

NMR STUDY OF ION MOTIONS IN $[\text{C}(\text{NH}_2)_3]_3\text{GaF}_6$ A. KOZAK^a, M. GROTTTEL^b AND Z. PAJAŁ^a^aInstitute of Physics, A. Mickiewicz University, Poznań, Poland^bDepartment of Physics, Academy of Agriculture, Poznań, Poland*(Received October 1, 1992)*

Proton and fluorine spin-lattice relaxation times as well as second moments were measured in guanidinium hexafluorogallate over a wide range of temperature. The analysis of all cross-relaxation effects occurring in the four unlike spin system revealed two cation motions and yielded their activation parameters. It was found that the anion size did not influence C_3 reorientation of cation nor isotropic reorientation of anion.

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1. Introduction

In our previous studies of various guanidinium salts a molecular dynamics of cation embedded in different anion sublattices was analyzed [1-5]. It was particularly interesting to examine a role of the cation-anion interactions and hydrogen bondings contributing essentially to potential barrier which hinders the considered cation reorientation. In all the compounds studied we found an evident existence of the reorientation of the whole guanidinium cation around its C_3 symmetry axis. The activation energies found for this reorientation vary from 26 kJ/mol for weak bonds up to 68 kJ/mol for strong hydrogen bonds. In our study of the guanidinium complexes containing fluorinated anions it was possible to describe dynamics of both ionic sublattices and reveal an interesting interaction of cations and anions leading to a coupling of the reorientational frequencies at phase transition [6]. In most compounds the onset of cation motion requires much higher energy as compared with that required for the anion motion. We have recently found the only exceptional behaviour in the guanidinium hexafluoroaluminate [5] wherein activation energy for the anion motion (67 kJ/mol) evidently exceeded that found for the cation (45 kJ/mol). Hence the relative rigidity of the anion sublattice in the wide temperature range enabled us to confirm an existence of another cation motion, suggested earlier in our previous works.

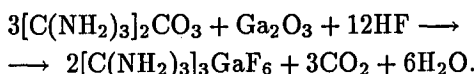
It seemed interesting to examine the hexafluorogallate, the compound which, besides hexafluoroindate, is isostructural with the guanidinium hexafluoroaluminate [7]. No essential difference in crystal and molecular structure has been observed in both compounds [5, 8]. The hexafluorogallate crystallizes in a cubic

system, in the space group $P2_1/a\bar{3}$, $a = 14.073(1)$ Å, $V = 2787.1$ Å³ and $Z = 8$. The molecular packing can be described as a framework of GaF_6 ions, hydrogen bonded to the guanidinium cations.

In the present work a study of ^1H and ^{19}F NMR second moment and spin-lattice relaxation time T_1 was undertaken to obtain information on the dynamics of both sublattices in the compound and compare it with those for the guanidinium hexafluoroaluminate. It seemed interesting to find out whether a size of an anion influences a height of the barrier hindering reorientations of both ions and to confirm an existence of a complex motion of the cation.

2. Experimental

The guanidinium hexafluorogallate $[\text{C}(\text{NH}_2)_3]_3\text{GaF}_6$ was obtained following the reaction:



Respective amounts of guanidinium carbonate and gallium oxide were treated with an excess of hydrofluoric acid HF (40% aqueous solution) and heated to a complete dissolution. After cooling small cubes of $[\text{C}(\text{NH}_2)_3]_3\text{GaF}_6$ crystallized from the solution. Analysis — found: N = 34.65, C = 9.91, H = 4.73%; calculated: N = 34.64, C = 9.90, H = 4.98%. To remove iron paramagnetic impurities, the compound was then recrystallized from 15% HF solution with a small amount of tartaric acid added. The product was then ground to a powder, dried, degassed and sealed off.

Measurements of proton and fluorine second moment were done over a wide range of temperature with our NMR spectrometer operating at the Larmor frequency of 28.0 and 26.3 MHz, for protons and fluorines, respectively. Measurements of the proton and fluorine spin-lattice relaxation times T_1 were performed in a function of temperature using a home-made pulse spectrometer operating at 40 MHz by a $\pi/2-\tau-\pi/2$ pulse sequence.

Temperature of the sample was controlled by means of a gas-flow cryostat and monitored with a Pt resistor to an accuracy of about 1 K. Differential thermal analysis was made with a Derivatograph UNIPAN (type DSC 605M).

3. Results

Experimental proton and fluorine NMR second moments in a function of temperature are presented in Fig. 1. The proton second moment of about 26 G² starts to decrease slowly at about 150 K to a value of 24 G² and then at 270 K sharply to a value of 5.2 G² achieved above 420 K. The fluorine second moment decreases from the value of 16.1 G² registered at low temperatures to a plateau value of about 7.5 G² at temperature range 350 K–440 K. At higher temperature the fluorine second moment further diminishes to a value of 1.4 G² registered at 530 K. The full curves in Fig. 1 are theoretically calculated for assumed model of the cation reorientation.

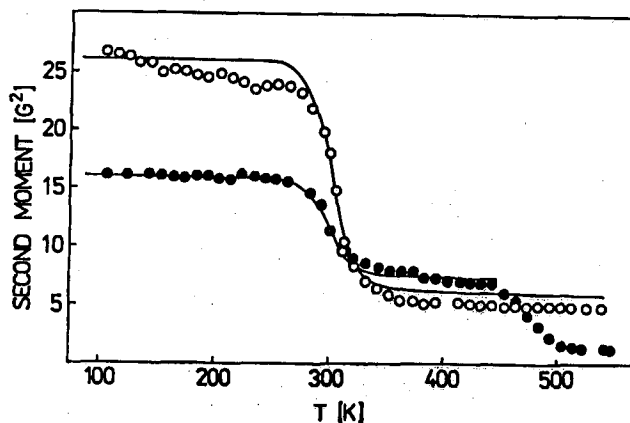


Fig. 1. Temperature dependencies of 1H (\circ) and ^{19}F (\bullet) NMR second moments. Full curves are theoretically calculated for the C_3 reorientation of the guanidinium cation.

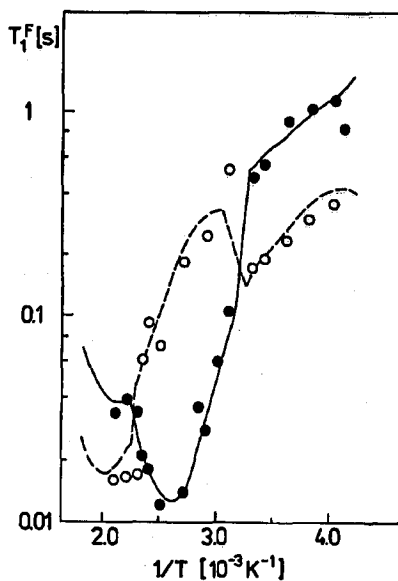


Fig. 2. Temperature dependence of the fluorine spin-lattice relaxation time: \bullet — components for magnetization amplitudes higher than 0.5; solid and dashed lines denote calculated λ_F^{-1} and λ_H^{-1} , respectively.

Figure 2 presents the fluorine spin-lattice relaxation time as $\log T_1^F$ plot against inverse temperature. The curves in the figure are theoretical fits to the experimental data. At all the temperatures studied a non-exponential magnetization decay was observed. The decay curves were decomposed into two exponential

terms with different T_1 values. In Fig. 2 the full circles denote T_1^F components for fluorine magnetization amplitudes higher than 0.5. One can see an evident minimum of 12 ms at about 385 K revealed in the plot of the short components.

Differential thermal analysis performed from room temperature to 600 K revealed that the compound started to decompose at about 560 K.

4. Calculations and discussion

4.1. NMR second moment

Experimental proton and fluorine second moments obtained in a function of temperature remind those found for $[\text{C}(\text{NH}_2)_3]_3\text{AlF}_6$ [5]. The lower value of the fluorine second moment (16.1 G^2) found for $[\text{C}(\text{NH}_2)_3]_3\text{GaF}_6$ (see Fig. 1) comes from the smaller intramolecular F–F (3.48 G^2) and F–Ga (1.20 G^2) contributions evidently resulting from the Ga–F distance (1.901 \AA) longer than Al–F length (1.818 \AA). Hence, the theoretical fluorine second moment of 16.1 G^2 is exactly the same as experimental value (16.1 G^2), thus proving the rigidity of the GaF_6 anion sublattice at low temperatures. Therefore, it follows that interionic fluorine–proton and proton–fluorine contributions to the respective second moments must be the same as for the isostructural $[\text{C}(\text{NH}_2)_3]_3\text{AlF}_6$. Hence the theoretical proton second moment value of 21.6 G^2 found for the aluminate can be accepted as corresponding to the rigid cation sublattice in the gallate, as well. The reduction of the proton and fluorine second moments observed upon increase in temperature can be interpreted similarly as in case of the aluminium analogue. The one-step reduction of the proton second moment can be ascribed to the reorientation of the guanidinium cation around its C_3 symmetry axis perpendicular to the cation plane. Theoretical plot calculated using the Bloembergen–Purcell–Pound formula [9] and activation parameters extracted from our relaxation data compared with the experiment evidently shows that there must exist another motion which precedes the C_3 reorientation and further reduces the second moment value at high temperatures. It is not clear what kind of motion it is and why it does not affect the measured fluorine second moment at low temperatures. It can be a reorientation of NH_2 groups or small angle over the barrier jumps of the whole cation. The respective theoretical plot calculated for fluorines proves that the plateau value observed for the fluorine second moment at temperature range 350–440 K reflects only the onset of the C_3 reorientation of the guanidinium cation and cannot be explained by any reorientation of the anion. The latter starts to reorient as late as at about 440 K. The value of 1.4 G^2 registered at the highest temperatures indicates that it is an isotropic reorientation hindered by a high potential barrier of about 68 kJ/mol , as estimated from the Waugh–Fiedin formula [10]. This value is comparable with that found for the AlF_6 anions. Since the barrier for the anion tumbling is of the interionic origin, the fluorine–proton interactions must be the same in both compounds.

4.2. NMR relaxation

To describe our experimental proton and fluorine relaxation data we had to consider all homo- and heteronuclear interactions occurring in the compound studied. Since it is a system of four unlike spins (H, F, N, and Ga), we could apply the solution of a set of coupled differential equations describing the time variation of nuclear magnetization derived in [4]:

$$\begin{bmatrix} dM_H/dt \\ dM_F/dt \\ dM_N/dt \\ dM_{Ga}/dt \end{bmatrix} = \begin{bmatrix} -R_{HH} & -R_{HF} & -R_{HN} & -R_{HGa} \\ -R_{FH} & -R_{FF} & -R_{FN} & -R_{FGa} \\ -R_{NH} & -R_{NF} & -R_{NN} & -R_{NGa} \\ -R_{GaH} & -R_{GaF} & -R_{GaN} & -R_{GaGa} \end{bmatrix} \begin{bmatrix} M_H - M_{0H} \\ M_F - M_{0F} \\ M_N - M_{0N} \\ M_{Ga} - M_{0Ga} \end{bmatrix}$$

To find the eigenvalues of the relaxation matrix and compare them with the experimental proton and/or fluorine values one must estimate all homo- and heteronuclear contributions to the reduced second moments for the assumed model of ion reorientation and calculate all diagonal (R_{II}) and off-diagonal (R_{IS}) elements according to the formulae:

$$R_{II} = (2/3)\gamma_I^2 \Delta M_2^{II} g_1(\omega_I, \tau) + (1/2) \sum_S \gamma_I^2 \Delta M_2^{IS} g_2(\omega_I, \omega_S, \tau),$$

$$R_{IS} = (1/2)\gamma_S^2 \Delta M_2^{SI} g_3(\omega_I, \omega_S, \tau) N_S/N_I,$$

where

$$g_1(\omega_I, \tau) = \tau/(1 + \omega_I^2 \tau^2) + 4\tau/(1 + 4\omega_I^2 \tau^2),$$

$$g_2(\omega_I, \omega_S, \tau) = \tau/[1 + (\omega_I - \omega_S)^2 \tau^2] + 3\tau/(1 + \omega_I^2 \tau^2)$$

$$+ 6\tau/[1 + (\omega_I + \omega_S)^2 \tau^2],$$

$$g_3(\omega_I, \omega_S, \tau) = -\tau/[1 + (\omega_I - \omega_S)^2 \tau^2] + 6\tau/[1 + (\omega_I + \omega_S)^2 \tau^2].$$

As it results from our second moment study, we have considered the C_3 reorientation of the guanidinium cation preceded by the other motion while the anions are still rigid. Hence we considered the relaxation matrix as a sum of two components

$$R = R_1 + R_2$$

corresponding to both motions. Then, we calculated eigenvalues λ_r of the relaxation matrix and their respective magnetization amplitudes $A(r)$ in a function of temperature. The inverses of the eigenvalues λ_H^{-1} and λ_F^{-1} were then compared with the respective experimental short and long components of the T_1 values.

For the fluorine experiment (see Fig. 2) a good agreement is observed at temperatures where only fluorine-proton interaction contributes to the fluorine magnetization. It turned out that in the whole temperature range the nitrogen and gallium contributions to the fluorine magnetization are negligibly small and can be neglected. Hence our compound can be treated as a two-spin system and a decomposition of fluorine magnetization recovery into two exponential decays is fully justified. Thus, the fluorine experiment appears to be sufficient to reveal the

molecular dynamics of the cation and confirms an existence of two motions. The relaxation at temperatures higher than 320 K is mainly due to the C_3 reorientation of the cation. The minimum observed at about 385 K is related to this reorientation through the heteronuclear proton-fluorine interaction $\tau \approx (\omega_H - \omega_F)^{-1}$. A significant shortening of the fluorine T_1 values at temperatures lower than 320 K and the inversion of the magnetization amplitudes must result from an existence of another cation motion, which precedes its C_3 reorientation. The best fitting of the theoretical eigenvalues λ_H^{-1} and λ_F^{-1} to the experimental T_1^F data yielded the Arrhenius activation parameters for the two motions considered (Table).

TABLE
Activation parameters for the cation motions.

	E_a [kJ/mol]	τ_0 [s]
C_3 reorientation	44.4	5.94×10^{-14}
The other motion	18.8	2.01×10^{-12}

From the fitting procedure it turns out that the motion preceding the C_3 reorientation only very slightly modulates the fluorine-proton interaction ($\Delta M_2(\text{F-H}) = 0.2 \text{ G}^2$). Therefore, it is not surprising that this motion does not affect, in the accuracy limit, the fluorine second moment at low temperatures. The geometry of the motion cannot be precisely defined, since an X-ray analysis does not reveal exact hydrogen atom positions [11].

For protons an agreement between the calculated eigenvalues and experimental components of T_1^H is somewhat worse due to more complicated heteronuclear interactions (nitrogen and gallium contributions cannot be neglected). However, the proton relaxation data also reveal and corroborate the model of cation reorientations derived from the fluorine experiment.

Our analysis shows that molecular dynamics of both sublattices in the compound studied is very similar to that of the guanidinium hexafluoroaluminate. The cation's freedom to reorient is much higher than the anion's one. It results from hydrogen bond pattern: each anion is involved in three times more hydrogen bonds than the cation. The relative rigidity of the anion sublattice in a wide temperature range allowed us to confirm once again the existence of the additional motion of the cation preceding its C_3 reorientation. Though the activation energies for the C_3 reorientation of cation and isotropic reorientation of anion are the same in the gallate and in the aluminate, it is not clear why the hindering barrier for the additional motion of the cation is evidently lower in the gallate. It could suggest its intraionic origin, resulting maybe from the tiny difference in the molecular structure of the cations in both salts. Hence one can suppose that the additional motion can be rather related to the NH_2 groups than to the whole cation. Since the crystal structure of both salts is nearly the same, a significant increase in the GaF_6 anion size compared with AlF_6 , revealed in the X-ray analysis, does not

essentially affect the height of the barriers hindering the C_3 reorientation of the cation nor the isotropic reorientation of the anion.

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