

Differential scanning calorimetric and Raman studies of phase transition V \rightleftharpoons IV of ammonium nitrate

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Abstract

Differential scanning calorimetry, alone and in conjunction with Raman spectrophotometry for simultaneous calorimetric and spectral measurements, was used to study the solid state phase transitions of ammonium nitrate between -50 and 100°C.

On heating, two transition paths were observed between -40 and 0°C: one showing two separate peaks in DSC and the other showing a single peak. The latter path became dominant when samples were thermally cycled. The double transition was followed by transition IV \rightarrow II at 51°C and the single transition by transitions IV \rightarrow III \rightarrow II at about 50 and 87°C.

Raman spectra showed that there were two phases present between the two DSC peaks at low temperature. The first peak was attributed to a transition from the phase here designated as V' to phase IV, and the second peak to a transition from V to IV. The single peak under 0°C was the transition V \rightarrow IV.

1. INTRODUCTION

Ammonium nitrate has six temperature-dependent solid state phases at normal pressure.^{1,2} The crystal structures of five these are known.²⁻⁶ The principal transitions are VII \rightleftharpoons V \rightleftharpoons IV \rightleftharpoons III \rightleftharpoons II \rightleftharpoons I \rightleftharpoons (I) with equilibrium temperatures T_e -170, -18, 32, 84, 124, and 169°C, respectively.^{1,2} In addition,

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transition IV \rightleftharpoons II is known at T_c 50°C.² The understanding of the factors giving rise to the different transition paths is far from complete, and attempts at explanation have focused mainly on impurities and thermal history.^{7,8} The existence of phase VII is not on firm ground, and the nature of the transitions between phases VII, V, and IV is unclear.⁹⁻¹¹

In this paper we report DSC and combined DSC and Raman spectroscopic experiments carried out to clarify the mechanism of transitions between -50 and 0°C and to determine whether the selection between paths IV \rightleftharpoons III \rightleftharpoons II and IV \rightleftharpoons II above room temperature depends on the cold state transitions.

2. EXPERIMENTAL

Ammonium nitrate (p.a. Baker) samples for DSC were prepared either by first melting and then cooling freely to room temperature or by recrystallizing from aqueous solution at room temperature over a period of two days. For combined DSC and Raman measurements the samples were melted straight into the DSC sample pans.

The Perkin Elmer PC Series DSC7 used for the separate DSC measurements was calibrated against indium m.p., $T_o = 156.6^\circ\text{C}$ and $\Delta H = 28.47 \text{ J g}^{-1}$ with rate $10^\circ\text{C min}^{-1}$, and against benzoic acid m.p. = 123.3°C . Aluminum 50- μl sample pans with holes were used. Running rates were 2 and 5°C min^{-1} .

For the combined DSC and Raman measurements a Perkin Elmer DSC-1B was installed into a Bruker FRA 106 FT Raman spectrometer as described earlier.¹² Low temperatures were achieved with an evaporating liquid nitrogen cooling cell.

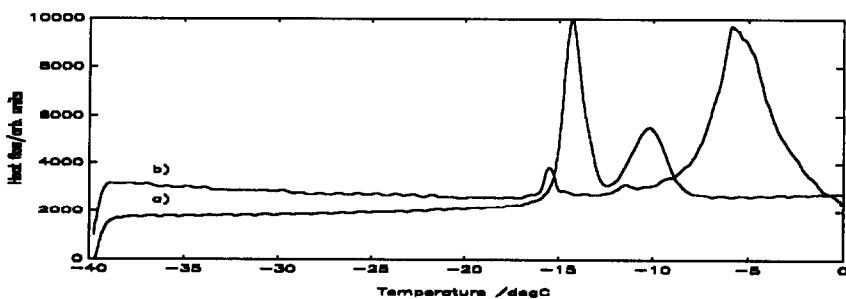


Figure 1. Normalized DSC heating curves of ammonium nitrate. Legend in text.

3. RESULTS AND DISCUSSION

Two typical DSC heating curves -40 to 0°C are shown in Fig. 1. In curve a) there are peaks at $T_0 = -15.2$ and -11.2 °C and in curve b) at $T_0 = -16.0$ and -8.1 °C. Above room temperature the transitions in a) were followed by transitions IV → III → II and the transitions in b) by a transition IV → II. When samples were cycled several times between -40 and 0°C, the peak at about -11°C gradually moved to -8°C and became dominant.

Simultaneous DSC and Raman measurements showed that the spectra recorded under -20°C are similar to those of phase V and those recorded above 0°C to those of phase IV, reported by Tang and Torrie¹¹; spectra recorded between the DSC peaks at -15 and about -11°C exhibited characteristic peaks of both phases. Examples of the spectra are shown in Fig. 2. Wave numbers are listed in Tab. 1.

Table 1. Observed Raman wave numbers and assignments to ammonium nitrate.¹¹

a) (cm ⁻¹)	b) (cm ⁻¹)	c) (cm ⁻¹)	Assign.
98	94	94	T(NO ₃)
132		146 178	L(NO ₃)
713 729	716 729	717	v ₄
1057	1045 1056	1045	v _t

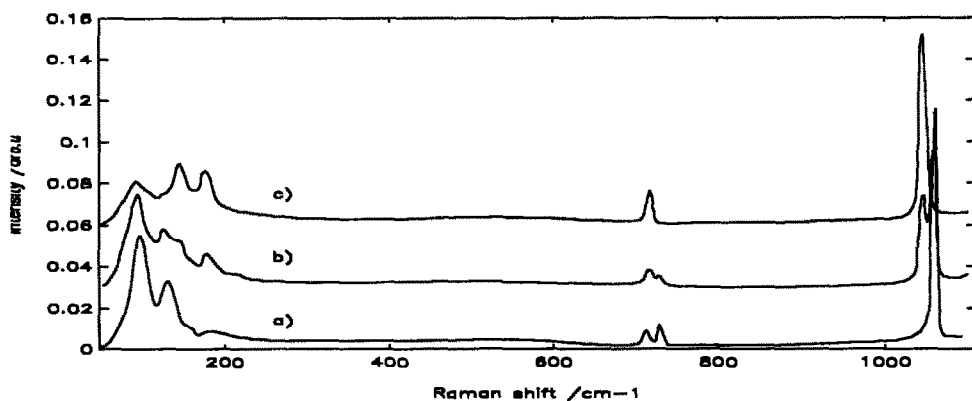


Figure 2. FT Raman spectra of ammonium nitrate recorded a) under -20°C, b) between the two DSC peaks of Fig. 1.a, and c) over 0°C.

Phase IV may thus be formed from the cold state phases in two ways. When a single transition takes place at about -8°C , the whole sample is transported into a structure that above room temperature undergoes transition to phase II. As the transition at -15°C gradually increases, however, more and more of the sample undergoes the transition IV \rightarrow III. This leads us to propose that phase IV is formed, through different transitions, into structures with different order parameters, and this is the basis for the divergent transitions at higher temperature.

4. CONCLUSIONS

Ammonium nitrate has two possible phase transitions in the temperature range -40 to 0°C . One is a transition from phase what we call V' to phase IV and the other transition is from phase V to phase IV. The latter transition may occur alone, but the first is always followed by the latter. If both transitions occur, the transitions IV \rightarrow III \rightarrow II will occur at higher temperature, but if only V \rightarrow IV occurs, the transition IV \rightarrow II will occur.

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