A quantitative kinetic study of the I to or from II phase transition of ammonium chloride

A quantitative kinetic study of the I↔II phase transition of ammonium chloride

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Abstract. The I↔II phase transition of ammonium chloride has been studied using energy-dispersive powder diffraction with a synchrotron source of x-radiation. The equilibrium transition temperature was found to be $184.5 \pm 0.5\,°C$ and the activation energy for the transformation was found to be $213 \pm 15\,kJ\,mol^{-1}$. The transition was satisfactorily described using the Avrami equation with a shape parameter of 3.

1. Introduction

Three phases of ammonium chloride have been found to exist at atmospheric pressure [1]: phase I above about $183\,°C$, phase II between $183\,°C$ and $-30\,°C$ and phase III below $-30\,°C$. Phases II and III have the CsCl structure with chlorine ions at the corners of a cube and an ammonium ion in the centre. There are two possible orientations of the ammonium ion with nitrogen–hydrogen bonds lying along threefold axes (body diagonals). Direct octopole–octopole interactions between neighbouring ammonium ions favour parallel ordering (ammonium ions in the same orientation) while an indirect octopole–dipole–octopole interaction via the chlorine ions favours anti-parallel ordering [2, 3]. The ammonium ions in phase III are completely parallel ordered while no long-range order exists in phase II [4]. Phase I has the NaCl structure with ammonium ions that are even less ordered than in phase II [1].

The transformation between phase I and phase II is reversible and thermodynamically first order [5]. It has been described as dilatational [6, 7] with a 40% contraction along the ⟨111⟩ direction of the face centred cell. Subsequently an orientational relationship was observed between the two phases both on heating and cooling [8–10] and Kennedy [11, 12] carried out a martensite analysis of the transition and developed an alternative description involving the translation of alternate (001) layers of phase II (or (220) layers of phase I).

A dilometric investigation of the I↔II transformation of both NH_4Cl and NH_4Br by Poyhonen [13] established a transition temperature of $183.1\,°C$ for the transition of NH_4Cl although consistent values for the rate of transformation were not obtained. Also, the values of the rate of transformation of NH_4Br presented by Poyhonen differed from those presented in a previous investigation by Erofeev and Mendeleev[14] by about two orders of magnitude.

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Chupakhin *et al* [15] have carried out an optical microscopic study of this transition. They used crystals of ammonium chloride measuring about 10 mm × 5 mm × 1 mm. They observed that phase II grew from the thin edge of phase I crystals; across the large face. Phase I was found to stop growing after it had penetrated some distance into the parent phase. The suggested reason for this is that the 19.3% volume increase on transforming from phase II to phase I produces a strain field in front of the growing phase which eventually is strong enough to prevent further growth.

We here present an investigation of the I↔II transition of NH_4Cl using energy-dispersive powder diffraction to monitor the rate of conversion between the two phases under both isothermal and non-isothermal conditions.

2. Experimental details

Analytical grade ammonium chloride was obtained from BDH Ltd and ground in liquid nitrogen to give a fine powder made up of small white evenly sized crystals.

Data were collected using the energy-dispersive powder diffraction (EDPD) facility at the UK synchrotron radiation source [16, 17] (figure 1). EDPD with a synchrotron source of radiation has the advantage that all of the diffraction pattern is collected simultaneously and rapidly (a few seconds in this case). Also, the high post-sample collimation and lack of moving parts lead to extremely clean spectra with little or no change to the background of the diffraction pattern while the material transforms between phases. The diffraction angle was optimized at about 9.9° so as to have as few overlapping peaks as possible (figure 2); most of the low-energy peaks are seen to be fully resolved and the background is virtually identical in both spectra.
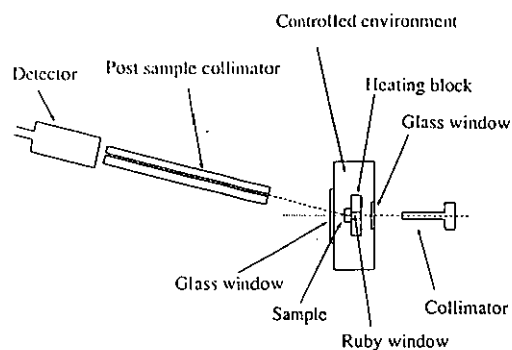

Figure 1. Schematic diagram of the experimental set-up.

Two methods of data collection were used: the MCA method [18] and the SCA method [19]. In the MCA method a series of whole diffraction patterns is collected for a set length of time each, and with a set time interval between them, during the course of the transformation (figure 3). The areas of the peaks of the two phases are then measured, using profile fitting, normalized and combined to give an estimate of the degree of transformation from one phase to the other. In the SCA method a number of strong, totally unoverlapped peaks are windowed electronically and all x-rays detected in these windows are counted for set time intervals during the course of the transformation (figure 4). An estimate of the degree of transformation was
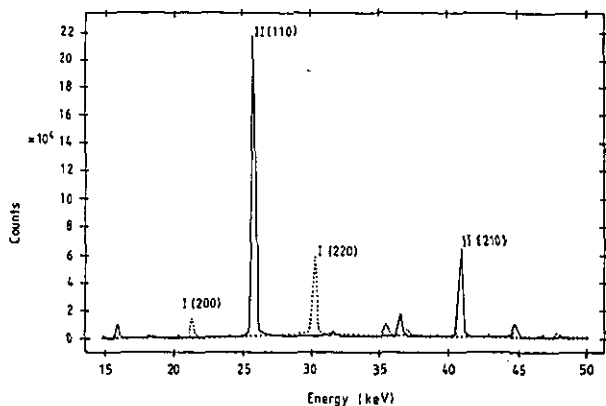
Figure 2. EDPD spectra of phases I (...) and II (–) of ammonium chloride collected at 250 °C and room temperature, respectively.

then made by normalizing and combining these spectra. The MCA method has the advantage that peak fitting allows the study of materials with complex spectra with no unoverlapped peaks while the SCA method has the advantages that data can be collected more rapidly, due to lower computational overheads, and that less data analysis is required. Data were collected using both MCA and SCA methods although, due to the simplicity of the diffraction patterns in this case, the majority of the data were collected using the SCA method. Three diffraction peaks were monitored using the SCA method: the (110) peak of phase II and the (200) and (220) peaks of phase I.
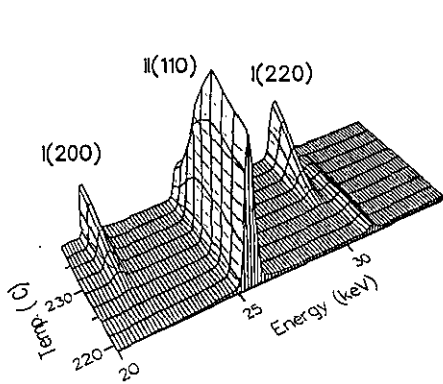

Figure 3. EDPD spectra of ammonium chloride collected using the MCA method during cooling from phase I to phase II.
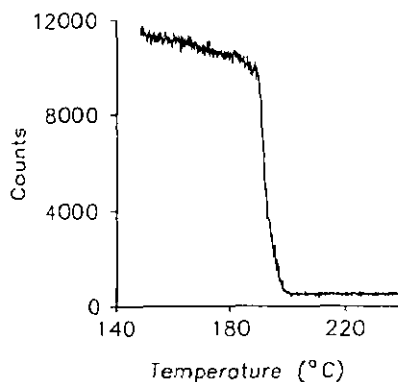

Figure 4. EDPD spectrum of the II↔I transformation of ammonium chloride collected using the SCA method.

A Linkham Scientific PH600 furnace, controlled by a PR600 controller, was used to vary the temperature of the sample. The furnace consists of a silver heating block, which encloses a platinum resistance thermometer, inside a water cooled jacket. X-rays pass through a sapphire window in the centre of the heating block. Samples were contained inside brass rings with thin glass slides as windows. These sample holders were held onto the heating block using two spring-loaded clips. Samples were 1–2 mm thick and about 1 cm in diameter. Some samples were pressed into pellets 6 mm in diameter using a 2 ton force in order to improve the ease of sample manipulation. Dry nitrogen gas was bled into the furnace in order to give an inert

atmosphere around the sample. Data were collected both isothermally and non-isothermally. For isothermal data collection the sample temperature was rapidly changed to a target temperature and then data were collected in equal time slices. For non-isothermal data collection the temperature was changed at a slower constant rate and data were collected in equal time, and therefore equal temperature, slices while the temperature was rising. The former data were used for a kinetic analysis of the transformation and the latter for determining the transition temperature. Data were collected isothermally on heating and cooling from pelletized and unpelletized samples. Readings from an incident flux monitor were used to normalize all spectra [16].

3. Determination of the transition temperature

The transition temperature as a function of ramp rate was determined by graphically estimating the temperature that corresponded to fifty per cent transformation for each of the non-isothermal datasets. These values were extrapolated to zero ramp rate (figure 5) to give an equilibrium transition temperature of $184.5 \pm 0.5\,°C$. It has been suggested that the strong departure from linearity of these curves could be due to a martensitic memory effect [20]. Alternatively, this behaviour could be due to the processes governing the kinetics of the transformation varying in different regions about the transition temperature. Such effects were not observed in the isothermal data presented in the next section of this paper. Despite the non-linear nature of these curves an accurate measure of the transition temperature was obtained without the need to use the curve-fitting procedure of the previous author [13].
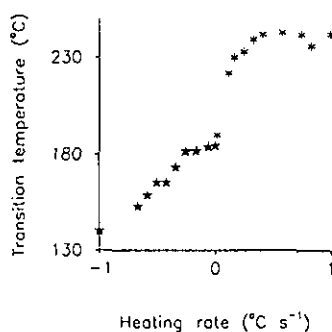

Figure 5. The transition temperature of the $I \leftrightarrow II$ transition of ammonium chloride, measured from heating (∗) and cooling (⋆) non-isothermal data, plotted as a function of heating rate.
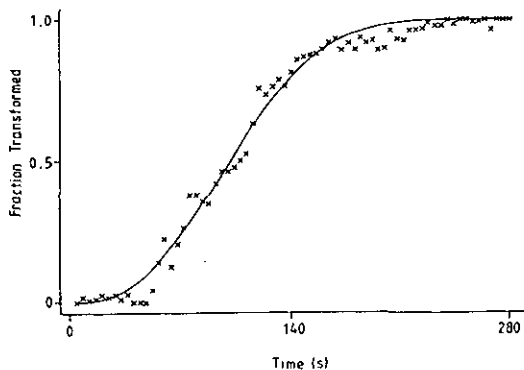
Figure 6. The rate of transformation of ammonium chloride from phase I to phase II determined from an isothermal measurement at $185\,°C$. A fit of these data ($\times$) to the Avrami equation (–) is shown.

Data collected from pelletized samples gave a slightly higher value for the equilibrium transition temperature ($193 \pm 2\,°C$) than the unpelletized samples.

4. Kinetic analysis

The isothermal data were found to fit the Avrami [22–24] equation well (figure 6). Each curve gave a shape parameter of about 3. The shape parameter was then fixed at 3 and the rate of transformation k was determined from the time for fifty per cent transformation $t_{1/2}$ using the relationship [21]:

$$k = \ln(2)/t_{1/2}^3. \tag{1}$$

Values for the rate determined at different temperatures were then used to produce Arrhenius plots (figure 7) for heating and cooling measurements using pelletized and unpelletized samples. Activation energies were then determined from the gradients of these graphs. The values obtained on heating and cooling were found to be the same within experimental error and an average value of $213 \pm 15 \, kJ \, mol^{-1}$ was determined for the unpelletized samples. The activation energies measured with pelletized samples failed to give consistent results although they were always lower than the activation energies measured for unpelletized samples.
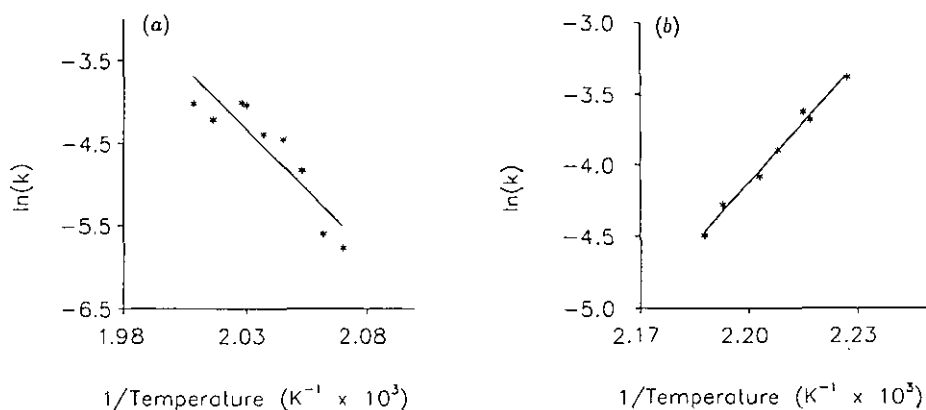

Figure 7. Arrhenius plots of the rate of transformation of ammonium chloride on heating (*a*) and cooling (*b*).

5. Discussion

The I↔II transition in ammonium chloride has been found to occur at $184.5 \pm 0.5 \, °C$ with an average activation energy of $213 \pm 15 \, kJ \, mol^{-1}$.

The value obtained for the transition temperature is slightly higher than that previously determined [13]. The higher transition temperature given by the pelletized samples could be due to there being some residual pressure inside the pellets. A residual average pressure inside the pellets of only $42.4 \, kg \, cm^{-2}$ is enough to produce an increase in transition temperature of $3 \, °C$ [13]. This is a small residual pressure when compared with a pressure of over $7000 \, kg \, cm^{-2}$ used to produce the pellets.

The value of the activation energy determined here is similar to that determined for other martensitic transformations, for example, the olivine–spinel transition $(205(2)\,kJ\,mol^{-1})$ [25]. On transforming from phase II to phase I an increase in the number of background counts was observed about the (220) reflection of phase I (figure 2). The martensitic discription of the transformation involves the translation of the (220) planes of phase I. The extra background could well be due to atomic disorder about this plane. It is possible that this disorder is due to some small regions of the sample being unable to transform into phase I due to the volume increase of the surrounding layers that have already transformed, causing a local increase in the activation energy. These small regions could then act as seeds for the growth of phase II on cooling, thus explaining the martensitic memory effect. This study supports the view that the transformation is martensitic.

The transformation was described adequately using the Avrami equation with a shape parameter of 3; suggesting two-dimensional crystal growth [21] which agrees well with previous optical microscopy observations [15]. The activation energy was the same on heating and cooling which suggests that no effect due to stress fields was experienced.

The inconsistencies in the value of the activation energy determined from pelletized samples could be due to the residual stress in the pellets annealing out with heating and cooling cycles. The activation energy for pelletized samples was consistently lower than that for unpelletized samples which indicates that the activation energy for this transformation decreases with pressure.

References

[1]   Pistorius C W F T 1976 *Prog. Solid State Chem.* **11** 1
[2]   Seymour R S 1971 *Acta Crystallogr.* A **27** 348
[3]   Huller A 1972 *Z. Phys.* **254** 456
[4]   Ross R G and Sandberg D 1979 *J. Phys. C: Solid State Phys.* **12** 3649
[5]   Staveley L A K 1949 *Q. Rev.* **3** 64
[6]   Buerger M J 1951 *Phase Transformations in Solids* ed R Smoluchowski *et al* (New York: Wiley)
[7]   Buerger M J 1961 *Fortschr. Miner.* **39** 9
[8]   Chatterji S, Mackay A L and Jeffery J W 1971 *J. Appl. Crystallogr.* **4** 175
[9]   Fraser W L and Kennedy S W 1972 *Acta Crystallogr.* B **28** 3101
[10] Fraser W L and Kennedy S W 1974 *Acta Crystallogr.* A **30** 13
[11] Kennedy S W 1973 *J. Appl. Crystallogr.* **6** 293
[12] Kennedy S W 1974 *J. Mater. Sci.* **9** 1043
[13] Poyhonen J 1960 *J. Ann. Acad. Sci. Fenn.* A VI **58** 1
[14] Erofeev B V and Mendeleev L T 1957 *Vestsi Akad. Navuk Belaruskoi SSSR, Fiz.-Tekh. Navuk* **1** 57
[15] Chupakhin A P, Sidel'nikov A A and Boldyrev V V 1987 *React. Sol.* **3** 1
[16] Clark S M 1989 *Nucl. Instrum. Methods* A **276** 381
[17] Clark S M 1992 *Rev. Sci. Instrum.* **63** 863
[18] Clark S M, Miller M and Pantos E 1989 *Daresbury Laboratory Technical Memorandum* DL/SCI/TM59E
[19] Clark S M and Miller M 1990 *Rev. Sci. Instrum.* **61** 2253
[20] Glaser A M 1992 Private communication
[21] Clark S M and Doorhyee E 1992 *Daresbury Laboratory Technical Memorandum* DL/SCI/TM87E
[22] Avrami M 1939 *J. Chem. Phys.* **7** 1103
[23] Avrami M 1940 *J. Chem. Phys.* **8** 212
[24] Avrami M 1941 *J. Chem. Phys.* **9** 177
[25] Lauterjung J and Will G 1986 *Physica* B **139 & 140** 343