A Pulsed $^{35}$Cl NQR Study on the Molecular Motions and Phase Transition of 4-Chlorobenzyl Alcohol*

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The spin-lattice and spin-spin relaxation times $T_1$ and $T_2$ of $^{35}$Cl NQR were measured for the high (I) and low (II) temperature phases of 4-chlorobenzyl alcohol in the range $50 < T / K < 338$ (transition and melting points: 236 and 343.5 K, respectively). In phase II the $T_1$ behavior in the range $50 < T / K < 90$ can be explained by lattice vibrations and that in the range $90 < T / K < 190$ by reorientation with an activation energy of ca. 3.8 kJ/mol. In phase I, the $T_1$ behavior at $T > 260$ K is explainable by another reorientation with $E_a \approx 4.7$ kJ/mol. The $T_2$ vs. $T$ curves revealed that in both phases the crystal dynamics is anomalous in the vicinity of the transition temperature. Lattice defects accumulated in phases I and II by the phase transition were found to be responsible for the extremely short inverse line width parameters ($T_2^*$).

Key words: Chlorine NQR, Spin-lattice relaxation, Phase transition, Molecular motions, Lattice defects.

Introduction

4-Chlorobenzyl alcohol ($\text{4-Cl}C_6H_5CH_2OH$) undergoes a phase transition at 236 K [1, 2]. Both the low (phase II) and high (phase I) temperature phases give one $^{35}$Cl NQR line. The crystal structure of the high temperature phase is known (monoclinic, space group $P2_1$) [2]. In the crystal there exist chains of molecules, each of which is formed along a $2_1$ axis oriented parallel to the crystallographic $b$ axis, and the crystal structure as a whole is build by van der Waals packing of the chains. Unfortunately the structure of phase II is unknown, but the small jump of the NQR frequency (ca. 20 kHz) at the transition temperature suggests that the structures of the two phases are similar, and one would assume that the chain structure is kept in phase II because cracks aligning parallel to the $b$ axis of phase I were observed for a single crystal which had experienced the phase transition several times.

Thermal studies have been carried out and are reported briefly in [2]. A characteristic feature of the phase transition is that the transition temperature depends strongly on the history of the specimen. Lattice defects accumulated in the crystal by the phase transition seem to be correlated to the hysteresis.

The molecular dynamics of the alcohol molecule is expected to play a role in the occurrence of the phase transition. In the present work, therefore, the spin-lattice and spin-spin relaxation times ($T_1$ and $T_2$, respectively) of $^{35}$Cl NQR were investigated. Since the inverse line width of the NQR ($T_2^*$) reflects the degree of lattice defects [3], one may expect to deduce information on the defects from the values of $T_2^*$.

Experimental

The commercial compound (Tokyo Kasei Organic Chemicals) was purified by recrystallization from chloroform (or benzene). The specimens (crystalline powder) used in the work were obtained by slow evaporation of chloroform (or benzene) solutions.

$T_1$, $T_2$, and the inverse line width parameter ($T_2^*$) of $^{35}$Cl NQR were measured with a conventional pulse spectrometer. $T_1$ was determined by the echo sequences $90^\circ - \tau - 90^\circ - \tau - 90^\circ - 180^\circ$ and $T_2$ by a conventional spin echo method. $T_2^*$, defined as the time required for a given induction signal to decay to $1/e$ of its maximum value, was obtained from the shape of echo signals. The width of the $90^\circ$ pulse was about 15 μs.
Results and Discussion

Temperature Dependence of the NQR Frequency and $T_2$

The NQR signal of phase II at temperatures below ca. 200 K could not be detected by a continuous wave (CW) NQR method [1]. In this work the NQR signals at temperatures higher than 50 K could be detected by the pulsed method. Figure 1 shows the temperature dependence of the $^{35}$Cl NQR frequency. The jump of the frequency at the transition point is small (ca. 20 kHz) but distinct, indicating that the transition is of first order. When a specimen (phase I) was cooled from ca. 290 K and kept at 210 K for ca. 1 h, the NQR signal of phase II began to give beat signals due to the mixing of the NQR signals of phases I and II. Then the I to II phase transition temperature was located at ca. 210 K in the present NQR experiment. In a similar manner, the II to I phase transition temperature was determined to be ca. 235 K. The overlap of the two curves in Fig. 1 in the region between 210 and 235 K corresponds to supercooling of phase I, which is also characteristic of the first order phase transition.

The temperature dependence of the NQR frequency was analyzed by the equation [4]

$$v(T) = v(0) - \frac{A}{\exp(B/T) - 1},$$

where $A = (3/4 \pi) (h v_Q/I_1 v_1)$, $B = h v_1/k_B$, and $v_Q = e^2 Q q^2/(2 h)$ $(v_Q, I_1, v_1, Q, q)$ are NQR frequency, moment of inertia, librational frequency, quadrupole moment, and electric field gradient (EFG), respectively. The values of $A$, $B$, and $v(0)$ were calculated by least squares fitting the observed data to (1). The value of $B$ for phase I was in good agreement with that for phase II, and hence the value of $v_1$ is thought to be approximately constant in both phases. On the contrary, the ratio of $A$ in phase I to that in phase II ($A_I/A_{II}$) is ca. 1.34, which results in the ratio of $q(q_1/q_0)$ of ca. 1.34. The latter ratio will be used in the discussion of $T_1$.

The temperature dependence of $T_2$ of the $^{35}$Cl NQR is shown in Figure 2. The transverse relaxation in phases I and II is considered to be governed mainly by magnetic dipolar broadening from the local fields due to the protons, since $T_2 \ll T_1$ in the whole temperature range investigated. Intramolecular interactions between the Cl atom and H atoms on the ortho positions with respect to the chlorine, and intermolecular ones between the Cl atom and an H atom in an adjacent molecule (see below) are considered to play a predominant role in the transverse relaxation.

$T_1$ in Phase II

In the range ca. $50 \leq T/K < 77$ the temperature dependence of $T_1$ is the explained by the usual $T^2$ law as depicted in Figure 3. The spin-lattice relaxation in this temperature region is considered to be dominated
by fluctuation of the EFG at the chlorine nucleus due to vibrations [5, 6].

The $T_1$ vs. $1/T$ curve in the region between ca. 77 and 190 K can be described by the equation

$$T_1^{-1} = b \exp(-E_a/RT).$$

(2)

The slope of the $\ln(T_1) \times 1/T$ curve in this temperature range gives $E_a \approx 3.8$ kJ/mol. This suggests the excitation of a reorientation of a neighboring atomic group which produces a fluctuation of the EFG at the chlorine nuclei. A 180°-flipping of the phenyl ring similar to that found in 4-chlorobenzamide [7] could be proposed as a possible mode of the reorientation. In the present case, however, the activation energy is too low to assume such a motion (as to the modes of motion, see the section, $T_1$ in phase I).

At temperatures between ca. 190 and 235 K $T_1$ depends anomalously on the temperature (see Figure 4). The temperature dependence of $T_1$ in this region exhibits a dip somewhat similar to that reported for dichlorotoluene [8] and NH$_4$H(CICH$_2$COO)$_2$ [9]. In these compounds, the dip corresponds to a second order phase transition. The drop of $T_1$ observed for phase II should not be regarded as a dip, because the phase transition in 4-chlorobenzyl alcohol is clearly of first order. Interestingly, a discontinuous increase in $T_1$ was observed at the II to I transition. The discontinuity is also an evidence for the first order phase transition. The anomalous $T_1$ behavior indicates that the crystal dynamics in phase II changes critically in the vicinity of the phase transition. A part of the increase in $T_1$ caused by the phase transition can be explained by the finding that $q$ in phase I is larger than that in phase II. Moreover, the increase of $T_1$ in phase I could be attributed to a change of distance(s) between the chlorine atom and the moving atom(s), which contributes to produce the fluctuation of the EFG.

$T_1$ in Phase I

In the region between ca. 260 and 338 K, the temperature dependence of $T_1$ can be described by (2). The value of $E_a$ calculated from the slope of the curve in this temperature region is ca. 4.7 kJ/mol. This value is very close to that found for the reorientation in phase II, but it is not clear whether the reorienting group is the same or not in phases I and II.

From the molecular and crystal structures of 4-chlorobenzyl alcohol one may assume reorienta-
tions of such groups as the phenyl ring, \(-\text{CH}_2\text{OH},\) \(-\text{OH},\) and a chain of molecules (formed by hydrogen bonds) as a whole. A definite conclusion on the re-orientational mode cannot be drawn here, but in any case a small angle reorientation seems to be acceptable. According to the crystal structure analysis of Phase I [2], the equivalent isotropic thermal parameters of the carbon and oxygen atoms in the \(-\text{CH}_2\text{OH}\) group (5.45 and 6.18 Å², respectively) are clearly larger than those of the other carbon atoms (3.88 Å² on average) [2]. This would imply the possibility of a small-angle reorientation of the \(-\text{CH}_2\text{OH}\) group. Furthermore, it is interesting to note that in phase I one (H71) of the two hydrogen atoms of the CH2 in the 

\[
\begin{align*}
\text{CH}_2\text{OH} & \\
\text{H} & \\
\text{O} & \\
\end{align*}
\]

is situated very near to the chlorine atom; the intermolecular Cl...H71 distance is 2.98 Å and is slightly smaller than the sum of the van der Waals radii [2]. Therefore, the motion of the \(-\text{CH}_2\text{OH}\) group is thought to produce the fluctuation of the EFG owing to the short Cl...H71 distance.

The ln(T1) vs. 1/T curve in the temperature region between ca. 260 and ca. 210 K deviates clearly from that predicted by (2) (see Figure 4). Thus the crystal dynamics of phase I in the vicinity of the I to II transition also seems to be anomalous.

**T2 and Lattice Defects**

The temperature dependence of T2* is shown in Figure 5. In phase I of the original sample (the sample which has not experienced the phase transition) the T2* vs. T curve is quite peculiar, giving a maximum (ca. 260 μs) at about 290 K. This temperature dependence of T2* is reversible.

The decrease of T2* of phase I observed below ca. 290 K, as well as that above ca. 290 K, should be attributed to a random distribution of EFGs due to a static origin because T2 is almost temperature independent and T1 is much longer than T2*. It is difficult to assign the decrease in T2* above 290 K to pre-melting, as that of CH2Cl2 [5], because the temperature where the decrease of T2* occurs is too low to expect pre-melting (mp. = 343.5 K). The behavior of T2* in phase I indicates that the characteristics of vacancies or other lattice defects are temperature dependent. The cause of this phenomenon is not clear at present.

When the I to II phase transition took place on cooling, T2* decreased drastically at the transition temperature (210 K), and T2* in phase II remained almost constant throughout the phase (see Fig. 5). After the II to I phase transition, the values of T2* in phase I were markedly shorter than those observed for the original sample. When a sample which had experienced the phase transition (sample-ex) was annealed at room temperature for a few days, T2* became longer (ca. 150 μs) but remained shorter than in the original sample (ca. 260 μs). The values of T1 and T2 of phase I of sample-ex coincided with those of the original sample. Thus the drastic decrease of T2* of phase I observed for the sample-ex can be attributed to a random distribution of EFGs due to lattice defects produced by the experience of the phase transition. The temperature variation of T2* of sample-ex was obscure owing to the very short values of T2*, but a temperature dependence similar to that found for the original sample seems to exist in the sample-ex, too. The extremely short T2* in phase II can also be attributed to lattice defects produced by the phase transition.

From thermal analysis by a differential scanning calorimeter (DSC), the I to II phase transition temperature for an original sample was determined as approx. 206 K. As mentioned above, however, the I to II phase transition was found to start even at 210 K in the original sample used in the present NQR experi-
ment when the specimen was kept for a long time at that temperature. The thermal analyses were carried out using a small single crystal (ca. 10 mg) at a constant cooling rate (typically, $-5 \text{ K/min}$). The difference in the experimental conditions between the NQR and DSC, especially the cooling rate, is considered to be responsible for the discrepancy of the transition temperatures.

The thermal analysis showed that the transition temperature of the sample-ex was raised up to ca. 215 K depending on the number of experiences of the transition. When the sample-ex was annealed at room temperature, the phase transition temperature approached the original value of 206 K. The rise and the recovery of the I to II transition temperature can be correlated with the accumulation and relaxation of lattice defects detected by the measurements of $T^*_2$, respectively. We recently reported a similar phenomenon for methylammonium hexatellurate as studied by $^{35}\text{Cl NQR}$ [10].