from aqueous solution by evaporation and growing these usually small crystals by recrystallization, maintaining them about one week within this temperature range. Crystals with rhombic, rather square outlines are obtained. The limiting faces belong to the form $\{110\}$. The accurate interfacial angle is 86° . The optic orientation given by GOODWIN and WHETSTONE (1947) was confirmed. The optic sign is positive and the optic axial angle $2V_\gamma = 86.5 \pm 1^\circ$, 1° being the average deviation of 115 determinations.

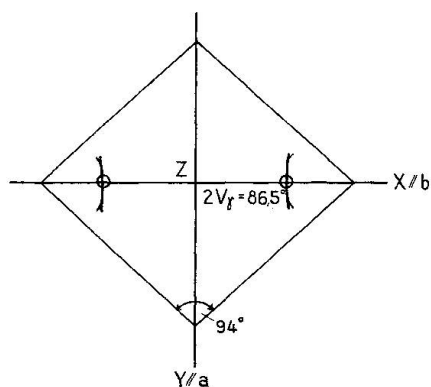
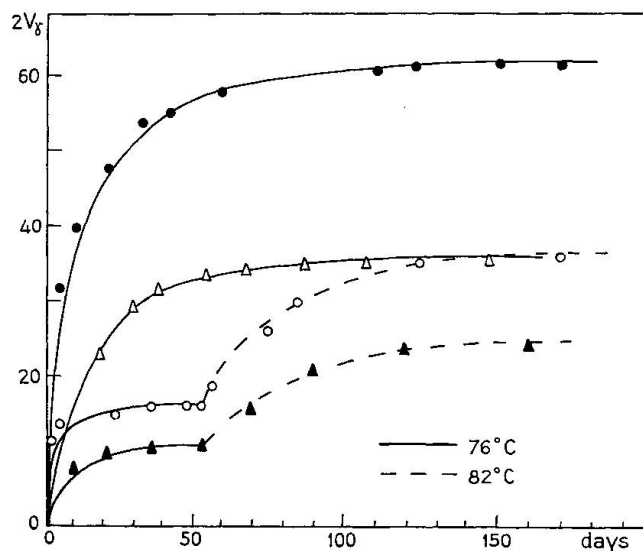


Fig. 1. Optical orientation of NH_4NO_3 III.

Fig. 2. Annealing II' in the stability range of III – the optic axial angle increases with time of heating and with temperature (TESSORE 1965).



The intermediate phase II' is obtained by annealing crystals of II in the stability range of III. Crystals of tetragonal or lower symmetry are obtained. After a certain length of time the crystals turn biaxial by annealing. $2V_\gamma$

increases with time and temperature. The largest value so far obtained is 62° after 250 days heating at 80°C .

Evidently the changes in the optical properties as shown in fig. 2 are due to transformations of the crystals. Their general behaviour is rather irregular from one crystal to the other and even in the same crystal. Interference figures are therefore rather poor and diffuse and exact extinction positions are not obtained. Observations made with these crystals when heated or cooled can be taken as evidence against alteration by decomposition or impurification. (Compare table 2b.) Normal crystals of modification II or IV are obtained from them by heating or cooling¹).

We have not been able to confirm so far whether II' is an intermediate phase between II and III as might be expected. Owing to the characteristics of the II' crystals there is little chance of confirming this fact by X-rays or spectroscopic methods.

The optical properties of mixed crystals of NH_4NO_3 - KNO_3 were determined by Mallard's method and confirmed with the universal stage for phase III. Results are given in fig. 3.

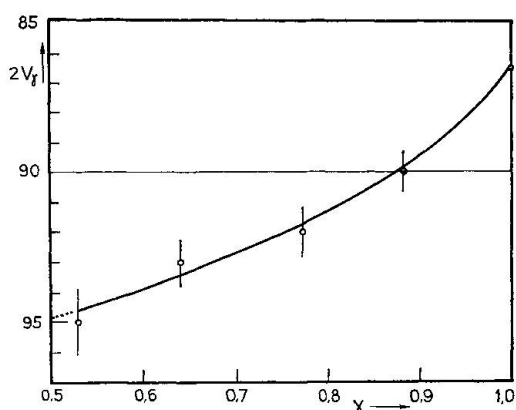


Fig. 3. Optic axial angle of mixed crystals $(\text{NH}_4)_x \text{K}_{1-x} \text{NO}_3$. The vertical lines represent the dispersion of the determinations made for each concentration (about 10) (see LEONE, 1970).

b) The pseudometastable transition temperature is generally given as "about 50°C ". BOWEN (1926) tried to make a rather accurate determination of this temperature obtaining the following values: 47 – 49° at cooling and 51 – 52.5 at heating. This author notes that according to his measurements, the value given by BEHN (1956) is certainly too low: 45°C . EVERETT and WATSON (1956) also mention that a difference exists between the transition temperature on heating and on cooling: these authors observe "a transition presenting hysteresis in the region of 50°C ."

The influence of addition of KNO_3 to NH_4NO_3 on this transition temperature was studied by LEONE (1969). From extrapolation of his values, as well as from

¹) Note: Decomposition was sometimes observed heating crystals for long periods of time with immersion oil or in loose crystals heated for long periods at higher temperatures. The decomposed parts are opaque and changes in the optical properties were never noted.

our direct determinations, the transition temperature is 45.3° on cooling and 47.8° on heating. As KNO_3 is added the transition temperature is lowered to 33.5°C for $(\text{NH}_4)_{0.75}\text{K}_{0.25}\text{NO}_3$ (see LEONE, 1970).

c) Crystallographic relations in the phase transitions

In disagreement with the observations of AMOROS and CANUT (1962) who state that $[100]$ of III approx. corresponds with $[100]$ of IV and $[010]$ and $[100]$ of III are approx. the diagonals of the rectangle formed by $[010]$ and $[001]$ of form IV, we found that the crystallographic orientation relations in the transitions III–IV and II–III are rather complex, but not random. 45 successive $\text{III} \rightleftharpoons \text{IV}$ transitions were made in humid crystals.

The behaviour in the transition II–III is somewhat more regular. In 50% of the transformations the c_{II} axis is inclined in one of the principal planes of III with the c_{III} axis. The most frequent inclination is $20\text{--}30^\circ$.

In the IV–II transition, in agreement with the above authors we also found that this transformation is a single crystal transition where the optic normal Y_{IV} (c-axis) is replaced by the optic axis of II (c-axis) (WALLERANT, 1906; SHINNAKA, 1956 and AMOROS and coworkers 1958, 1962). The reverse transition however produces polysynthetic twinning in the crystals of phase IV. The twinning is noted by the crosshatched appearance of the transformed crystals of IV, given by the contact faces (110). A peculiar interference figure is observed, exhibiting the isogyres of two different crystal individuals (figs. 4 and 5).

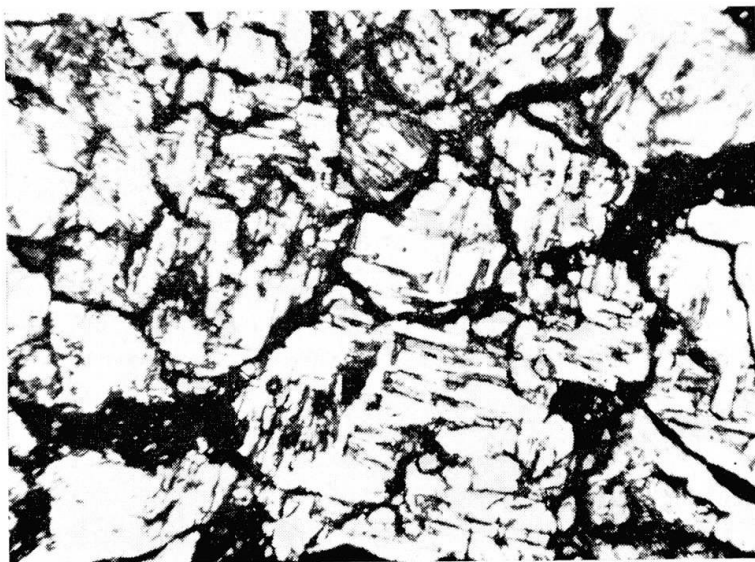
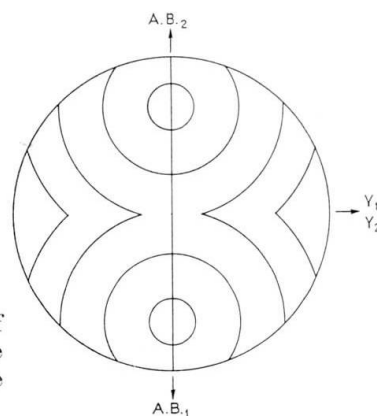


Fig. 4. Twinned crystal of NH_4NO_3 IV in the section perpendicular to Y . The contact planes of the multiple twinning (110) are seen.

Fig. 5. Peculiar interference figure, observed on (110) of polysynthetic transformation twins of NH_4NO_3 IV. The optic normal of both individuals lie parallel, their acute bisectrices at 90° from each other.



The orientation of the twins is: $c_{IV}-c_{II}$, and alternating $a_{II}-a_{IV}$ or $a_{II}-b_{IV}$.

The behaviour of the crystals seems quite reasonable if the structure proposed by SHINAKA (1959) is considered. One may also refer to AMOROS and BANERJEE (1960). It can be seen, by comparing the structures, that the twinned crystals of IV have the pseudosymmetry of phase II due to the multiple twinning. The finer the twinning, the larger the percentage of groups of intermediate positions along the contact planes of the twin individuals, related to the total volume of the crystal. Thus by finer twinning the crystal approaches a symmetry similar to that of II. The considerations given here on twinning are similar to comments on transformation twins in feldspars by LAVES (1950) and GOLDSMITH and LAVES (1961).

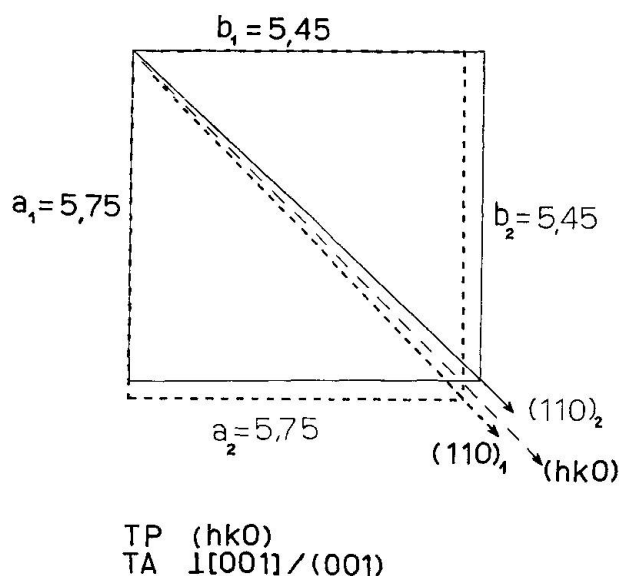


Fig. 6. Schematic drawing of the polysynthetic transformation twins. The crystallographic c -axes of both individuals are parallel. The drawing shows the deformation along the composition plane due to the superposition of the a and b axes of both individuals. It is also seen that the resulting pseudosymmetry is quadratic, corresponding to modification II. The irrational twinning plane $(hk0)$ is also the composition plane. It is the (110) plane of the pseudotetragonal twinned crystal.

DISCUSSION AND CONCLUSIONS

a) Nuclei or twins?

Many discussions exist in the literature on the rather peculiar behaviour of the NH_4NO_3 transitions. To a considerable extent it depends on the history of the samples presenting the typical behaviour of phase transitions with "memory". In table 2 the behaviour of samples with a different history is given. Our own observations differ from those of TANAKA and FUKUYAMA (1953) and AMOROS and CANUT (1962) in several aspects (compare papers quoted above). EVERETT and WATSON (1956) have tried to find an explanation for the memory phenomenon in the III-IV transition. They admit the existence of nuclei of one phase persisting, after the transition, in the other phase (e.g. nuclei of III in IV). These authors further elaborate upon the description of the nuclei, to the extent of giving details on their probable shape and size. Their conclusions are based on surface-free energy considerations.

The term nuclei is also used by SHINNAKA (1956). It could be simply employed as meaning "active centers" in the crystal, favouring the appearance of a certain phase. We would not disagree with such a definition. The term "nuclei" as employed by EVERETT and WATSON however means "unconverted regions of the original (and now unstable) phase" . . . "trapped in pockets formed by the meeting of the growth boundaries of the new phase, which has spread out from a number of scattered nuclei."

From the present study it seems highly improbable that considerations based on the continuous properties of the crystals can explain the behaviour of these phase transitions. The role of the molecular distribution in the crystal lattice and the importance of polysynthetic transformation twins must be taken into account. The importance of diffusion in these crystals, particularly when they are not perfectly dry seems also to be highly significant. Ion diffusion even in dry samples is considerable (see LEONE, 1970, this volume). In humid crystals it has in no case been possible to maintain unstable crystals in the presence of the stable phase. In a microscope slide it is observed that as soon as one crystal of II', for example, transforms into the stable form III, the remaining crystals of II' start dissolving and the now stable crystals grow rapidly at the expense of the latter. This happens even when both crystals are at the opposite ends of the slide. In rather dry crystals, those in contact with each other will usually transform in the same way. In no case has it been possible to maintain minute amounts of the unstable crystals in the presence of the stable ones if the samples were humid. Recrystallization in these crystals is very rapid. Idiomorphic crystals grow in short periods of time from irregular crystal aggregates (see also LEONE, 1970, this volume, fig. 3). It is therefore highly improbable that in the presence of saturated solution (working conditions of EVERETT and WATSON) residua of any shape could be maintained for an appreciable length of time in the presence of the stable phase.

Our present observations favour the possibility that polysynthetic transformation twin formation preserves the pseudosymmetry of the original crystal phase and can therefore account for the behaviour of the samples. In the transition IV-II' this is illustrated in fig. 6. The multiple twins of IV have the pseudosymmetry of the original crystals II. In the transition III-IV a similar process seems to occur, but it would be more complicated.

b) Influence of the history of the samples and other factors affecting the different phase transitions in the temperature range 15–90°C

The behaviour of the samples of NH_4NO_3 of modifications II', III and IV and their phase transitions have been studied by several authors: WALLERANT (1905), EARLY and LOWRY (1919), BOWEN (1926), HENDRICKS, POSNJAK and KRACEK (1932), TANAKA and FUKUYAMA (1953) SHINNAKA (1956), AMOROS,

ALONSO and CANUT (1958), THÉORÊT and SANDORFY (1963), M. DE SÁENZ, AMONINI and PRESA (1964), on related transformations KENNEDY and PATTERSON (1965) etc.

Most authors are surprised at the widely differing transformation speeds between samples prepared under somewhat dissimilar conditions or with a different thermal history. In fact, the time required to complete transformations varies, according to our observations, from more than 12 months to a few minutes. These observations should also be born in mind when dealing with hysteresis phenomena related to this type of crystal.

The main factors affecting these phase transformations are:

1. Presence of active sites in the crystal lattice. That is, crystallographically non-equilibrium sites such as surfaces, edges, corners, cracks, cleavages and slipping planes, twinning contact planes, grain boundaries or any altered lattice layers, due to misfit at the interface between two lattices, foreign inclusions etc.

2. Mobility of NO_3 ions. The most mobile ions are certainly located at the active sites mentioned above. Ion mobility is increased by increasing temperature.

3. Possibilities of recrystallization are increased mainly by the presence of the solution even in minute amounts. The stable phase can form by solution and reprecipitation. The stable, less soluble form crystallizes from the saturated solution, while the more soluble unstable phase dissolves until the transformation is complete.

4. Free transition energy increases with rising temperature differences from the equilibrium temperature and by non-equilibrium crystallographic ion distribution (active lattice sites).

5. Influence of oriented growth: pseudosymmetry due to transformation twinning and epitaxial overgrowth. (Study in progress.)

6. Ease of crystallization of the stable modification under the given conditions (compare GOLDSMITH, 1955).

Although these features do not give a quantitative explanation for the behaviour of these phase transitions they may represent a general scheme usually followed by them.

Finally, a practical example will be discussed: let us consider for instance crystals of modification IV heated into the stability range of III, below the IV-II' transition point. The following observations are made:

- a) Small crystals transform more easily than large ones and residual microcrystalline crusts enhance the transformations of the latter. Due to such a difference in size, transformation velocity changes so much that hardly any noticeable change occurs in several millimeter-large, rather perfect crystals whereas microcrystalline aggregates transform in a few days or weeks.

b) Previously transformed crystals are usually cracked and appear mosaic or twinned. They transform more easily than crystals that never had before. By means of about 10 successive transformations the time can be reduced from several months to a few minutes.

c) Perfectly dry crystals transform only very sluggishly, if at all, into phase III. (The crystals called here "perfectly dry" were dried for several weeks over silica gel and later for about one month over P_2O_5 . Longer drying did not change their behaviour.) Below 50° it is easy to maintain crystals for about 8 months above the transformation temperature without noting any transformation. THÉORÊT and SANDORFY (1964) were not able to transform their samples dried in vacuum into modification III at all. In a few cases, when our samples transformed after very long annealing, this may be due to some contamination with humidity which is very difficult to avoid during manipulations repeated so many times.

d) Crystal seeds of the stable modification increase very considerably the speed of transformation. Once the transition starts at one point it extends in a few minutes over the whole crystal. In the presence of the saturated solution, seeds cause the transformation of the unstable phase by dissolution and reprecipitation.

e) Transformations occur more rapidly at higher temperatures within the established temperature range if the formation of the rather complex structure of phase III is involved. So transformation $IV \rightarrow III$ may require three months at $33^\circ C$ but only half an hour at 40° . It is a common fact that the greater ion mobility at higher temperatures stimulates the formation of rather complex crystal structures, even if they belong to the "low temperature" variety of the substance.

REFERENCES

- AMOROS, J. L., ALONSO, P. and CANUT, M. L. (1958): Transformaciones polimorfas en monocristales II. Transición $IV-II$ (84°) del nitrato amónico y forma metaestable II' (55°). Bol. Real Soc. Esp. Hist. Nat. *56*, 77-91.
- AMOROS, J. L. and BANERJEE, R. L. (1960): El mecanismo de la transición $IV-II$ en el nitrato amónico. Bol. Real Soc. Esp. Hist. Nat. *58*, 165-180.
- AMOROS, J. L. and CANUT, M. L. (1962): El polimorfismo del nitrato amónico. Bol. Real Soc. Esp. Hist. Nat. *60*, 15-40.
- BEHN, U. (1908): On the polymorphic changes of ammonium nitrate. Proc. Roy. Soc. (London). A *80*, 444-457.
- BOWEN, N. L. (1926): Properties of ammonium nitrate. I. A metastable inversion in ammonium nitrate. J. Phys. Chem. *30*, 721-725.
- BRIDGMAN, P. W. (1916): Polymorphic changes under pressure of the univalent nitrates. Proc. Amer. Acad. Arts Sci. *51*, 581-625.

- EARLY, R. G. and LOWRY, T. M. (1919): The properties of ammonium nitrate. Part I. The freezing point and the transition temperatures. *Jour. Chem. Soc. London* 65, 1387–1404.
- EVERETT, R. G. and WATSON, A. E. P. (1956): Nucleation phenomena in the 32° transition of ammonium nitrate. *Tercera Reunion Internacional sobre Reactividad de los sólidos* (Madrid), 301–319.
- GOLDSMITH, J. R. (1953): A “simplexity principle” and its relations to “ease” of crystallization. *J. Geol.* 61, 439–451.
- GOODWIN, S. B. and WHETSTONE, J. (1947): The crystal structure of ammonium nitrate III and atomic scattering factors in ionic crystals. *J. Chem. Soc.*, 1455–1461.
- HENDRICKS, S. B., DEMING, W. E. and JEFFERSON, M. E. (1933): The refractive indices of ammonium nitrate. *Z. Krist.* 85, 143–155.
- HENDRICKS, S. B., POSNJAK, E. and KRACEK, F. C. (1932): Molecular rotation in the solid state. The variation of the crystal structure of ammonium nitrate with temperature. *J. Amer. Chem. Soc.* 54, 2766–2786.
- HÖVI, V., PÖYHÖNEN, J. and PAALASSALO, P. (1960): Anomalous thermal expansion of NH_4NO_3 at 125.8° and 84.1°. *Ann. Acad. Sci. Fennicae Ser. A VI Physica* 42, 3–11.
- KENNEDY, S. W. and PATTERSON, J. H. (1965): Mechanisms of structure transformations in thallos nitrate crystals. *Proc. Roy. Soc. London. A* (283), 498–508.
- LAVES, F. (1950): Lattice and twinning of microcline and other potash feldspars. *J. Geol.* 58, 548–571.
- LAVES, F. and GOLDSMITH, J. R. (1961): Polymorphism, order, disorder, diffusion and confusion in the feldspars. *Inst. Lucas Mallada Cursos y Conferencias* (Madrid), Fasc. VIII, 71–80.
- LEONE, R. (1970): Note on the phase transition II'–IV in the ammonium rich end of the mixed crystal series $(\text{NH}_4)_x\text{K}_{1-x}\text{NO}_3$. *Schweiz. Mineral. Petrogr. Mitt.* 50/2, 221–225.
- SÁENZ, I. MICHAELIS de, AMONINI, N. and PRESA, S. (1964): Changes of the specific gravity during the gradual III–IV transition. *Z. Phys. Chem. Neue Folge* 43, 119–122.
- SÁENZ, I. MICHAELIS and TESSORE, J. C. (1968): A directional constant derived from the optical indicatrix and its application in quantitative conoscopy. *Schweiz. Min. Petr. Mitt.* 48, 471–484.
- SHINAKA, Y. (1956): On the metastable transition and the crystal structure of ammonium nitrate (tetragonal modification). *Jour. Phys. Soc. Japan* 11, 393–396.
- (1959): X-ray study on molecular rotation in tetragonal ammonium nitrate. *Jour. Phys. Soc. Japan* 14, 1707–1716.
- TANAKA, K. and FUKUYAMA, I. (1953): On the metastable phase change of ammonium nitrate. *J. Phys. Soc. Japan* 8, 428–429.
- TESSORE, J. C. (1965): Transformation II'–IV del NH_4NO_3 (unpublished).
- THÉORÊT, A. and SANDORFY, C. (1964): Infrared spectra and crystalline phase transitions of ammonium nitrate. *Canadian J. Chem.* 42, 57–62.
- WALLERANT, F. (1906): Sur le polymorphisme et l'isomorphisme des azotates alcalins. *Bull. Soc. Min. France* 28, 311–374.