Dynamics of Nitrite Ions in the Ionic Plastic Crystal $TlNO_2$ studied by ^{15}N and ^{205}Tl NMR

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Z. Naturforsch. **50 a,** 871–875(1995); received June 16, 1995

The temperature dependences of the NMR spin-lattice and spin-spin relaxation times and the NMR spectra of ^{15}N in $Tl^{15}NO_2$ were observed in the plastic phase (282.4 K $< T <$ 459 K) and the low-temperature phase. From the analysis of ^{15}N NMR data, we attributed the motion reported in dielectric and Tl NMR studies in the low-temperature phase to the 180°-flip of NO_2^- ions which takes place with an activation energy of 14 kJ mol^{-1}. In the plastic phase, we detected isotropic NO_2^- reorientation with an activation energy of 13.5 kJ mol^{-1} and a new anionic motion with 10 kJ mol^{-1}.

Key words: Solid NMR, Spin-lattice relaxation, Plastic crystal, Phase transition, Chemical shift anisotropy.

Introduction

Alkali metal nitrites MNO_2 (M = K, Rb, Cs) and $TlNO_2$ transform into a plastic phase around room temperature [1-6]. Thermal measurements carried out on the respective salts [2-6] revealed that the heat capacity at the transition point is accompanied by a long tail on the low-temperature side extending over 100 K. This suggests the presence of some disorder in the low-temperature phase. In our previous NMR studies on KNO_2 [7] and $RbNO_2$ [8], a new anionic motion was found in the low-temperature phase of these salts. Excitation of a 180°-flip of the NO_2^- ions and their small-angle reorientation about the C_2-axis were shown to contribute to the anomalous heat capacity in this phase.

$TlNO_2$ has two solid phases [3]. The plastic phase (Phase I) obtainable between 282.4 K and 459 K (melting point) [1] forms a CsCl-type cubic lattice with the space group Pm3m and a_0= 421 pm [9]. The entropy change at the transition to this phase was determined to be 23.8 J K^{-1} mol^{-1}, being larger than the melting entropy of 15 J K^{-1} mol^{-1} [1-3]. This inverse relation is characteristic in plastic crystals. The low-temperature phase (Phase II) crystallizes in an orthorhombic lattice with Cmmm or Cmm2 [3]. In this phase the dielectric constant has been measured [3] and a marked dielectric dispersion, attributable to some anionic motion, with an activation energy of 19.5 kJ mol^{-1} was observed. Freezing of this motion is expected at the glass transition around 60 K [3]. Recent Tl NMR measurements carried out between 120 and 430 K [10], have revealed an anionic motion corresponding to the dielectric relaxation in Phase II and cationic self-diffusion in Phase I [10,11]. Tl NMR gives two T_1 components (long and short values, T_1^l, T_1^s) which have different dependences on temperature and Larmor frequency [10]. The mechanism of T_1^s has been discussed and assigned to the scalar relaxation, while that of T_1^l is still unknown.

In the present work, we study temperature dependences of the ^{15}N NMR relaxation time and spectra to get information about the mode of the anionic motion in Phase II and the plastic phase. We also measured ^{205}Tl NMR T_1 at 13.84 MHz to reveal the unknown relaxation mechanism for T_1^l in Phase II .

Experimental

$TlNO_2$ and $Tl^{15}NO_2$ were prepared from $NaNO_2$ (Wako Pure Chemical Industries Ltd.) and $Na^{15}NO_2$ (99 wt% ^{15}N, ICON Inc.), respectively, using a cation exchange resin (Diaion SK-1, Mitsubishi Kasei Corp.). The crude crystals were recrystallized from water; hygroscopic orange crystals were obtained.

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^{15}N ($I = 1/2$) NMR spectra and the spin-lattice and spin-spin relaxation times T_1 and T_2 were measured at a Larmor frequency of 30.42 MHz (7.041 T) using a Bruker MSL-300 spectrometer at 140-360 K, and a Bruker MSL-400 spectrometer (9.388 T) at 300-450 K. The saturation recovery and Carr-Purcell methods were employed to evaluate T_1 and T_2, respectively. The ^{15}N chemical shift values were determined using an external reference of $^{15}NH_4^+$ ($\delta_s = -354$ ppm) in a 4.5 M solution of ^{15}N enriched $^{15}NH_4NO_3$ in 3 M hydrochloric acid.

^{205}Tl ($I = 1/2$, natural abundance of 70.5 %) NMR T_1 was measured at a Larmor frequency of 13.84 MHz by the inversion recovery method using a Bruker SXP spectrometer at 160-270 K.

Results and Discussion

The temperature dependences of ^{15}N T_1 observed at 30.42 MHz in Phase I and II, and at 40.56 MHz in Phase I, and T_2 in Phase I of $Tl^{15}NO_2$ are shown in Figure 1. The magnetization recovery of ^{205}Tl nuclei observed after a 90° pulse showed marked non-exponential behaviour in Phase II, as already reported in [10]. We showed only the long component, T_1^l in the figure. The reported data observed at 34.61 MHz [10] in Phase II of $Tl^{14}NO_2$ are also shown in Figure 1. A shallow ^{15}N T_1 minimum of *ca.* 30 s was observed at 210 K in Phase II. A frequency dependent ^{205}Tl T_1^l was detected on the high-temperature side of the minimum. In Phase I, ^{15}N showed a T_1 maximum around 320 K at 30.42 MHz and a nearly constant T_2 of 30 ms at 350-450 K.

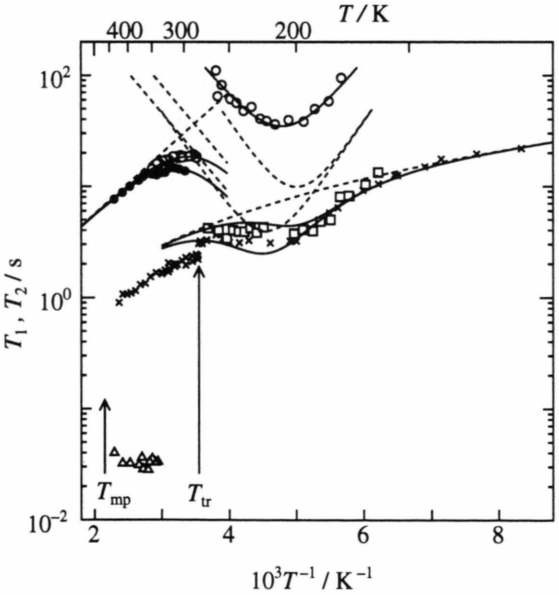

Fig. 1. Temperature dependences of ^{15}N NMR spin-lattice relaxation time T_1 observed at Larmor frequencies of 30.42 (○) and 40.56 MHz (●), and spin-spin relaxation time T_2 (△) in $Tl^{15}NO_2$, and ^{205}Tl T_1^l observed at 13.84 MHz (□) and reported at 34.61 MHz (×) [10] in $Tl^{14}NO_2$. Solid and dotted lines are the best fitted theoretical values. T_{tr} and T_{mp} are the phase transition and melting temperatures, respectively.

Phase II (Low-Temperature Phase)

The ^{15}N T_1 minimum observed in $Tl^{15}NO_2$ in this phase is attributable to the fluctuation of the chemical shift(CS) anisotropy and can approximately be expressed as [12]

$$\frac{1}{T_1} \simeq \frac{3}{10}\Delta\omega^2\frac{\tau}{1+\omega^2\tau^2}, \tag{1}$$

where τ, ω, and $\Delta\omega$ denote the correlation time of the expected anionic motion, the ^{15}N Larmor angular frequency, and the line-width narrowed by the CS averaging, respectively. We assume an Arrhenius-type temperature dependence of τ:

$$\tau = \tau_0\exp\left(\frac{E_a}{RT}\right). \tag{2}$$

(1) and (2) were fitted to the observed ^{15}N T_1 values and the obtained best-fitted T_1 curve is shown in Figure 1. Evaluated activation parameters are given in Table 1.

We assumed that the observed ^{205}Tl T_1^l results from two superimposed mechanisms:

$$\frac{1}{T_1^l} = \frac{1}{T_{1Mot}} + \frac{1}{T_{1Lat}}, \tag{3}$$

where T_{1Mot} is due to the NO_2^- motion contributing to the T_1^l minimum, and T_{1Lat} is due to lattice vibrations responsible for the gradual change of T_1^l at low temperatures, expressed as

$$\frac{1}{T_{1Lat}} = AT^2, \tag{4}$$

where A is a constant. Since the temperature dependent T_1^l was observed on the high-temperature side of

Phase	Motional Mode	E_a / kJ mol^{-1}	τ_0 / s	Nucleus
II	180°-Flip	14±2	1.8×10^{-12}	^{15}N
		17*	4.2×10^{-13}	^{205}Tl
I	C_2-Reorientation	10±2		^{15}N
	Isotropic Reorientation	13.5±1		^{15}N

Table 1. Motional modes and activation energies (E_a) and the pre-exponential factor (τ_0) for NO_2^- ions derived from spin-lattice relaxation time (T_1) of ^{15}N in $Tl^{15}NO_2$ and the long T_1 component (T_1^l) of ^{205}Tl in $Tl^{14}NO_2$.

* The same value reported for ^{205}Tl T_1^s [10] was assumed.

the minimum, we attributed the relaxation mechanism of T_{1Mot} to the fluctuation of the CS anisotropy which is given by (1). We fitted (1) - (4) to the present and reported data shown in Fig. 1, and obtained the activation parameters listed in Table 1. The best-fitted T_1^l curves shown in Fig. 1 approximately reproduce the observed data. Small deviations from the experimental data seen in the high-temperature range of this phase are attributable to the influence of the phase transition and/or the contribution from other relaxation mechanisms, such as magnetic dipole interactions. The present activation energy of 14 kJ mol^{-1} agrees roughly with the reported value of 17 kJ mol^{-1} derived from the Tl T_1^s data [10]. Since the reported temperature of the Tl T_1^l minimum (220 K) observed at 34.61 MHz is close to 210 K of the present ^{15}N T_1 minimum, we can conclude that the ^{15}N T_1 and Tl T_1^l minima correspond to the same anionic motion.

The fact that the marked anomaly of the dielectric dispersion has been detected in Phase II of $TlNO_2$ [2,3] indicates that the anionic motion is expected to be accompanied by the change of the electric-dipole direction of the NO_2^- ions. The activation energy E_a of 19.5 kJ mol^{-1} and the correlation time τ_0 of the order of 10^{-13} derived in the dielectric study are close to the present NMR results shown in Table 1, implying that the same motion is observed by these two different techniques.

Figure 2 shows the temperature dependence of ^{15}N NMR spectra. Each of the observed spectra consists of three different principal CS components in the studied temperature range of Phase II. This indicates that no change of symmetry in the NO_2^- ion takes place in the above motional process.

From these results of ^{15}N NMR and dielectric studies, we attributed this motion to the 180°-flip of NO_2^-, in which the NO_2^- dipole flips about one of the two axes perpendicular to the molecular C_2-axis.

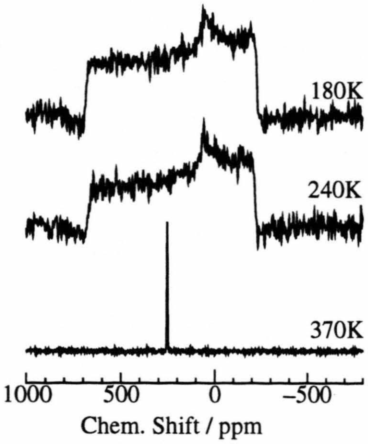

Fig. 2. ^{15}N NMR spectra observed at 30.42 MHz in Phase I and II of $Tl^{15}NO_2$. As the external reference of chemical shift, we employed $^{15}NH_4^+$ ($\delta_s = -354$ ppm) in a 4.5 M solution of ^{15}N enriched $^{15}NH_4NO_3$ in a 3 M hydrochloric acid.

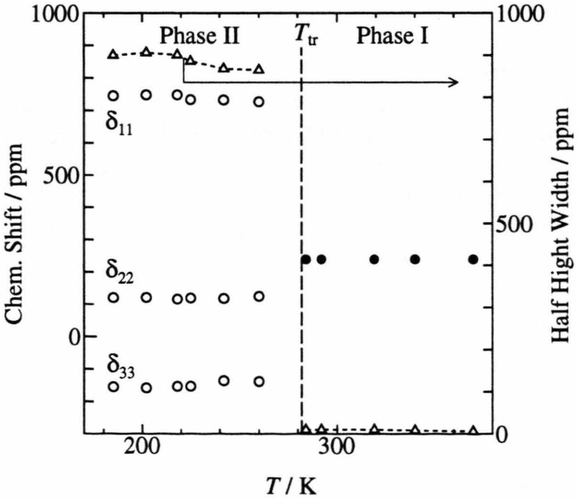

Fig. 3. Temperature dependences of three principal values (δ_{11}, δ_{22}, δ_{33}) (○) of the chemical shift tensor of ^{15}N observed in Phase II, isotropic-shift values in Phase I (●) and half-height-widths (△) of the observed spectra in $Tl^{15}NO_2$. T_{tr} denotes the phase transition temperature.

The onset of this motion in this phase is consistent with the orientational disorder of NO_2^- ions expected from the dielectric and thermal studies [3]. Since the 180°-flip becomes slow enough at low temperatures, we can accept the proposed model of the freezing of NO_2^- orientation at the glass transition observed at *ca.* 60 K [3].

We measured the temperature dependence of the principal values of the ^{15}N CS tensor in $Tl^{15}NO_2$ and showed it in Figure 3. The calculation of the ^{15}N CS tensor reported for $Na^{15}NO_2$ [13-15] afforded that the direction of the largest component δ_{33} is perpendicular to the molecular plane, the intermediate δ_{22} along the C_2-axis, and the smallest δ_{11} in the molecular plane. We can see from Fig. 3 that the absolute values of δ_{11} and δ_{33} gradually decrease upon heating in the high-temperature region, while δ_{22} changes little. This result suggests a marked increase of the amplitude of NO_2^- libration about the C_2-axis or the onset of a new reorientation with a small angle about the axis. A similar motion has already been found in the low-temperature phase of $Rb^{15}NO_2$ [8].

Phase I (Plastic Phase)

Phase I, which forms a CsCl-type cubic lattice with the space group Pm3m and a_0 = 421 pm at room temperature [9], contains isotropically disordered NO_2^- dipoles, as predicted from the structural and thermal studies [3]. We observed a narrowed single ^{15}N NMR spectrum at 320 K with a half-height width of *ca.* 300 Hz as shown in Figure 2. This spectrum is quite analogous to those in $K^{15}NO_2$ and $Rb^{15}NO_2$ observed in the respective plastic phase. These results indicate the onset of isotropic reorientation of NO_2^- ions. The CS, 239 ppm independent of temperature, equals almost the 248 and 249 ppm observed in the potassium and rubidium salt, respectively.

The temperature dependences of ^{15}N T_1 observed in this phase are shown in Figure 1. A T_1 maximum was observed around 320 K at 30.42 MHz. In $K^{15}NO_2$ and $Rb^{15}NO_2$, the T_1 showed a gradual decrease on heating in the low-temperature region of the plastic phase [7,8], and this result was explained by the onset of isotropic NO_2^- reorientation. In the present system, however, we observed a frequency dependent T_1 increase with temperature near the phase transition. This T_1 change can, accordingly, be attributed to some ionic motion, but not to effects of the phase transition. We approximately expressed the observed T_1 by the superposed two relaxation mechanisms:

$$T_1^{-1} = T_{1a}^{-1} + T_{1b}^{-1} \tag{5}$$

Here T_{1b} contributes in the low-temperature range and T_{1a} in the high-temperature range of the T_1 maximum in this phase. We assumed that these T_1 values can be written by (1) and (2) in which $\omega\tau \ll 1$ is assumed for T_{1a} and $\omega\tau \gg 1$ for T_{1b}. Using (1), (2) and (5), we evaluated the best fitted T_1 curve as shown in Fig. 1 and obtained the activation parameters listed in Table 1. We assigned T_{1a} to the isotropic reorientation of NO_2^- ions which has been expected in this phase from the structural and thermal studies [3]. The activation energy of 13.5 kJ mol^{-1} for the isotropic reorientation is slightly larger than 10 and 12 kJ mol^{-1} reported for the same motion in KNO_2 [7], and also 6.2 and 8.5 kJ mol^{-1} in $RbNO_2$ [8]. It has been reported in this phase that Tl T_1^s in $Tl^{14}NO_2$ gave a minimum around 400 K, which was explained by Tl^+ self-diffusion [10]. Although we can also expect the onset of NO_2^- diffusion in this phase, we can not attribute T_{1a} to this motion by the following reason. The observed ^{15}N T_2 values of *ca.* 30 ms were almost temperature independent in the range 350 to 450 K. This T_2 value can be derived by only considering the isotropic NO_2^- reorientation without its self-diffusion from the calculation of ^{15}N T_2, where we assume isotropic NO_2^- reorientation and Tl^+ self-diffusion and use the relations

$$\frac{1}{T_2} = \frac{\gamma_N}{2\pi}\sqrt{\langle\Delta H\rangle_N^2} \tag{6}$$

and

$$\langle\Delta H\rangle_N^2 = \frac{3}{5}\hbar^2\gamma_N^2 I_N(I_N+1)\sum\frac{1}{r_{ij}^6} \tag{7}$$

Here γ_N, I_N, r_{ij} denote the gyromagnetic ratio, spin quantum number of ^{15}N, and the ^{15}N-^{15}N internuclear distance, respectively. In this treatment, we considered magnetic dipolar interaction between the ^{15}N nuclei which is only the contribution to ^{15}N T_2 under the above motional modes of both ions. The estimated T_2 value of 29.5 ms agrees well with the observed T_2 and supports the assumed motional modes, namely, isotropic NO_2^- reorientation and Tl^+ self-diffusion.

The motional mode contributing to T_{1b} in the low-temperature range of this phase is, accordingly, attributed to some NO_2^- motion with an amplitude smaller than that of the isotropic reorientation. We may assign this mechanism to the NO_2^- reorientation about its C_2-axis, which is expected to take place in Phase II, but probably with a large amplitude in Phase I.

Conclusion

The anomalous increase of the heat capacity observed in $TlNO_2$ over a wide temperature range below the phase transition at 282.4 K was explained by the excitation of NO_2^- 180°-flip in Phase II. This motion was derived from the temperature dependence of the ^{15}N NMR spectra, which retained the three kinds of different CS components in the studied temperature range of Phase II, and also from the reported data of the dielectric dispersion and relaxation [2,3], and Tl NMR [10]. A new motion is expected in the high-temperature range of Phase II. This motion seems to be a large amplitude NO_2^- libration or a small-angle reorientation about its C_2-axis.

In the plastic phase (Phase I), the anionic isotropic reorientation and a new motion attributable to the NO_2^- reorientation about the C_2-axis, were deduced from the temperature and frequency dependences of ^{15}N NMR T_1. The activation energy of 13.5 kJ mol^{-1} determined for the isotropic NO_2^- reorientation in the CsCl-type cubic phase is close to 10 and 12 kJ mol^{-1} in KNO_2 [7], and 6.2 and 8.5 kJ mol^{-1} in $RbNO_2$ [8], both having the NaCl-type cubic structure. These results suggest that the hindrance for the isotropic reorientation is not strongly dependent on the kind of the cubic structure, in contrast to the barriers for the cationic self-diffusion [8] which have been shown to be quite different in these two kinds of cubic phases.

Acknowledgement

We are grateful to Dr. Y. Onoda and Dr. M. Tansho in National Institute for Research in Inorganic Materials for the use of the MSL-400 spectrometer. We also thank Professor Y. Furukawa in Hiroshima University for useful discussion in data analysis. This work was partly supported by a Grant-in-aid for Scientific Research No. 06453055 from the Ministry of Education, Science and Culture, Japan.

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