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## <sup>35</sup>Cl nuclear quadrupole resonance study of the structural phase transition in 1,2,4,5-tetrachlorobenzene

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**Abstract.** The crystallographic phase transition which 1,2,4,5-tetrachlorobenzene undergoes at about 188 K from a high-temperature monoclinic ( $P2_1/a$ ) structure to a low-temperature triclinic ( $P\bar{1}$ ) structure has been studied by means of the <sup>35</sup>Cl nuclear quadrupole resonance transition frequencies measured as a function of temperature from 77 to 300 K. The transition is shown to be first order displacive, determining the order parameter and its temperature dependence, and deducing a critical exponent  $\beta = 0.309 \pm 0.012$  which indicates that the system behaves as a 3D Ising-like model where the important forces are those of short range. Also, the measured spectra are shown to be consistent with the measured ( $P2_1/a$ ) and proposed ( $P\bar{1}$ ) crystal structures, producing an assignment of the spectra to the various chlorine sites in both primitive unit cells. Additionally, a wide temperature range (approximately 165–205 K) where both phases coexist in a stable form is found and analysed.

### 1. Introduction

During the last few years we have been involved in the study of chlorinated molecular crystals (Zuriaga and Martin 1983, 1986, Ramia *et al* 1988, Monti *et al* 1988), and in this paper we report the study carried out on the crystallographic phase transition, which takes place in 1,2,4,5-tetrachlorobenzene (TCB) at about 188 K, by means of <sup>35</sup>Cl nuclear quadrupole resonance (NQR).

X-ray and NQR studies (Dean *et al* 1958, Gafner and Herbstein 1960) have revealed that the crystalline high-temperature  $\beta$ -phase is monoclinic ( $P2_1/a$ ;  $a = 9.73 \text{ \AA}$ ,  $b = 10.63 \text{ \AA}$ ,  $c = 3.86 \text{ \AA}$ ;  $\alpha = \gamma = 90^\circ$ ,  $\beta = 103.5^\circ$ ) with two symmetry-related molecules per primitive unit cell, which are located at equivalent positions ( $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, 0)$  (Henry and Lonsdale 1965)) whose local point symmetry is that of inversion. The low-temperature  $\alpha$ -phase has been shown by means of x-ray and Raman studies (Herbstein 1965, Halac *et al* 1977) to be triclinic ( $P\bar{1}$ ,  $a = 9.60 \text{ \AA}$ ,  $b = 10.59 \text{ \AA}$ ,  $c = 3.76 \text{ \AA}$ ;  $\alpha = 95^\circ$ ,  $\beta = 102.5^\circ$ ,  $\gamma = 92.5^\circ$ ) with two symmetry-unrelated molecules per primitive unit cell located at  $(0, 0, 0)$  and at  $(\frac{1}{2}, \frac{1}{2}, 0)$ , which are points with inversion operation as the local point symmetry (Henry and Lonsdale 1965).

Various open questions need to be answered about the  $\alpha$ -to- $\beta$  phase transition. First, it has been pointed out by Pasquier and La Calvé (1977) that over a wide temperature range both phases coexist with no time evolution. This fact should clearly be exhibited

by the NQR spectra. Second, as is pointed out by Bonadeo *et al* (1978), the  $\alpha$ -phase NQR spectra is consistent with the  $P\bar{1}$  crystalline structure, although it is not clear whether more NQR lines could be expected. This is also a question that could be answered by a careful analysis of the intensities of the NQR spectra in both phases. Third, an assignment of the NQR spectra, i.e. which chlorine atoms contribute to which line, has been obtained in the  $\beta$ -phase (Dean *et al* 1958); is it possible to produce an assignment for the  $\alpha$ -phase spectra? Fourth, it has been proposed for TCB that the rotation angle  $\varphi$  of the molecules on approaching  $T_c$  may be used as an order parameter (Pasquier and La Calvé 1977). A similar situation holds for chloroanil (Ellenson and Kjems 1977). On the basis of the temperature dependence of the NQR spectra in the  $\alpha$ -phase this is shown to be the case, and therefore  $\varphi$  is chosen as the order parameter for the  $\alpha$ -to- $\beta$  phase transition. Additionally, a value for the order parameter critical exponent is deduced and the consequences analysed. The temperature dependence of the  $\beta$ -phase NQR spectra and the crystalline contributions to the electric field gradient (EFG) at the chlorine sites are discussed.

## 2. Experimental details

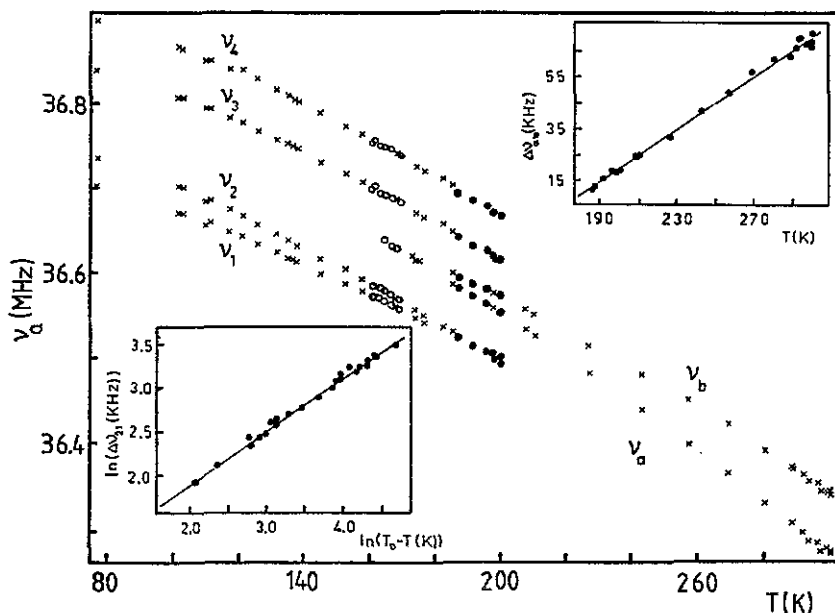
A commercial sample was provided by Fluka (catalogue number 87000) and used as received. Excellent signal-to-noise ratio spectra were recorded employing a standard super-regenerative-type spectrometer with side-band suppression; the temperature was measured by means of a copper-constantan thermocouple located inside the vial containing the sample. Frequency and temperature measurements are believed to be accurate to within  $\pm 2$  kHz and  $\pm 0.3$  K, respectively.

As mentioned above, both phases coexist over a wide temperature range. In order to make sure that this is not an impurity effect, an additional sample, from the same batch, was purified by recrystallizing TCB in *i*-butanole, resulting in a white fine powder. This recrystallized sample also produced excellent signals and reproduced all the previously obtained results. In order to eliminate possible surface-volume and strain effects, a third sample from the recrystallized batch was melted and slowly cooled to room temperature (about 24 h). The NQR frequency data obtained with this sample matched exactly those already determined with the two previous samples. These results indicate that impurities, surface-volume and strains may be eliminated as possible causes of the fact that both phases coexist in the temperature interval 165–205 K.

## 3. Results and discussion

The measured NQR spectra as a function of the temperature are depicted in figure 1. The crosses are the data collected when only either the  $\alpha$ -phase or the  $\beta$ -phase was present. The open circles are the data collected when both phases were present and while lowering the temperature. The full circles are the data gathered when both phases were present, but in this case while raising the temperature.

It is important to point out that all measurements were done about  $\frac{1}{2}$  h after the set temperature was reached, i.e. the data were collected in all cases under conditions of thermodynamic equilibrium. It should be mentioned that 10–15 min after setting the desired temperature no changes could possibly be detected in the measured frequencies. At those temperatures where both phases coexisted, much longer times were allowed



**Figure 1.** Temperature dependence of the NQR spectra in both phases:  $\times$ , data gathered with only one phase present either lowering or raising the temperature;  $\circ$ , data obtained when both phases were present during cooling;  $\bullet$ , data obtained when both phases were present during heating. The upper inset depicts the temperature behaviour of  $\nu_b - \nu_a$  in the  $\beta$ -phase, clearly showing a linear behaviour. The full line is described by  $\nu_b - \nu_a = 0.501(T - 160.8)$  (kHz). The lower inset represents the temperature dependence of  $\nu_2 - \nu_1$  in the  $\alpha$ -phase, clearly showing a critical behaviour describe by  $\ln(\nu_2 - \nu_1) = 0.632 + 0.618 \ln(185.4 - T)$ , which produces the full line.

(about 10 h), while recording the NQR spectra every hour. No changes were detected in the NQR spectra either in the frequencies or in the intensities of the various lines, therefore indicating that there was no time evolution of the system on a time scale of about 10 h. A similar situation was detected by means of Raman spectroscopy (Pasquier and La Calvé 1977). This may be understood on the basis that the driving thermodynamic force to keep the phase transition going is very small. Several arguments support this assumption.

- (a) The Helmholtz free energies for both phases are very similar (Bonadeo *et al* 1978).
- (b) The latent heat of the transition is very small:  $\Delta H = 34 \text{ J mol}^{-1}$  (Martin 1982).
- (c) The entropy changes associated with the transition are also very small:  $\Delta S = 0.18 \text{ J K}^{-1} \text{ mol}^{-1}$ .
- (d) The two crystalline structures are very similar (Halac *et al* 1977).

All these elements indicate that the transition is mainly displacive, although it is first order owing to the presence of hysteresis (Martin 1982).

The NQR spectra agree with the crystalline structure of both phases (Dean *et al* 1958, Gafner and Herbstein 1960, Henry and Lonsdale 1965, Herbstein 1965, Halac *et al* 1977). In the  $\beta$ -phase, both molecules in the primitive unit cell are located at equivalent

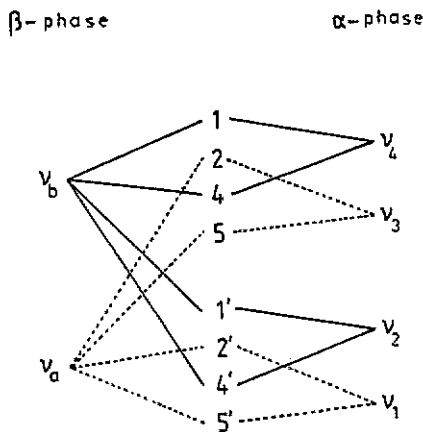


Figure 2. Assignment of the  $\beta$ -phase (monoclinic;  $P2_1/a$ ;  $z = 2$ ) and  $\alpha$ -phase (triclinic;  $P\bar{1}$ ;  $z = 2$ ) NQR spectra. The numbers 1, 2, 4, 5 and 1', 2', 4', 5' indicate the chlorine sites in the TCB molecules 1 and 2, respectively, and are taken from the work of Dean *et al* (1958), while the assignment of  $\nu_4 > \nu_3 > \nu_2 > \nu_1$  to the chlorine pairs (1, 2), (2, 5), (1', 4') and (2', 5') respectively is achieved as indicated in the text.

sites (i.e. symmetry related) with inversion symmetry, and the fact that two equal-intensity lines are detected indicates that the crystalline contribution to the EFG at the chlorine sites 1 and 4 of the TCB molecule is slightly different from that at sites 2 and 5 while, in the  $\alpha$ -phase, both molecules in the primitive unit cell are located at symmetry-unrelated sites with inversion symmetry and therefore each  $\beta$ -phase line splits into two lines, producing a spectrum with four equal-intensity lines, as is actually observed. Additionally, the area under the four  $\alpha$ -phase lines is equal to that under the two  $\beta$ -phase lines, indicating there is no need to search for other resonances.

An attempt to produce an assignment of the four  $\alpha$ -phase lines ( $\nu_1 < \nu_2 < \nu_3 < \nu_4$ ) to the two ( $\nu_a < \nu_b$ ) in the  $\beta$ -phase follows. The criterion used is based on the fact that the lattice distortion on going from the  $\alpha$ - to the  $\beta$ -phase is very small (Gafner and Herbstein 1960, Herbstein 1965, Halac *et al* 1977), i.e. we expect the temperature dependence of one  $\alpha$ -phase pair average to match smoothly that of one of the two  $\beta$ -phase lines. Excellent matching, which gives additional support to the smallness of the lattice distortion, is obtained by assigning the pairs ( $\nu_1, \nu_4$ ) and ( $\nu_2, \nu_3$ ) to the  $\nu_b$  and  $\nu_a$  lines, respectively. This assignment agrees with that given by Chihara and Nakamura (1973) in the case of chloroanil. The NQR spectrum in the  $\beta$ -phase has already been assigned by Dean *et al* (1958), and the result is as follows: the higher-frequency ( $\nu_b$ ) line is due to chlorine atoms 1 and 4 (Dean *et al* 1958, Halac *et al* 1977) in the TCB molecule, i.e. those chlorine atoms whose C-Cl bond directions are mainly parallel to the primitive  $b$  unit-cell axis; chlorine atoms 2 and 5 contribute to the lower-frequency ( $\nu_a$ ) line. In view of the above discussion, it is possible to figure out which chlorine atom pair in the primitive unit cell contributes to which line in the  $\alpha$ -phase. Both assignments are shown schematically in figure 2.

Since the two structures are very similar, it is reasonable to assume that the main effect of the transition is a rotation of the molecules about a given axis, similarly to the chloroanil case (Ellenson and Kjems 1977). Let us consider the TCB molecule located at the origin of the primitive unit cell in the  $\beta$ -phase, assuming it to be planar, and defining a Cartesian system of coordinates  $x$ ,  $y$  and  $z$ , labelled according to  $I_x > I_y > I_z$ , respectively, which are the eigenvalues of the molecular inertia tensor about the molecule centre of mass. The unit vectors  $\hat{i}$ ,  $\hat{j}$  and  $\hat{k}$  along the  $x$ ,  $y$  and  $z$  axes, respectively, are taken from the work of Dean *et al* (1958). Using the atomic positions for the same

molecule in the  $\alpha$ -phase given by Halac *et al* (1977), a rotation which takes the molecule from the orientation in the  $\beta$ -phase to that in the  $\alpha$ -phase is deduced and defined by an angle  $\varphi = 7.9^\circ$  about the axis defined by  $\nu = 0.2172i - 0.5082j + 0.8334k$ . As may be seen, the rotation of the molecule is quite small since it measures the rotation which the molecule undergoes on going from 300 to about 150 K (Dean *et al* 1958, Gafner and Herbstein 1960, Herbstein 1965, Halac *et al* 1977), and that may be decomposed in  $R_x = 5\%$ ,  $R_y = 26\%$  and  $R_z = 69\%$ , i.e. the main contributions to the rotation are those about the  $z$  and  $y$  axes. Considering the transition to be first order displacive,  $\varphi$  may be taken as the order parameter of the transition (Ellenson and Kjems 1977, Pasquier and La Calvé 1977); therefore it is to be expected that the lattice librational frequencies, mainly those related to  $R_z$  and  $R_y$ , will exhibit both a marked temperature dependence on approaching  $T_c$  and a discontinuity at the transition temperature (Samuelsen *et al* 1971). These facts are indeed observed in the case of TCB (Pasquier and La Calvé 1977), therefore confirming that  $\varphi$  may actually be considered an order parameter for the  $\alpha$ -to- $\beta$ -phase transition in TCB.

The temperature dependence of the order parameter  $\varphi$  should be reflected in the temperature dependences of the NQR transition frequencies at low temperatures. This temperature dependence is most clearly seen in the difference  $\Delta_{21} = \nu_2 - \nu_1$ , which is depicted as a function of the temperature, in the temperature range 77–170 K, in the lower inset in figure 1. The full circles are obtained by fitting the  $\Delta_{21}$  versus  $T$  data by means of  $\ln(\nu_2 - \nu_1) = P_1 + P_2 \ln(P_3 - T)$  with the following values for the parameters:  $P_1 = 0.63 \pm 0.11$ ,  $P_2 = 0.618 \pm 0.024$  and  $P_3 = 185.4 \pm 1.4$  K. The value for  $P_2$  may be understood by assuming that  $\Delta_{21}$  depends to a good approximation on  $\varphi^2$ , since in this case a value for the critical point exponent  $\beta = 0.309 \pm 0.012$  is deduced which indicates that this system shows 3D Ising-model-like ( $\beta = \frac{1}{8}$ ) behaviour (Stanley 1971). It may be argued that, owing to the  $\beta$ -phase crystalline symmetry, rotations of the TCB molecules in  $+\varphi$  or  $-\varphi$  should produce identical changes in both the static and the dynamic contributions to the thermodynamic free energies. Therefore  $\Delta_{21}$  as well as other quantities should depend only on even powers of  $\varphi$ . The Ginzburg (1961) criterion suggests that the Ising-like critical behaviour should be observed when the important forces of the system are those of short range, as is certainly the case for TCB since the weak bonding forces are those normally found in molecular crystals, i.e. those arising from induced dipole–induced dipole van der Waals terms which fall off rapidly with increasing distance. The repulsive forces between molecules are relatively strong and are these forces which are dominant in determining the molecular crystal packing. This critical behaviour on approaching  $T_c^-$  is also reflected in the softening of the mainly  $R_z$  and  $R_y$  librational modes (Pasquier and La Calvé 1977).

The temperature dependence of the NQR frequency may be written as  $\nu_a = \nu_0(1 - \frac{1}{2}\langle\theta^2\rangle) + \nu_c$  (Bayer 1951, Kushida 1955, McEnnan and Schempp 1973, Martin 1985), where  $\nu_0 + \nu_c$  is the NQR frequency in a rigid lattice,  $\nu_0$  and  $\nu_c$  describing the molecular and crystalline contributions, and  $\langle\theta^2\rangle$  describes the mean square value of the C–Cl bond direction rotation angle. Because of the high symmetry of the TCB molecule,  $\nu_0$  and  $\langle\theta^2\rangle$  are the same at all the eight chlorine sites in the primitive cell unit. Therefore, the different values of the transition frequencies must be look for in the crystalline contribution  $\nu_c$  at the various chlorine sites. These crystalline contributions, in the  $\beta$ -phase, are the same at the chlorine sites 1, 4, 1' and 4' but are different from that at chlorine sites 2, 5, 2' and 5' (see figure 2). The fact that  $\nu_b - \nu_a$  versus  $T$  decreases on lowering the temperature may be interpreted by saying that the  $P2_1/a$  monoclinic structure is approaching a more symmetric crystalline structure, i.e. one in which  $\nu_c$

takes on the same value for all the eight chlorine atoms in the primitive unit cell. This more symmetric structure is almost reached since below 180 K both lines merge into each other beyond resolution. However, the important forces in the system are unable to stabilize the more symmetric structure and the system finally evolves from the monoclinic  $P2_1/a$  to the triclinic  $P\bar{1}$ . This interpretation requires more experimental evidence such as, for example, x-ray structure determination as a function of temperature from 170 to 300 K. A final comment on the linear behaviour exhibited by  $\nu_b - \nu_a$  versus  $T$ , as depicted in the upper inset in figure 1, is in order. This behaviour simply reflects the distortions induced in the crystalline lattice by thermal expansion, these distortions being so small that, to a good approximation, the changes in  $\nu_c$  may be taken as linear functions of temperature.

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