LETTER TO THE EDITOR

The re-entrant phase transitions in malononitrile: specific heat capacity measurements

M T Dove†, G Farelly‡, A I M Rae and L Wright§
Department of Physics, University of Birmingham, Birmingham B15 2TT, UK

Abstract. The specific heat capacity of malononitrile has been measured in the vicinity of the low-temperature re-entrant phase transition, and the results are shown to be in good agreement with the predictions of a model for re-entrant phase transitions proposed by the authors.

The molecular crystal malononitrile $(C_3H_2(CN)_2)$ has recently been found to undergo a sequence of second-order re-entrant phase transitions at 141 and 294.7 K (Dove and Rae 1980, 1983), the intermediate temperature phase having a lower symmetry than the high- and low-temperature phases. The phase transitions have been studied experimentally using the techniques of nuclear quadrupole resonance (Zussman and Alexander 1968, Zussman and Rapaport 1977), Raman scattering (Savoie *et al* 1976, Le Calvé *et al* 1980) and x-ray diffraction (Dove and Rae 1980, 1983), and theoretically through calculations of the lattice energies of the different phases (Rae and Dove 1983). The re-entrant phase transitions are of the displacive type, driven by a soft optical phonon of zero wavevector (Le Calvé *et al* 1980), and the microscopic re-entrant order parameter has been shown to correspond to small rotations of the molecules which preserve the centre of symmetry of the unit cell and leave the size and shape of the unit cell essentially unchanged (Dove and Rae 1980). A more detailed review of the information available concerning the re-entrant phase transitions in malononitrile will be given elsewhere (Dove and Rae 1983). All the experimental evidence shows that both of the phase transitions are second order and describable by mean field theory. However, since the intermediate temperature phase is of lower symmetry than the other two phases, it might be expected that the heat capacity anomaly associated with the low-temperature transition will be of opposite shape to that associated with most second-order mean-field phase transitions; i.e. there will be a positive discontinuity in the heat capacity on warming through the phase transition. The specific heat capacity of malononitrile has been measured by Girdhar *et al* (1968) but these authors did not make detailed measurements in the vicinities of the phase transitions and so comparisons of their results with theoretical predictions are not possible. The aim of the present work therefore was to remeasure the specific heat capacity of malononitrile at temperatures

---

† Present address: Department of Physics, University of Edinburgh, Edinburgh EH9 3JZ, UK.
·‡ Present address: The Royal English College, Valladolid, Spain.
§ Present address: Mullard Southampton, Millbrook Trading Estate, Southampton, UK.

close to the transition temperatures in order to compare the results with theoretical models of the re-entrant phase transitions. However, we here report in detail only the measurements of the heat capacity in the vicinity of the low-temperature re-entrant phase transition since observations of a specific heat capacity anomaly associated with the high-temperature transition did not prove to be sufficiently reproducible to be considered reliable.

The specific heat capacity of malononitrile was measured using an adiabatic calorimeter that has been described elsewhere (Smith and Rae 1978). Measurements were made using two polycrystalline samples of approximately 15 g of malononitrile that had been purified by double distillation. Heating powers of between 14 and 45 mW were employed, and several experimental heating runs were performed. The results of these runs are shown in figure 1. It can be seen that there is an apparent irreproducibility
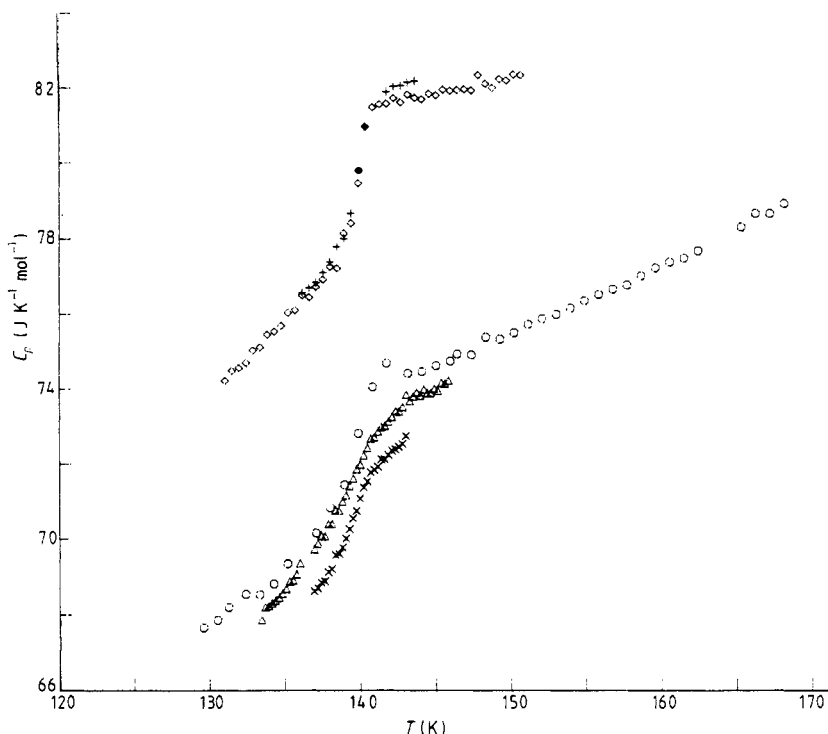

Figure 1. The specific heat capacity of malononitrile in the temperature range 130–170 K. The data represented by circles, triangles and diagonal crosses correspond to separate runs using one sample, and the data represented by diamonds and vertical crosses are for a second sample.

between the results from the two samples used, and it is believed that this is due to the possible presence of impurities, particularly since malononitrile is known to polymerise readily. The effect of such impurities would just be simply to add a small but indeterminate contribution to the total measured heat capacity: the shape and size of any specific heat anomalies will be expected to remain almost unchanged. It is seen from figure 1 that the results indicate the existence of an anomalous discontinuous increase of about 2–3 $J K^{-1} mol^{-1}$ in the heat capacity on warming through the transition temperature of 141 K. This feature is highlighted in figure 2, which shows a plot of each of
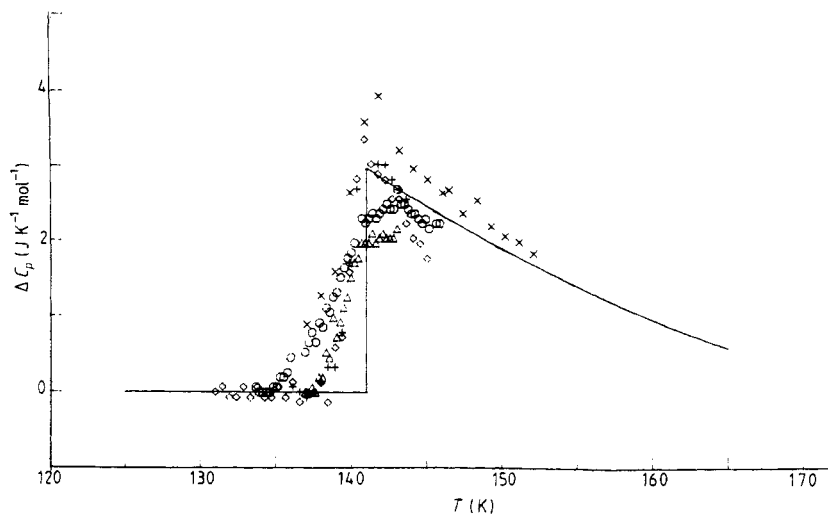
Figure 2. The specific heat capacity of malononitrile with appropriate background contributions subtracted. The data symbols are defined as in figure 1. The smooth curve represents the calculation described in the text.

these sets of data from which an approximate 'background' contribution obtained by linear extrapolation of the heat capacity below the transition temperature has been subtracted. Because the heat capacity of malononitrile at temperatures below 140 K is not strictly a linear function of temperature, this background subtraction procedure is only valid for a few degrees above the transition temperature.

In this spirit of Landau theory, the re-entrant phase transitions in malononitrile can be described using a free energy functional of the form

$$F = A(T)P^2 + C(T)P^4$$

where P is the order parameter, $A(T)$ is zero at the two transition temperatures and is negative between these two temperatures, and $C(T)$ is a slowly varying function of temperature. The equilibrium value of P follows directly from $(\partial F/\partial P)_T = 0$:

$$P^2 = -A/2c$$

We can then obtain an expression for the entropy S:

$$S = -(\partial F/\partial T)_P = -(\partial A/\partial T)P^2 - (\partial C/\partial T)P^4$$

$$= \tfrac{1}{2}P^2(\partial A/\partial T) - \tfrac{1}{2}A(\partial P^2/\partial T).$$

Now $A(T) = \tfrac{1}{2}I\omega^2$, where I is the moment of inertia of the malononitrile molecule about the axis of molecular rotation corresponding to the eigenvector of the soft mode, and ω is the soft mode frequency which has been measured as a function of temperature by Le Calvé *et al* (1980). Moreover, the temperature dependence of P can be obtained from the temperature dependence of the splittings of the NQR frequencies (Zussman and Alexander 1968) scaled to the value of the order parameter directly measured at 273 K by x-ray diffraction (Dove and Rae 1980). Using these data, the temperature dependence of the entropy S and the heat capacity ($= T\partial S/\partial T$) were calculated and are shown in figures 2 and 3. It can be seen that these results are in good agreement with the experimentally measured values.
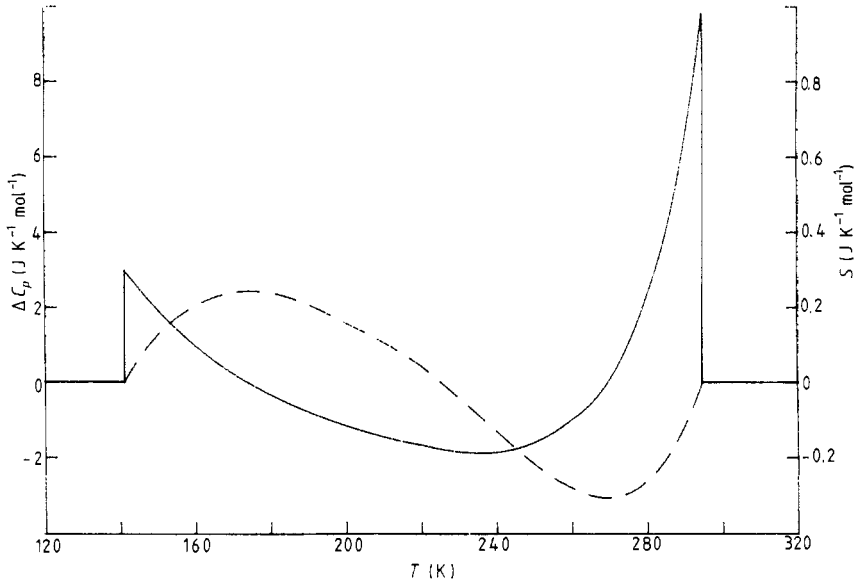
Figure 3. The calculated forms of the entropy S (broken curve) and specific heat capacity C (continuous curve) of malononitrile.

References

Dove M T and Rae A I M 1980 *Faraday Discuss.* **69** 98–106
—— 1983 to be published
Girdhar H L, Westrum E F and Wulff C A 1968 *J. Chem. Eng. Data* **13** 239–42
Le Calvé N, Pasquier B and Novak A 1980 *J. Chem. Phys.* **72** 6409–13
Rae A I M and Dove M T 1983 *J. Phys. C: Solid State Phys.* in press
Savoie R, Brousseau R and Nolin C 1976 *Can. J. Chem.* **54** 3293–302
Smith J H and Rae A I M 1978 *J. Phys. C: Solid State Phys.* **11** 1771–8
Zussman A and Alexander S 1968 *J. Chem. Phys.* **49** 3792–803
Zussman A and Rapaport E 1977 *J. Chem. Phys.* **66** 5330–4