Ionic Dynamics in Plastic Crystal KNO_2 Studied by ^{39}K and ^{15}N NMR *

Motoko Kenmotsu, Hisashi Honda, Hiroshi Ohki, and Ryuichi Ikeda
Department of Chemistry, University of Tsukuba, Tsukuba 305, Japan

Tomoki Erata and Akira Tasaki
Department of Applied Physics, University of Tsukuba, Tsukuba 305, Japan

Yoshihiro Furukawa
Faculty of School Education, Hiroshima University, Shinonome, Minami-ku, Hiroshima 734, Japan

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The spin-lattice relaxation time of ^{39}K NMR observed in the low-temperature phase ($T < 264.1$ K) of KNO_2 is explained by the quadrupole mechanism contributed from a newly found NO_2^- motion. The in-plane C_3 reorientation and the overvall NO_2^- rotation as well as the self-diffusion were shown in the intermediate phase ($T \leq 314.7$ K) and the high-temperature plastic phase ($T <$ melting point: 710 K), respectively, by observing ^{39}K and ^{15}N NMR relaxation times and ^{15}N lineshapes.

Key words: Solid NMR, Quadrupole relaxation, Plastic crystal, Phase transition, Chemical shift anisotropy

1. Introduction

Solid nitrites MNO_2 (M: K, Rb, Cs, Tl) have been reported to form a plastic phase in a wide-temperature range of ca. 400 K above room temperature [1]. In this phase of NaCl- or CsCl-type cubic structure [2–5], highly disordered NO_2^- orientations and rapid ionic motion of large amplitude are expected. The heat capacity curve at the transition to the plastic phase in each salt [6–8] (at the low-temperature transition for KNO_2 [9]) is accompanied by a long tail on the low-temperature side extending over 100 K, suggesting some disordered structure in the low-temperature phase. The presence of NO_2^- reorientation in this phase has been shown by dielectric, Raman, and NMR studies for the cesium and thallium salts [8, 10, 11]. On the other hand, no sign of disorder in the corresponding phase has been reported for $RbNO_2$ [6], and little is known about KNO_2. In KNO_2, three solid phases I, II, and III from the high-temperature side have been reported [9]. The plastic phase I forms an NaCl-type cubic lattice (Fm3m) [2] between 314.7 $K(T_{trI})$ and the melting temperature (T_m) of 710 K. Phase II, having a rhombohedral structure ($R\bar{3}m$) [2, 12], is stable above 264.1 $K(T_{trII})$. Detailed structure is unknown for Phase III, which was reported to form a monoclinic lattice below T_{trII} [2, 13]. In the present study, we intend to reveal the ionic dynamics in the plastic phase I and the disordered structure expected in Phase III of KNO_2 by measuring ^{39}K and ^{15}N NMR relaxation times and ^{15}N NMR spectra.

2. Experimental

Commercial KNO_2, purified by recrystallization from water, was used for the ^{39}K NMR measurement. $K^{15}NO_2$ was prepared from $Na^{15}NO_2$ (99.6 wt% ^{15}N, ISOTEC INC.) using a cation exchange resin in which the cations were at first completely replaced by K^+ ions and then aqueous $Na^{15}NO_2$ was adsorbed on the resin; $K^{15}NO_2$ was eluted with water. Crude crystals obtained by evaporating solvent were recrystallized from water.

We measured ^{39}K NMR spin-lattice and spin-spin relaxation times, T_1 and T_2, respectively, at a Larmor frequency of 12.66 MHz using a homemade spec-

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Reprint requests to Prof. R. Ikeda, Department of Chemistry, University of Tsukuba, Tsukuba 305, Japan.

trometer equipped with an Oxford superconducting magnet (6.37 T) in the range 77–660 K. We obtained ^{15}N NMR T_1 at 27.50 MHz using the same apparatus between 330 and 610 K, and at 30.42 and 40.56 MHz by Bruker MSL-300 and 400 spectrometers, respectively, in the range of 143–380 K. The inversion recovery and Hahn's spin echo methods were employed to determine T_1 and T_2, respectively. Since almost a single exponential recovery of ^{39}K magnetization was obtained in the whole temperature range studied, we assumed the presence of a single value of ^{39}K T_1 and T_2. Wideline ^{15}N NMR spectra were recorded at 30.42 MHz using the MSL-300 spectrometer between 147 and 330 K. The electrical conductivity was measured by the two-terminal method using an Ando Denki AG-4311 LCR meter for the powdered sample pressed into a pellet 1 cm in diameter and ca. 1 mm thick.

3. Results and Discussion

Low-Temperature Phase (III)

Temperature dependences of T_1 and T_2 for ^{39}K nuclei with $I = 3/2$ observed in Phase III are shown in Figure 1. The deep T_1 minimum of ca. 700 μs is explainable by the quadrupole relaxation caused by the fluctuation of the electric field gradient (EFG) due to ionic motions. Since nearly a single T_1 value was obtained at each temperature, we assume that the observed T_1 data are described by the BPP-type equation

$$T_1^{-1} = C[\tau/(1 + \omega^2 \tau^2)], \qquad (1)$$

where C, τ and ω are constants depending upon the motional mode, the correlation time of the motion and the angular Larmor frequency. We also assume an Arrhenius-type temperature dependence of τ:

$$\tau = \tau_0 \exp(E_a/RT). \qquad (2)$$

The observed T_1 values are unexplainable by a single T_1 curve. Therefore we introduce two superimposed minima T_{1a} and T_{1b}, expressed as

$$T_1^{-1} = T_{1a}^{-1} + T_{1b}^{-1}, \qquad (3)$$

where both T_{1a} and T_{1b} are given by (1). We fitted (1)–(3) to the observed data, and the best-fitted curves are shown in Figure 1. The obtained activation energies are listed in Table 1.

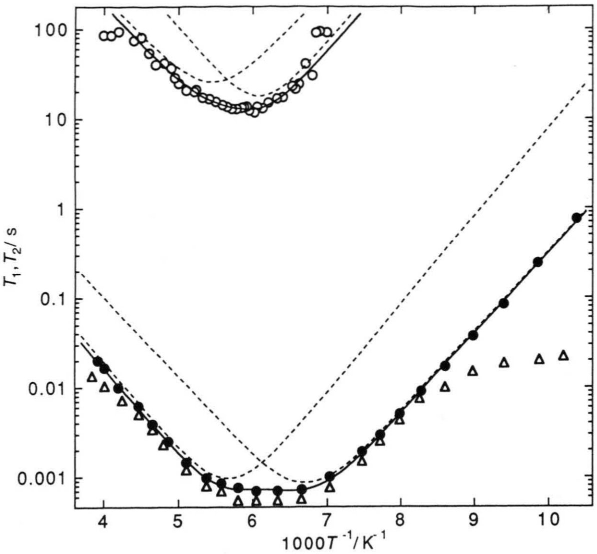

Fig. 1. ^{39}K NMR spin-lattice and spin-spin relaxation times, T_1 (●) and T_2 (△) observed at Larmor frequency of 12.66 MHz, and ^{15}N NMR T_1 (○) at 30.42 MHz observed in Phase III of potassium nitrite. The solid and broken lines are the best-fitted theoretical values using the BPP-type equations.

Table 1. Motional modes and activation energies (E_a) for ions in Phase I, II and III derived from the spin-lattice relaxation time of ^{39}K and ^{15}N NMR observed in potassium nitrite.

Phase	Motional Mode	E_a/kJ mol^{-1}	Nucleus
III	180°-Flip	17.1 ± 1	^{39}K
		18.8 ± 1	^{39}K
		16.5 ± 2	^{15}N
		18.8 ± 2	^{15}N
II	180°-Flip	11.5 ± 2	^{39}K
	C3-Reorientation	26 ± 2	^{15}N
I	C3-Reorientation	(26 ± 2*)	^{39}K
	Isotropic Rotation	10 ± 2	^{15}N
		12 ± 2	^{39}K
	Self-Diffusion	43 ± 3	^{39}K **
		48 ± 3	^{39}K

* The same value as in Phase II was assumed.
** Determined from T_2 data.

To get more information about the motion, we measured T_1 of $^{15}N (I = 1/2)$ in this phase of $K^{15}NO_2$. The observed T_1 shown in Fig. 1 gave an asymmetric minimum around the same temperature as ^{39}K T_1. This T_1 mechanism is attributable to the fluctuation of the ^{15}N chemical shift (CS) tensor caused by the anionic motion which is also responsible for ^{39}K T_1. If the linewidth is narrow by $\Delta\nu$ through the averaging of CS anisotropy, T_1 due to this relaxation process can roughly be expressed as [14]

$$T_1^{-1} \approx (2\pi\Delta\nu)^2 [\tau/(1+\omega_N^2\tau^2)] , \tag{4}$$

where ω_N is the ^{15}N Larmor frequency. The model of superposed two T_1 minima (3) can also be applied to the observed ^{15}N asymmetric T_1 minimum. Using (2)–(4), we calculated the best-fitted T_1 curve as shown in Fig. 1 and determined the activation energies listed in Table 1. These activation energies, in good agreement with those derived from ^{39}K T_1, indicate that the mechanisms for ^{39}K and ^{15}N relaxations are from the same anionic motion.

We measured ^{15}N NMR spectra to determine this motional mode. The observed temperature dependence of ^{15}N spectra is shown in Figure 2. One sees that the spectra below and above the T_1 minimum temperature have the same lineshape with three different principal CS components, but with a width narrowed by ca. 0.7 kHz. This value is close to $\Delta\nu = 0.9$ kHz which was roughly evaluated by substituting the observed T_1 minimum of 11 s into (4), implying the adequacy of the present assignment of relaxation. Nonequivalent three components of the CS tensor indicate that the NO_2^- ions are still almost rigid at low temperatures in this phase. Since the asymmetric CS tensor was retained even above the T_1 minimum, possible motional models are a 180° flip of the NO_2^- ion about an axis perpendicular to the C_2-axis, or a small angle reorientation of the whole anion about one of the three principal axes. These motions can create fluctuations of the EFG at ^{39}K nuclei, whereas there is a little change of ^{15}N CS anisotropy.

It has been reported [9] that an anomalous increase of the heat capacity begins already around 80 K, and this anomaly is extended over 170 K up to T_{trII}. This temperature range of anomaly agrees well with that of the ^{39}K T_1 minimum observed in this phase. The gradually liberated large entropy in this phase suggests a thermally activated orientational disorder taking place in a wide-temperature range. A similar result has been obtained from the analysis of the Raman spectrum lineshape [15] which suggests the presence of some disorder of NO_2^- in this phase. Referring to these results, the model NO_2^- 180° flip seems to be acceptable. Our explanation of assuming at least two T_1 minima with almost the same activation energy suggests is the presence of crystallographically nonequivalent NO_2^- ions in the crystal.

Intermediate Phase (II)

In this phase, forming a rhombohedral lattice ($R\bar{3}m$), the NO_2^- ion is on the C_3-axis which is perpen-

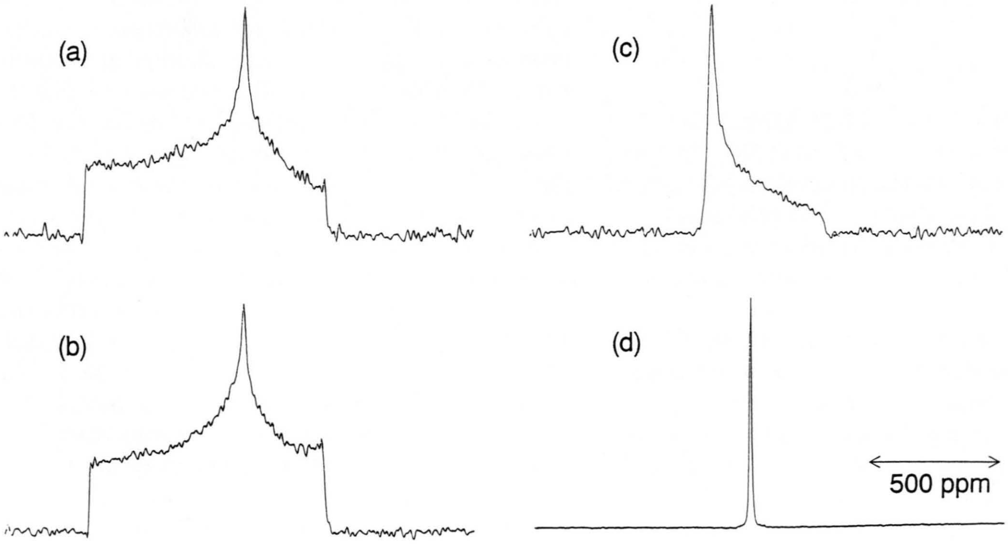

Fig. 2. The temperature dependence of ^{15}N NMR spectra in $K^{15}NO_2$ observed at a Larmor frequency of 30.42 MHz. (a): 147 K, (b): 198 K, (c): 273 K and (d): 330 K.

dicular to the molecular plane [2]. From these crystal data, in-plane disorder as for the anionic orientation is expected. In fact, the ^{15}N spectrum observed at 273 K as shown in Fig. 2 exhibits an axially symmetric CS tensor implying that the anionic C_3-reorientation is excited at the phase transition III to II.

^{39}K NMR T_1 and T_2, and ^{15}N T_1 observed in Phases I and II are shown in Figure 3. The frequency-independent steep ^{15}N T_1 decrease with increasing temperature is attributable to the averaging CS anisotropy by the anionic C_3-reorientation in the limit of $\omega\tau \gg 1$ in (4). The activation energy for the C_3-reorientation was evaluated from the slope of $\log T_1$ vs. T^{-1} plots and listed in Table 1. In contrast to ^{15}N T_1, we observed a gradual increase of ^{39}K T_1 with temperature, which can be reasonably attributed to a motion contributing in Phase III, probably the anionic 180°-flip which is still effective in this phase although its jumping rate is discontinuously increased at T_{trII}. The anionic C_3-reorientation seems to be too slow to contribute to ^{39}K T_1 in this phase. For the observed ^{39}K T_1 data, the BPP-type relaxation equation given by (1) can also be applied in the limit of $\omega\tau \ll 1$ and, from the slope of $\log T_1$, we determined an activation energy of 11.5 ± 2 kJ mol^{-1} for the 180° flip as given in Table 1. If the combined motions of C_3-reorientation and 180°-flip take place in this phase, a C_6-orientationally disordered structure is formed. In fact, it has been reported [16] that C_6-disordered anionic arrangements can be derived from structural and thermal analyses carried out in this phase.

High-Temperature Plastic Phase (I)

In Phase I (cubic, Fm3m, $a = 6.66$ Å), the presence of isotropically disordered orientations of NO_2^- ions was predicted from structural and thermal studies [2, 9]. In accordance with these results, a narrowed single ^{15}N spectrum with a width of ca. 0.4 kHz was observed at 330 K, indicating the onset of isotropic anionic rotation in this phase.

The temperature dependences of ^{39}K and ^{15}N T_1 and ^{39}K T_2 observed in Phase I are shown in Figure 3. These relaxation times changed gradually with temperature with no marked discontinuity at T_{trI}. The almost linear decrease of ^{15}N $\log T_1$ with no frequency dependency can be explained by averaging of the CS anisotropy caused by the overall NO_2^- reorientation and be expressed by (4) under the condition $\omega\tau > 1$. From the slope of $\log T_1$ in the low temperature region in Phase I we derived an activation energy of 10 ± 2 kJ ml^{-1} for the NO_2^- isotropic reorientation. ^{39}K T_1 data having a maximum around 500 K were separated and assigned to two different mechanisms in the low and high temperature regions. Here, we assume that the anionic isotropic rotation mainly contributes to ^{39}K T_1 through the quadrupolar mechanism as given by (1), and that another mechanism, which is also written by a BPP-type equation like (1), but in the limit of $\omega\tau \gg 1$, as discussed below, becomes important at high temperatures. To get a good fit to the observed data, we introduce one more mechanism in the low-temperature region, where C_3-reorientation taking place rapidly ($\omega\tau \ll 1$) is expected to contribute to T_1. Superposing T_1 values from these three mechanisms, the best fitted T_1 to the experimental data was calculated and shown in Figure 3. The evaluated activation energies are listed in Table 1. The calculated broad T_1 minimum was assigned to the isotropic anionic reorientation, in consistence with the ^{15}N T_1 analysis. The steep T_1 decrease observed at high temperatures is attributable to the ionic self-diffusion, which is always present in the high-temperature range of the plastic phase [17]. This explanation can be confirmed by the following analysis of ^{39}K T_2.

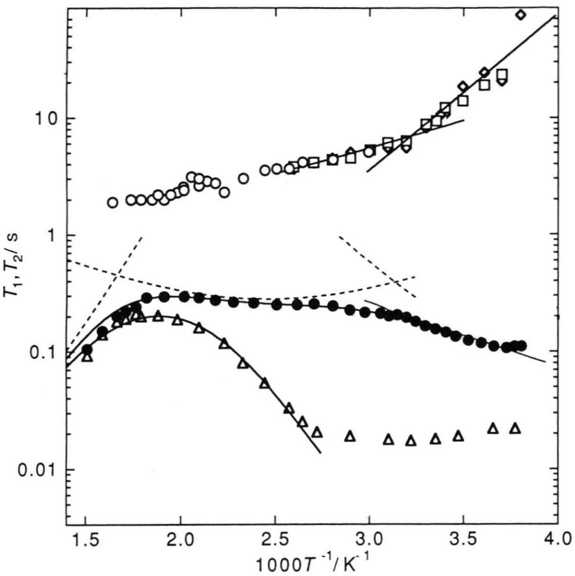

Fig. 3. ^{39}K NMR spin-lattice and spin-spin relaxation times, T_1 (●) and T_2 (△) observed at 12.66 MHz, and ^{15}N T_1 at 27.50 (○), 30.42 (◇) and 40.56 MHz (□) of potassium nitrite in Phases I and II. The solid and broken lines are the best-fitted theoretical values.

In Phase II and in the low-temperature region of Phase I, almost constant T_2 of ca. 20 ms was observed. We roughly estimated the magnetic dipolar linewidth ΔH for ^{39}K nuclei in the powdered sample using the relation [14]

$$(\Delta H)^2 = (3/5)\,\gamma_K^2\,\hbar^2\, I_K\,(I_K+1) \sum r_{ij}^{-6} + (4/15)\,\gamma_N^2\,\hbar^2\, I_N(I_N+1) \sum r_{ij}^{-6}\,, \tag{5}$$

where γ_K, γ_N, I_K and I_N are the magnetogyric ratios and nuclear spin quantum numbers of each nucleus, respectively. The first term includes the contributions from $^{39}K-^{39}K$ dipolar interactions and the second terms from $^{39}K-^{15}N$ interactions, where r_{ij} is the internuclear distance. The T_2 value evaluated from $(\Delta H)^2$, which was calculated in Phase I by employing the cubic structure with $a = 6.66$ Å, became 14 ms, being close to the observed value of 20 ms. This indicates that the ^{39}K linewidth is mostly of magnetic dipolar origin. Upon heating, T_2 was increased by 10 times and became ca. 200 ms, and then decreased by the effect of T_1 decrease. This T_2 increase is attributed to the averaging of the intermolecular magnetic dipolar interaction, which indicates the onset of ionic self-diffusion. We divided the T_2 data observed around its maximum into three components given by

$$T_2^{-1} = T_{2h}^{-1} + T_{2l}^{-1} + T_1^{-1}\,, \tag{6}$$

where T_{2h} and T_{2l} denote the contributions from the ionic self-diffusion in the high and low temperature ranges, respectively. We assumed an Arrhenius-type temperature dependence with the same activation energy for both T_2. The contribution to T_2 from the spin-lattice relaxation expressed as T_1 in (6) was assumed for simplicity to have a temperature independent value of ca. 300 ms. The best fitted T_2 curve is shown in Fig. 3, and a diffusional activation energy of 43 ± 3 kJ mol^{-1} was determined. This value agrees well with 48 kJ mol^{-1} evaluated from T_1 data.

We confirmed the ionic self-diffusion by measuring the electrical conductivity σ. The observed temperature dependence of σ multiplied by T is shown in Figure 4. The rapid increase of σ from ca. 10^{-6} to 10^{-1} Sm^{-1} upon heating this phase clearly shows the presence of ionic conduction, in conformity with the T_1 and T_2 analysis. The slope of $\log\sigma$ could not give a single activation process and the activation energy (50 kJ mol^{-1}) evaluated in the low-temperature range is close to those obtained from relaxation data, whereas large values amounting to ca. 100 kJ mol^{-1} were obtained from σ data in the high-temperature region. These results are explainable if we assume different activation energies for the anionic and cationic self-diffusions.

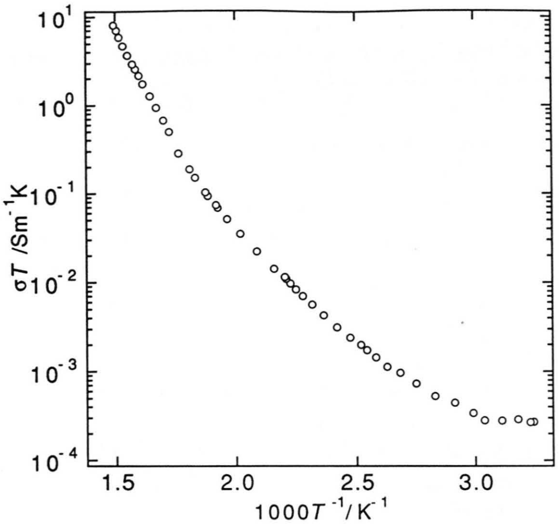

Fig. 4. Temperature dependence of the electrical conductivity σ observed in Phase I of potassium nitrite.

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