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THERMAL ANALYSIS OF AMMONIUM NITRATE BY ENERGY-DISPERSIVE X-RAY DIFFRACTION

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Ammonium nitrate was heated and cooled in consecutive steps in a high temperature device mounted on a X-ray goniometer. Diffraction patterns were measured at each temperature, using a Si-Li detector together with a multichannel analyzer. The results strongly support the existence of a phase II'. They show that the phase change IV/III goes via a transition state similar to or consistent with phase II'.

A new approach was made to elucidate the numerous phase transitions of ammonium nitrate. Until now, thermal analysis of this salt has generally consisted in tracing the DTA or DSC curves of the substance [1, 2]. The diagrams showed the transitions by the inherent thermal effects. However, this could not elucidate clearly the rather complex behaviour of the substance.

The new concept consists in combining a high-temperature device on an X-ray goniometer with the energy-dispersive X-ray diffraction method. In such a combination, using a Si-Li detector together with a multichannel analyzer, a fast recording of the X-ray diffraction patterns is possible at various sample temperatures. The sample can be heated in consecutive steps or linearly with a low heating rate.

The stored patterns give direct information on the parameters of the actual lattice during the special experiments as a function of temperature. This allows a better insight into the transition mechanisms and into the whole lattice dynamics generally.

Experimental

The investigations were made with a Siemens Kristalloflex IV and a "Lihl" high-temperature device on a goniometer of type F. The Si-Li detector was combined with a NS 880 MCA of Tracor Northern.

The Kristalloflex was run with a tungsten tube, quadratic focus, 35 kV, 20 mA, providing continuum radiation. Collimator aperture was 1/2°, detector aperture 0.3 mm, and measuring time 100 and 200 sec.

With a goniometer angle 2ϑ of 10 degrees, a region free of interfering peaks is available between about 30 keV. Below 13 keV tungsten fluorescence peaks and at about 29 and 30 keV platinum diffraction peaks of the sample holder were visible. The samples were heated in consecutive steps. The temperatures were set manually by a controllable transformer. The obtained spectra were recorded on magnetic tape. The channel width was 40 eV. Three runs were made with different samples of ammonium nitrate (Merck, reagent grade). Sample 1 had been dried thoroughly, samples 2 and 3 were used in the moist state. During the run, samples 1 and 2 were heated up to 150°, while sample 3 was cycled between 20 and 110°.

Results

The results are presented in Tables 1–3. Selected diagrams from run 1 are shown in Fig. 1.

Table 1

Diffraction peaks of dry ammonium nitrate, in keV

°C	II/IV (001)	I (100)	II/IV (110)	I (110)	II/IV (111)	II/IV (200) / (020)	Mod.
20	14.40–56		17.96		23.08	26.12–24	IV
65	14.16–44		17.36–72		22.64–96	24.76–25.08	II
80	14.20–56		17.48–60		22.56–92	24.60–84	II
97	14.20–60		17.40–64		22.56–72	24.68–25.00	II
139		16.20		22.96			I
137		16.28–32		22.8–23.24			I
129		16.28–44	17.64		23.04–24	24.52–76	I+II
94			17.56		22.92–23.08	24.52–96	II
77			17.56		23.00	24.76–25.08	II
63	14.32–64		17.68		22.88–23.20	24.64–92	II
50	14.36		17.68		22.96–23.20	25.24–52	II
39	14.36		18.00		23.12–40	25.88	IV
20	14.40		18.04–08		23.32	26.08	IV

Table 2

Diffraction peaks of humid ammonium nitrate, in keV

°C	II/IV (001)	III (101)	I (100)	II/IV (110)	III (111)	III (120)	I/II/IV (110/111)	II/IV (200/020)	Mod.
20	14.52			18.20			23.32	26.35	IV
59	14.5	15.72		18.04		22.16		25.36 26.04	IV+III
59		15.84			18.36	21.08–21.96		24.76	III
97	14.4			17.72			23.04	24.9–25.3	II
129			16.32	17.76			23.1–3	25.4–6	I+II
138			16.40				23.25		I
150			16.40				23.35		I
122	14.4			17.05			22.70	25.04	II
52	14.6			17.72			22.84	25.2	II
40	14.4						23.04	26.36	IV
20	14.52			17.9			23.12	26.56	IV

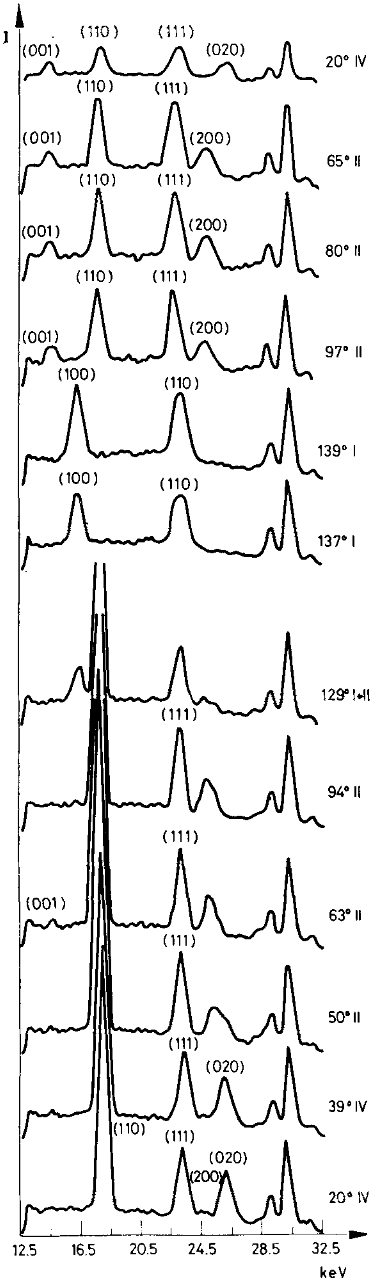

Fig. 1. Diffraction patterns of dry ammonium nitrate (series 1)

Table 3

Diffraction peaks of cycled humid ammonium nitrate, in keV

°C	II/IV (001)	III (101)	II/IV (110)	III (111)	III (120)		II/IV (111)	II/IV (200) / (020)		Mod.
20	14.6	16.3	18.12				23.42	24.6	26.42	IV
58	14.6	15.9	18.04		21.2	21.9	23.03	25.3–6		IV+III
58	14.5	16.0		18.36	21.2	22.2		24.2–25.5		III
111	14.6		18.00				23.2	24.60		II
57		16.0	18.0	18.70	21.2	22.6		25.0–6		III
20	14.5		18.20				23.28	26.3–5		IV
63		15.7		18.30	21.1	22.4		24.4	25.18	III
102	14.5		17.95				23.04		25.45	II
53		15.8		18.48	21.3	22.4		24.4–25.3		III
20	14.7		18.20				23.4	26.4	26.8	IV

Dry ammonium nitrate did not show the transition into phase III. Heating and cooling influenced the planes (110), (111), (200) and (020) of phases II and IV.

During heating of sample 2, phase III occurred as expected. Consecutive spectra at 59° showed that in the first step the peaks at 18.20, 23.32 and 26.36 keV were shifted to lower values. Further rearrangement of the lattices shifted the peak at 18.0 keV back to 18.36 keV and decreased the intensity of the peak at 23 keV. New peaks appeared at 13.72, 15.82 and 22 keV.

Further heating caused the transitions III/II and II/I. On cooling, the splitting of the peak at 23.35 keV of (110) of phase I into two sharp peaks at 22.7 and 25.04 keV, caused by expansion in the direction of c_{II} and by shrinkage in the plane (001), indicated the transition I/II, followed by transition II/IV. The peak intensities during cooling were different from those of run 1 due to recrystallization and texture effects in the sample.

During heating of sample 3 the same transition IV/III occurred as in run 2. Further cycling showed the expected transitions III/II, II/III and III/IV.

Discussion

In run 1 the phase transitions IV/II/I occur as expected. Careful checking of the diffraction patterns reveals slight differences of the peak positions of phase II on heating and cooling. Lattice parameters, calculated by Bragg's equation (Tables 4–5), reflect these differences.

The results can be interpreted in that heating will extend "b" to the value of "a", causing the transition into the tetragonal phase II. Further heating causes the transition into the cubic phase I. The transition extends a_{II} to $a_I \cdot \sqrt{2}$ and decreases c_{II} to the value of a_I.

Table 4

Variation of $a_{IV,\ II}$ and b_{IV} with temperature, in Å

Ser.	IV	II	I	II	IV
1	5.72 5.49	→ 5.71	→ 6.18	→ 5.75 → 5.60 – 9	5.74 5.43
2	5.74 5.40	→ III → 5.60 – 6	→ 6.14	→ 5.68 → 5.68	5.74 5.36
3	5.74 5.40	→ III → 5.60 – 3			5.72 5.37

Table 5

Variation of parameter "c" with temperature, in Å

Ser.	IV	II	I	II	IV
1	4.93 →	4.98	→ 4.37	→ 4.77 → 4.82	→ 4.95
2	4.90 → III	→ 4.90	→ 4.36	→ 4.95 → 4.87	→ 4.90 – 5
3	4.90 → III	→ 4.91 – 3	→ 4.34		

On cooling, the transition I/II requires an expansion in the direction of the c-axis and shrinkage in the other directions. Obviously, the expansion leading to c_{II} was not complete after the transition causing lower values on cooling with corresponding peak shifts.

At 50°, on cooling, diverging values for a_{II} were obtained. This tendency finally split a_{II} into a smaller axis b_{IV} and a larger a_{IV}, causing the transition II/IV.

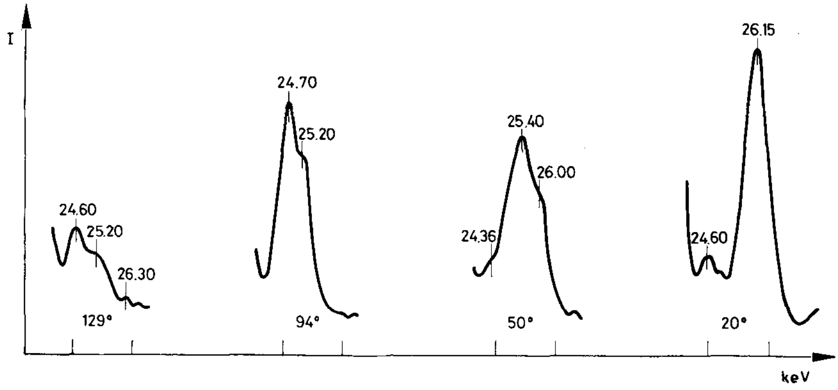

Fig. 2. Sections of diffraction patterns of dry ammonium nitrate (series 1)

The diffraction patterns of run 1 contain further interesting details, which are shown in Fig. 2. On cooling, three distinguished peak positions are observed. The lowest and the highest values stem from plane $(200)_{II, IV}$ and $(020)_{IV}$. The third must be attributed to a third phase II', which has been postulated in the literature [1, 3, 4] without conclusive proof of its existence.

The experiments with humid ammonium nitrate reveal that the transition IV/III occurs via a transition state, which might well be phase II'. Table 6, with concentrated information of series 3, confirms this statement.

Table 6

Phase transitions of humid AN
Peak shift in the diffraction patterns, in keV

IV	→			III	→	II
18.1	→	18.0	↗ ↘	15.9 18.3	↘ ↗	18.0
19.8	→	20.2	→	21.2		
23.4	→	23.0	→	24.2	→	22.7; 23.2
26.4	→	25.2	→	22.2	→	24.6

The discussion of the transition IV/III is not easy due to the essential differences of the two phases. Heating expands b_{IV} in the first step to the value of a_{II}. Further expansion causes adjacent layers in (001) of IV to shift in opposite directions, the shift being stronger for the tilting nitrate than for the ammonium groups. As a consequence, (110) of IV containing both groups disintegrates, giving rise to (101) and (111) of phase III, which contain the ammonium and nitrate groups, respectively.

The rearrangement being completed, a_{IV} remains essentially unchanged and corresponds to c_{III}; c_{IV} decreased, agreeing in direction with b_{III}; b_{IV} expanded strongly, corresponding with the direction of a_{III}.

Tables 4 and 5, containing the calculated parameters a, b and c for all series, allow some speculation about the conditions under which phase III will appear. There might be a correlation between the appearance of phase III and comparably low values for a_{II} and c_{II}.

Conclusions

The experiments proved that energy-dispersive X-ray diffraction can be successfully used for thermal analysis. Results could be obtained which strongly support the existence of a phase II'. It could further be shown that the phase change IV/III goes via a transition state which is similar to or consistent with phase II or II'. Finally a correlation may exist between the appearance of phase III and the values of the lattice parameters of phase II.

References

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Résumé — Le nitrate d'ammonium était chauffé et refroidi pas à pas dans un four fixé sur un goniomètre de rayons X. A chaque température, des diagrammes de diffraction étaient mesurés par un détecteur semiconducteur, combiné avec un sélecteur multicanaux. Les résultats supportent l'existence d'une phase II'. Ils montrent, que la transition des modifications IV/III procède par une phase de transition, qui ressemble à la phase II'.

Zusammenfassung — Ammoniumnitrat wurde in einer Hochtemperaturkammer auf einem Röntgengoniometer schrittweise aufgeheizt und abgekühlt. Bei jeder Temperatur wurde ein Beugungsdiagramm aufgenommen mit einem Si-Li-Detektor und angeschlossenem Vielkanalanalysator. Die Ergebnisse unterstützen die Annahme einer Phase II'. Sie zeigen, daß die Phasenumwandlung IV/III über einen Übergangszustand verläuft ähnlich oder identisch mit der Phase II'.

Резюме — Проведено последовательное ступенчатое нагревание и охлаждение нитрата аммония с помощью высокотемпературного устройства, смонтированного на рентгеновском гониометре. При каждой температуре были измерены дифрактограммы, используя Si—Li детектор совместно с многоканальным анализатором. Результаты в значительной степени дают доказательства существования фазы II'. Они свидетельствуют, что фазовое изменение IV/III проходит через переходное состояние, подобное или совпадающее с фазой II'.