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THERMAL ANALYSIS OF DRY AMMONIUM NITRATE BY ENERGY DISPERSIVE X-RAY DIFFRACTION BETWEEN -70 AND 150^{o}C.

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ABSTRACT

Series of x-ray diffraction spectra were measured in 2^{o}C intervals, while ammonium nitrate was cycled between -70/80 and -70/150^{o}C. On cooling from 150^{o}C the phase transitions I/II/IV/V and, on heating, the same transitions in reverse order occurred as expected.

After heating the sample to 80^{o}C phase II changed simultaneously into the phases IV and V below 50^{o}C. Further cooling to -70^{o}C changed the part existing in phase IV into phase V. During the succeeding heating cycle an incomplete transition V/IV was followed by the transitions IV/II and V/II.

INTRODUCTION

Ammonium nitrate (AN) crystallizes in at least five different polymorphic forms at atmospheric pressure. The transitions between these phases lead to serious problems for the utilization of AN in certain applications. Thermal methods like DTA and DSC applied to AN left numerous ambiguities, which also include the phase changes of dry AN.

$$\mathrm{V} \underset{50-\ -29^{0}}{\overset{-8\ -\ 0^{0}}{\rightleftharpoons}} \mathrm{IV} \underset{44-53^{0}}{\overset{47-55^{0}}{\rightleftharpoons}} \mathrm{II} \overset{125^{0}}{\rightleftharpoons} \mathrm{I}$$

tetragonal orthorhomb. tetragonal cubic

Whereas the literature values are rather consistent about the phase change II/I , the data about the transitions in the range of 50^{o}C differ essentially. The differences relate to the transition temperatures reported from 47-55^{o}C on heating and from 53-44^{o}C on cooling and, much stronger, to the phases involved (ref.1-4)

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Recent structure determinations for the phases IV and II and thermal analysis work suggest a phase transition IV/II for dry AN on heating (ref.5-6).Different interpretations exist, however, about the cooling cycle. Brown and McLaren propose a phase sequence I/II/IV/V (ref.x). Seiyama interprets microscopic results as a phase change II/V (ref.4) and Nagatani suggests an intermediate phase V^* during a phase change $II/V^*/V$ (ref.3).

In our own investigation of the phase changes measuring series of angle dispersive x-ray diffraction patterns between 20 and 80°C we found that phase II changes simultaneously into the phases IV and V on cooling (ref.8)

Our present work tries to elucidate the transition paths of AN from phase I to phase V. Different temperature cycles were run with upper limits of 80 and 150°C respectively. Series of more than 300 diffraction spectra were measured in 2°C intervals, while the sample was heated or cooled continuously. The measured diffraction data reflect changes of the AN lattice e.g. by phase changes, avoiding the ambiguities of DTA and DSC.

For the evaluation a concept of forming difference spectra was developed (ref.7).These are obtained by subtracting corresponding channels of the digitalized spectra. The sum of the absolute values over all channels then correlates with the amount of change from one spectrum to the other. The difference procedure performed with neighboured spectra plotting of the sums against temperature yields a DTA-like curve. If, however, the difference spectra are formed with one constant spectrum, normally the first one, a TG-like curve results.

EXPERIMENTAL DETAILS

The diffraction spectra were measured with a tungsten tube and a Si(Li) semiconductor detector using an angle 2 theta of 10°. The detailed experimental setup was described elsewhere (ref.7)

Ammonium nitrate, reagent grade of Merck, dried for 3 days at 80°C under vacuum was used.

The series were run with the following temperature programs:
1. 20/ 80/-70/80 °C, 2. 20/-70/ 80/-70/ 80°C,
3. 20/150/-70/150°C, 4. 20/-70/150/-70/150°C.

The samples were heated and cooled,resp.,with 1 and 2°C/min. The spectra were measured at intervals of 2°C.

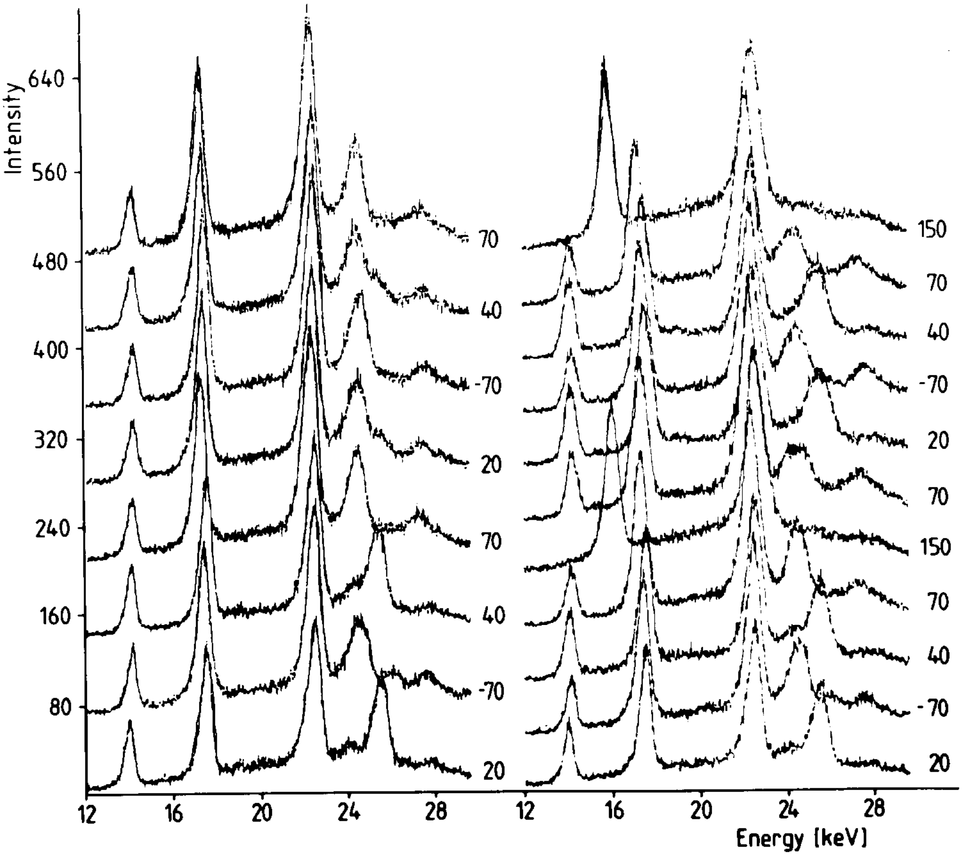

Fig. 1 Diffraction spectra after the transitions
left: series 2 cycled to 80°C
right: series 4 cycled to 150°C

RESULTS

The results are presented as selected x-ray spectra in fig.1 and as difference curves in fig.2-3, both from series 2 and 4. Fig. 2-3 contain the TG-like curves, which are obtained by forming difference spectra with the first spectrum in the series. The beginning of the series from 20 to -70°C as well as all DTA-like curves were omitted to keep the diagrams readable.

The difference curves were formed using the region from 24-27 keV of the spectra with the (200)- and (020)-peaks containing the interesting changes. The results are listed in tab.1.

TABLE 1

Phase changes detected in the difference curves (°C)

	V/IV	IV/II V/II	IV/II	II/I
ser.4	-63--39 ←	start		
	→ 3- 18		54-59	139-150
	-45--37		42-48	124-139 ←
	→ 3- 9		57-60	139-150
ser.2	-53--36 ←	start		
	→ -1- 14		50-54	
	-48--36	32-47	←	
	→ 5- 20	53-57		

DISCUSSION

The phases in dry ammonium nitrate appear in the order I/II/IV/V on cooling from 150°C. When the samples are heated to only 80°C, the transition II/IV is incomplete. The other part changes directly into phase V. On heating, the reverse transition order is observed in both cases.

The curve in fig 3 from the 150°C cycle shows clear steps, when transitions occur. In contrast the curve in fig. 2 contains only two distinct steps on heating to 80°C. Thereafter, the major part of the sample changes directly into phase V, which is not detected in the difference curve, as the spectra of the phases II and V are almost identical.

The parts of the sample changing into phase IV and V, however, are not constant. In series 1 with a higher percentage of phase IV the steps for the simultaneous transitions II/V and II/IV are more pronounced, as the spectrum of phase IV differs clearly from the phases II and V.

The transition temperatures in table 1 cannot be very accurate caused by the described difficulties to detect the steps and by the measurement interval of 2°C. Besides, especially the transitions including phase V are very sluggish. No attempt was made to improve the values, as the scope of this paper was to elucidate the transition paths and not the temperatures.

The phases involved in the transitions were identified by the original diffraction spectra. Fig 1 contains one characteristic

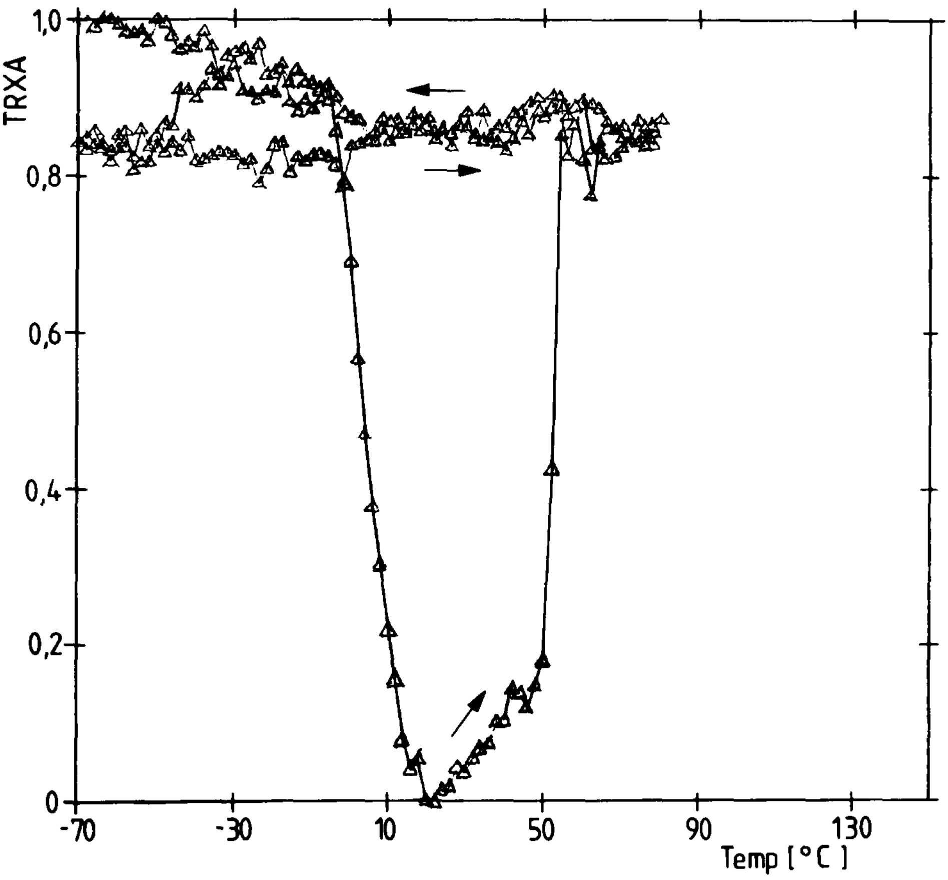

Fig. 2 Difference curve of series 2 cycled to 80^{o}C

spectrum after each transition starting with the first one at the bottom. It can be seen that in the 150^{o}C-cycle the spectra are all clearly different, whereas in the 80^{o}C-cycle the last five spectra are nearly the same..As already mentioned, this is,because the phases II and V are very similar, and indeed, cannot be easily distinguished by energy dispersive spectra. The differentiation was made by angle dispersive measurements (ref.8)

Peak fits were made to determine the intensities of the phases. When an incomplete transition occurs, the ratio of the phases IV and V is the same during cooling and succeeding heating. At low heating rates the percentage of phase IV increases because phases V slowly transforms into phase IV.

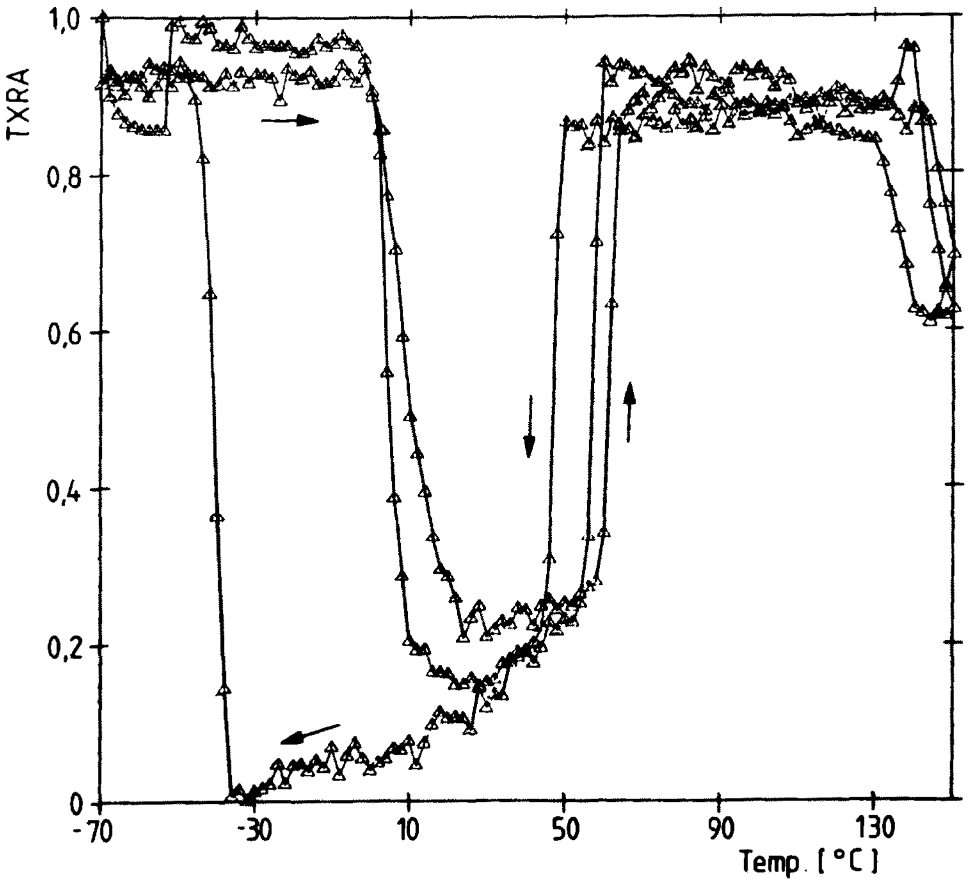

Fig. 3 Difference curve of series 4 cycled to 150^{0}C
Step nearest -70^{0}C was caused by the equipment.

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