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Cationic Self-Diffusion in Ionic Plastic Phases of Thallium Nitrite and Nitrate and in Thallium Thiocyanate

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Cationic self-diffusion in the ionic plastic phases of $TlNO_2$ and $TlNO_3$ was investigated by measuring temperature dependences of the $^{203,205}Tl$ NMR spin-lattice relaxation time and the electrical conductivity. The NMR results showed that the Tl^+ ions in these phases undergo rapid translational diffusion with the activation energy (E_a) of 48 and 77 kJ mol^{-1} for nitrite and nitrate, respectively. The E_a values agreed well with those obtained from the electrical conductivity, indicating that the cation is the electric carrier. The diffusion constants (D) estimated from the relaxation time and conductivity data were ca. 10^{-12} m^2 s^{-1} at the respective melting point (T_m) of plastic phase. The tendency that D at T_m has the characteristic value given above is recognized for other ionic plastic phases so far reported. The Tl^+ ionic conductivity in TlSCN, which makes no plastic phase, was reported in comparison.

Plastic crystals consist of molecules whose centers of gravity form a regular crystalline lattice, whereas each molecule is in a highly movable state as in liquid. Molecular motions characteristic in the plastic crystals are the isotropic overall rotation and the translational self-diffusion which are attributable to the origin of marked plasticity observed in this phase. Systematic NMR studies on this phase of molecular crystals have revealed that the average time for the self-diffusional jump to the neighboring vacant sites observed at the melting point is independent of molecules as well as temperatures, and becomes almost the same value (ca. 10^{-7} s).[1] Similar results have been obtained in plastic phases of ionic crystals containing methylammonium cations.[2–4]

The highest-temperature solid phases of thallium nitrite and nitrate have been reported to form plastic crystals.[5–8] It has been shown from the Tl NMR studies that the Tl^+ ions are diffusing in these phases.[9,10] In the present study, we intend to measure the electrical conductivity of $TlNO_2$ and $TlNO_3$ and the ^{205}Tl NMR spin-lattice relaxation time of $TlNO_3$ to get detailed information on the diffusional motions in the ionic plastic crystals.

Experimental

Commercially available $TlNO_3$ (Nacalai Tesque, GR) and $TlNO_2$ prepared by double decomposition of $Ba(NO_2)_2 \cdot H_2O$ and Tl_2SO_4 are recrystallized from aqueous solution. The ^{205}Tl spin-lattice relaxation time, T_1, was determined by the usual inversion recovery method using a homemade NMR spectrometer.[11] The electrical conductivity, σ, was measured by means of the complex impedance analysis using an Ando Denki AG-4311 LCR meter, which was interfaced to an NEC PC-9801 microcomputer by GP-IB. The impedance was determined over the frequency range between 0.1 and 100 kHz on pelletized samples with the electrodes of colloidal carbon. The sample temperatures were measured by a copper–constantan thermocouple within errors of ±1 K.

Results and Discussion

We have previously reported the temperature dependence of the spin-lattice relaxation times, T_1 and $T_{1\rho}$, in the laboratory and rotating frame, respectively, and the spin–spin relaxation time, T_2, of $^{203,205}Tl$ in $TlNO_2$.[10] These relaxation times were interpreted in terms of the reorientation of the NO_2^- ions in the low-temperature phase obtainable below the phase transitioin temperature (T_c) of 282 K and the translational self-diffusion of the Tl^+ ions in the high-temperature plastic phase above T_c. In the analysis of the relaxation times attributable to the Tl^+ ionic self-diffusion, the usual BPP-type spectral density functions were assumed.[12] A small discrepancy recognized in the motional parameters determined from T_1 and $T_{1\rho}$ analysis may be ascribed to this assumption because it has been expected that the BPP-type spectral density is a rough approximation for diffusing spins.[13]

The temperature dependence of the relaxation times in $TlNO_2$ above 263 K are represented in Fig. 1.[10] The magnetization recovery curve in the T_1 measurements of Tl nuclei usually becomes nonexponential because of the magnetic interactions between two kinds of Tl isotopes, ^{203}Tl and ^{205}Tl, which have only 1% difference in the gyromagnetic ratios.[9,10] From the observed recovery curves, we evaluated the long and short components of T_1 (T_1^l and T_1^s, respectively). The T_1^l values in the high-temperature phase of $TlNO_2$, which are known to be usually determined by lattice vibrations,[10] are ommited in Fig. 1. The T_2 increase observed on heating and the minima in both T_1^s and $T_{1\rho}$ are assignable to the translational self-diffusion of the Tl^+ ions.

The relaxation times of Tl nuclei are mainly governed by scalar (pseudo-exchange) interactions and approximated by[9,10,12]

$$(T_1^s)^{-1} = 2(\langle \delta\,\omega^2 \rangle_i + \langle \delta\,\omega^2 \rangle_j)\, j(\omega_{0i} - \omega_{0j}, \tau), \tag{1}$$

$$(T_{1\rho})_i^{-1} = \langle \delta\,\omega^2 \rangle_i \{j(\omega_{1i}, \tau) + j(\omega_{0i} - \omega_{0j}, \tau)\}, \tag{2}$$

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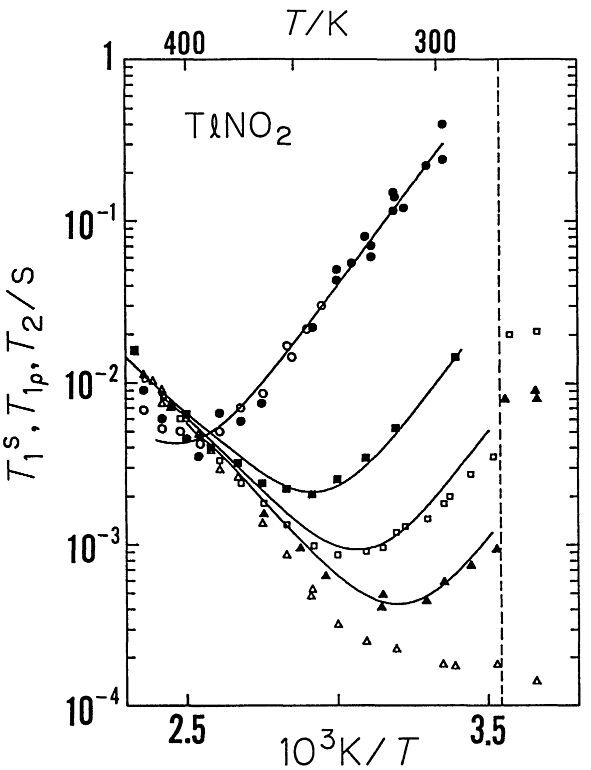

Fig. 1. Temperature dependences of T_1^s (short component), $T_{1\rho}$, and T_2 of ^{203}Tl and ^{205}Tl in TlNO$_2$ observed above 263 K.[10] T_1^s of ^{203}Tl and ^{205}Tl at 34.270 (●) and 34.613 MHz (○), respectively; ^{205}Tl $T_{1\rho}$ at $\omega_1=157$ (■), 68 (□), and 31 krad s^{-1} (▲); ^{205}Tl T_2 (△). ^{203}Tl $T_{1\rho}$ and T_2 were omitted for simplicity. The solid lines were calculated using Eqs. 1 and 2 and the spectral density numerically given for the self-diffusion in the sc lattice.[13] The vertical broken line indicates the phase transition point.

$$(T_2)_i^{-1}=\langle\delta\,\omega^2\rangle_i\,\{j(0,\tau)+j(\omega_{0i}-\omega_{0j},\tau)\}. \qquad (3)$$

Here, ω_{0i} and ω_{1i} are the Larmor frequencies of thallium-i spins (i=203 or 205) in the laboratory and rotating frame, respectively. $\langle\delta\omega^2\rangle_i$ is the NMR second moment of thallium-i spins determined by the scalar interactions with unlike thallium-j spins. Since the scalar interaction between like spins does not affect the second moment, one can obtain $0.295\langle\delta\omega^2\rangle_{203}=0.705\langle\delta\omega^2\rangle_{205}$ by referring to the natural abundances of ^{203}Tl and ^{205}Tl nuclei. This relation could be confirmed from the ratios of $T_{1\rho}$ or T_2 observed for ^{203}Tl and ^{205}Tl, indicating that the relaxations of the thallium nuclei are dominated by the scalar interactions.[10] τ is the correlation time of the Tl$^+$ self-diffusioin. $j(\omega,\tau)$ is the spectral density function, and under the assumption that the correlation function is exponential or of the BPP-type, it is expressed as[12]

$$j(\omega,\tau)=\tau/(1+\omega^2\tau^2). \qquad (4)$$

Barton and Sholl have reported numerical results of nuclear spin relaxation times due to dipole–dipole interacions between diffusive species in fcc, bcc, and sc lattices.[13] In order to reanalyze the relaxational data given in Fig. 1, we use their numerical values of $g_{\text{poly}}(y)$, where $y=\omega\,\tau/2$, for the sc lattice given in Ref. 13 instead of Eq. 4 by assuming that the spectral density for the scalar interactions is the same shape as that for the dipolar ones; the fitting calculation was carried out using the T_1^s and $T_{1\rho}$ data. The determined diffusional parameters are given in Table 1. These parameters are not significantly different from those given in Ref. 10, but the present analysis can account for the temperature dependence of both T_1^s and $T_{1\rho}$ using the same parameters.

Villa and Avogadro have studied the temperature dependences of T_1^l, $T_{1\rho}$, and T_2 of Tl nuclei in TlNO$_3$.[9] They, however, reported no T_1^s because, in most cases, it gives the same information as $T_{1\rho}$. Their derivation

Table 1. Tl$^+$ Diffusional Parameters Determined from Tl NMR Relaxation Times in the Ionic Plastic Phases of TlNO$_2$ and TlNO$_3$

Compound	$C^{a)}/10^7$ s^{-2}	$\log(\tau_0/\text{s})$	E_a/kJ mol^{-1}
TlNO$_2$	6.6±0.2	−12.3±0.1	48±1
TlNO$_3$	10.2±0.5	−15.6±0.4	77±5

a) $C=(\langle\delta\omega^2\rangle_i+\langle\delta\omega^2\rangle_j)/7.5$, where the factor 7.5 was introduced by comparing the maximum values of $\omega\, j(\omega,\tau)$ in Eqs. 1 and 2 with that of $y\, g_{\text{poly}}(y)$ in Ref. 13.

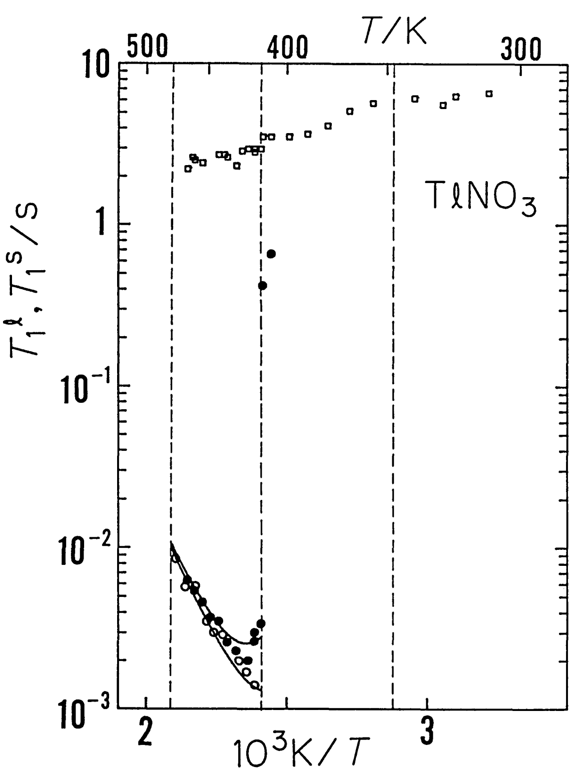

Fig. 2. Temperature dependences of ^{205}Tl T_1^l (□) and T_1^s (●) at 32 MHz, and T_1^s (○) at 16 MHz in TlNO$_3$. The solid lines for T_1^s were calculated in the same procedure as that for TlNO$_2$. Broken lines indicate the melting and two phase-transition points.

of ionic-diffusion correlation time from the $T_{1\rho}$ and T_2 is likely to be less reliable, because no $T_{1\rho}$ minimum was detected. It can be expected from their data that a T_1^{s} minimum in the highest-temperature phase of $TlNO_3$ will be detected, if one chooses a suitable resonance frequency. This can be derived from the fact that the NMR time scale of T_1^{s} $\{(\omega_{0i}-\omega_{0j})^{-1}\}$ is just between those of T_1^{l} $(\omega_0{}^{-1})$ and $T_{1\rho}$ $(\omega_1{}^{-1})$. Along this purpose, we measured the temperature dependence of T_1^{s} at 16 and 32 MHz. A T_1^{s} minimum could be observed at 32 MHz in the high-temperature plastic phase as shown in Fig. 2. The analytical procedure of the T_1^{s} is the same as above, and the obtained motional parameters are given in Table 1.

The diffusion constant (D_{NMR}) of the Tl^+ ions is related to the diffusion correlation times by

$$D_{\mathrm{NMR}}=\langle l^2\rangle/6\tau, \tag{5}$$

where, $\langle l^2\rangle$ stands for the mean-square jump distance of the ions. When l is assumed to be equal to the lattice parameter of the unit cell, D_{NMR} can be derived, and the values at the melting point (T_{m}) of $TlNO_2$ and $TlNO_3$ are given in Table 2.

Figure 3 shows the temperature dependence of the electrical conductivity of $TlNO_2$, $TlNO_3$, and TlSCN, where the last compound forms no plastic phase.[14] The diffusion constant (D_σ) of the ions can be related to the electrical conductivity by the Nernst–Einstein equation:

$$D_\sigma=\sigma\, kT/(Ze)^2c. \tag{6}$$

Here, Ze and c are the charge and concentration of the diffusing ions, respectively. Since the Arrhenius relation is assumed for D_σ, the conductivity activation energy (E_σ) can be determined from the slope of the $\log\sigma T$ vs. $1/T$ plot.

$TlNO_2$ gave σ of 2.4×10^{-4} S m^{-1} at 296 K. With increasing temperature, the σT vs. $1/T$ plot of $TlNO_2$ increased exponentially, yielding E_σ of 46.6 kJ mol^{-1}. This is in good agreement with that determined from the relaxation measurements, indicating that the Tl^+ ions are the electric carriers in $TlNO_2$. The σ value of $TlNO_3$ shows a break in the $\log\sigma T$ vs. $1/T$ curve at both phase transition points. The decrease in σ in the intermediate-temperature phase was observed by several authors,[6,9,15] and assigned to some effect of the sample humidity.[6] The highest-temperature plastic phase has E_σ of 79 kJ mol^{-1}, which agrees with 77 kJ mol^{-1} from

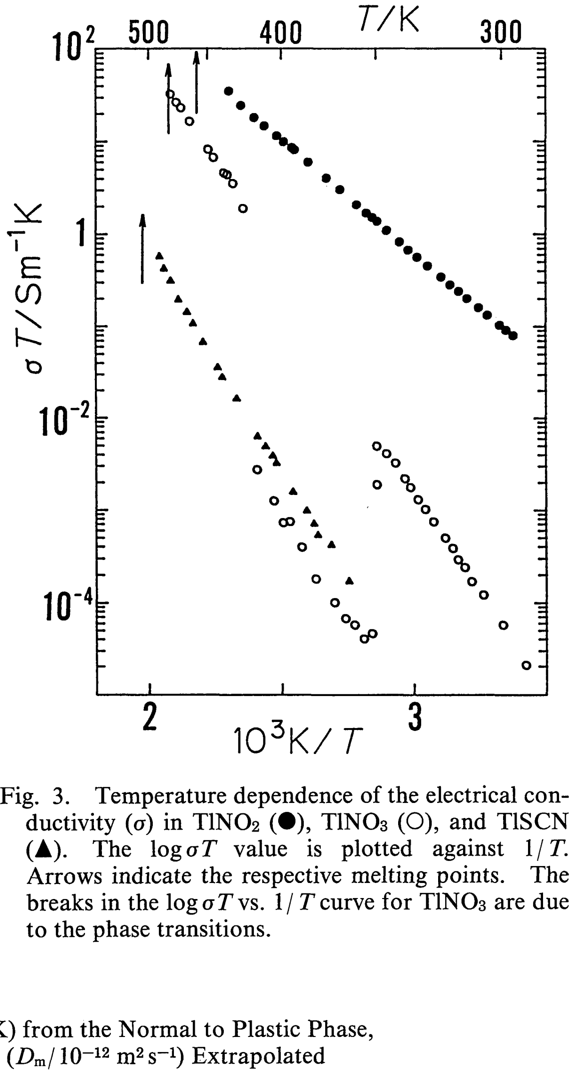

Fig. 3. Temperature dependence of the electrical conductivity (σ) in $TlNO_2$ (●), $TlNO_3$ (○), and TlSCN (▲). The $\log\sigma T$ value is plotted against $1/T$. Arrows indicate the respective melting points. The breaks in the $\log\sigma T$ vs. $1/T$ curve for $TlNO_3$ are due to the phase transitions.

Table 2. Phase Transition Temperature ($T_{\mathrm{c}}/$K) from the Normal to Plastic Phase, Melting Point ($T_{\mathrm{m}}/$K), Diffusion Constant ($D_{\mathrm{m}}/10^{-12}$ m^2 s^{-1}) Extrapolated to Their Melting Points of Several Ionic Plastic Crystals

Compound	$T_{\mathrm{c}}(T_{\mathrm{m}})$	NMR				Conductivity		
		Nuclei	$D_{\mathrm{m,NMR}}$	E_{a}	Ref[a)]	$D_{\mathrm{m},\sigma}$	E_σ	Ref[a)]
$TlNO_2$	282(459)	$^{203,205}Tl$	0.2	48	*	2.5	47	*
$TlNO_3$	417(480)	^{205}Tl	0.5	77	*	1.4	79	*
			—	77	9	—	77	9
$K[HF_2]$	470(512)	$^1H, ^{19}F$	0.5	80	17	0.3	87	18
$[C(NH_2)_3]ClO_4$	450(525)	^1H	0.4	41	19	1.0	43	19
$[(CH_3)_4N]SCN$	455(565)[b)]	^1H	1.5	110	20	2.9	100	20
$(CH_3NH_3)NO_3$	352(384)	^1H	0.4	29	2	2.5	45	2
$(CH_3NH_3)ClO_4$	451(528)	^1H	1.7	36	3	—	—	—
$(CH_3NH_3)I$	414(515)	^1H[c)]	0.8	48	4	10	51	4
TlSCN[d)]	371(507)	$^{203,205}Tl$	—	90	16	0.05	93	*

a) Asterisks represent the present work. b) Decomposition point. c) Derived from T_2 data. d) TlSCN forms no plastic phase up to T_{m}.

the T_1^s results. The fact that σ in TlSCN is lower than those of $TlNO_2$ and $TlNO_3$ may imply that TlSCN is not plastic. We have shown that the charge carriers in TlSCN are also the Tl^+ ions.[16] Under the assumtion that c is the total Tl^+ ion concentration, D_σ was estimated to be 2.5×10^{-12}, 1.4×10^{-12}, and 4.8×10^{-14} $m^2 s^{-1}$ at T_m of $TlNO_2$, $TlNO_3$, and TlSCN, respectively.

For many molecular plastic crystals, it has been observed that the diffusion constants at respective T_m are in the range 0.5—2.5×10^{-13} $m^2 s^{-1}$ and the correlation times of the diffusion approach 10^{-7}—10^{-6} s.[1]

In order to see whether the diffusion constant in ionic plastic phases approaches a characteristic value at T_m, as in molecular plastic crystals, we collected experimental data on the ionic diffusions studied by electrical conductivities and NMR relaxation times. The collected data of D_{NMR} and D_σ at T_m are summarized in Table 2. Both D values of each compound are in good agreement in spite of the different methods employed to deduce them. With no exception, D_{NMR} as well as D_σ tends to converge into ca. 10^{-12} $m^2 s^{-1}$. This value is thought to be characteristic for ionic plastic phases. It is surprising that these characteristic correlation times are almost the same in both ionic and molecular plastic crystals because the weak van der Walls interaction is the main cohesive force in the molecular crystals whereas the much stronger Coulombic force is opperative in ionic crystals.

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