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An Ionic Plastic Phase of 1,1-Dimethylhydrazinium Tetrafluoroborate Revealed by ^{1}H and ^{19}F NMR and Thermal Measurements

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Three solid phases of $(CH_3)_2NNH_3BF_4$ were found between 200 K and the melting point (415 K) by differential thermal analysis, differential scanning calorimetry, and ^{1}H and ^{19}F NMR measurements. The highest-temperature solid phase obtainable above 268 K was shown to be an ionic plastic phase, where the cations as well as the anions perform rapid translational self-diffusion and overall rotation about their center of gravity.

Various ionic crystals involving methyl-substituted ammonium and guanidinium cations are known to have an unusual crystalline phase named "ionic plastic phase", where the cations perform rapid isotropic reorientation and self-diffusion.[1-12] Such phases are expected to exist widely in the crystals containing not only the above cations but also other molecular cations of high-symmetry.

Stammler and Orcutt have reported that $(CH_3)_2NNH_3BF_4$ has a CsCl-type cubic structure and undergoes plastic-like deformation at room temperature.[13] We can interpret their results as an evidence that this salt forms an ionic plastic phase, in which both cation and anion may rotate freely and isotropically, and, at the same time, easily diffuse in the crystal lattice, resulting in the cubic structure and plastic deformation. The present investigation of ^{1}H and ^{19}F NMR, differential thermal analysis (DTA), and differential scanning calorimetry (DSC) on $(CH_3)_2NNH_3BF_4$ has been undertaken in order to reveal the presence of the ionic plastic phase of this salt.

$(CH_3)_2NNH_3BF_4$ was prepared by neutralizing dimethylhydrazine with tetrafluoroboric acid. The obtained crystals were recrystallized twice from isopropyl alcohol. Found: C, 15.69; H, 5.99; N, 19.01%. Calcd for $(CH_3)_2NNH_3BF_4$: C, 16.24; H, 6.13; N, 18.94%.

DTA and DSC were carried out using a home-made apparatus[14] and a Parkin-Elmer DSC7 calorimeter, respectively. The second moment (M_2) of ^{1}H and ^{19}F NMR absorptions was determined by use of a JEOL JNM-MW-40S spectrometer. The ^{1}H NMR spin-lattice relaxation time (T_1), spin-spin relaxation time (T_2), and linewidth parameter (T_2^*) were measured at 32 MHz using a pulsed spectrometer.[15] The 180° - t - 90° pulse sequence and the Hahn's spin-echo method[16] were employed for the determination of T_1 and T_2, respectively. T_2^* was determined from the shape of free induction decay after a 90° pulse by assuming the exponential behavior. Before the measurements, the samples were dried under vacuum (*ca.* 10^{-3} Torr) at room temperature for 5 h and then at 60 °C for 5 h.

Two solid-solid phase transitions at 265 and 268 K, and the melting at 415 K were located by DTA in the temperature range from 180 to 420 K. The revealed solid phases are designated in the order of decreasing temperature as Phases I, II, and III. The entropy changes (ΔS) determined by DSC were 9.5, 21, and 11 J K^{-1} mol^{-1} for the phase transitions taking place at the above temperatures (T_{tr}(III→II) and T_{tr}(II→I)) and fusion, respectively. The characteristic feature of the large ΔS_{tr}(II→I) and small ΔS_f implies that Phase I forms a plastic crystal,[17] where both cations and anions are expected to acquire the greatest part of their motional freedom.

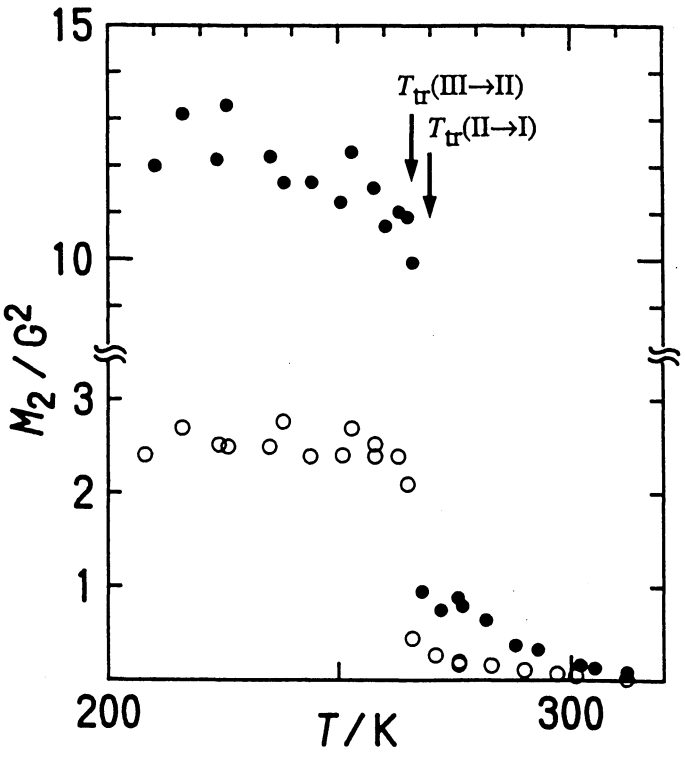

Fig. 1. Temperature dependences of the second moment (M_2) of ^{1}H (●) and ^{19}F (○) NMR absorptions.

The temperature variations of ^{1}H and ^{19}F M_2 determined above 200 K are shown in Fig. 1. The sudden decrease in ^{1}H and ^{19}F M_2 observed at T_{tr}(II→I) implies that rapid isotropic reorientations of both cations and anions occur in Phase I. This is because the observed ^{1}H and ^{19}F M_2 of < 0.95 and < 0.45 G^2, respectively, (1 G = 1×10^{-4} T), are smaller than the 1.35 G^2 calculated for these motional modes of both ions using the reported crystal data.[13] The further decrease in both M_2 to < 0.1 G^2 with increasing temperature in this phase indicates the onset of self-diffusion of both ions. The more rapid decrease in ^{19}F M_2 than that in ^{1}H M_2 on heating, implies that the anions diffuse faster than the cations, which is acceptable in view of the size difference of the two ions.

^{1}H and ^{19}F M_2 values observed below *ca.* 240 K are assignable to the CH_3 and NH_3^+ reorientations, and the isotropic reorientation of the anion, respectively, by comparing the observed data with the reported M_2 for trimethylammonium salts[8,18] and ammonium tetrafluoroborate.[19]

Temperature dependence of ^{1}H T_1, T_2, and T_2^* above 200 K is shown in Fig. 2. A discontinuous change in T_1 and a small thermal hysteresis were observed at each phase transition point. In Phase I, the T_1 change observed in the range of 270 < T/K < 290 is attributable to the isotropic reorientation of the cations by referring to the M_2 results; the T_2^* values less than 0.1 ms observed in this temperature range are consistent with this motional mode. The T_2 increase from 0.2 to 18 ms with increasing temperature from 290 K indicates that the cationic self-diffusion becomes rapidly with temperature, in accordance with the M_2 results. Above 290 K in Phase I, the observed T_1 showed the non-exponential recovery of ^{1}H magnetization attributable to the cross relaxation due to the magnetic dipole interaction between ^{1}H and ^{19}F nuclei.[20-22] The similar behavior of T_1 was also observed in Phase II. The recovery curve was separated into two relaxation times, T_{1s} and T_{1l} (T_{1s} < T_{1l}), according to the following equation:

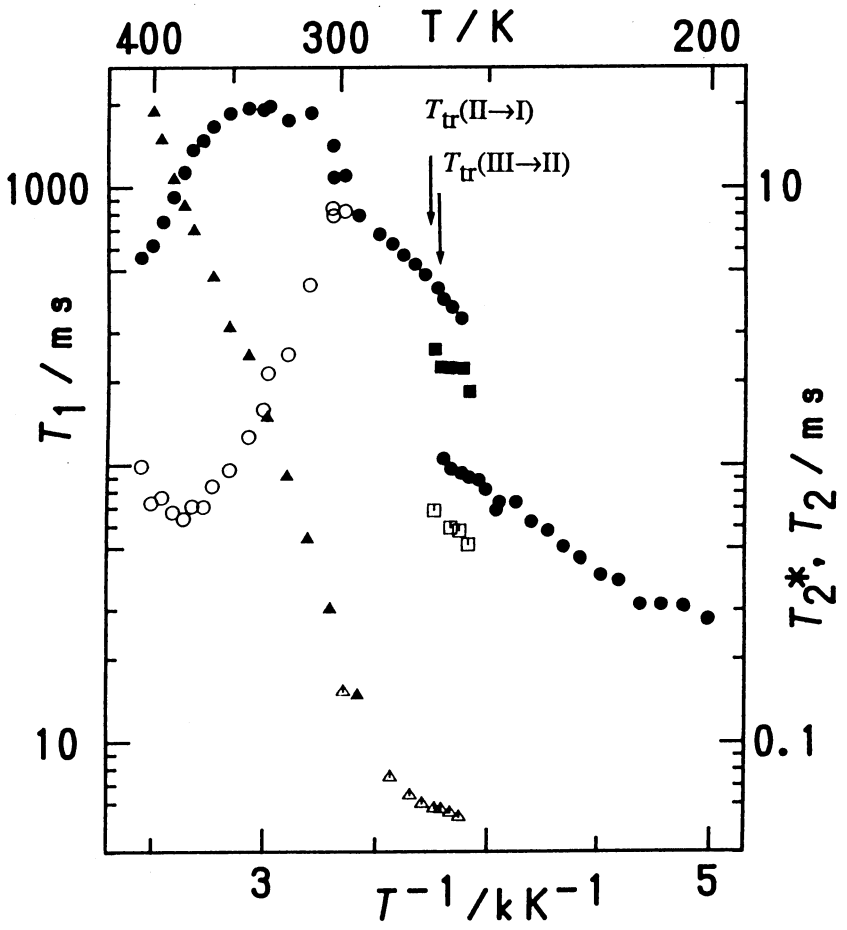

Fig. 2. Temperature dependence of ^{1}H T_1 (● : T_1 and T_{1l} in Phases I and III; ○ : T_{1s} in Phase I; ■ : T_{1l} in Phase II; □ : T_{1s} in Phase II), T_2 (▲), and T_2^*(△) observed at 32 MHz.

$$(M_0 - M_z(t)) / M_0 = A_s \exp(-t / T_{1s}) + A_l \exp(-t / T_{1l}).$$

Here, M_0 and $M_z(t)$ are the z-components of the ^{1}H magnetization at thermal equilibrium and at time t after 180° pulse, respectively, and A_s and A_l are the constants ($A_s + A_l = 2$).

^{1}H T_1 (T_{1s} and T_{1l}) above 290 K is determined by the ^{1}H-^{19}F cross relaxation controlled by the short ^{19}F T_1 originating from the anionic diffusion more rapid than that of the cations. We evaluated E_a for the cationic self-diffusion as 42.5 kJ mol^{-1} from the gradient of the ln T_2 *vs.* T^{-1} plots, and E_a for the anionic diffusion to be *ca.* 41 kJ mol^{-1} from the T_{1s} plots.

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