

A new ordered phase in *p*-chloronitrobenzene detected by NQR studies

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 L95

(<http://iopscience.iop.org/0953-8984/8/7/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.179

The article was downloaded on 13/05/2010 at 13:11

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

A new ordered phase in *p*-chloronitrobenzene detected by NQR studies

C A Meriles†, S C Perez and A H Brunetti‡

Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

Received 8 November 1995

Abstract. A study of NQR frequency (ν_Q) and line width as a function of temperature has revealed the existence of a new ordered phase in pure *p*-chloronitrobenzene (PCNB). This phase is stable below $T_c = 282.6$ K. For temperatures above T_c the disordered phase is the stable one.

It is known that if there is a certain disorder in the molecular arrangement, the x-ray technique detects the ‘average molecule’ by the superposition of all the molecules located in the same crystallographic position of the average unit cell. One of the most common examples of this kind of disorder is the formation of centrosymmetric crystals by molecules without a symmetry centre [2]. Such is the case of *p*-chloronitrobenzene (PCNB), that, for a long time, was assumed to be an example of rigid stable disorder in the solid state. In fact, Mak and Trotter [1] showed that this compound exhibits monoclinic symmetry described by space group $P2_1/c$ with two molecules per unit cell, so that a molecular centre of symmetry is required. This is achieved by a disordered arrangement of molecules involving random interchange of the positions of the chlorine atom and nitro group.

Efforts have been made to induce order in PCNB. Semin *et al* [3] attempted to do this by zone melting, in mixtures with *p*-iodonitrobenzene and *p*-bromonitrobenzene. They obtained, after a year, a narrower line of frequency $\nu_Q = 35.412$ MHz at 80 K. We will show that this phase is different from the ordered phase found in pure PCNB.

In the present study, the NQR temperature dependence of ν_Q (figure 1) shows the existence of a phase transition from an ordered state to a disordered one at $T_c = 282.6$ K. That the low-temperature phase is an ordered one can be seen from the NQR line shape. Figure 2 shows the line shape just above and below T_c . Above T_c , we observed a line width of about 200 kHz and below T_c the line width observed was about 10 kHz (this is a typical line width in ordered molecular crystals [4]).

It is worth noting that the NQR frequency of this new phase in the pure compound at 80 K is $\nu_Q = 35.1482$ MHz. This frequency is quite different from that obtained by Semin *et al* in mixtures of PCNB with *p*-iodonitrobenzene or *p*-bromonitrobenzene.

Figure 1 also shows that the disordered phase can persist below T_c by quenching it at liquid nitrogen temperature. The temperature dependence of ν_Q in both phases shows a normal Bayer behaviour.

$$\nu_Q(T) = \nu_0 \left(1 - (3\hbar^2/2I\omega) \cot(\hbar\omega/2kT) \right).$$

† Holder of a fellowship of SeCyT–UNC.

‡ Fellow of the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

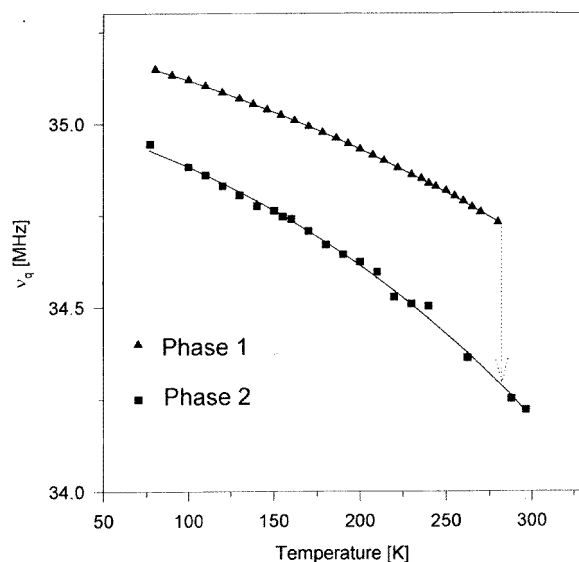


Figure 1. The temperature dependence of ν_Q in PCNB.

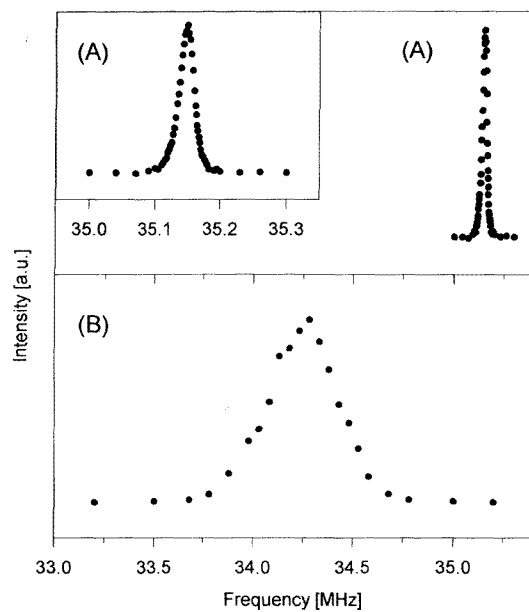


Figure 2. The line shape of PCNB close to T_c in the ordered and disordered phases. The intensities have been normalized in each case.

In this expression $\omega = \omega_0(1 - gT)$ is an average torsional frequency, ν_0 is the limiting static value of the resonance frequency and I is an average moment of inertia of the molecule. A least-squares fit of this equation to the experimental data, in the temperature range 80–300 K using the I value calculated from the molecular structure, yielded the

parameters shown in table 1. These values of ω_0 and g are typical for substituted benzene [5].

Table 1.

Phase I (ordered)	Phase II (disordered)
$\nu_0 = 35.2939$ MHz	$\nu_0 = 35.093$ MHz
$\omega_0 = 95.3$ cm ⁻¹	$\omega_0 = 88.6$ cm ⁻¹
$g = 6 \times 10^{-4}$	$g = 9 \times 10^{-4}$

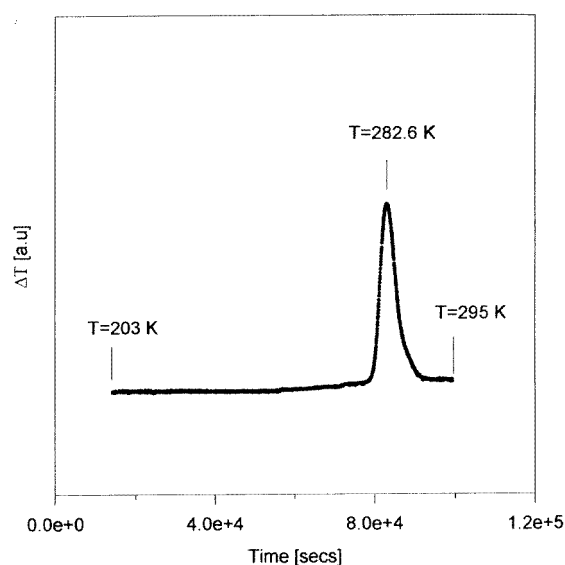


Figure 3. DTA in PCNB.

The phase transition is of first order as shown by the abrupt change in the NQR frequency. Differential thermal analysis also confirms this statement: a typical endothermic peak at T_c is found (figure 3). An estimated value of the enthalpy change associated with this transition is $\Delta H = 921$ cal mol⁻¹.

Concluding, $\nu_Q(T)$, line width and DTA allow us to interpret that *p*-chloronitrobenzene undergoes an order–disorder phase transition at $T_c = 282.6$ K. Therefore, the pure compound has indeed a stable ordered phase and it is different from the one found by Semin *et al.* At present we are studying the characteristics of this phase transition and analysing NQR data in the ordered phase. This will be the subject of a future paper.

References

- [1] Mak T C and Trotter J 1962 *Acta Crystallogr.* **15** 1078
- [2] Kitaigorodsky A I 1973 *Molecular Crystals and Molecules (Physical Chemistry 29)* (New York: Academic) p 86
- [3] Semin G K, Babushkina T A and Robas V I 1967 *Sov. Phys.–Dokl.* **11** 697
- [4] Pérez S C, Armstrong R L and Brunetti A H 1993 *J. Phys.: Condens. Matter* **5** 4045
- [5] Moross G C and Story H S 1966 *J. Chem. Phys.* **45** 3370