Phase Transition and Crystal Dynamics of 4-Bromobenzyl Alcohol*

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For the title compound a phase transition from Phase II to Phase I (low and room temperature phases, respectively) was found at ca. 217 K. The temperature dependence of the ^{81}Br NQR frequency and that of the dielectric constant showed anomalies at ca. 195 K that were tentatively attributed to a higher order phase transition. A similar anomaly was found at ca. 218 K for 4-chlorobenzyl alcohol which showed a II-I transition at 236 K. The dielectric dispersion observed for both compounds at low temperatures indicates an excitation of a molecular motion with the dielectric relaxation rate of ca. 1 kHz. The temperature dependence of the ^{81}Br NQR frequencies of 2- and 3-bromobenzyl alcohol, measured at $T > 77$ K, gave no evidence of phase transition in their crystals.

Key words: NQR, Phase Transition, Molecular Motion, Dielectric Dispersion.

Introduction

Our previous study on the temperature dependence of the spin lattice relaxation time (T_1) of ^{35}Cl NQR has revealed molecular motions in the high and low temperature phases (Phase I and II, respectively) of 4-chlorobenzyl alcohol (pCBA) [1]. It has been pointed out that the crystal dynamics is unusual in the vicinity of the II-I phase transition (236 K). As an extension of the previous work we investigated ^{81}Br NQR of 4-bromobenzyl alcohol (pBBA) in the present work, since both compounds are known to be isomorphous [2]. The temperature dependence of the ^{35}Cl NQR frequency of pCBA was reinvestigated precisely in the vicinity of the phase transition temperature because we found an anomalous temperature variation of the ^{81}Br NQR frequency in the course of the present investigation. We also measured the ^{81}Br NQR of the two related compounds 2- and 3-bromobenzyl alcohol (abbreviated as oBBA and mBBA, respectively).

Anomalies of the NQR and dielectric properties and the molecular motions in the crystals of pBBA and pCBA will be discussed. Furthermore, the temperature dependence of T_1 of pCBA reported in the previous paper will be reexamined on the basis of the present observations.

Experimental

Commercial pCBA, pBBA and oBBA (Tokyo Kasei Organic Chemicals) were purified by recrystallizations from appropriate solvents. Commercial mBBA (the same source) was used for the ^{81}Br NQR experiment without further purification.

The thermal analysis was carried out in the temperature range ca. $100 < T/\mathrm{K} <$ ca. 350 by using a differential scanning calorimeter (Rigaku DSC-8058).

The ^{81}Br and ^{35}Cl NQR spectra were detected by a home made super-regenerative oscillator detector [3] and by a conventional pulsed NQR spectrometer [4], respectively. The accuracy of the frequency measurement was 20 and 0.5 kHz, for the Br and

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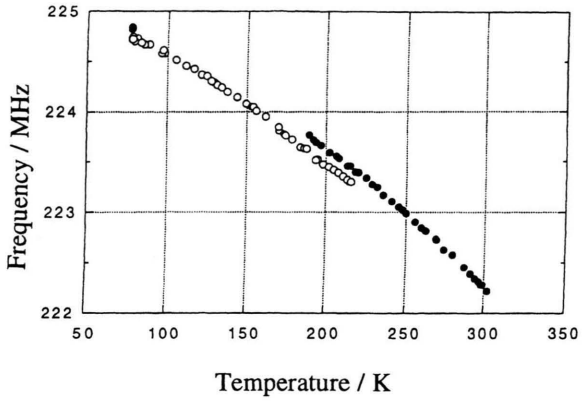

Fig. 1. Temperature dependence of the ^{81}Br NQR frequency of 4-bromobenzyl alcohol (pBBA). Solid and open circles for Phase I and Phase II, respectively. Solid circle at 77 K corresponds to super-cooled Phase I.

Cl NQR, respectively. The errors in the temperature measurements were within 1 K (for pBBA) and 0.1 K (for pCBA).

An LCR meter (Ando AG-4311B) was employed for the dielectric measurements on the compressed disks of pCBA and pBBA. The frequency range was $0.1 < f/\mathrm{kHz} < 100$.

Results

The thermal analysis of pBBA revealed a phase transition at 216.7K (heat of transition of ca. 1.1 kJ/mol). The transition is similar to that of pCBA (at 236.0 K and heat of transformation of 1.3 kJ/mol).

The ^{81}Br NQR frequencies of the bromobenzyl alcohols at 77 K are listed in Table 1. The temperature dependence of the ^{81}Br NQR frequencies of pBBA are shown in Figs. 1 and 2 and that of the ^{35}Cl NQR of pCBA in Figs. 3 and 4. Figures 5 and 6 show the temperature dependence of the dielectric constant measured for pBBA and pCBA, respectively. Their dielectric dispersions at various temperatures are shown in Figs. 7 and 8.

Discussion

Anomaly in the vicinity of the II-I transition

As shown in Fig. 1, the ^{81}Br NQR frequency of the Phase II of pBBA jumps by about 150 kHz at ca. 217 K owing to the II-I phase transition. In addition, the ^{81}Br NQR frequency vs. temperature curve exhibits

Table 1. ^{81}Br NQR frequencies of 2-, 3-, and 4-bromobenzyl alcohol (oBBA, mBBA, and pBBA, respectively) at 77 K.

Compound	Frequency / MHz
oBBA	222.80
mBBA	225.2, 224.00
pBBA (Super-cooled Phase I)	224.83
pBBA (Phase II)	224.72

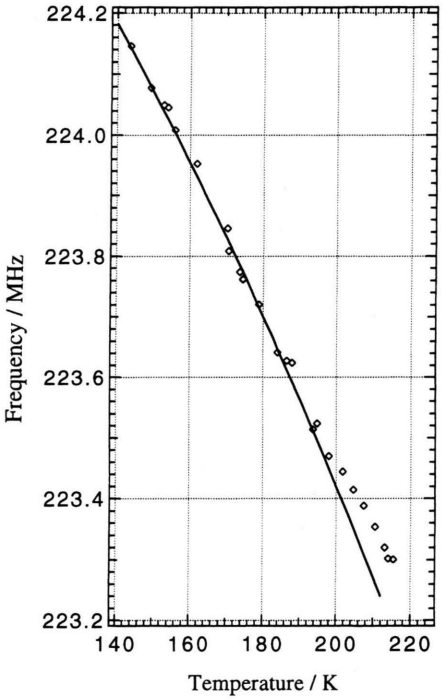

Fig. 2. ^{81}Br NQR frequency vs. temperature in the range $140 < T/\mathrm{K} < 217$ for 4-bromobenzyl alcohol (pBBA) (for the solid line, see text).

an unusual upward shift in the range ca. $195 < T/\mathrm{K} < 217$ (see Figure 2). The solid line in the figure was obtained by a least squares fitting of the observed data in the range $77 < T/\mathrm{K} < 180$ to the Bayer type function [5]

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

where $A = (3/4\pi)(h\nu_Q/2\pi I_1\nu_1)$, $B = h\nu_1/k_B$, and $\nu_Q = e^2Qq/2h$ (ν_Q, I_1, ν_1, Q, and e are NQR frequency, moment of inertia, librational frequency, quadrupole moment, and electric field gradient, respectively).

The ^{35}Cl NQR frequency of pCBA jumps to a lower frequency at 236 K as a result of the II-I phase transition (Figure 3). As can be seen in Fig. 4, the frequency

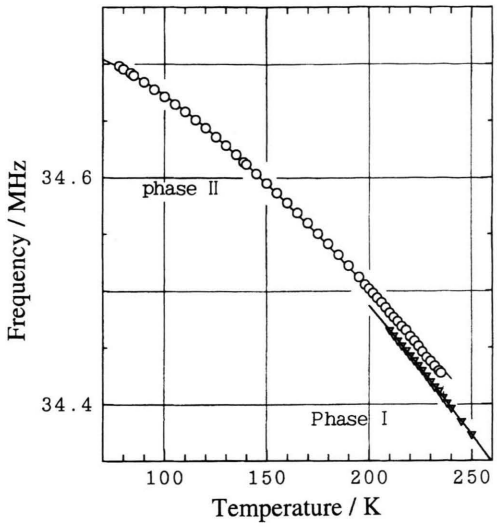

Fig. 3. Temperature dependence of the ^{35}Cl NQR frequency of 4-chlorobenzyl alcohol (pCBA). Triangles and circles for Phase I and Phase II, respectively.

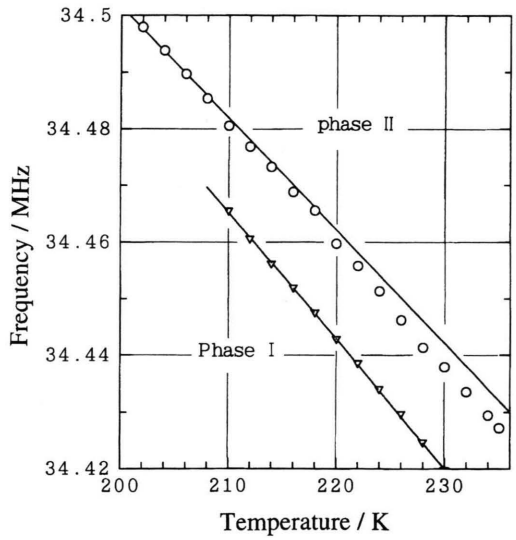

Fig. 4. ^{35}Cl NQR frequency vs. temperature in the range $200 < T/\mathrm{K} < 235$ for 4-chlorobenzyl alcohol (pCBA) (for the solid lines, see text).

vs. temperature curve of Phase II (circles) in the range ca. $218 < T/\mathrm{K} < 235$ shows an appreciable deviation from the solid line, which was obtained by the least squares fitting of the observed frequencies at $T <$ 210K to (1). The deviation found for pCBA is very slight compared to the case of pBBA, but seems significant. On the temperature dependence of T_1 of ^{35}Cl NQR of pCBA (Fig. 9), one can see a break at around

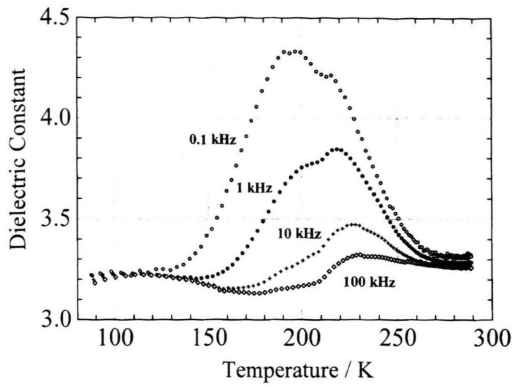

Fig. 5. Temperature dependence of the dielectric constant of 4-bromobenzyl alcohol (pBBA).

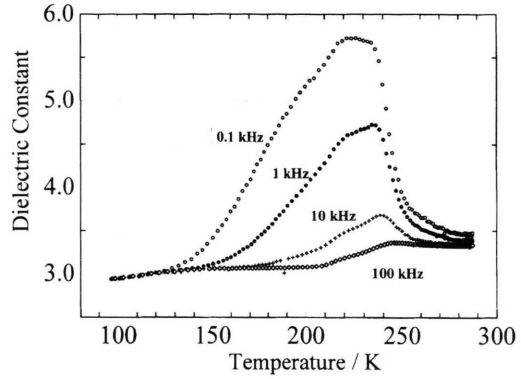

Fig. 6. Temperature dependence of the dielectric constant of 4-chlorobenzyl alcohol (pCBA).

220 K (the figure has been reported in [1], but it is given here again for the sake of convenience).

The temperature dependence of the dielectric constant of pBBA has a break at about ca. 190 - 195 K besides that at ca. 217 K corresponding to the II-I transition (Figure 5). In the case of pCBA, a beak appears at ca. 218 K in addition to that of the II-I transition at 236 K (Figure 6). The breaks are more remarkable at lower frequencies. These NQR spectroscopic and dielectric observations suggest the presence of an anomaly of the nature of the crystal in the vicinity of the II-I transition. We propose tentatively a higher order phase transition for pCBA (at ca. 218 K) and pBBA (at ca. 195 K.).

The jump of the NQR frequency due to the II-I transition is rather small in the two compounds. This fact indicates the similarity of the crystal structures of both phases. The structure seems to become closer to that of Phase I, since the shift of the NQR frequency

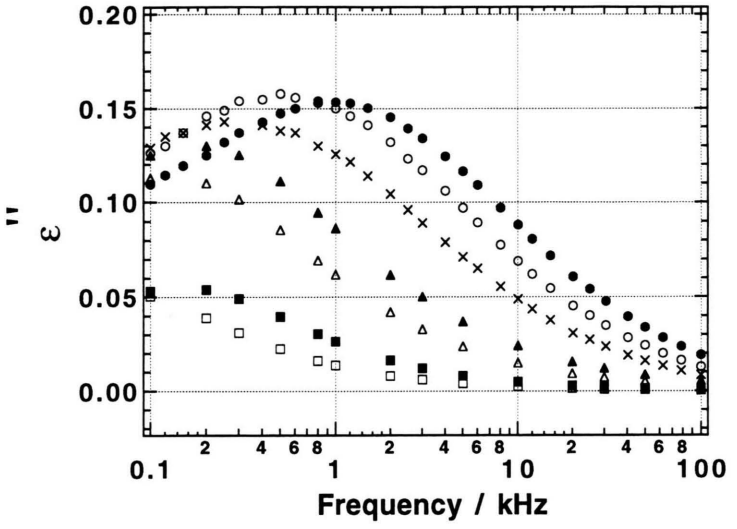

Fig. 7. Dielectric dispersion of 4-bromobenzyl alcohol (pBBA) at various temperatures (from top to bottom, 210, 200, 195, 190, 180, 170, and 160 K).

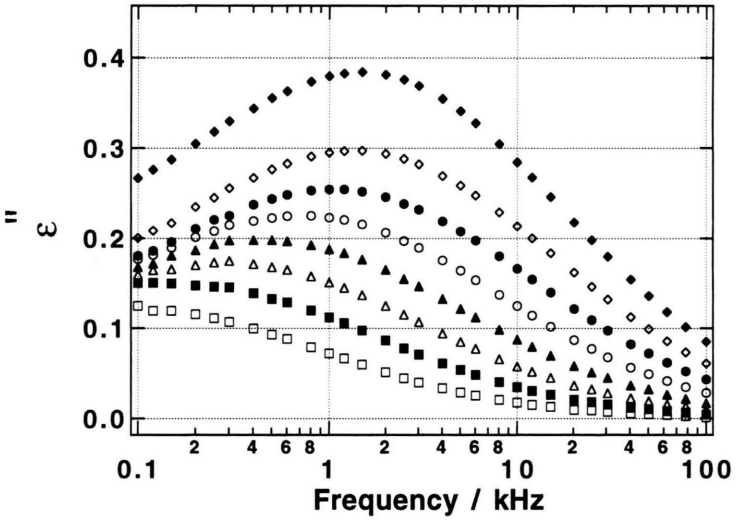

Fig. 8. Dielectric dispersion of 4-chlorobenzyl alcohol (pCBA) at various temperatures (from top to bottom, 230, 220, 210, 200, 190, 180, 170, and 160 K).

in each compound is directed toward the frequency of Phase I.

An increase in the temperature coefficient of the ^{81}Br NQR frequency was observed for pBBA at $T >$ ca. 195 K, while the reverse was found for pCBA. Therefore, the change in the temperature dependence of the NQR frequency should not be attributed to that in the crystal dynamics.

Molecular Motions at Low Temperatures

It has been shown from the analysis of the temperature dependence of T_1 of the ^{35}Cl NQR of pCBA that a reorientation of some atomic group with a potential barrier of ca. 3.8 kJ/mol is excited in the range ca. 90 < T/K < ca. 190. In addition, another molecular motion was found by the present dielectric measurements.

The dielectric dispersion observed for pBBA and pCBA at low temperatures (Figs. 7 and 8) is well reproduced by the empirical equation corrected for the distribution of the relaxation time [6]. The strong temperature dependence of the magnitude of the dispersion can be accounted for by assuming a reorientation of an electric dipole between asymmetric potential wells [7]. The analyses of the dielectric dispersion of pCBA gave 11.3±0.3 and 19.7±0.6 kJ/mol for the higher and lower potential barriers, respectively (pBBA; 10.5±1.3 and 18.0±1.6 kJ/mol). (The details of the analyses of dielectric dispersion will be reported in a separate paper.)

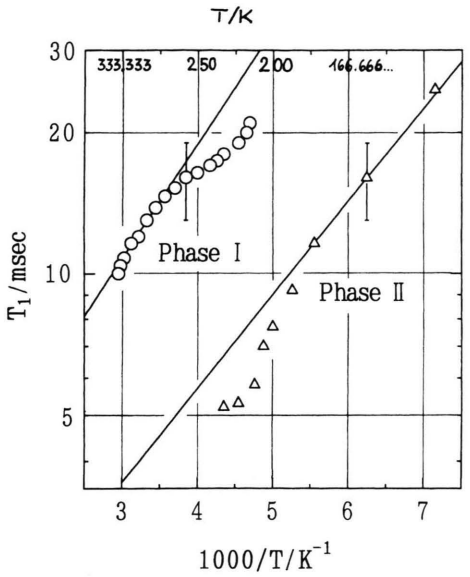

Fig. 9. Spin lattice relaxation time (T_1) of ^{35}Cl NQR vs. reciprocal temperature for Phase I and Phase II of 4-chlorobenzyl alcohol (pCBA).

As pointed out in [1], T_1 of the ^{35}Cl NQR of pCBA exhibits an anomalous decrease in the range ca. 190 < T/K < ca. 220 (Figure 9). One may expect a correlation between the decrease in T_1 and the reorientation related to the dielectric dispersion, since they take place almost in the same temperature region. It seems difficult, however, to attribute the decrease in T_1 to the fluctuation of the electric field gradient due to this reorientation because the dielectric relaxation rate (ca. 1 kHz) is far lower than the ^{35}Cl NQR frequency.

The signal to noise (S/N) ratio of the ^{81}Br NQR signal was found to depend strongly on the thermal history of the sample. When a specimen was cooled quickly in liquid nitrogen, the S/N ratio at 77 K was about 50. On the subsequent heating cycle the ratio remained almost constant up to ca. 170 K. Then it began to increase at ca. 180 K and reached about 90 at ca. 200 K. When the specimen was cooled again from ca. 200 K, the S/N ratio was about 120 at 77 K. The irreversible increase in the S/N ratio observed at around 190 K is attributable to relaxation of lattice defects [8]. The pronounced increase in the S/N ratio was found in the temperature region where the dielectric dispersion became remarkable. Therefore, the relaxation of the defects is considered to proceed through the reorientation corresponding to the dielectric dispersion.

As to possible molecular motions in the crystalline state of pCBA or pBBA, one can assume reorientations associated with intramolecular rotations: the reorientation of the hydroxyl H atom around the O-CH_2 axis and that of -C_6H_4Cl group around the CH_2-C(1) axis. The latter is not responsible for the dielectric dispersion, because it does not accompany a change in the direction of the electric dipole associated to this group. The potential barriers hindering the reorientations were preliminarily estimated by means of the molecular orbital method [9]. The calculations were carried out for the free molecule and a cluster of molecules which consists of two pCBA molecules arranged in the same way as in the crystal (Phase I). The magnitudes of the potential barriers obtained were of the same order as the observed ones. Thus, both motions seem acceptable, although further study is needed to obtain a definite conclusion.

^{81}Br NQR of oBBA and mBBA

The temperature variations of the ^{81}Br NQR frequencies of oBBA and mBBA are normal in the range 77 < T/K < melting point of each compound, indicating the absence of phase transitions. The temperature coefficients of the ^{81}Br NQR frequency at 150 K were found to be 13.3, 15.7, and 11.5, and 11.5 kHz/K for oBBA, higher and lower frequency lines of mBBA, and pBBA, respectively. Thus, lattice vibrations in the crystal of pBBA seem to be normal as in the crystals of the other compounds.

The frequency separation of the two ^{81}Br NQR signals of mBBA (ca. 1.2 MHz) is a measure of the magnitude of the crystal field effect on the ^{81}Br NQR frequency. Since the frequency of oBBA is lower than those of mBBA and pBBA by ca. 2 MHz in the average, there is a slight difference in the nature of the C-Br bond between the former and the latter two compounds. This difference can be attributed to the electronic effect of the -CH_2OH group [10].

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