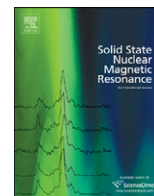




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# Characterization of solid phases and study of transformation kinetics in m-chlorofluorobenzene by $^{35}\text{Cl}$ nuclear quadrupole resonance

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## ABSTRACT

Polymorphism is of widespread occurrence in the world of molecular crystals. In this work we present experimental results showing the existence of four solid phases in m-chlorofluorobenzene. A glass structure is achieved by quenching the liquid phase at 77 K. This glassy state crystallizes in a disordered phase at  $T \sim 143$  K, which in turn transforms to the high-temperature stable phase (phase I) at  $T \sim 153$  K. Depending on the thermal history of the sample, a different ordered phase (phase III) can be obtained. The disorder is attributed to a molecular orientational disorder. There is no evidence of molecular reorientation in any phase. A study of the disorder-order phase transformation kinetics, using nuclear quadrupole resonance, is presented. The results are analyzed following Cahn's theory. Nucleation seems to take place at grain boundaries. Growth rates for different temperatures have been determined.

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## 1. Introduction

Several investigations have been performed on p-chlorohalobenzenes to study both their static and dynamics properties [1–9]. In particular, p-chlorobromobenzene and p-chloriodobenzene exhibit long-range positional order and long-range orientational disorder, while p-chlorofluorobenzene shows polymorphisms [10]. By contrast there is little information available in o-dihalobenzenes or m-dihalobenzenes. The nuclear quadrupole resonance frequencies of some of them are reported [11,12] and only the crystal structures of m- and o-dichlorobenzene are known above 220 K [13].

Nuclear quadrupole resonance (NQR) is a useful technique for characterizing different solid phases and phase transitions in molecular crystals because the magnitude of the electric field gradient (EFG) is an extremely sensitive function of its near-neighbor environment [14]. When some kind of disorder is present, the resonance line width, which reflects the local structural order, is considerably broadened. Line widths of the order of MHz are associated with the glassy state and line widths of the order of hundreds of kHz are related to orientational disorder. Commonly used techniques for characterization of order-disorder phase transformation are X ray diffraction, DSC, NMR and vibrational spectroscopy; some works have been carried out using NQR [15–18]. Another important property of NQR technique is that the number of resonance frequencies observed

is related to the crystal structure. For these reasons it proved to be a useful non-invasive technique to detect, for example, polymorphism and pseudo-polymorphism in pharmaceutical compounds, particularly because, unlike X-ray diffraction and solid state NMR, is not influenced by the presence of excipients [19–21]. Finally, the dynamic properties of different crystalline states can be inferred from the temperature behavior of spin-lattice relaxation time ( $T_1$ ) and spin-spin relaxation time ( $T_2$ ). Studies of molecular reorientations are a common example. Particularly, the dynamic of a very simple kind of glass former was recently reported [22].

On the other hand, the subject of the kinetics of phase transitions in condensed matter is important not only in science, but also in technology. Transformations between crystalline phases have been studied by scientists in many disciplines and in widely varying materials. Most of the work in this field examines the overall rate of transformation or its dependence on the thermal history rather than the nucleation rate itself. This is understandable in view of the experimental and theoretical difficulties surrounding nucleation, in general, and nucleation in crystalline phases, in particular. Among the techniques used to study kinetic of phase transformations are X-ray diffraction methods, second harmonic generation, vibrational spectroscopy, high-resolution transmission electron microscopy, etc. In the literature there are at least two NQR studies reported on this subject [15,23].

The present study includes Differential Thermal Analysis (DTA) measurements and  $^{35}\text{Cl}$  NQR measurements in m-chlorofluorobenzene. This compound is liquid at room temperature and crystallizes below 194 K. Different solid phases were obtained

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depending on the cooling rate. As in p-chlorohalobenzenes, a disordered phase has been found. A characterization of the different phases has been made, as well as a study of the kinetics of the disorder-order phase transformation.

## 2. Experimental

The m-chlorofluorobenzene used in the experiments was obtained from Aldrich Chemical Co (#162299) and used without further purification. The sample container was a glass cylinder of length 3 cm and diameter 1 cm, closed under vacuum.  $^{35}\text{Cl}$  NQR measurements were done using a Fourier transform pulse spectrometer with a Tecmag NMRkit II unit and a Macintosh-based real time NMR station. To obtain the NQR spectra, the nuclear spin-echo Fourier transform mapping spectroscopy (NSEFTMS) method [24,25] was used with  $\pi/2=10\ \mu\text{s}$ . The value of  $\tau$  was set to  $70\ \mu\text{s}$  ( $\tau \gg T_2^*$ ) in order to eliminate distortions from the FID of the second pulse. The mapping frequency step used was 20 kHz and the number of scan was 1000 in the glass state, 400 in the disordered phase and 100 in the ordered phase.

$T_1$  measurements were made upon the echo by the standard  $\pi/2-\pi/2$  two-pulse sequence with  $\pi/2=13\ \mu\text{s}$  and  $\tau=70\ \mu\text{s}$ . The number of points in relaxation curves was around 20 and the repetition rate was ten times  $T_1$  in all the experiments.

The temperature was controlled to within 0.1 K using a homemade cryogenic system with a Lakeshore temperature controller. The temperature range covered was between 80 and 190 K.

The DTA runs were recorded with a properly calibrated homemade system with heating rate of  $0.2\ \text{K min}^{-1}$ . The sample and reference container are cylinders of length 1 cm and diameter 0.4 cm. The reference sample used was benzoic acid. The DTA experiments were carried out on a specimen that was cooled down to liquid nitrogen temperature in two different ways: (i) slow cooling at a rate of  $0.3\ \text{K min}^{-1}$ , and (ii) rapid cooling from the liquid state at room temperature down to 77 K by plunging the specimen into liquid nitrogen.

## 3. Results and discussion

### 3.1. DTA measurements

Fig. 1 shows two DTA records obtained while heating the sample. In Fig. 1a, the sample was cooled down slowly ( $0.3\ \text{K min}^{-1}$ ) from room temperature to liquid nitrogen temperature, while in Fig. 1b the sample was cooled by quenching the liquid phase at 77 K. In the first case, two phase transitions are observed: the exothermic peak at 170 K and the fusion at 193 K. In Fig. 1b, four phase transitions are detected. The first one at 126 K is a glass transition. Two crystalline transitions are detected at 143 K and 153 K and finally the fusion is observed at 193 K. Since in both cases the fusion occurs at 193 K, it is possible to assume that the crystalline phase existing prior to the fusion is the same in both scans. Therefore, it can be concluded from DTA that m-chlorofluorobenzene presents a total of four different solid phases.

### 3.2. NQR frequency and line shape study

In order to characterize each of these phases, the NQR frequency ( $\nu_Q$ ) and  $T_1$  were measured as a function of temperature. Fig. 2 shows the line shape that characterizes the m-chlorofluorobenzene in different temperature ranges after the sample was quickly cooled to liquid nitrogen temperature. For  $T < 126\ \text{K}$ ,

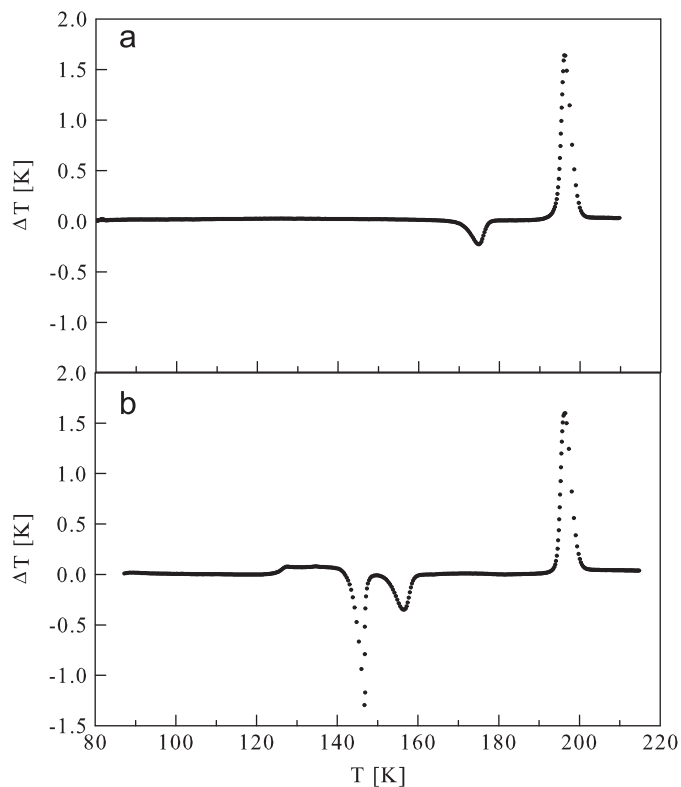


Fig. 1. DTA heating records: (a) sample cooled down slowly and (b) sample quenched at 77 K.

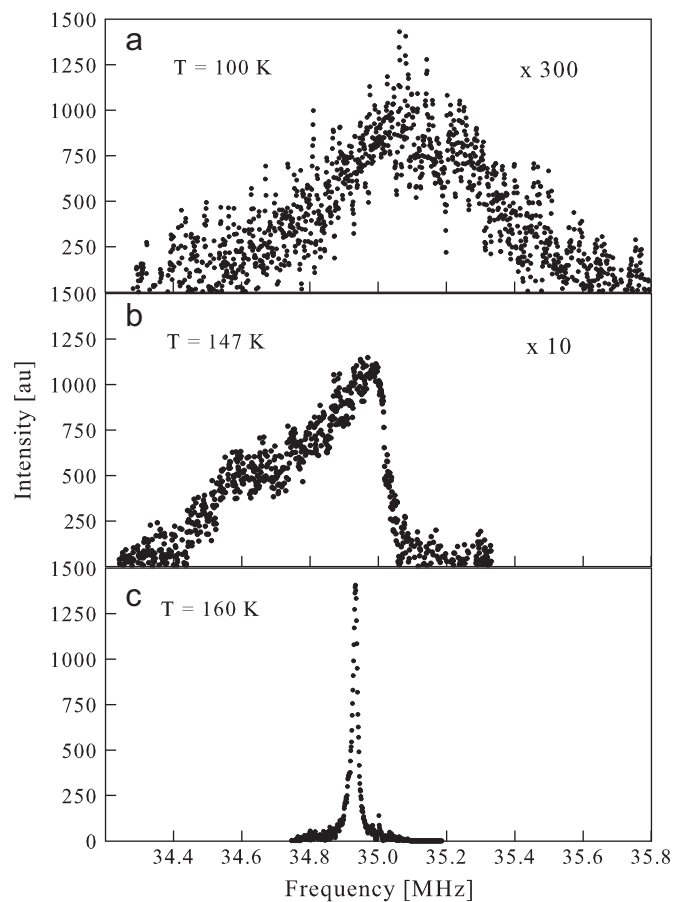
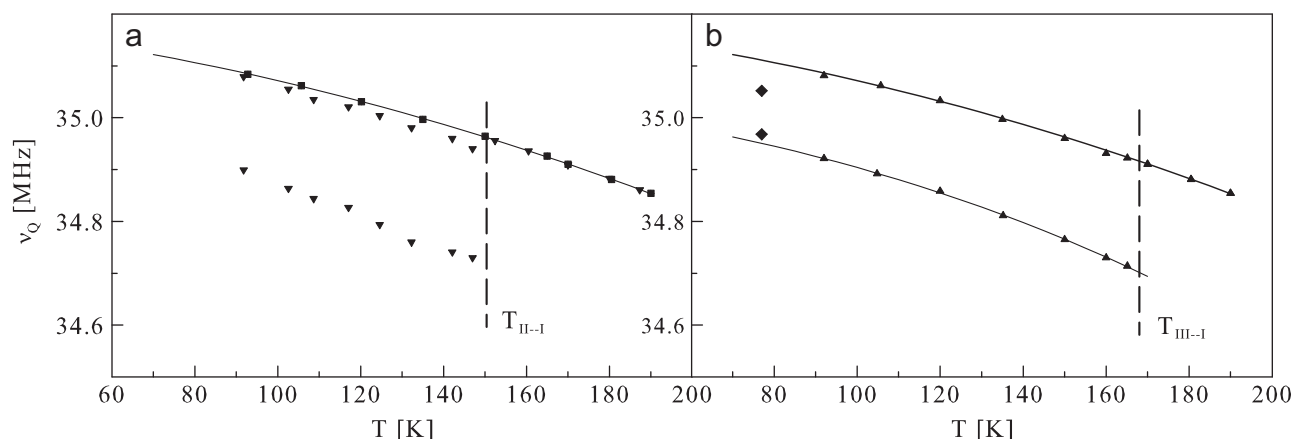
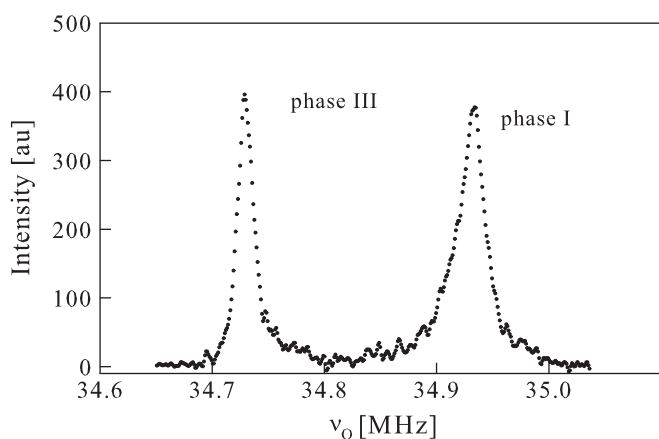


Fig. 2. (a) NQR line shape below 126 K, (b) NQR line shape between 143 K and 153 K and (c) NQR line shape above 153 K.



**Fig. 3.** Temperature dependence of NQR frequency (a) ▼ phase II to phase I, ■ phase I and (b) ▲ phase III to phase I, ◆ frequencies reported in Ref. [18].



**Fig. 4.** NQR profile observed after obtaining phase III at 160 K.

the line width is about 1 MHz. This is typical of a glassy state [26,27]. In the range 126–140 K, the quadrupole signal was not observed. This implies that the sample is a supercooled liquid where the electric field gradient is averaged to zero by molecular motions. Between 143 and 153 K, the line width is about 400 kHz, whereas above 153 K is about 20 kHz. A line width of the order of hundreds of kHz is usually associated with orientationally disordered phases [8,9,16,18], while the line width of 20 kHz represents an ordered crystalline phase. The temperature at which the disordered phase occurs after the glass transition is consistent with that observed in the DTA record (b).

From now on we will call phase II to the ordered phase, and phase II to the disordered phase. Once phase II is obtained, it is possible to cool this phase to 77 K. To follow its behavior, going up with temperature, the central frequency of two Gaussians, used to fit the line shape, are chosen. The temperature dependence of these frequencies is shown in Fig. 3a. At  $T \sim 150$  K, a jump in the value of the NQR frequency is observed indicating a phase transition. This phase transition is from phase II to phase I. The temperature at which this phase transition occurs is consistent with that observed in the (b) DTA record. Phase I is observed up to the melting point. Also in this case is possible to cool down Phase I to 77 K. Its NQR frequency as a function of increasing temperature is shown in Fig. 3a.

When phase II is maintained at 147 K for one day and then it is kept for 32 h at 160 K, a new spectrum with two peaks is obtained (see Fig. 4). If this state was cooled to 77 K, it is possible to follow the temperature behavior of the two frequencies as the temperature increases (Fig. 3b). It is observed that at 170 K, the low

**Table 1**  
NQR frequencies of *m*-dichlorobenzene.

T (K)	$\nu_1$ (MHz)	$\nu_2$ (MHz)	$\nu_3$ (MHz)	$\nu_4$ (MHz)
77	34.809	34.875	35.030 (x2)	
196	34.724	34.732	34.503	34.523

frequency peak disappears while the high frequency peak has the same frequency that phase I at all temperatures. It is clear then, that the lower peak it is related to a new phase that it will be called, from now on, phase III. This phase transforms to phase I at 170 K in agreement with the transition observed through DTA when the sample was cooled down slowly. The area ratio between the two NQR lines is constant in the temperature range 90–165 K and it is of the order of 3/2, with more nuclei in phase I.

It is important to mention that line shape of phase II after 24 h at 147 K is the same that obtained without any waiting time. It is also important to note that after one day of being the sample at 147 K, the transformation at  $T \sim 153$  K is still observed and the spectrum at 160 K differs in the appearance of a very small peak at the frequency characterizing phase III.

Since a single resonance frequency is characteristic of both phase I and phase III, one can ensure that in each case, there is only one molecule in the asymmetric unit of the crystal structure. However, in the literature there are reported two NQR frequencies (35.052, 34.968 MHz) at 77 K [28] and they are represented in Fig. 3b with a diamond. The lowest frequency could correspond to phase III (the small difference in frequency may be due to temperature calibration), while it is clear that the highest frequency does not correspond to the frequency associated with phase I. Therefore, one can conclude that a fifth crystalline phase could exist in this compound; but it has not been obtained in this work.

As mentioned above, *p*-chlorobromobenzene and *p*-chloroiodobenzene are typical examples of crystals with rigid disorder and their line shapes have a line width of hundreds of kHz [8,9]. Also *p*-chloronitrobenzene is a typical example of rigid disorder [29,30]. These compounds crystallize in the centrosymmetric space group  $P2_1/c$  with  $Z=2$ . Because molecules are not centrosymmetric, they can only crystallize under the condition of statistical symmetry.

*m*-Dichlorobenzene crystallizes in the space group  $P2_1/c$  with  $Z=8$  and two molecules in the asymmetric unit [13]. Since each molecule has two chlorine atoms, four NQR frequencies were reported as shown in Table 1 [11,12]. Therefore, assuming that *m*-chlorofluorobenzene has a structure like that of

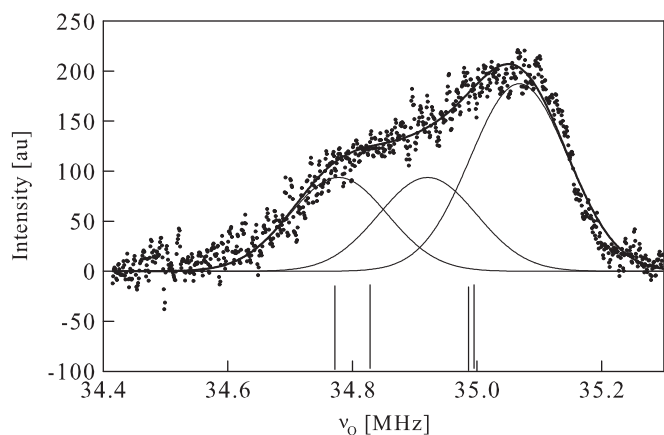


Fig. 5. Least-square fittings of Gaussian functions to line shape in phase II at 92 K.

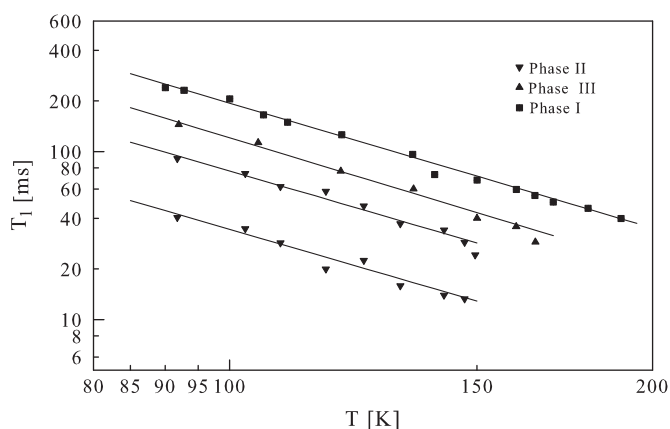


Fig. 6. Temperature dependence of  $T_1$ .

m-dichlorobenzene, a long-range orientational disorder is necessary to generate a centrosymmetric crystal. In this particular case, one can assume that there is a disordered arrangement of molecules consisting of random exchange of the positions of atoms of chlorine and fluorine. Under these conditions, the  $^{35}\text{Cl}$  NQR spectrum of m-chlorofluorobenzene should consist of four lines of equal intensity and width, but each of them is inhomogeneously broadened due to disorder. Fig. 5 shows, as an example, a fit of the data performed under these conditions. As it is observed the fit is quite good. The line width of each line is 180 kHz and their central frequencies are

$$\nu_1 = 34.778 \text{ MHz} \quad \nu_2 = 34.921 \text{ MHz} \quad \nu_3 = 35.069(x2) \text{ MHz}$$

A line width of 180 kHz is of the order of that observed in p-chloriodobenzene ( $\Delta\nu=150$  kHz) and p-chloronitrobenzene ( $\Delta\nu=200$  kHz). Frequencies, on the other hand, are in the range of frequencies observed in m-dichlorobenzene, as indicated by the four straight lines in Fig. 5, keeping a similar relationship: there are two that are very close and two that are separated. Therefore it seems reasonable to assume the existence of the kind of disorder that has been proposed.

Summarizing, DTA and NQR measurements show, depending on the thermal history of the sample, the existence of at least four different states: a glassy state, below  $T_g \sim 126$  K, an orientationally disordered phase which can exist in the range 92–153 K and two ordered phases. One of these is stable in the temperature range 92–193 K and the other one is stable below 170 K. Both, the orientationally disordered phase and phase III, are metastable states.

Table 2  
Fitting parameters of  $T_1(T)$ .

	$B$	$\lambda$
Phase I	$5.9 \times 10^{-8}$	2.47
Phase II ( $\nu_{\text{low}}$ )	$1.8 \times 10^{-7}$	2.43
Phase II ( $\nu_{\text{high}}$ )	$4 \times 10^{-7}$	2.43
Phase III	$7.2 \times 10^{-8}$	2.53

### 3.3. Nuclear quadrupole spin–lattice relaxation time

The temperature dependence of  $T_1$  in phases I, II and III of m-chlorofluorobenzene are shown in Fig. 6.  $T_1(T)$  has a normal behavior due to torsional oscillations

$$\frac{1}{T_1} = BT^\lambda \quad (1)$$

A least squares fit of data with Eq. (1) gives the parameters shown in Table 2.

A  $\lambda > 2$  means that the crystal is quite anharmonic [31]. Unlike what it is observed in p-chlorohalobenzenes (p-Cl- $\Phi$ -Br, p-Cl- $\Phi$ -I) and in p-chloronitrobenzene [8,9], there is no evidence of molecular reorientation in any of the phases.

### 3.4. Disorder–order phase transformation kinetics

An order–disorder phase transformation follows a mechanism of nucleation and growth [32,33]. Nucleation brings the atoms/molecules to new positions corresponding to the product phase. This new region, within the parent phase, is known as an “embryo”. When the embryo reaches a critical size, can continue to grow and is called a “nucleus” of the product phase within the parent phase. Depending on the nature of the material and the phase change involved, it is possible to distinguish two types of nucleation: homogeneous and heterogeneous. Since all solids contain a variety of defects (grain boundary, impurities, vacancies), perfectly homogeneous nucleation never occurs. Instead, nucleation takes place at defect centers. Cahn calculated the isothermal reaction curves for nuclei that are formed preferentially at grain boundaries (where two grains meet) or at edges or corners [34]. When nucleation occurs at grain boundaries, the transformed volume fraction  $\zeta$  at time  $t$  is given by

$$\zeta = 1 - e^{-(b^B)^{-1/3} f^B(a^B)} \quad (2)$$

where

$$a^B = \left( \frac{\nu I_B \gamma^2}{3.35} \right)^{1/3} t$$

$$b^B = \frac{\nu I_B L^4}{3.35(6.7)^3 \gamma}$$

$$f^B(a^B) = a^B \int_0^1 [1 - e^{(-\pi/3)(a^B)^3(1-2\xi^2+2\xi^3)}] d\xi$$

$\nu I_B$  is the grain boundary nucleation rate per unit volume of the assembly,  $\gamma$  is the isotropic growth rate and  $L$  is the mean grain diameter.

When  $a^B$  is very small, Eq. (2) approaches the limiting form

$$\zeta = 1 - e^{-\pi^3 \nu I_B \gamma^3 t^4 / 3} \quad (3)$$

When  $a^B$  is very large, Eq. (2) has another limiting form

$$\zeta = 1 - e^{-6.7 \gamma t / L} \quad (4)$$

Therefore, the  $\{\log_{10}[\ln(1/(1-\zeta))]\} - \{\log_{10} t\}$  plot consists of two straight lines with slope 4 and 1 separated by an intermediate region

over which the slope decreases from 4 to 1. Instead, when nucleation occurs at grain edges, the limiting straight lines have slopes 4 and 2 and when it takes place at grain corners, slopes are 4 and 3.

It is known that the area under the NQR line shape is proportional to the number of nuclei being observed and its central frequency is typical of the sample's crystalline phase. Therefore the transformed volume fraction  $\zeta$  will be proportional to the area of this signal. Since the NQR line width does not change with time,  $\zeta$  will be proportional to the NQR amplitude  $A$ . The time dependence of the amplitude of the ordered phase,  $A$ , is a good parameter to describe the kinetics of the transformation. This amplitude is obtained from the FFT of the second half of the echo signal using a  $\pi/2-\tau-\pi$  pulse sequence with  $\tau=70\ \mu\text{s}$  [35]. For normalization purposes, the NQR signal amplitude of phase I ( $A_0$ ) as a function of temperature for  $T > 155\ \text{K}$  was measured. Under these conditions the transformed fraction from the disordered phase to phase I or phase III is represented by

$$\zeta \propto \frac{A}{A_0} \quad (5)$$

To measure  $A$  as a function of time at a fixed temperature, the sample is rapidly cooled from the liquid to liquid nitrogen temperature and then brought it to the desired temperature. This procedure was repeated for each measured temperature.

Fig. 7 shows the time dependence of the fraction transformed to phase I at five different temperatures. It is observed that the transformation rate ( $d\zeta/dt$ ) has a maximum close to 180 K. Also shown in this figure the transformed fraction of phase III at  $T=160\ \text{K}$  in two cases. Open circles correspond to the case in which the sample was subjected to a cooling process as explained above. Black circles represents the case in which the sample was, first, frozen at liquid nitrogen temperature, then was kept at 147 K for 24 h (in disordered phase) and finally was maintained to 160 K. In the first case, phase transformation to phase III is hardly observed, while in the second case, part of the sample transforms into phase III and another transforms into phase I.

Using the scale representation of Fig. 8, it is observed that, for phase I, the time dependence is linear for fractions lower than 55% at  $T=160, 165$  and  $167\ \text{K}$ , fractions lower than 32% at  $T=170\ \text{K}$  and fractions lower than 25% at  $T=175$  and  $180\ \text{K}$ . Then a change in behavior is observed. These characteristics in the disorder–order transformation are the same observed in p-chloronitrobenzene [23]. After fitting the linear dependence, the slopes of the curves are 1 at 167, 170, 175 and  $180\ \text{K}$  and 1.22 at 160 and 165 K. These values of slopes are compatible with grain boundary nucleation.

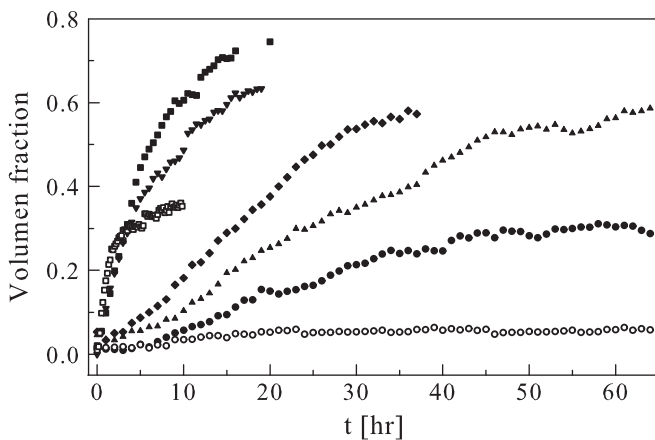


Fig. 7. Transformed volume fraction  $\zeta$  as a function of time. Phase I:  $\blacktriangle$  160 K,  $\blacklozenge$  165,  $\blacksquare$  167 K,  $\blacktriangledown$  170 K and  $\square$  180 K. Phase III:  $\bullet$  160 K after being kept at 147 K  $\circ$  160 K without being kept at 147 K.

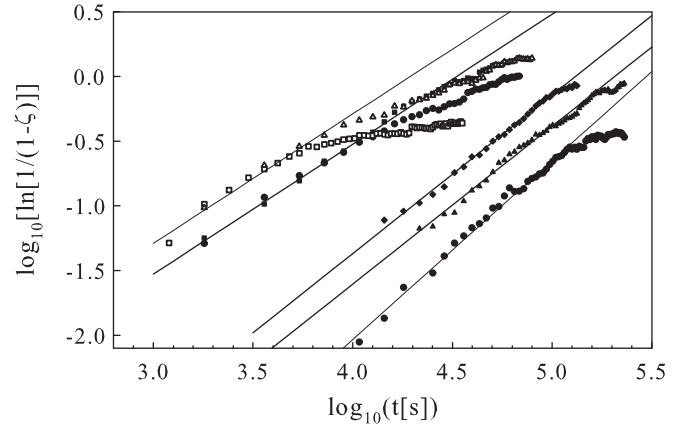


Fig. 8. Kinetics of the transformation.  $\{\log_{10}[\ln(1/(1-\zeta))]\}$  vs  $\{\log_{10} t\}$  plot. Phase I:  $\blacktriangle$  160 K,  $\blacklozenge$  165,  $\blacksquare$  167 K,  $\blacktriangledown$  170 K,  $\triangle$  175 K and  $\square$  180 K. Phase III:  $\bullet$  160 K after being kept at 147 K.

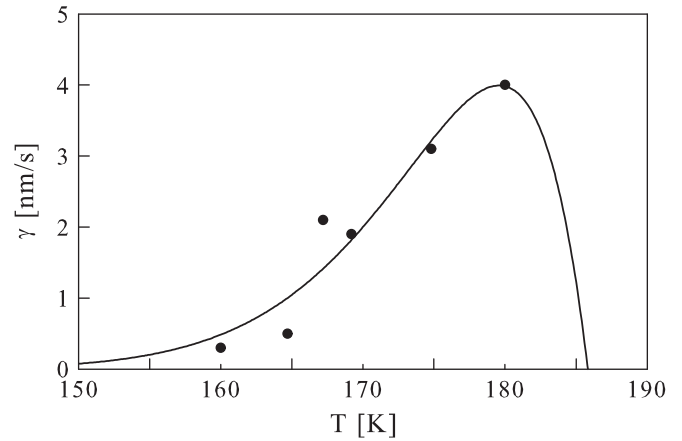


Fig. 9. Growth rate plotted as a function of temperature.

For phase III, the time dependence is linear for fractions lower than 25% and the slope is 1.41. Since the slope is lower than 2, it is possible to assume that also in this case nucleation takes place at grain boundaries.

According to Cahn formalism, when data do not show asymptotic behavior, it is possible to obtain  $\gamma$  from experimental data through the expression [32]

$$\gamma = \frac{L}{6.7} 10^{A-B}$$

where  $A$  and  $B$  satisfy

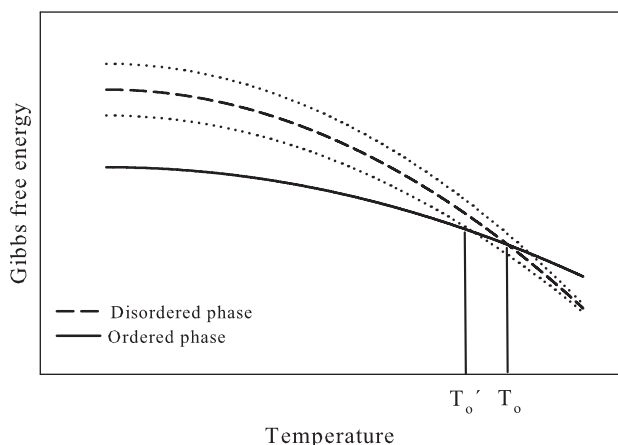
$$\log_{10} \left[ \ln \left( \frac{1}{1-\zeta} \right) \right] + B = \log_{10} f^B (a^B)$$

$$\log_{10} t + A = \log_{10} a^B$$

When the slope has the limiting value 1 it is possible to determine  $\gamma$  from Eq. (4). Fig. 9 shows the temperature dependence of  $\gamma$  for the disorder-phase I transformation calculated assuming a mean grain diameter of  $500\ \mu\text{m}$ .

If we consider the growth to be achieved through a molecule by molecule transfer across the interface between the two phases, the expected behavior for  $\gamma$  is given by the expression [33]

$$\gamma = C \left( \frac{1}{T} - \frac{1}{T_0} \right) e^{-E_a/kT} \quad (6)$$



**Fig. 10.** Schematic representation of the free Gibbs energy as a function of temperature.

$E_a$  is the free energy of activation for molecules to cross the interface from the parent phase to the new phase and  $T_0$  is the order–disorder transition temperature. A least squares fit of Eq. (6) to the experimental data gives

$$T_0 = 185.8\text{K} \quad E_a = 10.7\text{Kcal/mole}$$

$E_a$  has a value of the order of that found in the disordered–order phase transformation of *p*-chloronitrobenzene [23], compatible with that expected for molecular reorientation in aromatic compounds [36].

$T_0$  is quite different from the transition temperature obtained from DTA and NQR frequency data. It is important to take in account that phase II is a metastable state. A metastable state transforms to stable states with a minimum free energy, when sufficient energy is made available to them. Such transformations are irreversible. Therefore, it is not possible to assign any critical transformation temperature for an irreversible transformation. Because of kinetic factors, such transformations are functions of both time and temperature and one can only define a temperature below which an irreversible transformation does not take place [33]. In this case the transition temperature obtained from DTA and NQR data is the minimum temperature at which the transformation from the metastable state to the stable state takes place. On the other hand, as it was stated in Ref. [23], the Gibbs free energy of a disordered crystal is the average value of a distribution that contemplates the existence of different environments. This distribution has a finite width, reduced by thermal agitations as temperature increases (see Fig. 10). For a nucleus to form and grow, it is necessary to have a local temperature fluctuation with a net negative free energy. The existence of an energy distribution makes it possible that some of them do not satisfy this condition prematurely. As a result, it is observed an effective value ( $T_0'$ ) lower than the transition temperature. It is likely that the order–disorder transition temperature is above the melting temperature (193 K).

#### 4. Conclusions

Four different solid states have been found in *m*-chlorofluorobenzene. A structural glass is obtained, below 126 K, when the sample is quickly frozen to 77 K. This glass state transforms to a disordered phase at about 143 K. From experimental evidence, this disorder may be associated with random orientations of molecules,

as in *p*-chlorohalobenzenes and *p*-chloronitrobenzene. Two ordered phases, each with one molecule in the asymmetric unit cell, are also reported. One of them is stable below 170 K and only obtained if the sample is kept at 160 K after being held in the disordered phase for 24 h. From kinetic studies, the transformation process from disorder to order seems to take place at grain boundaries and the activation energy for molecules to cross the interface from the parent phase to the product phase is 10.7 kcal/mole. This value is approximately the activation energy found in *p*-chloronitrobenzene for the same process and it is compatible with that expected for molecular reorientation in aromatic compounds.

#### Acknowledgments

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