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THE TWO-STEP CHARACTER OF THE II→IV TRANSITION IN ND_4NO_3

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ABSTRACT

The DTA method has been applied for the investigation of the metastable II→IV transition in ND_4NO_3. This transition which differs from the usual one in NH_4NO_3, was found to occur in two steps, with the consequent observation of a double peak in the differential temperature curve. The difference between the two steps varied between about 1.9 and 0.2°C, depending on thermal cycling and on annealing. When the number of heating–cooling cycles was raised from 1 to about 60, the energy fraction $W_1/(W_1+W_2)$ increased from 0.22 to 0.28, and after that remained constant. Energies W_1 and W_2 above represent the high and low temperature steps of the transition, respectively. When the number of heating–cooling cycles exceeded 47, a supercooling effect was observed in the low temperature step of the transition, but not in the high temperature step.

INTRODUCTION

Ordinary ammonium nitrate (NH_4NO_3) has for a long time been the subject of a great deal of experimental study. According to Sowell et al.[1], phase III normally exists between 32.1 and 84.2°C at atmospheric pressure. However, under certain conditions phase III disappears, and a metastable II→IV transition is observed at about 50°C. In previous investigations[2,3], it has been found that with deuterated ammonium nitrate (ND_4NO_3) the corresponding transition, as an exception, occurs in two steps.

The purpose of the present investigation was to examine this unusual behaviour of the II→IV transition in ND_4NO_3, and of complementing the results obtained previously[2,3]. It is impossible to draw any comparison between findings made by other investigators, since very few studies of ND_4NO_3 are available in the literature[4–6], and there is no paper particularly concerned with the II→IV transition.

Details of the method of measurement, DTA, have been reported previously[2]. The recorder employed was a Honeywell Electronic 19, with simultaneous registration on its chart of the absolute sample temperature, and of the differential temperature between the reference material ($NaNO_3$) and the sample (ND_4NO_3). It was guaranteed that the deuteration grade of the ND_4NO_3 (E. Merck AG, G.F.R.) was 99.72%, with an ND_4NO_3 content of at least 98%. The $NaNO_3$ used as a reference was of the quality "pro analysi", and was supplied by the same manufacturer. To avoid pretreatment during the packing operation, the sample to be studied was not melted, but pressed into the calorimeter vessel as tightly as possible. The mass of the sample was 580.0 mg, and that of the reference 887.5 mg.

RESULTS

An examination was made of the effect of systematic thermal treatment on the II → IV transition. Figures 1 and 2 illustrate three examples of the temperature curves obtained. Temperatures T_1 and T_2 in the sample temperature curve are attributable

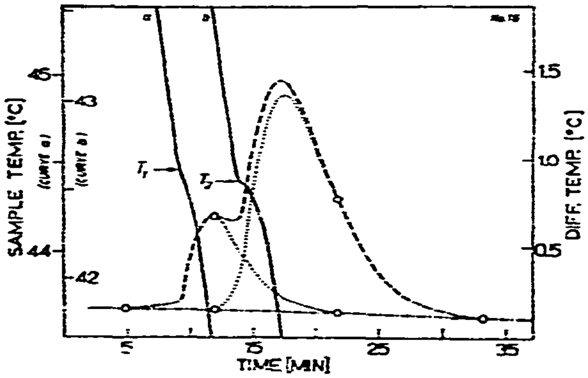

Fig. 1. Temperature curves of the II→IV transition in ND_4NO_3 for a cooling number of 16 (no annealing). ———, sample temperature; – – –, differential temperature; ······, sides of the two separated peaks; –·–·–, baseline, T_1 and T_2 are the temperatures of the high and low temperature steps of the transition, respectively.

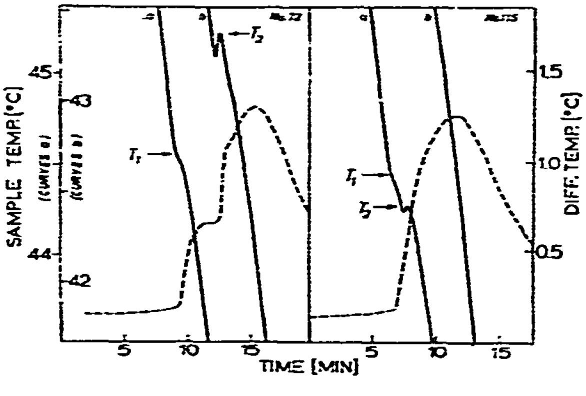

Fig. 2. Temperature curves of the II→IV transition in ND_4NO_3 for cooling numbers (a) of 72 (no annealing) and (b) of 115 (annealed 85 h at 120 °C). ———, sample temperature; – – –, differential temperature. T_1 and T_2 are the temperatures of the high and low temperature steps of the transition, respectively.

to the two steps of the transition. In view of the small temperature difference $T_1 - T_2$, the corresponding two peaks in the differential temperature curve overlap. The shift of the second step of the transition, and the almost stable position of the first step are visible in these figures. Figure 1 describes the situation in which the difference $T_1 - T_2$ attains its maximum value, in Fig. 2a the second step has shifted nearer to the first one, and in Fig. 2b the two steps are so close to each other that the double peak character in the differential temperature curve is barely discernible. However, the two steps can be seen in the sample temperature curve. In Fig. 3 the difference $T_1 - T_2$ is indicated as a function of the cooling number (cooling number = number of heating–cooling cycles).

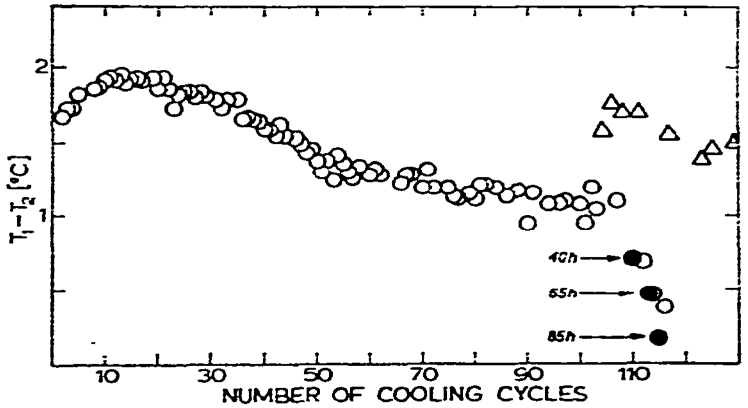

Fig. 3. Temperature difference between the two steps of the II→IV transition in ND_4NO_3 as a function of the cooling number. ○, Treatment 1—maximum temperature attained before cooling, 140 °C (phase I), no annealing; ●, treatment 2—maximum temperature attained before cooling, 140°C (phase I), annealing times within a stability range of phase II (120 °C) 40, 65, and 85 h, respectively; △, treatment 3—maximum temperature attained before cooling, 120 °C (phase II).

The area of the double peak in Fig. 1 represents the total transition energy, and equals the sum of the areas of the two separate peaks determined graphically. No determinations have been made of the absolute energies of the two different steps of the transition, but in Fig. 4 an energy fraction $W_1/(W_1 + W_2)$ is plotted against the cooling number. Energies W_1 and W_2 above represent the high and low temperature steps of the transition, respectively.

Figures 2a and 2b reveal the existence of a supercooling effect, but only in the low temperature step of the transition. Supercooling can be observed as a peak in the sample temperature curve, and as a very steep rise in the differential temperature curve.

The thermal treatment of the sample took three dissimilar forms, which are reported below.

Treatment 1. The sample was heated from room temperature to the stability range of phase I (140°C), and then immediately cooled to room temperature (open circles in Fig. 3). The appearance of the metastable II→IV transition was thus assured[3].

Due to the shift in the low temperature step of the transition, variation occurred in the difference $T_1 - T_2$, which attained its maximum value of 1.9°C when the cooling number was about 15. Subsequent to attainment of the maximum, the difference gradually diminished and approached a value of 1.1°C until the cooling number reached 100. The three deviating points for cooling numbers in excess of 110 in Fig. 3 are discussed below.

The energy fraction in Fig. 4 initially increased from 0.22 to 0.28, and then remained constant within the limits of experimental errors, which have been estimated on the basis of uncertainty in graphical integration of the peak areas.

Supercooling, to the extent of 0.3°C, occurred for the first time at a cooling number of 47, and subsequently appeared in almost every case of Treatment 1.

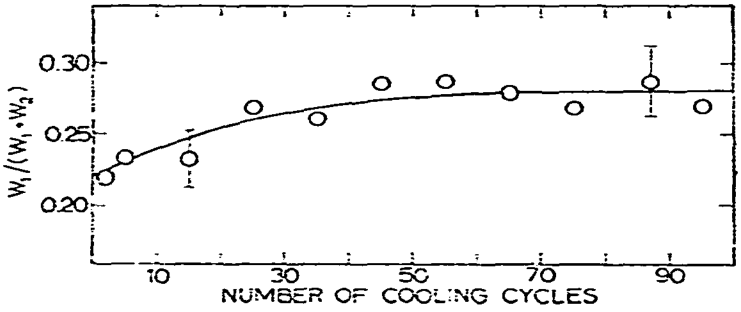

Fig. 4. Energy fraction $W_1/(W_1 + W_2)$ as a function of the cooling number. Here, W_1 and W_2 are the energies of the high and low temperature steps of the II→IV transition, respectively.

Treatment 2. The sample was heated from room temperature to the stability range of phase I (140°C), and then immediately cooled, through the I→II transition point, to the temperature range of phase II (120°C), at which temperature annealing was performed (filled circles in Fig. 3). As a result of the annealing, the difference $T_1 - T_2$ diminished, and attained its lowest value, 0.2°C, for the longest annealing time applied, 85 h. Annealing of this type seemed to leave a kind of "memory" in the sample, since the subsequent heating–cooling cycle, in accordance with Treatment 1, gave a difference $T_1 - T_2$ that was lower than had been expected (three open circles near the filled circles in Fig. 3).

In the case of small peak distance, accurate determination of the areas of the two separate peaks was difficult due to the marked overlapping of the peaks. In this case, accordingly, the energy fraction $W_1/(W_1 + W_2)$ was not taken into account.

A slight supercooling effect was observed at the low temperature step of the transition.

Treatment 3. The sample was heated from room temperature to the stability range of phase II (120°C) and then, either with or without annealing, it was cooled to room temperature (triangles in Fig. 3). When this treatment was carried out, the sample underwent either transition II→IV or II→III, depending upon its thermal history[3]. If the II→IV transition occurred, the difference $T_1 - T_2$ was always greater than that in the case of Treatment 1 or Treatment 2 with a cooling number of the same order of magnitude.

The energy fraction $W_1/(W_1+W_2)$ was in agreement with the values of Treatment 1.

In this case, when only phase II was attained on heating but not phase I, supercooling was not observed.

DISCUSSION

In this work, confirmation was made of the unique phenomenon of the II → IV transition peak in the differential temperature curve being split into two when D was substituted for H in NH_4NO_3. It was observed that the shift of the low temperature peak towards the high temperature peak depended upon thermal cycling and upon annealing; and when thermal treatment was extended, the peak distance T_1-T_2 diminished, but complete fusion of the peaks was not confirmed. The starting value of T_1-T_2 in Fig. 3 is in close agreement with the value of 1.6 °C reported previously[2]. The existence of the maximum in Fig. 3 can be regarded as reliable, on the basis of the proofs obtained from both the sample temperature and differential temperature curves.

It has been proved[3] that the double peak cannot represent transitions II → III → IV. Furthermore, the possibility of moisture is eliminated, since after drying in a vacuum above the melting point, the double peak remained. An increase in moisture achieved by passing steam over the sample did not result in disappearance of the double peak.

The reverse IV → II transition on heating, although not noticed previously[2,3], it was observed in this work after the sample had been cooled from the melt. Although the information gained about this transition was very slight, it seemed that the transition occurred at a fixed temperature just below 50 °C, and that no signs existed of the two-step character.

According to previous studies, the II → III transition point can shift even to the extend of tens of degrees. In the current investigation the high temperature step of the II → IV transition was found to take place at a fixed temperature. It can thus be stated that the II → IV transition, despite the lack of clarity in regard to the origin of the two-step character, rather than the unstable II → III transition, is one of the normal transitions undergone by ND_4NO_3 between the melting point and room temperature.

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