

A Phase Transition and Molecular Dynamics in Crystalline $C_6H_5CHCl_2$ by ^{35}Cl NQR Investigations *

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The NQR frequency ν and the spin-lattice relaxation time T_1 of ^{35}Cl nuclei in crystalline (ω, ω)-dichlorotoluene, $C_6H_5CHCl_2$, have been measured at temperatures above 77 K. The existence of a second-order phase transition was discovered at $T_c = 94$ K. At this point the low-temperature NQR spectrum consisting of five lines passes into the high-temperature doublet. The behaviour of ν and T_1 as functions of temperature near the critical point T_c is investigated and corresponding parameters are obtained. The NQR signals fade out about 185 K due to the reorientational motion with the potential barrier of 33.9 kJ/mole.

Introduction

In crystals with molecules containing partly chlorinated methyl groups the NQR spectral and relaxation parameters reveal an anomalous behaviour [1–3]. In the present paper a $C_6H_5CHCl_2$ crystal was investigated as to the temperature dependence of the ^{35}Cl NQR frequencies ν and the spin-lattice relaxation time T_1 . Some peculiarities in $\nu(T)$ and $T_1(T)$ of this crystal connected probably with a continuous phase transition were reported formerly [3]. It was the purpose of this paper to study more in detail the internal molecular dynamics in the crystal and to clarify the character of the transition.

Experimental

A home-made pulsed NQR spectrometer was used. The chosen temperatures (77 K – 256 K) were obtained by means of cold nitrogen gas ($T > 90$ K) and a mixture of liquid nitrogen and oxygen ($77\text{ K} < T < 90$ K). A copper-constantan thermocouple was used to measure the temperatures with a precision not worse than ± 0.5 K. The errors of the ν and T_1 measurements do not exceed 0.01% and 10%,

respectively, with the exception of a narrow interval near the phase transition point $T_c = 94$ K where both the signal intensity and the spectral resolution essentially diminished.

Firstly a ^{35}Cl NQR spectrum consisting of two lines at 77 K was reported in [4]. Our investigations show that this spectrum consists of 5 well resolved lines having the frequencies 36.519 (1), 36.383 (2), 35.831 (1), 35.734 (1), 35.622 (1) MHz (here the relative intensities of the lines are marked by 1 and 2, the second line possessing double intensity).

The temperature dependence of the line frequencies (see Fig. 1) shows that with increasing temperature the lines tend to come nearer to one another within two separated groups and at $T > T_c$ the spectrum becomes a doublet. This shows that the crystal structure changes whereby the number of non-

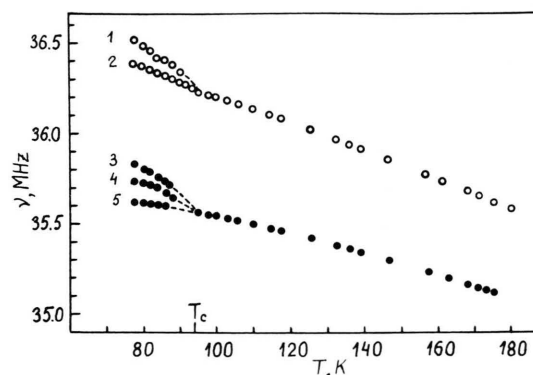


Fig. 1. Temperature dependence of the NQR frequencies ν in (ω, ω)-dichlorotoluene. The NQR lines corresponding to the inequivalent chlorine atoms are marked 1, ..., 5.

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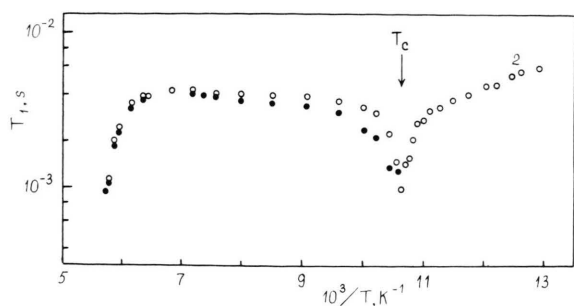


Fig. 2. Temperature dependence of the ^{35}Cl spin-lattice relaxation time T_1 in (ω, ω) -dichlorotoluene. The curves are marked as in Figure 1.

equivalent molecules per unit cell is reduced from three (below the phase transition) to one (above it). There is no discontinuity at T_c in the frequencies (see e.g. the most intensive line 2).

In Fig. 2 the temperature dependence of T_1 is shown. One sees that the curve $T_1(T)$ possesses a deep and sharp minimum at the transition point which probably is due to a critical change of the crystal dynamics near this point. The line intensities near T_c diminishing in the low-temperature phase, a detailed study of $T_1 = f(T)$ near T_c was made only for the most intensive line 2 (see Figure 2). As to the high temperature phase, the T_1 values for both lines become almost equal and remain anomalously small. No temperature hysteresis in the dependences $\nu(T)$ and $T_1(T)$ was observed.

The character of the temperature dependences of ν and T_1 described above makes it probable that the phase transition observed is of second order.

Above 160 K a strong shortening of T_1 takes place, and at about 185 K (far from $T_{mp} = 256$ K) the NQR signals fade out. Obviously this indicates an intensification of thermally activated molecular motions in the crystal. The form of the function $T_1(T)$ in this temperature region is nearly exponential, which may indicate a reorientational relaxation mechanism to be active.

Discussion

Phase transition

It is known (see [5]) that the second order phase transitions are characterized by order parameters $p_n(T)$ depending on temperature according to the

power law

$$p_n(T) = A_n(-\varepsilon)^{\beta_n}, \quad n = 1, \dots \quad (1)$$

with $\varepsilon \equiv (T - T_c)/T_c$, where T_c is the transition point. The quantities β_n are called the critical indices; they are of great importance to the second-order phase transition theory and its applications to concrete problems. Attempts were made [6, 7] to use the theory mentioned in the study of some second-order transitions by means of the NQR methods. In these attempts one used as order parameters quantities which are proportional to the frequency differences $\Delta_n \nu \equiv (\nu_i - \nu_j)_n$ vanishing at T_c :

$$p_n(T) \sim \Delta_n \nu(T), \quad n = 1, \dots \quad (2)$$

The same approach is accepted in this paper. The structure of the crystal in question being unknown, this approach is to be considered as a supposition. The phase transition observed being supposed of second-order, it is natural to try to find the corresponding critical indices. They may be found easily using (1) and (2) and all the experimental data obtained including $T_c = 94.0 \pm 0.5$ K. The results for the low-temperature phase of $C_6H_5CHCl_2$ are presented in Table 1, where S denotes the mean square error. In the temperature region $0.04 < |\varepsilon| < 0.2$ the mean value of β_n is 0.58, which is near to 0.5, the value following from Landau's theory (see [5]). Figure 3 shows the experimental data representing the temperature dependence of three frequency differences and corresponding calculated curves obtained with the parameters from the Table 1.

In the phase transition region the dependence $T_1(T)$ is essentially influenced by the "critical" change in the molecular dynamics. For $T < T_c$ it probably is the main factor determining $T_1(T)$. In fact, even for the lowest temperatures in the region in question $T_1^{-1}(T)$ may be approximated as aT^m

Table 1. The least-squares coefficients of the equation $\log(\Delta_n \nu) = \log A_n + \beta_n \log |\varepsilon|$ for the low-temperature phase of (ω, ω) -dichlorotoluene.

NQR frequency differences $\Delta_n \nu$ (kHz)	$\log A_n$	$S_{\log A}$	β_n	S_β
$\Delta \nu_{1-2}$	2.48	0.11	0.49	0.11
$\Delta \nu_{3-4}$	2.42	0.22	0.59	0.25
$\Delta \nu_{4-5}$	2.52	0.11	0.61	0.12
$\Delta \nu_{3-5}$	2.80	0.07	0.64	0.08

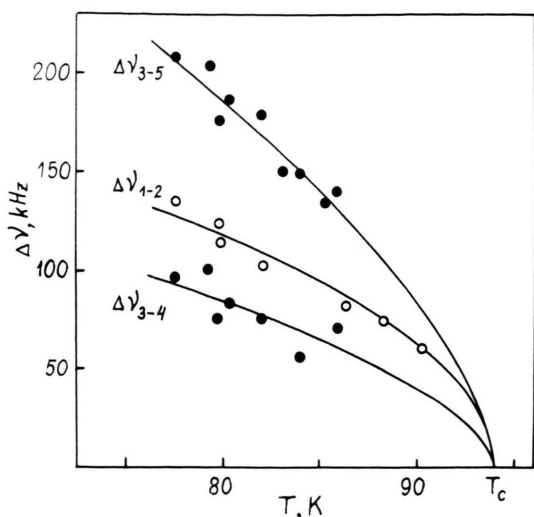


Fig. 3. Temperature dependence of the frequency differences $\Delta\nu$ in the NQR spectrum of (ω, ω) -dichlorotoluene. The marking as in Figure 1. The solid curves were calculated from (1) and (2) using the parameters A_n and β_n listed in Table 1.

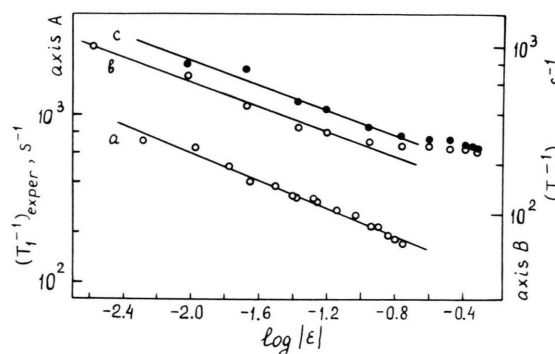


Fig. 4. Log-log plot of the experimental ^{35}Cl spin-lattice relaxation rate T_1^{-1} vs. $\varepsilon = (T - T_c)/T_c$ for (ω, ω) -dichlorotoluene near T_c : a = low-temperature phase, the NQR line No. 2 (axis A); b, c = high-temperature phase (axis B), the experimental points belong to crystallographically inequivalent chlorine atoms and are marked as in Figure 1.

with $m \sim 4$ whereas in the case of the normal librational regime m is near to 2 [8]. The most adequate approximation of $T_1(T)$ in the low-temperature phase for the line 2 is (see Fig. 4)

$$(T_1^{-1})_{\text{exp}} \sim |\varepsilon|^\gamma \quad (3)$$

with $\gamma = -(0.41 \pm 0.02)$ in the temperature region $0.005 < |\varepsilon| < 0.2$. In the high-temperature phase, where $T_1(T)$ was investigated for two chlorine atoms in one molecule, the expression (3) may be used as a good approximation as well with $\gamma = -(0.37 \pm 0.03)$ for both curves in the temperature region $0.005 < |\varepsilon| < 0.1$ (see Figure 4). So $T_1(T)$ is almost symmetric with respect to T_c (Figure 2).

Reorientational mobility

As already said, above 160 K activation of the reorientational motions is probable. To get information on the kind of these motions (for example, are they motions of molecules as a whole or of the groups CHCl_2 ?), special investigations are necessary. Nevertheless, it seems that the reorientation axis must always be near to the long axis of a molecule and that the asymmetry of the partly chlorinated methyl group does not exclude the possibility of reorientations. In any case, it is reasonable to try to clarify the role of the reorientational motion in calculating $T_1(T)$. The high-temperature experimental curve $T_1(T)$ being very complicated, the usual method [9] would be ineffective; so only the exponential part of this curve was used to estimate the reorientational motion parameters. The result is

$$\begin{aligned} (T_1^{-1})_{\text{reorient}} &= b \exp(-V_0/RT) \\ &= 10^{(13.1 \pm 1.4)} \exp \left[-\frac{(8.1 \pm 1.1) 10^3}{RT} \right] \end{aligned} \quad (4)$$

(T_1^{-1} and b are in s^{-1} , V_0 is in cal/mole).

Conclusions

By ^{35}Cl NQR it is possible to investigate the peculiarities of the internal dynamics in the (ω, ω) -dichlorotoluene crystal which are connected with a second-order phase transition and with reorientational motion in the high-temperature phase. The method permits to find some important parameters: the critical exponents, describing the temperature behaviour of the NQR spectrum and the relaxation rate of the chlorine nuclei near the transition temperature T_c , and the potential barrier hindering the reorientations.

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