

Order-disorder phase transition in *p*-chloronitrobenzene studied by NQR and DTA

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(Received 20 November 1995; revised manuscript received 24 May 1996)

A study of the temperature dependence of nuclear-quadrupolar resonance frequency (ν_Q) and spin-lattice relaxation time (T_1) in *p*-chloronitrobenzene has revealed the existence of an order-disorder phase transition at $T_c=282.6$ K. Nitro groups reorient in the quenched disordered phase but such reorientations are not detected in the ordered phase. The entropy change, ΔS , associated with the phase transition has been measured by differential thermal analysis and these results are discussed. [S0163-1829(96)03534-5]

I. INTRODUCTION

p-chloronitrobenzene (PCNB) provides a typical example of rigid disorder since the molecules in the crystal occupy well defined sites but they can have two possible orientations in order to generate a centrosymmetric crystal.¹ Several studies have been carried out on this compound^{2,3} and none of them revealed the existence of a stable ordered phase. Semin *et al.*³ were able to induce order in PCNB by zone melting in mixtures with *p*-iodonitrobenzene (PINB) or *p*-bromonitrobenzene (PBNB). Nevertheless, we will show that the ordered phase they obtained is affected by the impurities they added.

The present work was undertaken primarily to measure the electric field gradient distribution in the disordered crystal and molecular dynamical properties by means of the temperature dependence of ³⁵Cl nuclear quadrupole resonance (NQR) parameters. The temperature dependence of ν_Q revealed the existence of a phase transition to an ordered phase. This phase, stable below 283 K, was also studied by NQR.

Differential thermal analysis (DTA) was used to characterize the phase transition to the disordered state. An experimental value of entropy change (ΔS) for the transition was obtained and explained on the basis of configurational disorder.

II. EXPERIMENT

The PCNB used for the experiments was obtained from Aldrich Chemical Co. (N C5, 912-2) and used without further purification after three days of annealing. The sample container was a cylinder of 1 cm diameter; the amount of sample used was 2.1 g. The measurements were taken using a Fourier transform pulse spectrometer.⁴ The temperature was controlled to within 0.1 K using a homemade cryogenic system. Copper-constantan thermocouples were employed for the temperature measurements. Due to the line broadening in the disordered phase of this compound, measurements were made using the second half of the echo signal at 100 μ s after the second pulse. The line shape was obtained by reconstruction considering intervals up to 5 kHz. The spin-lattice relaxation time was determined from a $\pi/2$ - $\pi/2$ pulse sequence data synchronized at the central frequency. Pulses of 30 μ s length were used in each case. The temperature

range covered was between 80 K and room temperature.

DTA was carried out in a properly calibrated homemade system.⁵

III. RESULTS

Two different phases were found in this compound as indicated in Fig. 1 where the dependence of $\nu_Q(T)$ for the ³⁵Cl nuclei is plotted as a function of temperature. The chronological order of the measurements is indicated by capital letters. First, the sample was cooled down to liquid nitrogen temperature and the frequency we obtained (A) was that reported for this compound (phase I).⁶ Then the sample was heated up till 250 K (B) where it undergoes a phase transition to a new phase (phase II) (C). The sample was cooled down again and the temperature dependence of ν_Q in this new phase was measured from 80 K (D) to 282 K (E). At this point, the sample undergoes a phase transition to phase I (F). In this phase $\nu_Q(T)$ was measured from this temperature to 300 K. After that, the sample was cooled down from 300 to 260 K and contrary to expectation, phase I was still present (H). Phase II was recovered at that temperature after

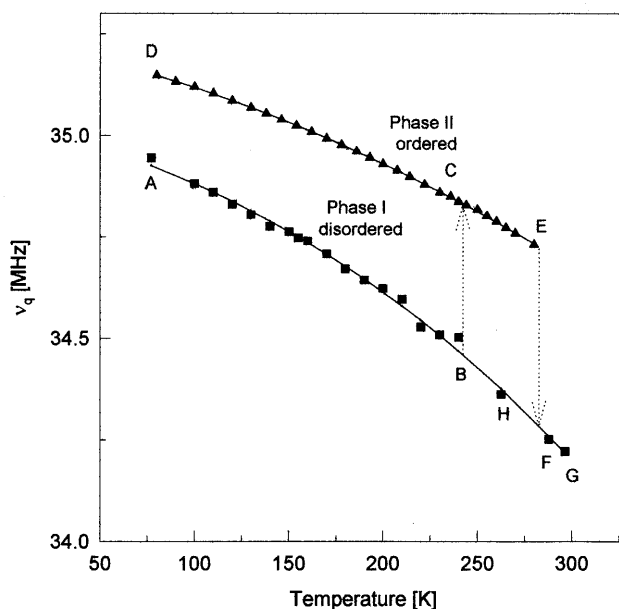


FIG. 1. Temperature dependence of ν_Q in PCNB.

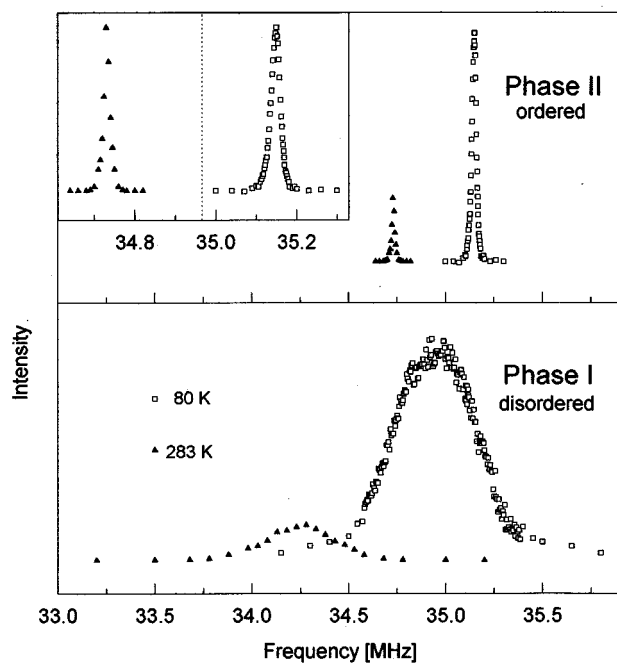


FIG. 2. Line shape of PCNB at 80 K and close to T_c . Intensities have been normalized in each case.

some weeks. It is worth noting that the phase transition at point (B) is extremely slow and that the two phases coexist for about a day. On the other hand, phase transition at point (E) occurs in a few minutes.

In order to check that phase II was not arising from impurity effects, another sample was purified and kept at 248 K for a one month period, after which, phase II was recovered at the expected frequency.

Figure 2 shows the line shape of both phases at two different temperatures. Linewidth in phase II is of the order of 10 kHz while in phase I is about 200 kHz. This shows that phase II represents a crystallographically ordered phase while phase I represents a crystallographically disordered one. The linewidth in both phases is constant with temperature.

The temperature dependence of T_1 for both phases is shown in Fig. 3. In phase II, $T_1 \propto T^{-\lambda}$, but this is not the case for phase I. Above 140 K, T_1 begins to decrease more rapidly with temperature showing a local minimum around 170 K. This suggests the existence of an extra relaxation mechanism besides the torsional oscillations.

Differential thermal analysis (DTA) was carried out in order to characterize the phase transition. Two different samples **a** and **b** were used. Sample **a** was kept at 248 K for a month while sample **b** was kept at that temperature for only two weeks. Sample **a** completely transformed to the ordered phase II, while such transformation was only partial in sample **b**. Figure 4(a) shows a DTA scan of sample **a** recorded while heating the sample. It is possible to observe an endothermic transformation at 282.6 K indicating an order-disorder phase transition. On the other hand, Fig. 4(b) shows a second DTA scan heating sample **a** once the sample was disordered after heating to 300 K in scan 1. In this graph no order-disorder phase transition at 282.6 K was observed. The onsets in Fig. 4(a) and 4(b) are drawn in order to show that

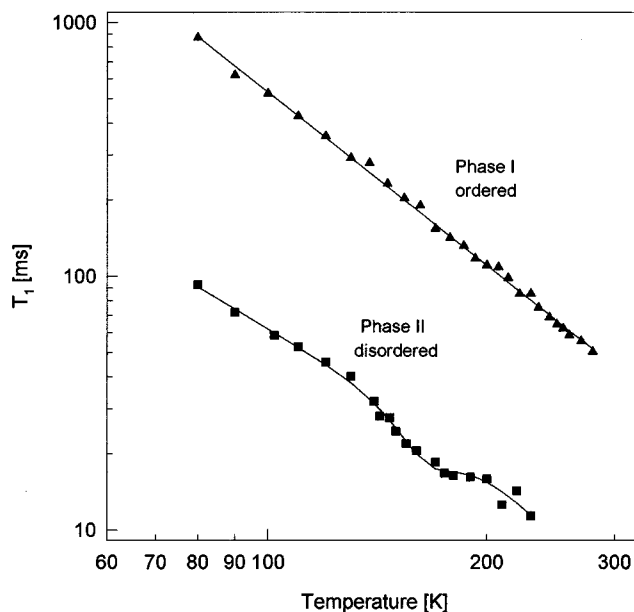


FIG. 3. Temperature dependence of T_1 in PCNB.

when phase II (ordered) is heated nothing is observed between 220 and 260 K. On the other hand, when phase I (disordered) is heated there is a change in ΔT as a function of T similar to the type *G* (glasslike) transitions in solids.⁷ The two transitions observed in Fig. 5 (sample **b**) are essentially those indicated by $B \rightarrow C$ and $E \rightarrow F$ in Fig. 1. The first transition at 245 K is an exothermic one and it is related to a disorder-order transition. The second one is the order-disorder phase transition at 282.6 K also observed in sample **a**. It is worth noting that the area of both peaks is different. The area of order-disorder transition corresponds to 300 mg

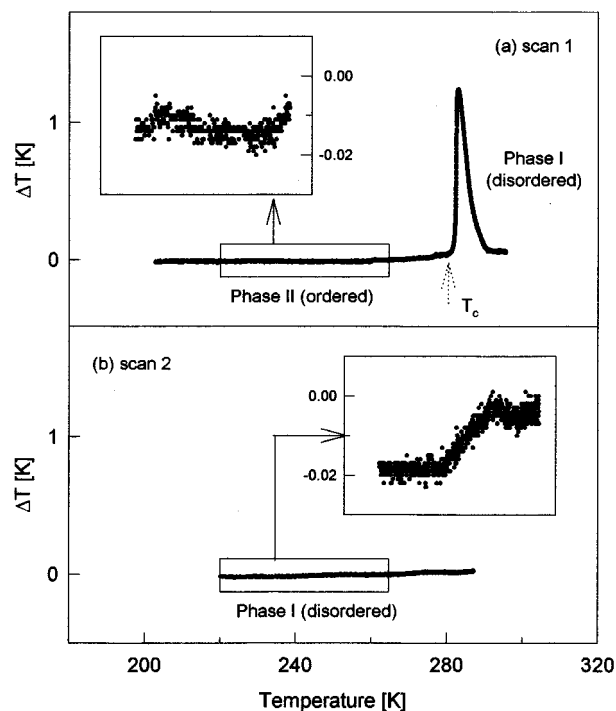


FIG. 4. Differential thermal analysis in PCNB, sample **a**.

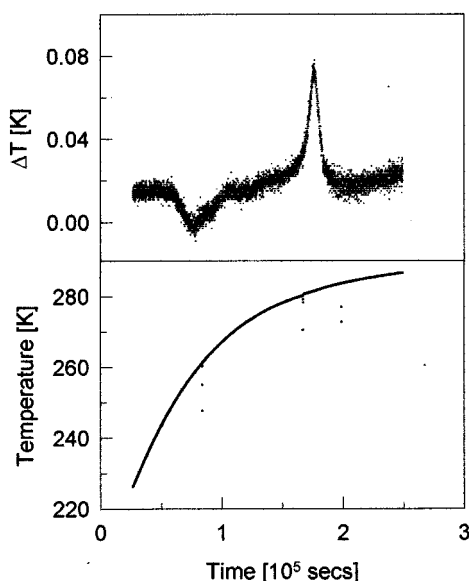


FIG. 5. Differential thermal analysis in PCNB, sample b.

of sample while the first one represents 150 mg of material. Since we had 1 g of sample, this means that part of the sample (150 mg) was ordered, previous to quenching, and acted as a seed to induce the incomplete disorder-order transition.

IV. ANALYSIS AND DISCUSSION

NQR frequency and line shape

The temperature dependence of ν_Q in both phases shows a normal Bayer behavior⁸

$$\nu_Q(T) = \nu_0 \left(1 - \frac{3\hbar^2}{2I\omega} \coth\left(\frac{\hbar\omega}{2kT}\right) \right).$$

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 square 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 following parameters:

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

These values of ω_0 and g are typical for substituted benzene.⁹

The phase transition is of first order as it is shown by the abrupt change in the NQR frequency. From Fig. 2 it is observed that phase I is a disordered one since line widths of 200 kHz represent a wide distribution of electric field gradients. On the other hand, linewidths of 10 kHz for phase II correspond to an ordered phase. This phase represents a different crystallographic structure of PCNB. A comparison of ν_Q value at 80 K of pure ordered PCNB with that obtained

by Semin *et al.* in mixtures ($\nu_Q = 35.412$ MHz) shows a difference of 350 kHz. This indicates that the ordered phase obtained by them depends on the impurities they added.

The line shape and linewidth remained nearly the same in the temperature range measured (see Fig. 2).

Spin-lattice relaxation time

The temperature dependence of T_1 in the ordered phase (phase II) has a normal behavior due to torsional oscillations:

$$\frac{1}{T_1} = AT^\lambda.$$

A least square fit of data gives the following parameters:

$$A = 7.3 \times 10^{-8}, \quad \lambda = 2.21.$$

On the other hand, T_1 in the disordered phase I is observed not to be proportional to $T^{-\lambda}$ (see Fig. 3). From 80 to 140 K the dominant relaxation mechanism is associated with torsional oscillation. Above 140 K, another relaxation mechanism becomes important. Based on studies previously reported,¹⁰⁻¹² it is possible to associate this extra contribution with the reorientation of nitro groups. Therefore,

$$\frac{1}{T_1} = AT^\lambda + \frac{1}{6} (q'/q)^2 \frac{\omega_q^2 \tau}{1 + \omega_q^2 \tau^2},$$

where (q'/q) and τ denote the fluctuating fraction of electric field gradient and the correlation time for the reorientation of the NO₂ group, respectively. The correlation time follows the Arrhenius law, $\tau = \tau_0 \exp(E_a/k_B T)$, where E_a is the activation energy for this motion. From a least square fit of the data, the following results are obtained:

$$A = 5.78 \times 10^{-6}, \quad \lambda = 1.72,$$

$$(q'/q) = 1.8 \times 10^{-4}, \quad \tau_0 = 2.2 \times 10^{-14} \text{ s},$$

$$E_a = 17.1 \text{ K J/mol}.$$

These values of activation energy, (q'/q) and τ_0 , are in good agreement with previously reported values.¹⁰⁻¹²

The discrepancy in the behavior of $T_1(T)$ permits us to make the following analysis: detection by NQR of reorientations of nitro groups requires

$$\omega_q \tau_0 \exp\left(\frac{T_a}{T_0}\right) \approx 1,$$

where T_0 is the temperature at which this relaxation mechanism has maximum efficiency (local minimum in T_1 plot) and $T_a = E_a/k_B$. Then

$$T_0 = \frac{T_a}{\ln(1/\omega_q \tau_0)}.$$

If it is assumed that the crystalline potential a nitro group sees is the same in both phases, the shift in frequency cannot account for an appreciable variation in T_0 . If this were true, we should be able to observe the local minimum in the ordered phase. As this is not the case, it is possible to conclude that the potential barrier has to be at least twice that of the

disordered phase. In this way, the activation of the nitro group would remain hindered for NQR studies.

Differential thermal analysis

With the aim to measure the enthalpy change in the order-disorder phase transition and to calculate the entropy change associated with it, DTA was carried out.

The peak area in Fig. 4(a) gives the value of $\Delta H=3.8$ K J/mol. This implies $\Delta S=\Delta H/T_c=13.6$ J/mol/K.

The total increase in entropy in an order-disorder transition is made up of electronic, vibrational, rotational and configurational contributions:

$$\Delta S = \Delta S_{\text{elec}} + \Delta S_{\text{vib}} + \Delta S_{\text{rot}} + \Delta S_{\text{conf}}.$$

ΔS_{elec} can be ignored because it is only important in metal-insulator or similar transitions. ΔS_{rot} becomes important if free rotation occurs in the disordered phase. This is not the case here. ΔS_{conf} is the truly dominant term in most order-disorder transitions. If in the ordered and disordered phases, the total number of configurations (be it positional or orientational in origin) is N_1 and N_2 , respectively, then¹³

$$\Delta S_{\text{conf}} = R \ln \left(\frac{N_2}{N_1} \right).$$

The vibrational entropy change ΔS_{vib} , which is determined by the vibrational spectrum of the material in the ordered and disordered phases, is considerable when the change in volume at the transition, is very high and when the disordered state has a different crystal symmetry.¹⁴

Having in mind the kind of disorder proposed by Mak and Trotter for this compound, the expected value for ΔS_{conf} should be not less than $R \ln(2)=5.76$ J/mol/K.

Clearly, the experimental value obtained in the present work is approximately twice the minimum expected one. This is an indication of an extra contribution to entropy change probably related with ΔS_{vib} .

With this in mind, we proceeded to estimate the contribution to ΔS_{vib} from the change in the potential shape of the nitro group. To proceed with the calculations we proposed in both cases (ordered and disordered states) a potential energy of the form¹⁵

$$V = \frac{V_2}{2} (1 - \cos(2\theta)),$$

where θ represents the torsion angle.

In the disordered case, it was assigned to V_2 the value obtained from T_1 data for the potential barrier ($V_2=17.1$ K J/mol). In order to explain the excess of entropy change with respect to the configurational contribution, a potential barrier of approximately eight times V_2 must be considered for the calculations in the ordered case, resulting in $\Delta S_{\text{vib}} \sim 6$ J/mol/K.

It is important to remark that if the potential shape for the disordered phase is changed in a way to give an effective well width greater than the one considered previously, then the potential height in the ordered phase could be decreased giving the same contribution to ΔS_{vib} .

V. CONCLUSIONS

A stable ordered phase of pure PCNB is found with an order-disorder phase transition at $T_c=282.6$ K. This transition is of first order and the entropy change associated with it is $\Delta S=13.6$ J/mol/K.

This value of ΔS can be explained considering two contributions: configurational and vibrational in origin. Each of these is of the order of $R \ln(2)$. The vibrational contribution has been calculated considering the change in the potential energy of the nitro groups. T_1 data reveals the existence of reorientations of these groups in the disordered phase with an activation energy of $E_a=17.1$ K J/mol. This value is in good agreement with values reported.¹⁰⁻¹² Furthermore between 240 and 250 K, disordered PCNB undergoes a possible type *G* transition, the exact nature of which remains to be established.

ACKNOWLEDGMENTS

The authors wish to express their thanks to CONICET of Argentina for financial support. They are also grateful to Dr. C. Shurrer and Dr. J. Schneider for their permanent cooperation.

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