Ionic Dynamics in the Ionic Plastic Crystal NH_4NO_2

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Using ^{1}H NMR T_1 and $T_{1\rho}$ measurements self-diffusion of NH_4^+ with an activation energy of (80 ± 10) kJ mol^{-1} was detected in the highest-temperature phase of NH_4NO_2 crystals. Narrow ^{15}N NMR spectra of $^{15}NH_4NO_2$ and $NH_4{}^{15}NO_2$ revealed that the isotropic reorientation rates of NH_4^+ and NO_2^- ions are rapid in the high-temperature solid phase. These results suggest that the high-temperature phase of NH_4NO_2 crystals forms an ionic plastic phase.

Key words: Plastic Crystal; ^{1}H NMR; ^{15}N NMR.

1. Introduction

Crystals of metal nitrites MNO_2 [M = K, Rb, Cs, Tl(I)] have been found to exhibit ionic plastic properties [1 – 29]. These compounds undergo a phase transition into a plastic phase in which isotropic reorientation of NO_2^- ions and self-diffusion of M^+ and NO_2^- ions are detected by metal and ^{15}N NMR spectroscopy [20 – 25]. In the low-temperature phase just below the plastic phase, NMR and dielectric studies have revealed the onset of two-site jump motion of NO_2^- ions [12 – 25]. Calorimetric measurements show molar entropy changes of 17.3 – 35.9 J K^{-1} mol^{-1} at the transition from the low-temperature phase to the plastic phase; these values are larger than those obtained at the melting point (14.0 – 17.8 J K^{-1} mol^{-1}). Molar heat capacity measurements display an anomalous long tail on the low-temperature side extending over 100 K [10 – 15].

In contrast, $NaNO_2$ and $LiNO_2$ crystals have no plastic phase. The former has been reported to show two order-disorder phase transitions with a small entropy change of 5.3 J K^{-1} mol^{-1}. In the highest-temperature solid phase, two-site jump motion of NO_2^- was detected [30 – 35]. The middle phase is incommensurate antiferroelectric with a sinusoidal modulation of the long-range order, and the low-temperature phase is ferroelectric with all nitrite ions aligned in parallel. In $LiNO_2$ crystals, no phase transition occurs within a temperature range of 80 K – 473 K (melting point) [11]. The entropy change of 36.2 J K^{-1} mol^{-1} at the melting point is much larger than those of the ionic plastic crystals of MNO_2, and is comparable to that of $NaNO_2$ (29.6 J K^{-1} mol^{-1}) [36]. ^{7}Li and ^{15}N NMR measurements [37] revealed that two-site jump motion of NO_2^- ions occurs by excitation in $LiNO_2$ crystals; the activation energies (42 – 44 kJ mol^{-1}) are much larger than those of plastic crystals of MNO_2 (8.7 – 18.8 kJ mol^{-1}), and similar to that of $NaNO_2$ (27 kJ mol^{-1}).

From the above facts, it may be deduced that there are certain conditions which must be fulfilled in a crystal so that an ionic plastic phase is formed; one is small melting entropy (less than 20 J K^{-1} mol^{-1}) and another is small activation energy for two-site jump motion in the low-temperature phase. The former condition has been reported by Timmermans [38 – 40] for organic plastic crystals. The other has been recently proposed for ionic plastic crystals based on previous studies [25, 37]. Pre-isotropic reorientation motions, such as two-site jump motion, make space for NO_2^- isotropic reorientation against the Coulomb force in crystals. If energies of pre-isotropic and isotropic reorientation are comparable with the lattice force, orientational disorder among NO_2^- ions can occur with retention of the crystal lattice. Since the activation energies of the NO_2^- two-site jump in $LiNO_2$ and $NaNO_2$ are larger than those of MNO_2 (M = K, Rb, Cs, Tl), it can be assumed that the ionic radius is a key parameter for plasticity. In this study, ^{1}H and ^{15}N NMR measurements of NH_4NO_2 were carried out to study the contribution of the ionic radius. The reported spherical

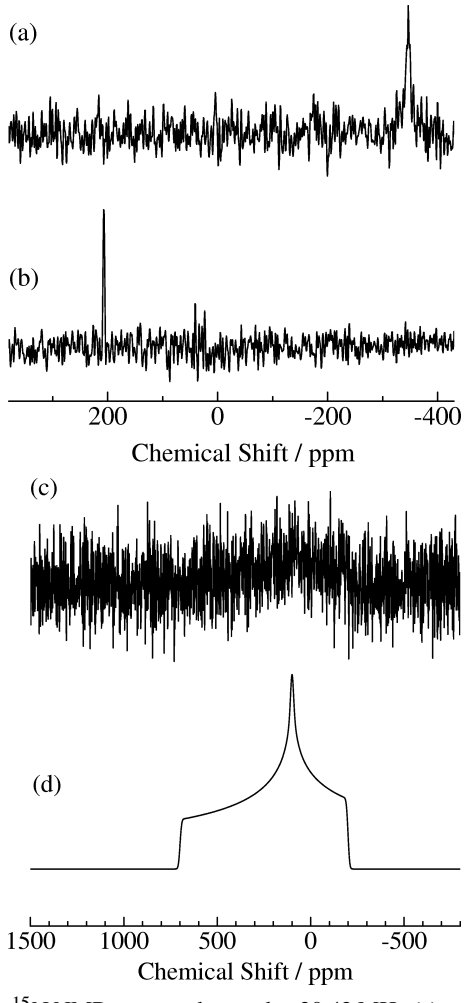

Fig. 1. ^{15}N NMR spectra observed at 30.42 MHz (a) at 160 K (Phase III) of $^{15}NH_4NO_2$, and (b) at 298 K (Phase I) and (c) at 260 K of $NH_4{}^{15}NO_2$. (d) Calculated line shape with three differential chemical shift principal values, where a reported line width of ca. 900 pm is employed [22 – 25, 37]. ^{15}N-enriched $^{15}NH_4NO_3$ in 3 M hydrochloric acid was employed as an external reference for the chemical shift.

radius of an NH_4^+ ion (148 pm) is similar to that of Rb^+ (152 pm).

It has been reported that NH_4NO_2 crystals undergo two phase transitions, at 181 and 276 K, and violent decomposition at 346 K [41, 42]. The reported decomposition entropy of ca. 20 $J\,K^{-1}\,mol^{-1}$ is similar to the fusion entropies of MNO_2-type plastic crystals: 14.0 (M = K), 16.0 (Rb), 17.8 (Cs), and 15.0 $J\,K^{-1}\,mol^{-1}$ (Tl), and smaller than melting entropies of normal crystals: 36.2 ($LiNO_2$) and 29.6 $J\,K^{-1}\,mol^{-1}$ ($NaNO_2$). The molar heat capacity of NH_4NO_2 shows an anomalous long tail on the low-temperature side of 276 K. Since the observed frequency dependences of the dielectric permittivity are reported to be around 276 K [42], orientational disorder of NO_2^- ions is predicted in the high-temperature phase. However, activation parameters and crystal structures of high-temperature solid phases have not been reported due to sample decomposition.

2. Experimental

NH_4NO_2 and $NH_4{}^{15}NO_2$ were prepared from $NaNO_2$ (Wako Pure Chemical Industries Ltd.) and $Na^{15}NO_2$ (99 wt% ^{15}N, ICON Inc.), respectively, by use of the cation exchange resin Diaion SK-1 (Mitsubishi Kasei Corp.). $^{15}NH_4NO_2$ was obtained by passing a $^{15}NH_4NO_3$ solution through a column packed with the anion exchange resin Dowex 1-X8 (Dow Chemical Company). The resulting hygroscopic crystals were dried in a desiccator. Since NH_4NO_2 crystals easily decompose to N_2 and H_2O, the crystals were kept in a freezer.

The ^1H spin-lattice relaxation time, T_1, and T_1 in a rotating frame, $T_{1\rho}$, were measured using a Bruker SXP spectrometer. The inversion recovery method was employed for the determination of T_1. A radio frequency field amplitude of 0.3 mT was used for the $T_{1\rho}$ measurement. ^{15}N ($I = 1/2$) NMR spectra were recorded at 30.42 MHz using a Bruker MSL-300 spectrometer by the solid echo method with a recycle time of 500 s. Powdered NH_4NO_2 crystals were sealed in a sample glass tube. The ^{15}N chemical shift was estimated based on an external reference of $^{15}NH_4^+$ ($\delta_s = -354$ ppm) in a 4.5 M solution of $^{15}NH_4NO_3$ in 3 M HCl.

3. Result and Discussion

The ^{15}N NMR spectrum obtained at 160 K (Phase III) of $^{15}NH_4NO_2$ is displayed in Figure 1a. The narrowed peak at -355 ppm, whose value is consistent with the reported ^{15}N NMR chemical shift of $^{15}NH_4NO_3$ [43], suggests that the isotropic reorientation rate of NH_4^+ ions is sufficiently rapid for the nuclear relaxation rate in Phase III. On the other hand, a sharp ^{15}N NMR peak of $NH_4{}^{15}NO_2$ was detected (ca. 250 ppm) only in Phase I, as displayed in Figure 1b. In the low-temperature phases, no narrow absorption spectrum was recorded, as shown in Fig. 1c,

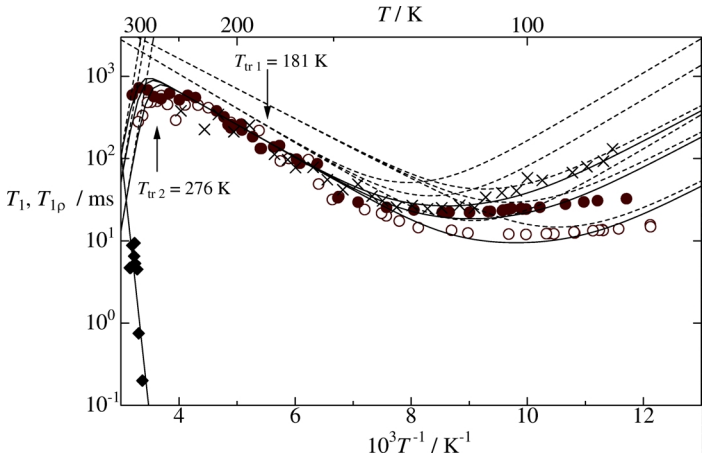

Fig. 2. Temperature dependences of ^{1}H NMR spin-lattice relaxation times in the laboratory frame (T_1) observed at 20.2 (○), 40.6 (●), and 57.6 MHz (×), and in the rotating frame [$T_{1\rho}$ (♦)] at $H_1 = 0.3$ mT in NH_4NO_2. Solid and dotted lines represent best-fit theoretical values. T_{tr} is the phase transition temperature.

although ^{15}N NMR spectra with three different principal values (ca. 700, 150 and −200 ppm) are reported for low-temperature solid phases of $M^{15}NO_2$ (M = Li, K, Rb, Cs, Tl) [22–25, 37]. The reported chemical shifts give us a theoretical envelope as shown in Figure 1d. Since the observed line width is similar to that of the simulated spectrum, any NO_2^- motion averaging chemical-shift-anisotropy is not considerable in Phase II. A reason of a low signal-to-noise ratio of the observed ^{15}N NMR spectrum can be attributed to a little amount of NH_4NO_2 crystals in the glass tube because NH_4NO_2 crystals are violently decomposed by heat. In order to get more detailed information, measurements of ^{1}H NMR relaxation times were carried out.

The obtained magnetization-recovery curve could be fitted by a single exponential function in all recorded temperature ranges. The temperature dependences of ^{1}H NMR T_1 observed at 57.6, 40.6, and 20.2 MHz and $T_{1\rho}$ are shown in Figure 2. T_1 minima and maxima were obtained around 110 and 290 K, respectively. The obtained T_1 slope in a high-temperature range of the minima was different from that of the low-temperature side and a single T_1 process model was difficult to express the observed data. Therefore, two relaxation times, $T_{1,L1}$ and $T_{1,L2}$, for low temperatures and a relaxation time, $T_{1,H}$, in the high-temperature range above the T_1 maxima were assumed:

$$\frac{1}{T_1} = \frac{1}{T_{1,L1}} + \frac{1}{T_{1,L2}} + \frac{1}{T_{1,H}}. \tag{1}$$

Since the T_1 values strongly depend on the observed frequencies below and around the temperature of the T_1 minima, the BPP-type equation [44] was used to estimate the activation parameters:

$$\frac{1}{T_1} = C\left(\frac{\tau}{1+\omega^2\tau^2} + \frac{4\tau}{1+4\omega^2\tau^2}\right), \tag{2}$$

$$C = \frac{2}{3}\gamma^2\Delta M_2, \tag{3}$$

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right). \tag{4}$$

Here C, τ, γ, ΔM_2, τ_0, E_a and ω denote a constant depending on the motional mode, correlation time of the motion, gyromagnetic ratio of ^{1}H nucleus, second moment, correlation time at infinite temperature and activation energy, and the ^{1}H Larmor angular frequency, respectively. Fitting (1)–(4) to the observed T_1 values, the activation parameters are listed in Table 1. Theoretical M_2 values can be calculated for various motional modes by using the Van Vleck equation [45]. An M_2 value of intra-molecular contributions could be estimated to be $28 \cdot 10^{-8}$ T^2 by assuming the N-H bond length of 105 pm in the tetrahedral shape of the NH_4^+ ion. Since negligible contributions of NO_2^- ($0.1 \cdot 10^{-8}$ T^2) and adjacent NH_4^+ ions ($0.4 \cdot 10^{-8}$ T^2) were roughly estimated, M_2 calculations for molecular motions were carried out for only intra-molecular contributions. If C3 reorientation of the NH_4^+ ion is excited, the theoretical M_2 value becomes $12 \cdot 10^{-8}$ T^2; ΔM_2 of $16 \cdot 10^{-8}$ T^2 can be obtained from rigid state C3 reorientation. Since the experimental ΔM_2 values of $13.6 \cdot 10^{-8}$ and $10.5 \cdot 10^{-8}$ T^2 are, respectively, comparable with calculated ones of $16 \cdot 10^{-8}$ and $12 \cdot 10^{-8}$ T^2, it is considerable that isotropic rotation rates of NH_4^+

Motional modes	E_a / kJ mol^{-1}	τ_0 / s	C / s^{-2}	ΔM_2 / T^2
C3	7 ± 1	$6.5 \cdot 10^{-13}$	$6.5 \cdot 10^{9}$	$13.6 \cdot 10^{-8}$
Isotropic reorientation of NH_4^+	8 ± 1	$8.0 \cdot 10^{-13}$	$5.0 \cdot 10^{9}$	$10.5 \cdot 10^{-8}$
Self-diffusion of NH_4^+	80 ± 10			

Table 1. Motional modes and activation parameters of NH_4NO_2, derived from ^{1}H NMR T_1 and $T_{1\rho}$.

M	r / pm	E_a / kJ mol^{-1}	a_0 of MNO_2 / pm	a_0 of MBr / pm
Li	68	80 – 90 [37]		550 (NaCl) [48]
Na	97	119 [47]	Orthorhombic [11]	597 (NaCl) [48]
K	133	60 [22]	666 (NaCl) [11]	660 (NaCl) [49]
NH_4	148	80		690 (NaCl) [50, 51]
Rb	152	75 – 110 [23]	693 (NaCl) [11]	687 (NaCl) [49]
Tl	152	47 [24]	411 (CsCl) [11]	398 (CsCl) [52]
Cs	170	33 – 47 [25]	439 (CsCl) [11]	430 (CsCl) [53]

Table 2. Cationic radii (r) [46], activation energies of self-diffusion (E_a) in the highest-temperature solid phase of MNO_2, and lattice constant (a_0).

ions in Phase III reach to the observed NMR frequencies. This result is consistent with the obtained ^{15}N NMR spectrum of $^{15}NH_4NO_2$.

Since $T_{1,H}$ also showed the observed frequency dependences, dipole-dipole interaction contributes to the ^{1}H relaxation mechanism. The rapid NH_4^+ isotropic reorientation in Phase I averages out ^{1}H-^{1}H dipole-dipole interaction, indicating that there is an additional motion which has enough large rates to relax ^{1}H spins in high-temperature ranges just below the decomposition point. The increase in $T_{1\rho}$ with temperature also suggests additional motion with a lower speed than that of isotropic reorientation. The estimated activation energy of (80 ± 10) kJ mol^{-1} from $T_{1\rho}$ is similar to that from $T_{1,H}$. Therefore it can be considered that self-diffusion occurs in Phase I and that crystalline NH_4NO_2 is a member of the new family of ionic plastic crystals. The obtained activation parameters are listed in Table 1.

^{1}H NMR measurements of T_1 and $T_{1\rho}$ and ^{15}N NMR spectra revealed that NH_4NO_2 exhibits a plastic phase in which the rates of isotropic reorientation and self-diffusion are sufficiently rapid. Since the ionic radius of NH_4^+ (148 pm) is between that of K^+ (133 pm) and Rb^+ (152 pm), the activation parameters of NH_4NO_2 can be compared with those reported for MNO_2 (M = K, Rb, Cs, Tl) [22 – 25] as listed in Table 2. Because the diffusional activation energy of NH_4NO_2 is almost identical to those of KNO_2 and $RbNO_2$, it can be considered that disordered NH_4^+ behaves as spherical cation. However, if an NO_2^- ion performs an isotropic reorientation motion, its spherical radius is close to that of Br^- (196 pm): lattice constants in the plastic phase of MNO_2 take similar values to those of MBr, as shown in Table 2. However, diffusional energies in the plastic phase of MNO_2 are much smaller than those of MBr. This tendency is also observed in NH_4NO_2:

Table 3. Activation energies of NH_4^+ isotropic reorientation and self-diffusion (in kJ mol^{-1}).

	Isotropic reorientation	Self-diffusion
NH_4NO_2	8 ± 1	80 ± 10 (this study)
NH_4Cl	17 ± 2 [53]	120 ± 10 [54]
NH_4Br	10 ± 3 [53]	120 ± 10 [54]

the obtained activation energies for NH_4^+ isotropic reorientation, (8 ± 1) kJ mol^{-1}, and self-diffusion, (80 ± 10) kJ mol^{-1}, are smaller than those of NH_4X (X = Cl and Br), as shown in Table 3. From these results it is clear that both ionic radius and ionic shape are important factors in plasticity. When a planar NO_2^- ion undergoes isotropic reorientation, it occupies a space similar to that of a Br^- ion in a crystal. However, the rate of isotropic reorientation in a crystal is much smaller than the jumping rate from one site to another (self-diffusion); therefore, from the point of view of the jumping ion, the orientation of NO_2^- ions is frozen over a short timescale of the order of picoseconds. This mechanism can be illustrated in terms of a revolving door.

4. Conclusion

Using ^{1}H NMR T_1 and $T_{1\rho}$ measurements self-diffusion of NH_4^+ with an activation energy of (80 ± 10) kJ mol^{-1} was detected in the highest-temperature phase of NH_4NO_2 crystals. This energy is similar to that of ionic plastic crystals, MNO_2 (M = K, Rb), and is smaller than that of normal crystals, NH_4X (X = Cl, Br). ^{15}N NMR spectra of $^{15}NH_4NO_2$ revealed that the isotropic reorientation rates of NH_4^+ ions are sufficiently rapid in the low-temperature solid phase. In contrast, NO_2^- isotropic reorientation was found only in the high-temperature solid phase. These results suggest that the high-temperature phase of NH_4NO_2 crystals forms an ionic plastic phase. From these results it

can be concluded that crystalline NH_4NO_2 is a member of the new family of ionic plastic crystals.

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