^{1}H and ^{19}F NMR Studies on Molecular Motions in Two Solid Phases of t-Butylammonium Tetrafluoroborate

Hiroyuki Ishida

Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan

Z. Naturforsch. **53 a,** 796–800 (1998); received May 30, 1998

Differential thermal analysis (DTA), differential scanning calorimetry (DSC), and the temperature dependence of the spin-lattice relaxation time (T_1) and the second moment (M_2) of ^{1}H and ^{19}F NMR were studied in $(CH_3)_3CNH_3BF_4$ and $(CH_3)_3CND_3BF_4$. DTA and DSC revealed a solid-solid phase transition at 219 K for $(CH_3)_3CNH_3BF_4$ and at 221 K for $(CH_3)_3CND_3BF_4$. The motions of cations and anions in the two solid phases were studied by T_1 and M_2 experiments. The motional modes of the ions and their motional parameters were determined.

Key words: Molecular motion; Phase transition; Nuclear magnetic resonance.

Introduction

In previous papers we have studied $(CH_3)_3CNH_3NO_3$ [1] and $(CH_3)_3CNH_3ClO_4$ [2] by ^{1}H NMR and thermal measurements. The nitrate was found to have seven solid phases (including three metastable phases) between 80 K and the melting point (418 K). The perchlorate has four solid phases (including a metastable phase) between 80 K and the melting point (414 K). We discussed the molecular motions of the cation in each phase and the relation between the motions and the polymorphic phase transitions.

Since a BF_4^- ion is expected to be able to move easily in crystals because of its highly symmetric shape and its size similarity to ClO_4^-, and since ^{19}F NMR can be measured as easily as ^{1}H NMR, t-butylammonium tetrafluoroborate seems to be an interesting candidate for studying the motions of both cation and anion, and the phase transition triggered by the molecular motion. In the present study, ^{1}H and ^{19}F NMR, differential thermal analysis (DTA), and differential scanning calorimetry (DSC) have been performed on $(CH_3)_3CNH_3BF_4$ and its partially deuterated analog, $(CH_3)_3CND_3BF_4$, to characterize the molecular motions of both cation and anion and to investigate possible phase transitions.

Reprint requests to Prof. Dr. H. Ishida;
Fax: +81 86 251 8497.

Experimental

$(CH_3)_3CNH_3BF_4$ was prepared by neutralizing t-butylamine with tetrafluoroboric acid. The obtained crystals were recrystallized twice from isopropyl alcohol. Found: C, 29.80; H, 7.45; N, 8.61%. Calcd for $(CH_3)_3CNH_3BF_4$: C, 29.85; H, 7.52; N, 8.70%. $(CH_3)_3CND_3BF_4$ was prepared from purified $(CH_3)_3CNH_3BF_4$ by three times repeated crystallization from D_2O (99.8 D%). Because of the hygroscopicity of the purified crystals, they were handled in a dry bag and dried under a vacuum (ca. 10^{-1} Pa) at room temperature for 5 h and then at 70 °C for 5 h before the NMR, DTA, and DSC measurements. The phase transition temperatures and the corresponding enthalpy changes were determined on a home-made DTA apparatus [3] and a Perkin-Elmer DSC7, respectively, at 100 to 410 K. The second moment of the ^{1}H and ^{19}F NMR linewidths (abbreviated to M_{2H} and M_{2F}, respectively) was determined by use of a JEOL JNM-MW-40S spectrometer. The spin-lattice relaxation times of ^{1}H and ^{19}F NMR (abbreviated to T_{1H} and T_{1F}, respectively) were measured using a pulsed NMR spectrometer [4] with the 180° - t - 90° pulse sequence.

Results and Discussion

DTA and DSC

A solid-solid phase transition and the melting point were located at 219 ± 1 and 404 ± 1 K, respectively,

0932–0784 / 98 / 0900–0796 $ 06.00

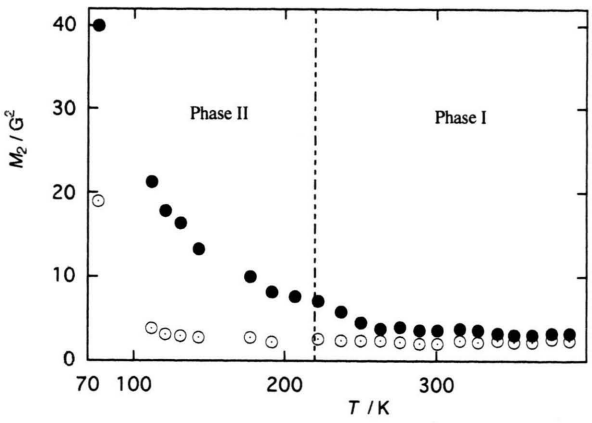

Fig. 1. Temperature dependence of the ^{1}H (•) and ^{19}F (⊙) NMR second moment (M_2) observed in $(CH_3)_3CNH_3BF_4$. The broken line shows the phase transition temperature determined by DTA.

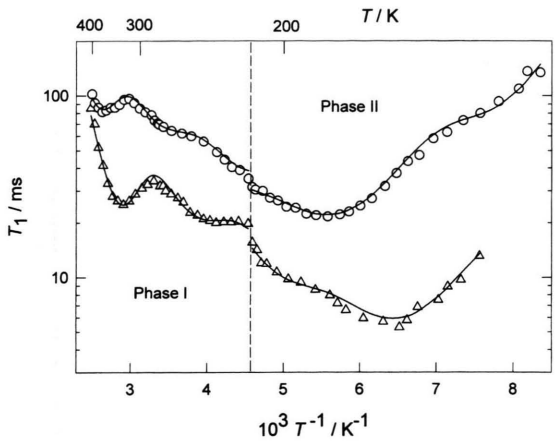

Fig. 2. Temperature dependence of ^{1}H NMR spin-lattice relaxation time (T_{1H}) observed at 8.5 (△) and 32 (○) MHz in $(CH_3)_3CNH_3BF_4$. The solid lines indicate the best-fit theoretical values; the broken line shows the phase transition temperature determined by DTA.

for $(CH_3)_3CNH_3BF_4$ by DTA. Since the heat anomaly at the solid-solid phase transition showed a long tail on the low temperature side on both heating and cooling runs, we have assigned the peak temperature to the transition temperature. The revealed solid phases are designated in the order of decreasing temperature as Phases I and II. The enthalpy changes at transition and fusion determined by DSC were 0.49 ± 0.05 and 12.6 ± 0.5 kJ mol^{-1}, respectively; thus the associated entropy changes were calculated to be 2.2 ± 0.2 and 31 ± 1 J K^{-1} mol^{-1}, in the same order. The solid-solid transition temperature determined for $(CH_3)_3CND_3BF_4$ by DTA was 221 ± 1 K.

Second Moment (M_2) of ^{1}H and ^{19}F NMR Linewidths

The temperature dependences of M_{2H} and M_{2F} observed for $(CH_3)_3CNH_3BF_4$ are shown in Figure 1. The M_{2H} and M_{2F} values at 77 K are 40 ± 0.5 and 19 ± 0.3 G^2 (1 G = 1 × 10^{-4} T), respectively. These values imply that both cation and anion are rigid at 77 K because the observed M_{2H} and M_{2F} values are much larger than 25.7 G^2 [2] and 14.5 G^2 [5], respectively, as calculated for the rigid states of the isolated cation and anion. The differences between the observed and calculated values are attributable to intermolecular contributions. With increasing temperature, M_{2F} decreased rapidly and a constant value of 2.3 ± 0.2 G^2 was obtained above 120 K. This value can be attributed to the isotropic reorientation of the BF_4^- ion, referring to the M_{2F} results obtained in NH_4BF_4 [5, 6], in which an M_{2F} of 2.5 - 2.8 G^2 was reported for the anionic motion. M_{2H} decreased, on the other hand, in three steps and reached a constant value of 3.2 ± 0.2 G^2 above 340 K. This value agrees fairly well with the 3.8 G^2 calculated for the cation which performs the C_3' reorientation of the t-butyl group about the C-N bond axis together with the C_3 reorientations of the CH_3 and NH_3^+ groups about the C-C and C-N bond axes, respectively [2]. The result that the observed M_{2H} value is smaller than the calculated M_{2H} value is explainable in terms of the contribution to M_{2H} from the large-amplitude librations of the cation about its C-C and/or C-N bond axes as discussed in previous papers [2, 7 - 9].

Spin-lattice Relaxation Time (T_{1H}) of ^{1}H NMR

The temperature dependence of T_{1H} observed for $(CH_3)_3CNH_3BF_4$ at Larmor frequencies of 8.5 and 32 MHz is shown in Figure 2. T_{1H} at 8.5 MHz showed three minima at 155, 245 and 345 K, and a shoulder around 200 K. No marked change in T_{1H} was observed at the transition point of 219 K. The temperature dependences of T_{1H} at 8.5 and 32 MHz in $(CH_3)_3CND_3BF_4$ are shown in Figure 3. T_{1H} at 8.5 MHz shows two minima at 155 and 345 K, and a shoulder around 200 K. Among the three kinds of cationic motions observed, i. e., the CH_3, NH_3^+, and t-butyl groups reorientations, the NH_3^+ group motion was found to correspond to the T_{1H} minimum at

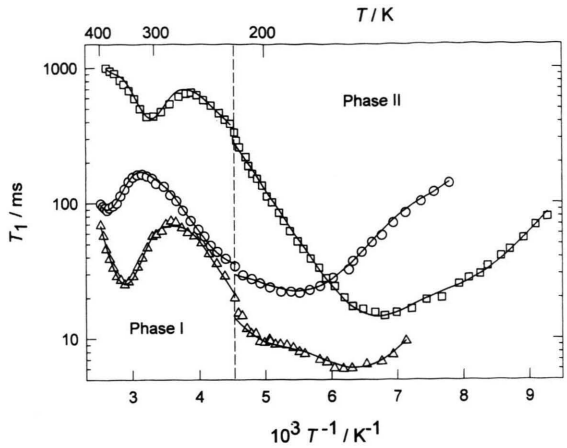

Fig. 3. Temperature dependence of spin-lattice relaxation time for $^1H(T_{1H})$ and ^{19}F (T_{1F}) observed in $(CH_3)_3CND_3BF_4$. T_{1H} (△) observed at 8.5 MHz; T_{1H} (○) at 32 MHz; T_{1F} (□) at 30.1 MHz. The solid lines indicate the best-fit theoretical values; the broken line shows the phase transition temperature determined by DTA.

245 K in $(CH_3)_3CNH_3BF_4$, comparing the T_{1H} data in $(CH_3)_3CNH_3BF_4$ with those in $(CH_3)_3CND_3BF_4$. The T_{1H} minimum and the shoulder in Phase II can, therefore, be attributed to the CH_3 group reorientation and the T_1 minimum at 345 K in Phase I to the t-butyl group motion because the CH_3 group motion is expected to occur more easily, i.e., at lower temperatures than the t-butyl group motion.

The broad and asymmetric T_{1H} minimum in Phase II, assignable to the CH_3 group motion, can be explained in terms of the existence of crystallographic non-equivalent CH_3 groups. Assuming two kinds of CH_3 groups in this phase, T_{1H} can be expressed by considering the ^1H-^1H and ^1H-^{19}F magnetic dipolar interactions [10 - 12],

$$\frac{1}{T_{1H}} = C_{HH(1)}g(\omega_H, \tau_{H(1)}) + C_{HH(2)}g(\omega_H, \tau_{H(2)}) + C_{HF(1)}g(\omega_{HF}, \tau_{H(1)}) + C_{HF(2)}g(\omega_{HF}, \tau_{H(2)}); \quad (1)$$

$$g(\omega_H, \tau_{H(i)}) = \frac{\tau_{H(i)}}{1+\omega_H^2\tau_{H(i)}^2} + \frac{4\tau_{H(i)}}{1+4\omega_H^2\tau_{H(i)}^2}, \quad (2)$$

$$g(\omega_{HF}, \tau_{H(i)}) = \frac{\tau_{H(i)}}{1+(\omega_H-\omega_F)^2\tau_{H(i)}^2} + \frac{3\tau_{H(i)}}{1+\omega_H^2\tau_{H(i)}^2} + \frac{6\tau_{H(i)}}{1+(\omega_H+\omega_F)^2\tau_{H(i)}^2} \quad (3)$$

$(i = 1, 2)$.

Table 1. Activation energies E_a, correlation times τ_0 at the limit of infinite temperature, and motional constants evaluated for anionic and cationic motions in Phases I and II of $(CH_3)_3CNH_3BF_4$ and $(CH_3)_3CND_3BF_4$ by measurement of ^1H and ^{19}F NMR spin-lattice relaxation time.

E_a / kJ mol^{-1}	τ_0 / 10^{-13} s	C / 10^8 s^{-2}	Reorienting group
$(CH_3)_3CNH_3BF_4$, Phase I:			
40*	0.11*	12.3 ± 0.1 (C'_{HH})	t-butyl
		0.25 ± 0.02 (C'_{HF})	
16*	4*	34 ± 1 (C_{HH})	CH_3
24 ± 1	1.4 ± 0.1	11.5 ± 0.5 (C''_{HH})	NH_3^+
		0.30 ± 0.05 (C''_{HF})	
$(CH_3)_3CNH_3BF_4$, Phase II:			
13 ± 1	4.9 ± 0.5	50 ± 2 ($C_{HH(1)}$)	$CH_3(1)$
		2.0 ± 0.1 ($C_{HF(1)}$)	
16 ± 1	7.5 ± 0.5	23 ± 1 ($C_{HH(2)}$)	$CH_3(2)$
		0.9 ± 0.1 ($C_{HF(2)}$)	
$(CH_3)_3CND_3BF_4$, Phase I:			
40 ± 2	0.11 ± 0.3	13.3 ± 0.1 (C_{HH})	t-butyl
		0.25 ± 0.02 (C_{HF})	
16 ± 2	4 ± 1	40 ± 1 (C_{HH})	CH_3
10 ± 1	—	—	BF_4^-
$(CH_3)_3CND_3BF_4$, Phase II:			
13 ± 1	5.2 ± 0.5	53 ± 1 ($C_{HH(1)}$)	$CH_3(1)$
		1.0 ± 0.2 ($C_{HF(1)}$)	
16 ± 1	8.0 ± 0.5	25 ± 1 ($C_{HH(2)}$)	$CH_3(2)$
		0.5 ± 0.1 ($C_{HF(2)}$)	
10.3 ± 0.4	3 ± 1	34 ± 3 ($C_{FF(1)}$)	$BF_4(1)^-$
17.2 ± 0.8	0.07 ± 0.04	34 ± 3 ($C_{FF(2)}$)	$BF_4(2)^-$

* Values obtained in Phase I of $(CH_3)_3CND_3BF_4$.

Here $\tau_{H(1)}$ and $\tau_{H(2)}$ denote the reorientational correlation times of the two kinds of CH_3 groups giving the T_{1H} minimum at the low and high temperatures, respectively; ω_H and ω_F are the ^1H and ^{19}F Larmor frequencies. $C_{HH(i)}$ and $C_{FH(i)}$ stand for the motional constants related to the reduction of M_{2H} through the ^1H - ^1H and ^1H - ^{19}F interactions, respectively, due to the i-th CH_3 group motion. Equations (1) - (3) were fitted to the T_{1H} observed in Phase II of $(CH_3)_3CNH_3BF_4$ and $(CH_3)_3CND_3BF_4$. In the calculations, we assumed an Arrhenius-type relationship between $\tau_{H(i)}$ and the activation energy $(E_{a(i)})$ $(i = 1, 2)$ of the motional process expressed as

$$\tau_{H(i)} = \tau_{0(i)} \exp(E_{a(i)}/RT), \quad (4)$$

where $\tau_{0(i)}$ is the correlation time at the limit of infinite temperature. The optimum values of $C_{HH(i)}$, $C_{HF(i)}$, $\tau_{0(i)}$, and $E_{a(i)}$ are shown in Table 1 and the fitted curves are shown in Figs. 2 and 3. We obtained

$C_{HH(1)} = 50 \times 10^8$ and $C_{HH(2)} = 23 \times 10^8$ s^{-2} for $(CH_3)_3CNH_3BF_4$ and $C_{HH(1)} = 53 \times 10^8$ and $C_{HH(2)} = 25 \times 10^8$ s^{-2} for $(CH_3)_3CND_3BF_4$, implying that the nonequivalent CH_3 groups can be classified into two groups with an abundance ratio of 2:1. The activation energies of 13 and 16 kJ mol^{-1} obtained for the CH_3 reorientations are comparable to the potential barrier of 17.21 kJ mol^{-1} for the internal rotation of the CH_3 group in an isolated t-butylammonium ion calculated by ab initio MO [13], when one takes into account the zero-point energy. The reorientation of the CH_3 group in this phase is, therefore, expected to be mostly hindered by the intra-cationic potential barrier, and the intermolecular hindrance to the reorientation is considered to be small.

The T_{1H} minima at 8.5 and 32 MHz in Phase I of $(CH_3)_3CND_3BF_4$ are attributed to the t-butyl group reorientation, as mentioned above. The T_{1H} increase with temperature in the low-temperature range of Phase I is attributable to the CH_3 group motion. Since the correlation time (τ_H) for the CH_3 group motion is considered to be much shorter than that (τ'_H) for the t-butyl group, as predicted from the T_{1H} results in Phase II, T_{1H} in Phase I can be approximately expressed [10 - 12, 14] by considering ^1H-^1H and ^1H-^{19}F dipolar interactions, as

$$\frac{1}{T_{1H}} = C'_{HH}g(\omega_H,\tau'_H)+C'_{HF}g(\omega_{HF},\tau'_H)+C_{HH}g(\omega_H,\tau_H). \tag{5}$$

Here C'_{HH} and C'_{HF} are the motional constants related to the t-butyl group motion, and C_{HH} is related to the CH_3 group motion. We assumed a single correlation time for the CH_3 group motion and ignored the contribution from the ^1H-^{19}F interaction caused by the CH_3 group motion for simplicity. Equation (5) is fitted to the T_{1H} data using the Arrhenius-type relation-ship as given by (4) for these two motions.

The T_{1H} data in Phase I of $(CH_3)_3CNH_3BF_4$ can be explained by the t-butyl, NH_3^+ and CH_3 group motions, referring to the T_{1H} data of $(CH_3)_3CND_3BF_4$ and the M_{2H} results. T_{1H} can, therefore, be expressed as

$$\begin{aligned}\frac{1}{T_{1H}} &= C'_{HH}g(\omega_H,\tau'_H) + C'_{HF}g(\omega_{HF},\tau'_H)\\ &+ C''_{HH}g(\omega_H,\tau''_H)\\ &+ C''_{HF}g(\omega_{HF},\tau''_H) + C_{HH}g(\omega_H,\tau_H),\end{aligned} \tag{6}$$

where τ''_H is the correlation time of NH_3^+ reorientation, and C''_{HH} and C''_{HF} are the motional constants. The motional parameters (C''_{HH}, C''_{HF}, E_a, and τ''_{0H}) for the NH_3^+ motion were evaluated using a fitting calculation with the E_a and τ_0 values of the t-butyl and CH_3 group motions obtained from the T_{1H} data in Phase I of $(CH_3)_3CND_3BF_4$. The E_a value of 24 kJ mol^{-1} obtained for the NH_3^+ motion is considerably smaller than 38.5 - 44.2 kJ mol^{-1} for the same motion in t-butylammonium chloride and bromide [15], in which a strong hydrogen bond N-H···X (X = Cl, Br) is expected. The value of 24 kJ mol^{-1} is, however, much larger than 12.41 kJ mol^{-1}, the calculated potential barrier for the internal rotation of NH_3^+ [13]. This implies that the primary origin of the hindering force for the NH_3^+ reorientation is intermolecular interactions including N-H···F hydrogen bonds.

Spin-lattice Relaxation Time (T_{1F}) of ^{19}F NMR

The T_{1F} data of $(CH_3)_3CND_3BF_4$ observed at 30.1 MHz are shown in Figure 3. The deep T_{1F} minimum of 18 ms around 160 K is assignable to the isotropic rotation of the BF_4^- ion based on the above discussion on M_{2F}. Since the observed T_{1F} yielded an asymmetric log T_{1F} vs. T^{-1} curve, we can expect that at least two kinds of crystallographically nonequivalent anions exist in Phase II. Here we assume that the ^{19}F - ^{19}F and ^{19}F - ^{11}B magnetic dipole-dipole interactions are the dominant relaxation processes affecting T_{1F} and that two kinds of anion exist with an abundance ratio of 1:1, in which case T_{1F} can be expressed approximately as [10 - 12]

$$\begin{aligned}\frac{1}{T_{1F}} &= C_{FF(1)}g(\omega_F,\tau_{F(1)}) + C_{FB(1)}g(\omega_{FB},\tau_{F(1)})\\ &+ C_{FF(2)}g(\omega_F,\tau_{F(2)}) + C_{FB(2)}g(\omega_{FB},\tau_{F(2)});\end{aligned} \tag{7}$$

$$g(\omega_F,\tau_{F(i)}) = \frac{\tau_{F(i)}}{1+\omega_F^2\tau_{F(i)}^2} + \frac{4\tau_{F(i)}}{1+4\omega_F^2\tau_{F(i)}^2}, \tag{8}$$

$$\begin{aligned}g(\omega_{FB},\tau_{F(i)}) &= \frac{\tau_{F(i)}}{1+(\omega_F-\omega_B)^2\tau_{F(i)}^2} + \frac{3\tau_{F(i)}}{1+\omega_F^2\tau_{F(i)}^2}\\ &+ \frac{6\tau_{F(i)}}{1+(\omega_F+\omega_B)^2\tau_{F(i)}^2}\end{aligned} \tag{9}$$

$(i = 1, 2)$.

Here $\tau_{F(i)}$ and ω_B are the correlation time of isotropic reorientation of the i-th anion and the Larmor frequency of ^{11}B. The motional constants, $C_{FF(i)}$ and $C_{FB(i)}$, are the contributions to M_{2F} caused by ^{19}F-^{19}F and ^{19}F-^{11}B interactions, respectively, due to the i-th anionic motion. Since the intra-anionic interaction is dominant for the ^{19}F-^{11}B interaction, $C_{FB(i)}$ is expressed as [10 - 11]

$$C_{FB(i)} = \frac{1}{4}\gamma_F^2\gamma_B^2\hbar^2 r_{FB}^{-6} \quad (10)$$

where γ_F, γ_B, and r_{FB} are the gyromagnetic ratios of ^{19}F and ^{11}B, and the B-F bond distance, respectively. Assuming an Arrhenius-type relationship given by (4), (7) - (9) were fitted to the observed T_{1F} values, where the theoretical value, $C_{FB(1)} = C_{FB(2)} = 15 \times 10^8$ s^{-2} (r_{FB} = 1.43 Å) [5], was used. The motional parameters determined are given in Table 1, and the best-fit curves are shown in Figure 3.

The T_{1F} minimum observed in Phase I is thought to originate from the inter-ionic ^{19}F-^{1}H dipolar interactions modulated by the t-butyl group motion because in Phase I intra-anion ^{19}F-^{19}F and ^{19}F-^{11}B dipolar interactions are considered to be completely averaged out by the anionic isotropic reorientation whose onset is detected in Phase II. T_{1F} in Phase I can be stated in terms of τ'_H and τ_F, the correlation times of the t-butyl group and the anion isotropic reorientation, respectively, as

$$\frac{1}{T_{1F}} = C'_{FH}g(\omega_{FH}, \tau'_H) + (5C_{FF} + 10C_{FB})\tau_F. \quad (11)$$

Here a single correlation time τ_F which is short enough to satisfy the condition of $\omega_F\tau_F$, $(\omega_F + \omega_B)\tau_F \ll 1$, is assumed for the anionic motion. Using the correlation time of t-butyl group obtained from the T_{1H} data of $(CH_3)_3CND_3BF_4$, (11) was fitted to the T_{1F} data in Phase I. The results are shown in Fig. 3 and Table 1.

Conclusion

The three kinds of cationic motions (reorientations of the CH_3 groups about their C-C bond axes, the NH_3^+ group about its C-N bond axis, and the t-butyl group about the C-N bond axis) and the anionic isotropic reorientation were observed in the two solid phases (Phases I and II) of t-butylammonium tetrafluoroborate. Since the entropy change at the solid-solid phase transition is small compared with that (> Rln 2) expected for the transition accompanying a gain in orientational disorder of ions [16], and since no marked change in M_{2H}, M_{2F}, T_{1H}, or T_{1F} was observed, the crystal structure change here is considered to be so slight that the motional states of the cation and anion are little affected; probably only the correlation times of the motions in Phase II decrease to some extent at the transition.

[1] H. Ishida, T. Iwachido, N. Hayama, R. Ikeda, M. Hashimoto, and D. Nakamura, Z. Naturforsch. **44a**, 71 (1989).
[2] H. Ishida, T. Iwachido, N. Hayama, D. Nakamura, and R. Ikeda, Bull. Chem. Soc. Jpn. **64**, 3613 (1991).
[3] Y. Kume, R. Ikeda, and D, Nakamura, J. Magn. Reson. **33**, 331 (1979).
[4] H. Ishida, T. Iwachido, N. Hayama, R. Ikeda, M. Terashima, and D. Nakamura, Z. Naturforsch. **44a**, 741 (1989).
[5] D. Pendred and R. E. Richards, Trans. Faraday Soc. **51**, 468 (1955).
[6] A. P. Caron, D. J. Huettner, J. L. Ragle, L. Sherk, and T. R. Stengle, J. Chem. Phys. **47**, 2577 (1967).
[7] K. N. Trueblood, Acta Crystallogr. **C43**, 711 (1987).
[8] H. Ishida, S. Inada, N. Hayama, D. Nakamura, and R. Ikeda, Ber. Bunsenges. Phys. Chem. **95**, 866 (1991).
[9] H. Ishida, T. Higashiyama, N. Hayama, and R. Ikeda, Z. Naturforsch. **47a**, 1087 (1992).
[10] A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press, London 1961.
[11] D. E. O'Reilly, E. M. Peterson, and T. Tsang, Phys. Rev. **160**, 333 (1967).
[12] S. Albert and H. S. Gutowsky, J. Chem. Phys. **59**, 3585 (1973).
[13] H. Ishida, Y. Kubozono, S. Kashino, and R. Ikeda, Z. Naturforsch. **47a**, 1255 (1992).
[14] M. B. Dunn and C. A. McDowell, Mol. Phys. **24**, 969 (1972).
[15] H. Ishida, S. Inada, N. Hayama, D. Nakamura, and R. Ikeda, Z. Naturforsch. **46a**, 265 (1991).
[16] N. G. Parsonage and L. A. K. Staveley, Disorder in Crystals, Clarendon Press, Oxford 1978.