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# Determination of the equilibrium temperatures and enthalpies of the solid–solid transitions of rubidium nitrate by differential scanning calorimetry

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## Abstract

The equilibrium temperatures of the three solid–solid phase transitions of high purity rubidium nitrate have been measured accurately by stepwise heating and by the extrapolation to zero heating rate method. Mean values of 164.9 ± 0.1 °C (transition 1), 222.2 ± 0.5 °C (transition 2) and 284.0 ± 0.1 °C (transition 3) were obtained using two different types of heat flux DSC instruments. The enthalpies of transitions 1 and 2 were determined using both heat flux and power compensated DSC instruments. The mean values were 3.83 ± 0.02 kJ mol$^{-1}$ (transition 1) and 3.14 ± 0.03 kJ mol$^{-1}$ (transition 2). For transition 3 the shape of the DSC curve prevented an unequivocal determination of the enthalpy. Values obtained using two alternative interpretations of the DSC peak shape are discussed in the text.

*Keywords:* Rubidium nitrate; DSC; Transition; Temperature; Enthalpy

## 1. Introduction

Rubidium nitrate exhibits three reversible solid–solid phase transitions prior to fusion, which takes place at about 310 °C. These are:

- Transition 1 (160–166 °C): trigonal to CsCl (cubic)
- Transition 2 (219–228 °C): CsCl (cubic) to rhombohedral
- Transition 3 (278–291 °C): rhombohedral to NaCl (cubic)

The temperatures shown in brackets represent the ranges of the literature values [1–9]. These are listed in Table 1 and show that even in the most recent publications there are discrepancies of several degrees between the reported temperatures. The reason for the poor agreement is uncertain. $RbNO_3$ is reported to be stable to temperatures well above the transition temperatures and although thermal history was found to influence the temperature of transition 2, transitions 1 and 3 were reported to be free from such effects [10]. In view of the discrepancies in the literature values we have determined accurate values for the equilibrium transition temperatures by means of DSC. In addition, we have measured the enthalpies of the transitions. Previous enthalpy measurements are rather few in number and are summarised in Table 2 [3,4,6,8,11,12].

There are two possible approaches to the accurate measurement of equilibrium temperatures of melting or solid-state transitions by DSC. In one, the extrapolated onset temperature of the peak ($T_e$) is measured at a number of heating rates (typically from 1 to 10 °C min$^{-1}$) and the equilibrium temperature is obtained by extrapolating the results to zero heating rate [13]. In the other approach the equilibrium temperature is obtained from the final step of a stepwise heating programme in which the temperature is raised in small increments (0.1 or 0.05 °C) with isothermal periods between the increments. In this method the melting or transition takes place under near-equilibrium conditions

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Table 1
Literature values for the temperature of the solid–solid phase transitions of rubidium nitrate

| First author | Year | Temperature (°C) | | | Reference | Method |
|---|---|---|---|---|---|---|
| | | Transition 1 | Transition 2 | Transition 3 | | |
| Rostkowski | 1930 | 166 | 229 | – | 1 | Heating curve |
| Plyushchev | 1956 | 164 | 219 | 291 | 2 | Heating curve |
| Mustajoki | 1958 | 160 | 218 | 281 | 3 | Calorimetry |
| Arell | 1961 | 164.4 | 219.2–220.7 | – | 4 | Calorimetry |
| Brown | 1962 | 160 | 220 | 290 | 5 | Microscopy |
| Rao | 1966 | 166 | 228 | 278 | 6 | DTA |
| Protsenko | 1973 | 164 | 220 | 285 | 7 | DTA |
| Secco | 1999 | 166 | 222 | 285 | 8 | DSC |
| Hichri | 2002 | 164 | 227 | 282 | 9 | DSC |

[14]. The procedure is similar to that adopted in adiabatic calorimetry and is easy to implement using modern DSC equipment.

A study of organic melting point temperature standards established that the melting temperatures obtained by the extrapolation to zero heating rate method corresponded to the near-equilibrium values [15]. Both methods were applied to the measurement of the equilibrium temperature of the solid-state transition of $CsNO_3$ and identical values were achieved [16].

For enthalpy determinations the conventional approach is to measure the area enclosed by the transition peak and a linear baseline. However, delineation of the base line becomes less straightforward when contributions from changes in heat capacity become significant. Richardson [14] has commented on the changes in heat capacity that accompany the transitions in $RbNO_3$. These are both positive (transition 1) and negative (transitions 2 and 3). Various DSC base line constructions have been discussed by Hemminger and Sarge [17]. The DSC software supplied by the instrument manufacturers has a number of constructions with the aim of eliminating the effect of the change in heat capacity on the measured transition enthalpy.

We have adopted the approach recommended by Richardson [14] in which the overall enthalpy change $\Delta H$ is expressed in terms of the isothermal enthalpy change at an assigned temperature $\Delta H(T)$ and contributions from the initial and final heat capacities where $\Delta H(T) = \Delta H - C_i(T - T_1) - C_f(T_2 - T)$. $C_i$ and $C_f$ are the initial and final heat capacities and $T_1$ and $T_2$ are the initial and final temperatures over which the area is to be calculated. In accordance with Richardson's recommendation the thermal analysis curves should be plotted with heat capacity and temperature as the ordinate and abscissa, respectively. In common with other base line constructions this procedure is not without difficulty in assigning the temperatures $T_1$ and $T_2$. However, in principle the procedure leads to thermodynamically valid enthalpies of transition.

## 2. Experimental

The rubidium nitrate (Alfa Aesar) used in these studies had a purity of 99.975% and was crushed with a pestle and mortar and dried at 105 °C before use. The calibration materials (LGC Limited) were high purity samples (99.995%) of indium, tin and lead. The certified values for both the equilibrium temperature and enthalpy of melting of these materials, which were obtained using adiabatic calorimetry, are shown in Table 3.

The temperature determinations were carried out using a Mettler Toledo 822$^e$ heat flux DSC (operated with the 'tau lag' correction disabled) and a TA Instrument 2920 heat flux DSC. The Mettler Toledo DSC was also used for the enthalpy measurements together with a PerkinElmer Diamond power compensated DSC.

The DSC instruments were calibrated for temperature using the stepwise heating method with temperature increments of 0.05 °C and either 10 or 20 min isothermal periods between the increments. The measurements were performed on 5 mg samples in non-hermetically sealed aluminium crucibles. The temperature of melting of the metals was normally found to be reproducible to within a single temperature step.

The enthalpy calibration was carried out using a sample mass of 10 mg and a heating rate of 3 °C min$^{-1}$. For both the tem-

Table 2
Literature values for the enthalpies of the solid–solid phase transitions of rubidium nitrate

| First author | Year | Enthalpy (kJ mol$^{-1}$) | | | Reference | Method |
|---|---|---|---|---|---|---|
| | | Transition 1 | Transition 2 | Transition 3 | | |
| Mustajoki | 1958 | 3.90 | 3.21 | 0.96 | 3 | Calorimetry |
| Arell | 1961 | 3.86 | 3.24 | – | 4 | Calorimetry |
| Rao | 1966 | 3.97 | 2.72 | 1.26 | 6 | DTA |
| Höhne | 1983 | 3.82 | 3.15 | 1.37 | 11 | DSC* |
| Höhne | 1985 | 3.82 | 3.13 | 1.27 | 12 | DSC‡ |
| Secco | 1999 | 4.00 | 3.29 | 1.47 | 8 | DSC |

* Unweigted mean from 2 instruments.
‡ Unweigted mean from round-robin study. Value for Transition 3 obtained using linear baseline.

Table 3
LGC limited temperature/enthalpy standards

| Material | Reference number | Melting temperature (°C) | Enthalpy of fusion ($\mathrm{kJ\,mol^{-1}}$) |
|---|---|---|---|
| Indium | LGC 2601 | 156.61 ± 0.02 | 3.296 ± 0.009 |
| Tin | LGC 2609 | 231.92 ± 0.02 | 7.187 ± 0.011 |
| Lead | LGC 2608 | 327.47 ± 0.02 | 4.765 ± 0.012 |

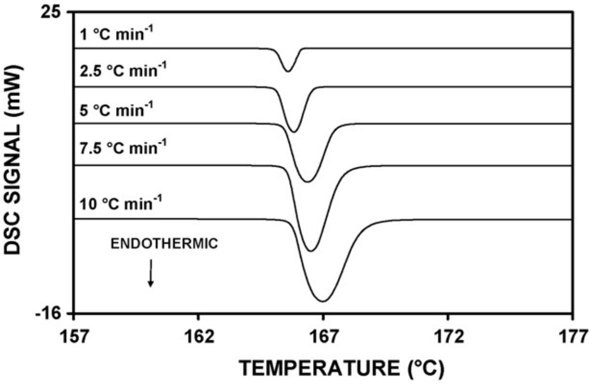

Fig. 2. Influence of heating rate on the DSC curves for transition 1 of rubidium nitrate (sample mass, 5 mg; atmosphere, argon).

perature and enthalpy calibration using lead the crucibles were pre-oxidised by heating in air at 550 °C for 2 h to minimise reaction between the sample and crucible.

The stepwise temperature and enthalpy measurements on rubidium nitrate were carried out under the same conditions as for the calibration materials. The measurements were made in triplicate using a new sample for each determination. The extrapolation to zero heating rate measurements were performed over the range 1–10 °C $\mathrm{min^{-1}}$ and a new sample was used at each heating rate.

The atmosphere used for the experiments was argon (80 $\mathrm{cm^3\,min^{-1}}$). Regular performance checks were carried out during the programme of work to ensure consistency in the results.

The calibration factors for temperature and enthalpy at the transition temperatures were obtained by linear interpolation between the values measured at the melting temperatures of the reference materials. In applying Richardson's method for the determination of enthalpies of transition of rubidium nitrate we have adopted a linear temperature extrapolation of the initial and final heat capacities. The assigned temperature was the measured equilibrium transition temperature. A small correction for thermal lag was incorporated into the calculations. The heat capacity ordinate was calculated from the instrument signal and the measured heating rate. The variation of the enthalpy calibration factor across the temperature breadth of the peaks was <0.2%.

## 3. Results and discussion

### *3.1. Determination of equilibrium transition temperatures*

A DSC curve for rubidium nitrate obtained at a heating rate of 10 °C $\mathrm{min^{-1}}$ shows three sharp peaks for the solid–solid transitions (Fig. 1). The influence of heating rate on the peak for transition 1 is shown in Fig. 2. It can be seen that the peak is well-defined over the range of heating rates studied. In contrast, the peak for transition 2 become less well-defined and increasingly noisy as the heating rate was reduced. This is exemplified in Fig. 3 which shows the peak obtained at a heating rate of 1 °C $\mathrm{min^{-1}}$. The peaks for this transition were smoothed using the software supplied by the instrument manufacturers to facilitate the evaluation of $T_\mathrm{e}$.

Transition 3 appeared to give a well-defined peak. However, when plotted at higher sensitivity it became clear that there was a slow increase in the heat capacity $C_\mathrm{p}$ before the main peak, with small peaks superimposed at about 265 and 275 °C (Fig. 4). These peaks were observed in all our experiments and appeared to increase slightly in magnitude in repeated cycles of the sample through the transitions. Thermogravimetric measurements showed that they were not associated with a mass change. The significance of these superimposed peaks is not clear and they have been ignored in obtaining the enthalpy values.

The equilibrium transition temperatures obtained by extrapolating the values of $T_\mathrm{e}$ to zero heating rate are shown in Table 4. The uncertainties are the standard deviations and include the uncertainty in the calibration factor. The measurements for transition 1 and transition 3 showed excellent reproducibility and the values obtained using the two DSC instruments were in close

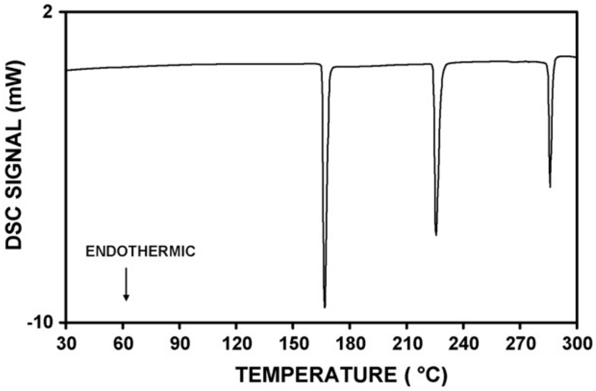

Fig. 1. DSC curve showing the solid–solid transitions of rubidium nitrate (sample mass, 5 mg; heating rate, 10 °C $\mathrm{min^{-1}}$; atmosphere, argon).

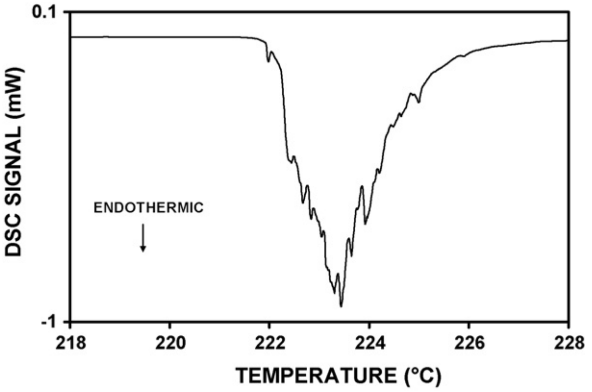

Fig. 3. DSC curve for transition 2 of rubidium nitrate (sample mass, 5 mg; heating rate, 1 °C $\mathrm{min^{-1}}$; atmosphere, argon).

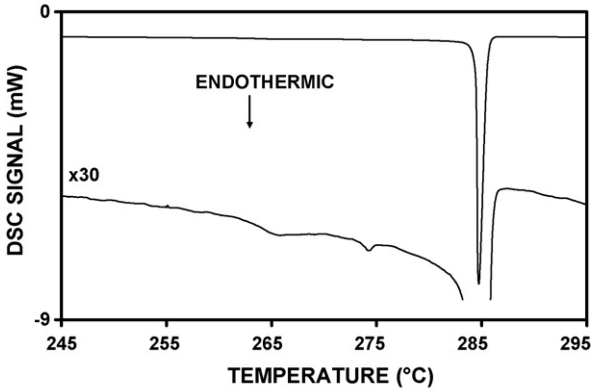

Fig. 4. DSC curve for transition 3 of rubidium nitrate (sample mass, 10 mg; heating rate 10 °C min$^{-1}$; atmosphere, argon).

Table 4
Equilibrium temperature for the solid–solid phase transitions of rubidium nitrate obtained using the extrapolation to zero heating rate method

| Instrument | Equilibrium temperature (°C) | | |
|---|---|---|---|
| | Transition 1 | Transition 2 | Transition 3 |
| Mettler DSC 822$^e$ | 164.95 ± 0.05 | 221.7 ± 0.4 | 283.98 ± 0.04 |
| TA DSC 2920 | 164.86 ± 0.03 | 222.7 ± 0.5 | 284.07 ± 0.07 |
| Mean | 164.91 ± 0.03 | 222.2 ± 0.5 | 284.03 ± 0.04 |

agreement. The mean values given in Table 4 are the weighted means with the corresponding uncertainties. The temperatures obtained for transition 2 showed greater variability, which is not unexpected in view of the difficulty in measuring $T_e$ for this transition. In this case we have calculated the mean and assigned an error, which encompasses the results from the two instruments.

The gradients of the curves obtained by plotting $T_e$ against the heating rate $\beta$ for the three transitions showed large differences which were well outside the experimental uncertainties. The mean values of $dT_e/d\beta$ from the two instruments were $0.079 \pm 0.003$ min (transition 1); $0.27 \pm 0.03$ min (transition 2) and $0.11 \pm 0.02$ min (transition 3). These marked variations within a single compound illustrate the potential errors in calibration at a single heating rate when the calibrant and sample may have significantly different heating rate dependencies.

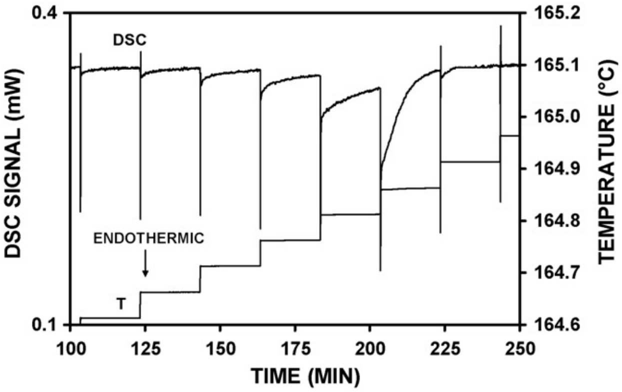

Fig. 5. DSC curve for transition 1 of rubidium nitrate obtained under stepwise heating conditions (sample mass, 5 mg; step size, 0.05 °C; atmosphere, argon).

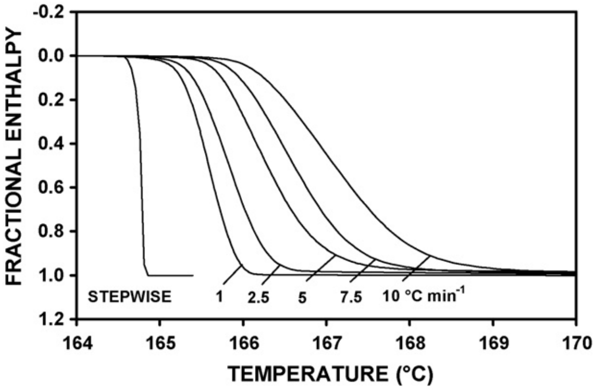

Fig. 6. Plot of fractional enthalpy against temperature for transition 1 of rubidium nitrate obtained under stepwise and linear heating conditions.

The DSC curve from a typical stepwise experiment for transition 1 is shown in Fig. 5. Plotting the incremental enthalpy against temperature enabled a direct comparison to be made between results from the stepwise and the linear heating rate methods. This is illustrated in Fig. 6 and demonstrates the very narrow temperature range over which the transition takes place under stepwise heating conditions compared with heating under linear conditions. The temperatures obtained for transitions 1 and 3 are summarised in Table 5. The results for the two instruments were in agreement and the overall uncertainty exemplifies the excellent reproducibility that can be obtained using this technique. It was not possible to measure transition 2 using the stepwise technique because the DSC curves were too diffuse and noisy.

The results for transitions 1 and 3 in Tables 4 and 5 clearly show the close agreement between the temperatures obtained by the two experimental approaches. This provides further confirmation that the extrapolated onset temperature at zero heating rate corresponds to the temperature at near-equilibrium conditions. The overall values from the two approaches are $164.9 \pm 0.1$ °C (transition 1) and $284.0 \pm 0.1$ °C (transition 3) where the uncertainties have been rounded to a single decimal place. For transition 2 we have the value $222.2 \pm 0.5$ °C from the extrapolation to zero heating rate method.

Our temperatures for transitions 1 and 3 fall between the values reported by Secco and Secco [8] and Hichri et al. [9] which are also based on measurements by DSC. These authors claim uncertainties of ±2 and ±1 °C, respectively in their temperature measurements. Our results show a 10-fold improvement in precision with values that can be traced to the certified reference

Table 5
Equilibrium temperature for the solid–solid phase transitions of rubidium nitrate obtained using the isothermal stepwise heating DSC method

| Instrument | Equilibrium temperature (°C) | |
|---|---|---|
| | Transition 1 | Transition 3 |
| Mettler DSC 822$^e$ | 164.90 ± 0.03 | 283.79 ± 0.03 |
| TA DSC 2920 | 165.02 ± 0.04 | 283.84 ± 0.04 |
| Mean | 164.96 ± 0.03 | 283.82 ± 0.03 |

temperatures and unlike the previous DSC measurements our values relate to thermodynamic equilibrium. For comparative purposes we have used our heating rate coefficients to adjust our values to correspond to the heating rates used in the previous measurements. At the heating rate of 10 °C $\mathrm{min}^{-1}$ used by Secco and Secco [8] our values become 165.7 °C (transition 1), 224.9 °C (transition 2) and 285.1 °C (transition 3). The agreement between the values of Secco and Secco and our calculated values is particularly striking for transitions 1 and 3.

The temperatures obtained by Mustajoki [3] are of obvious interest since they originate from calorimetric measurements of heat capacity as a function of temperature. The result for transition 1 is in marked contrast to that obtained by the other authors with the exception of Brown and McLaren [5] who claimed only that their value was about 160 °C. The value of 164.4 °C obtained by Arell and Varteva [4] by differential calorimetry, using a heating/cooling method, is close to that of the present work.

### *3.2. Determination of transition enthalpies*

Table 6 shows our results for the transition enthalpies measured using the approach adopted by Richardson [14]. There was no significant difference between the results from the Mettler Toledo and PerkinElmer instruments which is of particular interest in view of their different operating principles.

For transitions 1 and 2 there is broad agreement between the published values and those obtained in the present work, with the exception of the result of Rao and Rao [6] for transition 2. As previously mentioned we have assumed a linear dependence of heat capacity on temperature. However, any errors are likely to be small since the sharpness of the peaks for transitions 1 and 2 limits the extent of the heat capacity extrapolations. We have included in the uncertainty an estimate of the sensitivity of the results to the assignment of temperatures $T_1$ and $T_2$. The uncertainty in our results is about 1% which is similar to that given by Mustajoki [3], Arell and Vateva [4] and Höhne et al [11] (1–1.5%). The uncertainty reported by Secco and Secco [8] was slightly greater (3%).

The accuracy of the measurement of the enthalpy of transition 3 is reduced by the slow increase in $C_p$ heat capacity before the main peak which introduces considerable uncertainty in the assignment of $T_1$. The presence of pre-transition $C_p$ curvature is not without parallel in other systems [14]. In the present work the initial temperature $T_1$ has been assigned to a temperature before the onset of the $C_p$ curvature. A further cause of uncertainty is in the assignment of $T_2$ due to the lack of a well-defined linear baseline following the transition peak. By using a treatment common to all the curves we have obtained results reproducible to about 3%. The values shown in Table 6 exclude the contribution from the small superimposed peaks (~0.03 kJ $\mathrm{mol}^{-1}$)

Table 6
Enthalpy values for the solid–solid phase transitions of rubidium nitrate

| Instrument | Enthalpy (kJ $\mathrm{mol}^{-1}$) | | |
|---|---|---|---|
| | Transition 1 | Transition 2 | Transition 3 |
| Mettler DSC 822[e] | 3.83 ± 0.04 | 3.15 ± 0.04 | 1.74 ± 0.06[a] |
| PerkinElmer Diamond | 3.82 ± 0.02 | 3.13 ± 0.05 | 1.72 ± 0.06[a] |
| Mean | 3.83 ± 0.02 | 3.14 ± 0.03 | 1.73 ± 0.04[a] |

[a] These values were obtained by assigning $T_1$ to a temperature before the onset of $C_p$ curvature (see text).

The presence of a systematic error in our results cannot be ruled out. If we set $T_1$ to a temperature following the superimposed peaks we obtain an enthalpy of transition of 1.56 ± 0.03 kJ $\mathrm{mol}^{-1}$ which is closer to the value of 1.47 kJ $\mathrm{mol}^{-1}$ obtained by Secco and Secco [8]. We have no explanation for the very low value reported by Mustajoki [3].

The point has been already been made that the aim in using Richardson's method for enthalpy measurements is to obtain values which have thermodynamic validity. Thus our enthalpies of transition are determined at the equilibrium transition temperatures. It is of interest to compare these values with those obtained using commercial software. We obtained mean values of 3.83 ± 0.02 kJ $\mathrm{mol}^{-1}$ (transition 1), 3.12 ± 0.02 kJ $\mathrm{mol}^{-1}$ (transition 2) and 1.73 ± 0.03 kJ $\mathrm{mol}^{-1}$ (transition 3) using Mettler Toledo 'integral tangential' software and PerkinElmer 'sigmoidal' base line constructions. These values are based on iterative procedures in which the initial and final temperatures are assigned and are virtually the same as those obtained using Richardson's method. However, the use of a conventional straight base line construction would lead to a significant difference in the results for transitions 1 and 3 which would be outside the errors in the present results.

## 4. Conclusions

Accurate values for the equilibrium temperatures of the three solid–solid phase transitions in high purity rubidium nitrate have been measured by two different experimental methods using two different types of heat flux DSC instruments. Transitions 1 and 3 showed good reproducibility and gave overall mean values of 164.9 ± 0.1 and 283.9 ± 0.1 °C, respectively. These values show a significant improvement in precision over those published previously. The DSC peak for transition 2 was less well-defined at lower heating rates and the equilibrium temperature could not be measured using the stepwise technique. A value of 222.2 ± 0.5 °C was obtained by extrapolating $T_e$ to zero heating rate measurements.

The enthalpies of the transitions have been measured at the equilibrium temperatures using both heat flux and power compensation DSC instruments. For transitions 1 and 2 there was good agreement for the two sets of results and mean values of 3.83 ± 0.02 and 3.14 ± 0.03 kJ $\mathrm{mol}^{-1}$, respectively were obtained. For transition 3 there is considerable uncertainty in the results because of the slow increase in the heat capacity before the main transition peak. When the pre-transition region (excluding the small superimposed peaks) is included we obtained the value 1.73 ± 0.04 kJ $\mathrm{mol}^{-1}$, whereas if this region is excluded a value of 1.56 ± 0.03 kJ $\mathrm{mol}^{-1}$ is obtained. Similar results were given for the enthalpies of the three transitions using the dedicated software supplied by the instrument manufacturers.

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