THE TRANSITIONS IN PHASES II—III—IV IN HIGH PURITY AMMONIUM NITRATE*

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The phase changes in high-purity ammonium nitrate were studied by a differential thermal analysis (DTA) apparatus designed for constant heating and cooling rates and continuous cycling for ~3-gram samples. On the basis of DTA and X-ray diffraction data very consistent behavior is observed. Phase IV → III transformation on heating in the range 43° to 51° and Phase II → IV transformation on cooling in the range 49° to 53° are demonstrated. The III → II transition at about 86° is seen with repeated temperature cycling. This repeatable behavior not consistently seen by investigators using other techniques is believed to be due to the high purity material and constant heating and cooling rates.

The literature on the thermal behavior of NH_4NO_3 (ammonium nitrate) is voluminous; and although it extends back for more than 50 years, it still leaves the reader without a statement of the unambiguous phase relations for the material. Each investigator has reported on a special set of conditions, and the reader has the dilemma of deciding whether the anomalies described are related to the special conditions imposed by the experimenter, are the peculiar characteristics of the salt, or are both.

The crystalline modification of NH_4NO_3 are given as follows [1]:

Phase I	cubic	169.6° to 125.2°
Phase II	tetragonal	125.2° to 84.2°
Phase III	orthorhombic	84.2° to 32.1°
Phase IV	orthorhombic	32.1° to −16°
Phase V	tetragonal	below −16°
Phase VI		above 160° at pressure >9000 kg/cm^2
Phase VII		below −170°

The fusion temperature and the 125.2° temperature inflections are unambiguous, and Phases VI and VII are not in the scope of this paper. The behavior of the material at 32° and 85° appears to be irregular.

Hendricks et al. [2] noted a difference in behavior between thick and thin samples in the 32° to 85° range. These samples had been prepared by melting a small amount of material on a microscope slide and pressing it down with a cover glass. Thin samples showed the 32° and 85° transitions on heating; but when cooling was begun from above 125°, the 32° and 85° transitions were not seen. Instead, a transition at 50° replaced both of these. Hendricks states that for thick slides the 50° "metastable inversion" will revert a limited number of times, but that for thin slides this reversal can persist almost indefinitely. His investigation did not attempt to study the effect of variable heating and cooling rates.

Volfkovich et al. [3] used the same technique. For a 1- to 2-milligram sample on a slide at cooling rates of 1° to 1.5°/min, the normal Phases I through IV were obtained. When the cooling rate exceeded 2°/min, again the 32° and 85° transition points were replaced by the one at 50°.

Theoret and Sandorfy [1] sublimed reagent grade NH_4NO_3 at 0.1 torr and obtained infrared spectra on reasonably thin samples at given temperatures at a cooling rate of 1°/min.

Other investigators [4—6] have studied the effect of the presence of water on thermal transformations in ammonium nitrate. Brown and McLaren [4] observed that the Phase IV ⇄ III transitions involve drastic structural changes, and therefore do not occur in the dry solid. Their observations further indicate that the Phase II → III transition also involves a severe structural change and takes place only in the presence of moisture. Hendricks et al., and Brown and McLaren have suggested that these transitions take place by a dissolution and recrystallization process.

In order to obtain the given transitions, it would appear from the literature that samples must be small and must be cooled at rates of 1.5°/min or less. However, none of these papers gives the analysis of the salt used, and they rarely report repetition of the events by cycling.

The purpose of this paper is to report thermal behavior by differential thermal analysis (DTA) of high-purity material in vacuum with a controlled heating and cooling rate and with cycling. The solid state changes are compared with the data reported by the U.S. National Bureau of Standards [7]. In addition, X-ray diffraction results which support the observations obtained from DTA are given.

Experimental procedure

The DTA equipment incorporated automatic cycling between adjustable limits, proportioning features for a constant heating and cooling rate using refrigeration and heating as needed. The automatic cycling capability was considered important because both reproducibility of the testing and relevance of thermal history could be determined.

The recording apparatus consisted of a Leeds and Northrop (L & N) threepen automatic ranging millivoltmeter, a 2-millivolt display and automatic ranging to ±20 millivolts using two pens.

The differential temperature was recorded by the third pen, whose range was ±0.6 millivolt with zero-centering, amplified by an L & N microvolt amplifier. Three (platinum sheathed) iron-constantan thermocouples were used, one to the sample for the absolute temperature, one to the Al_2O_3 (aluminum oxide) reference, and the third to the temperature controller.

The sample holder was a three-hole capped brass cylinder. Platinum crucibles placed in the 7/8-inch cavities contained the sample, the reference Al_2O_3 and the Al_2O_3 for the temperature control thermocouple.
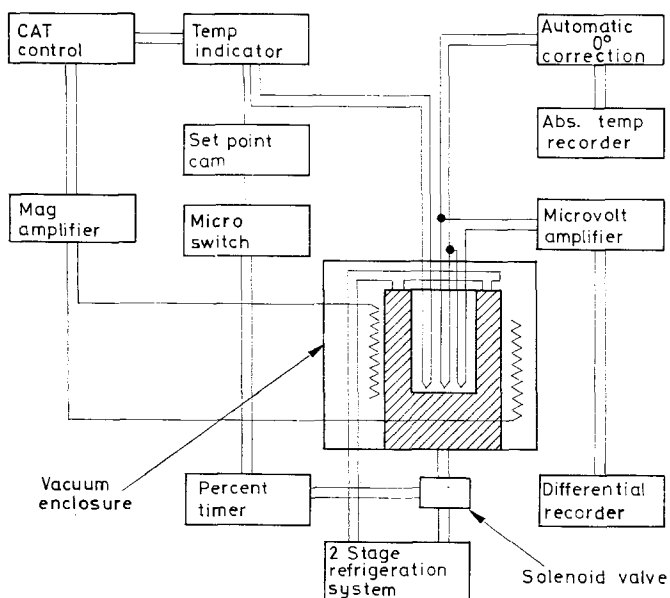

Fig. 1. Schematic representation of DTA unit

The cap was drilled to accommodate Teflon bushings which centered the thermocouples in the platinum crucibles. The thermocouple "beads" were positioned $^1/_4$ inch above the bottom of the crucible to approximate a spherical geometry when filled with the sample. The cell itself was 10 inches tall and was made of a double walled cylinder within which Freon 13 circulated.

Around the outside of the cell were an aluminized glass reflector and a resistance wire heater wrapped on glass cloth. The whole system was mounted on a base plate with ceramic feedthroughs for thermocouples, power leads and refrigerant lines. A bell-jar cover permitted operation in a vacuum to prevent condensation of moisture at low temperature.

The furnace was controlled by an L & N Series 60 Current Adjusting Type (CAT) control unit with a magnetic amplifier. Figure 1 shows a schematic representation of all of the components.
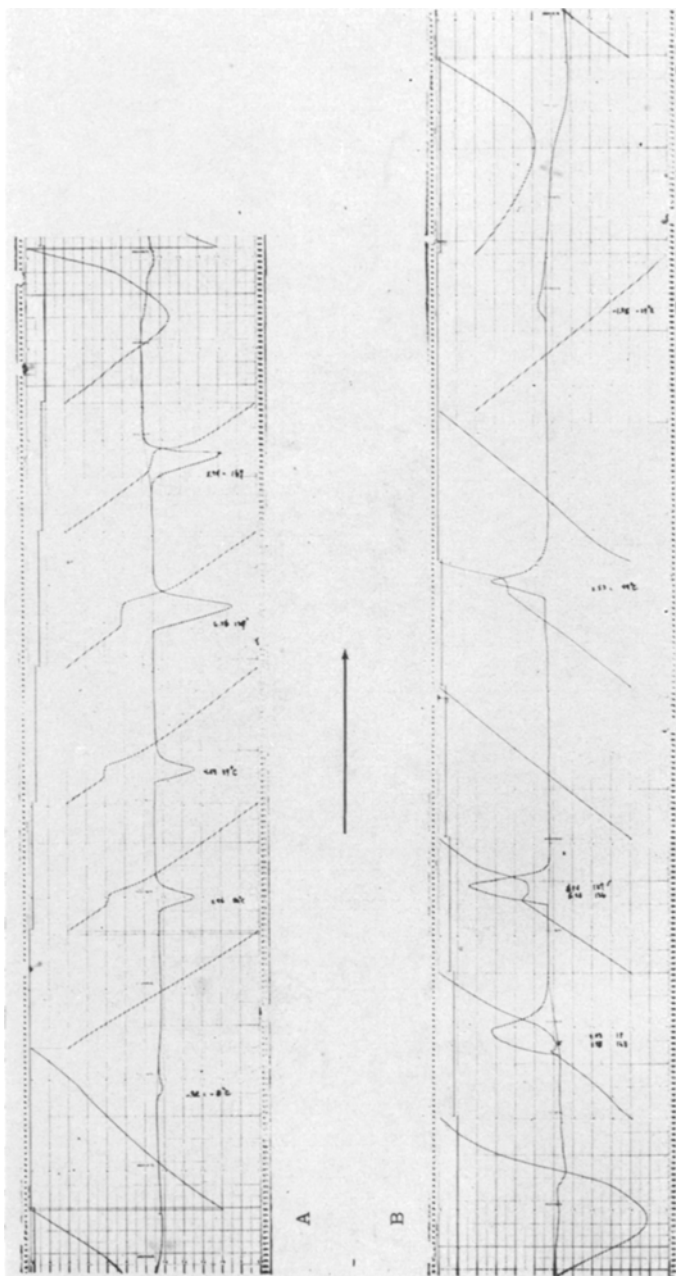
Fig. 2. Working DTA record (normally 10½-inch wide). Top of B fits bottom of A. Arrow indicates direction of travel

Figure 2 is a reproduction (reduced) of the DTA record for a portion of Table 3; the cooling portion of Cycle 1 and the heating portion of Cycle 2 are shown from B to A.

The chart shows three lines; the range index at the extreme left of each strip and the second line, the record of the absolute temperature. Each vertical subdivision (most clearly viewed at the bottom of A) is equal to 5 minutes. The third line records the amplified differential between the sample and the reference and is the continuous line through the zero center and shows the events as displacements when they occur.

The X-ray diffraction measurements were made on a Norelco X-ray diffractometer. Copper K_{α} radiation was used and the sample was heated with a focused heat source [8]. To minimize contamination of the sample, it was in contact only with glass in the sample holder. Nitrogen was allowed to flow over the samples during the measurements to avoid the effects of water. The sample was held at constant temperature for 20 minutes before the diffraction scan was initiated. The phases present in the sample were determined by comparing the obtained

Table 1

Spectrochemical analyses of NH_4NO_3 residues in ppm

Element	Fisher reagent grade NH_4NO_3	Specially prepared and used in this study
Ca	0.1—	0.05—0.1
Sr	< 0.05	[a]N < 0.05
Ba	0.1—0.5	N < 0.1
Be	N < 0.05	< 0.05
B	N < 0.05	N < 0.05
Mg	≈ 0.05	< 0.05
Al	1—2	N < 0.1
Si	0.1—0.5	0.1—0.5
Cr	0.1—0.5	N < 0.05
Fe	0.5—1.0	< 0.1
Ni	0.05—0.1	N < 0.05
Zn	1—2	N < 0.5
Cu	0.05—0.1	0.5—0.1
Ag	< 0.05	N < 0.05
Pt[b]	10—100 μg	10—100 μg
	N < 0.1	N < 0.1
Na	0.2—1	< 0.05
K	0.2—1	N < 0.2
Na[c]	0.9	0.09

Notes:

[a]N < indicates not detected at the indicated concentration level.

[b]The attack on platinum by NH_4NO_3 provided this level. The second value is the platinum value established from a separate evaporation in BN crucibles.

[c]Sodium analyses by neutron activation on separate samples.

diffraction profile with patterns given in the ASTM file of powder diffraction data for the various phases of NH_4NO_3.

The material used in this study was prepared with the goal of eliminating all possible impurities. The preparations included crystallization from solutions of purified HNO_3 and anhydrous NH_3. Crystallized material was exposed only to Teflon and a platinum spatula.

The determination of trace elements was provided by an evaporation technique and an analysis of the residue by emission spectroscopy. The analysis is shown in Table 1. Note that approximately 10 ppm of metallics, Ca, Ba, Al, Cr, Fe, Ni, Zn, Na and K, could be present in the reagent material and less than 1 ppm in the high-purity material.

Results

The DTA data obtained from ~3-gram samples of purified NH_4NO_3 at heating and cooling rates of 0.7°/min are shown in Tables 2 and 3.

Tables 2 and 3 are duplicate series of cycles on different portions of the purified material and are included to show the repetition of the temperatures of events on different samples.

Table 2

Thermal events from DTA II[a]

Cycle	Heating	Cooling	IV→III Heating	IV←II Cooling	III→II Heating	Cooling	II→I Heating	II←I Cooling	Heating	Cooling
1	start		43		86		127		168	
		—29		50				127		169
2	—8		47		87		128		168	
		—29		50				127		169
3	—9		47		87		128		168	
		—30		49				127		169
4	—8		43		88		128		168	
		—29		49				127		169
5		— loss of power	46		87		128		168	
				49				127		169

[a]Temperatures in degrees centigrade.

Table 4 shows the results of the X-ray diffraction measurements. The temperatures at which the diffraction scans were obtained were chosen to straddle the temperature events in question. The present DTA work revealed transitions at temperatures that were in conflict with previously reported transition temperatures. For example, a 32° transition was not observed with DTA but 50° transitions were

Table 3

Thermal events from DTA III[a]

Cycle	Event		Event		Event		Event		Event	
	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling
1	start	—21	51	49	87.5		126	127.5	168	170
2	—7	—29	47	50	86		126	125	167	168.5
3	—9	—29	49	51	86		126	126	166	168
4	—8	—29	44	52	86		126	126	166	169
5	—8	—29	48	53	86		126	126	165	168.5
6	—9	—29	50	53	86		126	126	166	169

[a] Tabulation of events throughout six cycles of heating and cooling from —60° to +200°

observed. Therefore, it was reasonable to examine the phases present at a temperature between 32° and 50° and also at a temperature between 50° and 84.2°. In addition, cycling samples to progressively higher maximum temperatures demonstrated the effect of thermal history on the transition temperatures.

Discussion of results

DTA results

Transitions at 125° and 169° were found as expected; however, there are several apparent anomalies shown in Tables 2 and 3. The Phase III → II transition is seen on heating at 86° to 88° in all cycles. The area under the differential temperature-time curve does not change with repeated cycling. By DTA, Brown and McLaren found that in dry material the Phase III → II transition peak diminished with repeated cycling but they did not report that it disappeared completely. However, Hsu [9], in a rather complete review of the transformations in ammonium nitrate, credited Brown and McLaren with giving sufficient evidence to show that transitions IV → III and III → II only take place in the presence of moisture. This is a step further than Brown and McLaren actually went. They stated that the Phase II → III transition required the presence of moisture but did not go so far as to state unequivocally that the Phase III → II transition required the presence of moisture.

Table 4

X-ray diffraction results

Sample 1

	Temperature (°C)	Phases
Heating	24	IV
	39	IV
	66 (max)	III & IV[a]
Cooling	39	III & IV
	24	III & IV

Sample 2

	Temperature (°C)	Phases
Heating	25	IV
	40	IV
	65	III
	111	II
	120 (max)	
Cooling	111	II
	66	III
	40	III
	25	III
	25[b]	IV

Sample 3

	Temperature (°C)	Phases
Cycle 1		
Heating	23	IV
	39	IV
	65	III & IV
	110	II & III
	140	I & II
	168 (max; not melted)	
Cooling	140	I & II
	110	I & II
	66	II
	42	IV
	24	IV
Cycle 2		
Heating	23	IV
	180 (max, melted)	Not measured
Cooling	140	I & II
	110	II
	65	II
	42	IV
	24	IV

Sample 4

	Temperature (°C)	Phases
Cycle 1		
Heating	24	IV
	42	IV
	64	III & IV
	210	II
	140	I & II
	(max)	
Cooling	109	II
	66	II
	41	IV
	24	IV
Cycle 2		
Heating	23	IV
	40	IV
	66	III & IV
	110	II
Cycle 3		
Heating	24	IV
	140 (max)	Not measured
	110	I & II
Cooling	65	II
	40	IV
	26	IV

[a]First phase mentioned is the predominant one.
[b]The sample remained as Phase III upon cooling to 25°. It was stirred in place and then another diffraction scan was obtained. The sample had then transformed to Phase IV. It is possible that moisture was introduced during the stirring since the system was open to laboratory atmosphere during this operation.

From DTA data alone it must be deduced that the transformations at approximately 50° reported in Tables 2 and 3 and shown graphically on the DTA record in Fig. 2 clearly are structurally different on heating and on cooling. The electrical conductance data of Brown and McLaren and the evidence from ultraviolet absorption obtained by Cleaver, Rhodes and Ubbelohde [11] support the premise. The destruction of Phase III nucleation sites by "heat treatment" as proposed by Tanaka and Fukuyama [5] and demonstrated by Shinnaka [6] in the Phase IV ⇄ II transition in dry ammonium nitrate obviously does not occur under the conditions of these experiments. X-ray diffraction data offer evidence which substantiates this premise and will be presented in that part of the discussion.

To evaluate the effect of sample size, 40- and 16-milligram samples were run through a single cycle in a separate semimicro DTA apparatus [11]. Confirming data were obtained and showed the transitions at 50° and 86° on heating and the absence of the Phase II → III transition on cooling but showed the presence of the 50° event. A 32° event was seen neither in this work nor in Northrop's [11] on this purity material.

During the course of the DTA studies of high-purity material, a run on an undried sample of Fisher certified reagent grade ammonium nitrate was made under the same conditions described for the high-purity samples. The results are not tabulated here but the salient feature observed was the presence of a transition at 36° to 41° on heating and of transitions at 48° to 50° on cooling through five cycles. X-ray diffraction patterns obtained from this material at 25° and 42° confirmed that the Phase IV → III transition had occurred on material containing this level of impurities.

Temperature cycling was continuous and under vacuum, and it is reasonable to expect that complete drying would have been accomplished after one, or at most, two cycles. The results suggest that water may not be the only foreign substance (i.e., impurity) which permits the Phase IV ⇄ III transitions.

X-ray diffraction results

The transitions observed by DTA are in agreement with the behavior observed in X-ray diffraction studies by Amorós and Canut [12]. Since an analysis of the NH_4NO_3 used in their work was not given, X-ray diffraction measurements were made to determine whether or not the phase above and below transition temperatures in question were the same in the high purity material used for DTA as those reported by Amorós and Canut.

No attempt was made to determine exact transition temperatures. In all cycles, both upon heating and cooling, a transition at 32° did not occur. However, in Samples 1, 2, and Cycle 1 of Sample 3 the Phase IV → III transition did appear on heating between approximately 39° and 66°.

Sample 4, which was stored for several months in a vacuum desiccator was examined to confirm the consistent behavior of the transformations of interest. Before X-ray diffraction patterns were taken the sample was placed in a vacuum

oven at 105° for a short time and allowed to cool to 70° and held at that temperature for four days. Cycles 1 and 3 show repetition of II → IV on cooling.

These results verify that a IV → III transformation takes place on heating and explain the consistent occurrence of the III → II transition observed by both DTA and X-ray diffraction. Taken together, both methods clearly define the transformations at approximately 50° to be IV → III on heating and II → IV on cooling.

Phase III did not appear in Sample 3, Cycles 1 and 2, upon cooling after the samples had been heated to maximum temperatures of 168° and 180°, respectively. Rather, Phase II transformed directly to Phase IV at a temperature between approximately 66° and 42°. These results agree with the present DTA results where a transition was not observed at 86° upon cooling. Sample 2 did show a transition of Phase II to Phase III between 111° and 66° upon cooling. However, this sample was heated to a maximum temperature of 120°. Hendricks et al. found that when cooled from below 125°, the Phase II to Phase III transition was observed at 85°.

The results shown in Table 4 indicate the presence of two phases in temperature regions where only one phase should be stable. Coexistent phases have been reported by other investigators [1, 12]. However, the DTA peaks were sharp and thus did not indicate slow transformations. This discrepancy is explained by the fact that the heating and cooling rates used in the DTA apparatus were 0.7°/min while heating and cooling rates for the furnace on the X-ray diffractometer were at least ten times faster and these rates were not controlled. Even though the samples were held at temperature for 20 minutes before diffraction traces were taken, it is possible that longer holding times or slower heating and cooling rates would have resulted in complete transformations. In all cases where two phases were present, the diffraction peaks from the stable phase were predominant, which indicates that the sample was largely composed of the stable phase.

Conclusions

DTA evidence obtained under the conditions of (1) high purity, (2) constant heating and cooling rates, (3) cycling, and (4) a vacuum environment and verification by X-ray diffraction indicate the following:
1. The Phase IV → III transformation (heating) occurs in the range 43° to 51° rather than at 32° as commonly reported.
2. The Phase III → II transition is obtained consistently at approximately 86°.
3. The Phase II → IV transformation (cooling) occurs in the range 49° to 53°.
4. The transformations at 125° and 169° are unambiguous.
5. The temperatures of transformation are independent of sample size.

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RÉSUMÉ — On a étudié les changements de phase du nitrate d'ammonium de haute pureté à l'aide d'un analyseur thermique différentiel conçu pour réaliser des vitesses d'échauffement et de refroidissement constantes ainsi que des cycles thermiques avec environ 3 g d'échantillon. Les résultats d'ATD et de diffraction X indiquent un comportement tout à fait constant. La tranformation de la phase IV en phase III se produit entre 43 et 51° à l'échauffement et celle de la phase II en phase IV entre 49 et 53° au refroidissement. On observe la transition III → II à 86° environ, avec des cycles thermiques répétés. On explique ce comportement bien défini, qui n'a pas été toujours remarqué par les chercheurs utilisant d'autres techniques, par l'emploi d'un échantillon de haute pureté et de vitesses d'échauffement et de refroidissement constantes.

ZUSAMMENFASSUNG — Die Phasenübergänge von hochreinem Ammoniumnitrat wurden mit Hilfe einer differentialthermoanalytischen Apparatur mit konstanten Aufheiz- und Abkühlungsgeschwindigkeiten und mit kontinuierlichen Temperaturzyklen für ungefähr 3 g betragende Proben geprüft. Diese Untersuchung, weiterhin röntgendiffraktometrische Aufnahmen zeigten ein sehr übereinstimmendes Verhalten. Die Phasenumwandlung IV → III erfolgte beim Erhitzen zwischen 43—51°, die Phasenumwandlung II → IV beim Abkühlen zwischen 49—53°. Die Umwandlung III → II bei ungefähr 86° wurde im wiederholenden Temperaturzyklus beobachtet. Dieses reproduzierbare Verhalten, welches nicht mit Untersuchungen durch andere Methoden übereinstimmt, wird der hohen Reinheit der Substanzen und den konstanten Aufheiz- und Abkühlungsgeschwindigkeiten zugeschrieben.

Резюме — Исследованы переходы фаз в нитрате аммония большой чистоты методом дифференциального термического анализа (ДТА). Установка, сконструированная для изучения перехода фаз, работает с постоянной скоростью нагревания и охлаждения в непрерывном цикле при количестве образца — 3 г. На основании данных ДТА и диффракции рентгеновских лучей обнаружено совместимое поведение. Показано превращение фазы IV→III при нагревании в области температуры 43—51° С и II—IV при охлаждении в области температуры 49—53° С. Превращение III→II наблюдалось около 86° С при повторном температурном цикле. В случае других методов исследования совместимое поведение не заметно и, видимо, присуще веществу высокой чистоты при постоянной скорости нагревания и охлаждения.