ELSEVIER Thermochimica Acta 254 (1995) 377–380

thermochimica
acta

Note

Phase transition in crystalline $[Ni(NH_3)_6](NO_3)_2$ as seen by the dependence of nucleation rate on temperature

Małgorzata Rachwalska

Faculty of Chemistry of the Jagiellonian Unversity, Department of Chemical Physics, ul. Ingardena 3, 30–060 Kraków, Poland

Received 14 January 1994; accepted 11 July 1994

Abstract

An analysis of the shape of the specific heat anomaly at 197 K in $[Ni(NH_3)_6](NO_3)_2$ shows that the transition occurs in a very wide temperature region, i.e. from about 115 to 197 K.

Keywords: Nickel ammonium nitrate; Nucleation rate; Phase transition; Temperature dependence

1. Introduction

Crystalline $[Ni(NH_3)_6](NO_3)_2$ was investigated by the adiabatic calorimetry method [1] and its dependence of specific heat versus temperature was measured in the temperature region 83–256 K. Two anomalies were discovered showing the existence of phase transitions. These anomalies appeared during the heating of the sample: at about 197 K, connected with the transition from phase III to phase II (a small anomaly); and at about 247 K, connected with the transition from phase II to phase I (a large anomaly).

The first phase transition is characterized by a large hysteresis, as stated in Refs. [1] and [2], and the second by a small hysteresis of just several degrees.

In the region of the small anomaly one observes a relatively large scattering of the experimental points, larger than that usually observed (0.6% at most) in the region. In addition, one can see that in particular experimental runs, the scattering of experimental points is much smaller.

This study is an attempt to explain this effect.

SSDI 0040-6031(94)01990-8

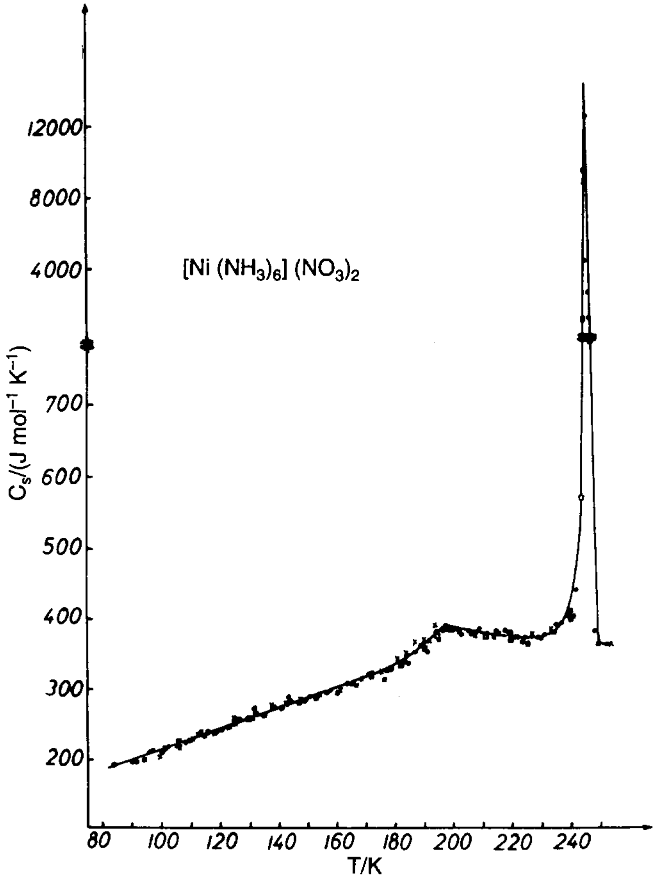

Fig. 1. Specific heat vs. temperature for $[Ni(NH_3)_6](NO_3)_2$: ×, run II; ○, run IV; ●, run V; □, run 2 [1].

2. Experimental data

The experimental results analysed in this work are presented in Fig. 1. As mentioned above, a comparison of the experimental runs, which gives an impression of a large scattering of experimental points, shows that the shapes of the small anomaly differ slightly.

3. Discussion

In order to understand this, Table 1 lists the values of ΔH which is the enthaply change of the entire calorimeter + sample in the temperature region of the small anomaly.

Table 1
ΔH values of the calorimeter + sample system in the region of the small anomaly

Number of experimental run	Temperature region in which ΔH was calculated/K	ΔH/J
II	170–230	9209 ± 8
IV	170–230	9176 ± 8
V	170–230	9155 ± 8

Table 2
ΔH values of the calorimeter + sample system over a wider temperature range

Number of experimental run	Temperature region in which ΔH was calculated/K	ΔH/J
II	115–230	16205 ± 13
IV	115–230	16200 ± 13
V	115–230	16184 ± 13

Looking at Table 1, we can see that ΔH decreases if the number of runs increases. If we take into account a larger temperature region (Table 2) the situation becomes different. In this case, ΔH remains constant within error limits.

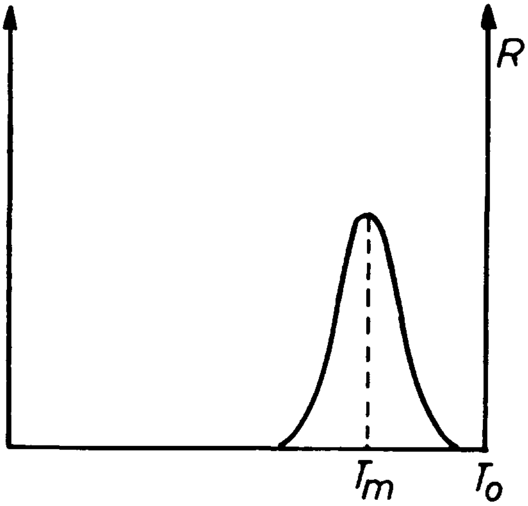

Fig. 2. The rate of nucleation R vs. temperature [3]. T_0 is the real temperature of transition; T_m is the temperature at which the rate of nucleation is maximal.

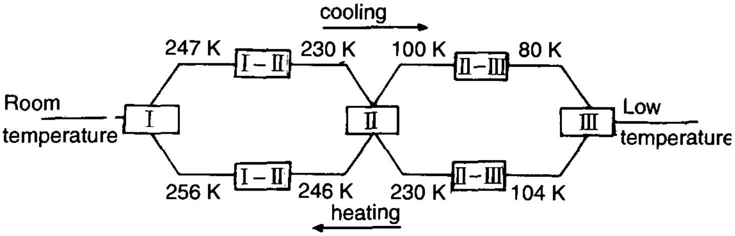

Fig. 3. Formation of particular phases in the diffraction experiment for $[Ni(NH_3)_6](NO_3)_2$ [2].

These facts may be explained from Fig. 2 which shows the nucleation rate versus temperature dependence. It seems that for the phase transition connected with the small anomaly, the nucleation rate changes in the large temperature region covering practically all the low temperature part of the specific heat curve, the small anomaly included. Thus the last set of ΔH values shows that one gets the same values of ΔH for subsequent runs in the large temperature region only. In other words, in this case phase III changed completely into phase II and the process continued, to be completed in the large temperature region.

Therefore for the phase transition III–II in Fig. 2, we should assume a temperature of 197 K for T_m and the left part of the maximum should be extended to the region from about 115 to 197 K. A good confirmation of this hypothesis can be found by taking into account the structural data [2] which show that the phase transition III–II takes place in a wide temperature region, see Fig. 3.

It is expected that the dimensions of the grains of $[Ni(NH_3)_6](NO_3)_2$ would influence the values of ΔH. This is connected to the observation made in Ref. [2] that $[Ni(NH_3)_6](NO_3)_2$ monocrystals break up at a temperature below that of the appearance of the small anomaly. Our calorimetric measurements clearly show the pulverization of the material during measurement: the sample when put into the calorimetric vessel was composed of small crystals of an intense violet colour, and then changed in colour, a result of visible pulverization. The pulverization brought about a change in the dimensions of grains and according to Ref. [4], this should influence the ΔH value of the small anomaly. This is the case because with small grain sizes, an excess of surface energy affects the ΔH value [4]. From the results of Table 2, we can assume that in this case such an influence is negligible. This is also the case for the large anomaly which was not considered here.

References

[1] A. Migdał-Mikuli, E. Mikuli, M. Rachwalska, T. Stanek, J.M. Janik and J.A. Janik, Physica B, 104 (1981) 331.
[2] S. Hodorowicz, J. Czerwonka, J.M. Janik and J.A. Janik, Physica B, 111 (1981) 155.
[3] C.N. Rao and K.J. Rao, Phase Transitions in Solids, MacGraw-Hill, New York, 1978.
[4] M. Natarajan, A.R. Das and C.N.R. Rao, Trans. Faraday Soc., 65 (1969) 3081.