^1H and ^{19}F NMR Relaxation Time Studies in $(\text{NH}_4)_2\text{ZrF}_6$ Superionic Conductor

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Abstract. ^1H and ^{19}F spin–lattice relaxation times in polycrystalline diammonium hexafluorozirconate have been measured in the temperature range of 10–400 K to elucidate the molecular motion of both cation and anion. Interesting features such as translational diffusion at higher temperatures, molecular reorientational motion of both cation and anion groups at intermediate temperatures and quantum rotational tunneling of the ammonium group at lower temperatures have been observed. Nuclear magnetic resonance (NMR) relaxation time results correlate well with the NMR second moment and conductivity studies reported earlier.

1 Introduction

Nuclear magnetic resonance (NMR) is one of the most powerful local probes to investigate diffusion and internal motions in solids and is therefore used to study molecular dynamics and mobility of conducting species in a variety of inorganic solids. Many of the ammonium-based inorganic solids exhibit superionic conduction. The diffusion of ammonium ions in these superionic solids is known to make a major contribution to the ionic conductivity. In the present study, proton and fluorine spin–lattice relaxation time (T_1) measurements are undertaken in ammonium hexafluorozirconate (AHFZ) for the following reasons: the two reorienting groups NH_4 and ZrF_6 are well suited for NMR studies, and it is interesting to explore the proton–fluorine dipolar interactions by cross relaxation. T_1 measurements as a function of temperature would provide complementary evidence for the processes governing the superionic conductivity, which may be due to the translational diffusion of ions. Further, AHFZ is a promising candidate for technological applications, for example, in organometal catalyst compositions; to increase the polymerization activity with silica gel-supported chromium oxide catalysts; as a fluorinating agent for curable resin composition; as an excellent corrosion-resistant material and in making lithographic printing plates [1].

2 Materials and Methods

In the present study, commercially available AHFZ from Aldrich Chemical Co., (39, 729-6) is used directly without further purification. The compound is finely powdered and vacuum-sealed into glass ampoules with a diameter of 5 mm in helium atmosphere and then used for NMR measurements. Zalkin et al. [2] have reported the crystal structure of AHFZ at room temperature. The crystal structure of AHFZ indicates that it consists of Zr_2F_{12} units extended in infinite chains along the *c*-axis with ammonium ions being hydrogen-bonded in a complex three-dimensional network to these chains. Each Zr atom is coordinated to eight F atoms. A triangle of three F atoms at the center of the Zr_2F_{12} group is sandwiched between two Zr atoms [2]. $(\text{NH}_4)_2\text{ZrF}_6$ has also been studied by wide-line NMR, direct current, conductivity, infrared, Raman and other techniques [3–13]. Infrared and Raman active NH_4 -vibrations in AHFZ [4] are found to occur at relatively high wavenumbers, which are characterized by moderate to weak hydrogen bonds [14]. Kavun et al. [11] have estimated the activation energy for the translational diffusion of ions. Lalowicz et al. [3] have carried out a proton NMR line shape calculation and analysis for AHFZ at 4.2 K and attributed their results to the tunneling rotations of the ammonium ion. However, to the best of our knowledge, T_1 measurements have not been reported for AHFZ.

In the present study, ^1H and ^{19}F NMR T_1 measurements are carried out as a function of temperature in the range of 400–11 K at 21.34 MHz on a homemade pulsed NMR spectrometer described earlier [15]. The inversion recovery pulse sequence is used for measuring T_1 and the magnetization recovery is found to be monoexponential within the experimental error throughout the temperature region studied. The T_1 measurements in the temperature region of 400–300 K are carried out using a modified high-temperature setup. The low-temperature measurements are done using a continuous-gas-flow helium cryostat (CF200 Oxford Instruments Cryosystem) and the temperature is controlled to an accuracy of ± 0.5 K with the aid of a ITC-503 temperature controller (Oxford Instruments intelligent temperature controller). The sample temperature is measured with a Pt100 sensor for temperatures down to about 75 K and with a germanium sensor for temperatures below 75 K.

3 Results

Figure 1 shows the variation of ^1H and ^{19}F NMR T_1 over the entire temperature range studied. For ^1H at room temperature, the T_1 value is about 38 ms; it decreases monotonically upon increasing the temperature up to 395 K, above which it reduces sharply from 8 ms to less than 1 μs . We have also observed an increase in the duration of the free induction decay (FID) by several times when the temperature was increased from 388 to 410 K. Upon decreasing the tempera-

Fig. 1. ^1H (closed diamonds) and ^{19}F (open circles) NMR T_1 data at 21.34 MHz for AHFZ in the entire temperature range studied. Solid lines are guides to the eye.

ture from room temperature, T_1 increases, exhibiting a maximum of about 48 ms around 240 K. Below 240 K, T_1 decreases and passes through a minimum of about 6.6 ms around 160 K, below which it further increases to about 11 ms at 146 K. Below 146 K, T_1 decreases to about 8.8 ms and remains constant (within the experimental error) till about 50 K. Below 50 K, T_1 again increases, and below 30 K, it shows another minimum of 51 ms around 22 K. Below 20 K, T_1 increases monotonically to a few seconds till the lowest measurement temperature (11 K) in the present investigation. ^{19}F spin-lattice relaxation time shows a behavior similar to that of proton T_1 and is about 3 times greater than that of proton. At room temperature, the T_1 value is about 48 ms. It decreases upon increasing the temperature up to 395 K, above which it reduces sharply to less than a millisecond similar to proton T_1 . In the same temperature region, FID duration also increases severalfold as the temperature is increased from 388 to 410 K. Upon decreasing the temperature from room temperature, T_1 increases and shows a relatively broad maximum (as compared to that of proton) of about 60 ms around 220 K. Below 200 K, T_1 decreases and passes through a shallow minimum of about 35 ms around 160 K (at which the proton minimum is also observed). Below 160 K, fluorine T_1 goes through another minimum of 19.7 ms and then increases to about 31 ms at 106 K. Below this temperature, T_1 remains constant (within the experimental error) till about 50 K, and on further reducing the temperature, T_1 again increases monotonically to about 500 ms at 20 K. Below 20 K the signal could not be measured due to a poor signal-to-noise ratio till the lowest temperature of measurements (11 K).

4 Discussion

4.1 Analysis of ^1H NMR T_1

The proton and fluorine second moment (M_2) results reported earlier [5] for this compound are shown in Fig. 2 along with the present T_1 results for the purpose of comparison and analysis. In the temperature region of 135–290 K, the ^1H NMR spectra of AHFZ showed a single and comparatively broad line [5]. Above 295 K, a narrow component appears in the center of the spectrum and the second moment also decreases from 5.5 to 2.3 G^2 . Above 370 K, the ^1H NMR line width starts decreasing and finally reaches a very small value (0.15 G) around 400 K similar to that of a liquid.

Narrowing of the NMR signal and the corresponding decrease in T_1 indicates the diffusion of both NH_4 and ZrF_6 ions through the lattice and the high ionic conductivity observed by Kavun et al. [11] above 400 K also supports our observation. The ^1H NMR line width above 400 K measured by Kavun et al. [11] reaches a limit of the modulation width indicating the diffusion of ammonium ions. The observed T_1 maximum at 240 K may be attributed to the competition between the diffusion and the reorientational motion of the NH_4 ions.

Fig. 2. NMR spin-lattice relaxation times (present study at 21.34 MHz) (a) and second moments [5] (b) of proton (closed squares) and fluorine (open circles) for AHFZ in the entire temperature region of measurements.

Fig. 3. ^1H NMR T_1 data at 21.34 MHz for AHFZ in the high-temperature region (>300 K). Solid line shows the fitting of T_1 data to Eq. (1).

The spin-lattice relaxation due to the translational diffusion can be explained by a random walk model as given by Torrey [16]. At high temperatures, when $\omega_0\tau \ll 1$, the relaxation rate due to the translational diffusion can be written as

$$T_{1\text{td}}^{-1} = \left(\frac{8\pi N}{15a^3} \right) I(I+1) \gamma^4 \hbar^2 \left[\frac{\tau/2}{1 + (\omega_0\tau/2)} + \frac{\tau}{1 + \omega_0^2\tau^2} \right], \quad (1)$$

where ω_0 is the Larmor frequency (operating frequency), a is the distance of the closest approach, N represents the density of spins per cubic centimeter, I represents the nucleus spin (1/2 for ^1H) and τ represents the correlation time for the NH_4 diffusion which is assumed to obey the Arrhenius equation given by

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

Here τ_0 and E_a are called the preexponential factor (correlation time at infinite temperature) and activation energy for the diffusion of the ammonium ions, respectively. The high-temperature T_1 data (>300 K) are fitted to Eq. (1) and are shown in Fig. 3. The best fitting parameters corresponding to the translational diffusion of the NH_4 ion are as follows: $E_a = 23.2 \pm 1$ kJ/mol and $\tau_0 = (8.8 \pm 1) \cdot 10^{-12}$ s. These motional parameters agree well with those reported for NH_4 in SnCl_3 [17].

By assuming that the NH_4 ion reorients in such a way that each proton spends the same amount of time at any of the hydrogen sites in the NH_4 tetrahedron, the proton relaxation time can be expressed using the Bloembergen–Purcell–Pound (BPP) approach as [18–20]

$$T_{1\text{H}}^{-1} = \frac{27\gamma^4\hbar^2}{40r^6} \left[\frac{\tau_{\text{H}}}{1 + \omega_0^2\tau_{\text{H}}^2} + \frac{4\tau_{\text{H}}}{1 + 4\omega_0^2\tau_{\text{H}}^2} \right], \quad (3)$$

Fig. 4. ^1H (squares) and ^{19}F (circles) T_1 data in the temperature range of 220–146 K. Solid line represents the BPP fit to ^1H T_1 data and dotted line shows the simulated graph of the BPP curve for ^{19}F T_1 data.

where τ_{H} represents the correlation time of the NH_4 reorientational motion and is assumed to obey the Arrhenius equation given in Eq. (2). E_a is the activation energy for the ammonium ion reorientational motion. In Eq. (3), γ is the gyromagnetic ratio of the proton and r is the interproton distance in the NH_4 tetrahedron.

Equation (3) fits well to the present experimental ^1H T_1 data in the temperature region from 240 to 146 K and is shown in Fig. 4. The best fitting parameters corresponding to the NH_4 reorientational motion are as follows: $E_a = 13.6 \pm 0.3$ kJ/mol and $\tau_0 = (19 \pm 1) \cdot 10^{-14}$ s. The ^1H second moment studies of the same compound [5] suggest that the activation energy corresponding to the reorientation of the ammonium ion should be less than 17 kJ/mol. The activation energy obtained from the present investigation (13.6 kJ/mol) agrees with the predicted value [5]. The observed motional parameters are of the same order as those obtained in other $(\text{NH}_4)_2\text{MCl}_6$ compounds [21, 22].

Below 146 K, the T_1 behavior can be explained on the basis of the quantum rotational tunneling of the ammonium ion. Lalowicz et al. [3] have also attributed the line shape of the proton NMR signal at 4.2 K to the quantum rotational tunneling.

4.2 Theory

At lower temperatures, the quantum rotational tunneling of the NH_4 ion becomes dominant. The observation of low activation energy for the reorientation of the NH_4 ion along with tunneling at low temperatures has been reported for similar compounds by several authors [23, 24]. The low hindering barrier observed for the NH_4 ion facilitates the tunneling process [25–26]. The Haupt model [27] was modified by Köksal et al. [23] to estimate the relaxation rate for the methyl group

tunneling. Later Punkkinen [28] extended this model to the ammonium ion. Four proton spins in an ammonium ion combine to form a fivefold degenerate A state ($I_{\text{tot}} = 2$), three sets of threefold degenerate T states ($I_{\text{tot}} = 1$) and a twice degenerate E state ($I_{\text{tot}} = 0$). The states are further split by the static magnetic field.

In the present study, T_1 is found to be temperature-independent from 146 down to 50 K, which suggests that only the ground tunnel state is occupied. A similar T_1 behavior has been observed in many compounds at lower temperatures [17, 23, 29–31]. Below 50 K, T_1 goes through a minimum. By assuming a very narrow tunnel splitting distribution and that the torsional ground state is well separated from the first excited state, the relaxation rate can be given by [28]

$$T_{1\text{AT}}^{-1} = C_{\text{AT}} \left[\frac{\tau_{\text{T}}}{1 + \bar{\omega}_{\text{T}}^2 (\tau_{\text{T}})^2} + \frac{\tau_{\text{T}}}{1 + (\bar{\omega}_{\text{T}} \pm \omega_0)^2 (\tau_{\text{T}})^2} + \frac{\tau_{\text{T}}}{1 + (\bar{\omega}_{\text{T}} \pm 2\omega_0)^2 (\tau_{\text{T}})^2} \right] \quad (4)$$

for the transitions between A and T states, where $\bar{\omega}_{\text{T}}$ is the average tunnel frequency for the A–T transitions. The three terms on the right-hand side of Eq. (4) correspond to the transitions $\Delta m = 0, \pm 1$ and ± 2 , respectively. Similarly, for the transitions between A and E states, the relaxation rate is given by

$$T_{1\text{AE}}^{-1} = C_{\text{AE}} \left[\frac{\tau_{\text{E}}}{1 + \bar{\omega}_{\text{E}}^2 (\tau_{\text{E}})^2} + \frac{\tau_{\text{E}}}{1 + (\bar{\omega}_{\text{E}} \pm \omega_0)^2 (\tau_{\text{E}})^2} + \frac{\tau_{\text{E}}}{1 + (\bar{\omega}_{\text{E}} \pm 2\omega_0)^2 (\tau_{\text{E}})^2} \right]. \quad (5)$$

Here $\bar{\omega}_{\text{E}}$ is the average tunnel frequency for the A–E transitions. The tunneling frequencies used in Eqs. (4) and (5) can also be approximately estimated from the value of the observed $T_{1\text{min}}$ (when $\omega_{\text{T}} \gg \omega_0$) with the relation [32]

$$T_{1\text{min}}(\text{obs})/T_{1\text{min}}(\text{class}) \approx \bar{\omega}_{\text{T}}/\omega_0. \quad (6)$$

Guttler and von Schutz [33] have used Eq. (6) for NH_4ClO_4 . Equation (5) is reasonable if the tunnel motion is considered to have a power spectrum centered around $\bar{\omega}_{\text{T}}$ (tunneling frequency) instead of around ω_0 (Larmor frequency) similar to the classical random motion. In the case of the ammonium ion, an estimate of the tunneling frequency can be made from the classical value of $T_{1\text{min}}$ by the relation [28]

$$\bar{\omega}_{\text{T}} \approx 25.13 \cdot 10^9 T_{1\text{min}}, \quad (7)$$

where $\bar{\omega}_{\text{T}}$ is in hertz when T_1 is in seconds. An empirical relation between the activation energy and the tunneling frequency can be approximately given as [26]

$$\bar{\omega}_{\text{T}} \approx 26.5 \cdot 10^{12} \exp[-10.4 \cdot (E_{\text{a}})^{1/2}],$$

where $\bar{\omega}_{\text{T}}$ is in hertz when E_{a} is in kilocalories per mol.

Fig. 5. ^1H NMR T_1 data at 21.34 MHz for AHFZ in the temperature region of 30–16 K. Solid line shows the fit of T_1 data to Eq. (8).

When $\bar{\omega}_T \geq \omega_0$, Eqs. (4) and (5) can be modified as

$$T_{\text{IAT}}^{-1} = C_{\text{AT}} \left[\frac{\tau_T}{1 + \bar{\omega}_T^2 \tau_T^2} \right] \quad (8)$$

for the A–T transition and

$$T_{\text{IAE}}^{-1} = C_{\text{AE}} \left[\frac{\tau_E}{1 + \bar{\omega}_E^2 \tau_E^2} \right] \quad (9)$$

for the A–E transition. τ_T and τ_E follow the usual Arrhenius behavior.

By Eq. (6) or (7), an approximate estimate of tunneling frequency is made and used in Eqs. (8) and (9) to give the best fit for the T_1 data at temperatures below 28 K (shown in Fig. 5). The fitting parameters are used to calculate the quantum parameters corresponding to the A–E or A–T transitions, respectively. The tunneling frequency is estimated to be 405 MHz. The tunneling frequencies measured in a few ammonium hexahalometallates are found to vary over a wide range from 1.4 to 600 MHz [26]. The energy of the torsional splitting is estimated as 1.98 kJ/mol and the preexponential factor is $8.38 \cdot 10^{-15}$ s. By comparing the tunneling parameters with that of NH_4SnBr_3 [30], the observed tunneling frequency is found to be higher than that of the A–T splitting and lower than that of the A–E tunnel splitting. The torsional splitting between the ground state and the first excited state (1.98 kJ/mol) is fairly in agreement with that of the A–T tunneling.

4.3 Analysis of ^{19}F NMR T_1

In the temperature range of 120–200 K, the ^{19}F wide-line NMR signal [5] consists of a single asymmetric line, in the range of 210–275 K, the spectrum has

shown a number of components with different widths, and above 275 K, the additional peaks have disappeared. The complexity of the ^{19}F NMR spectrum is due to the polymeric nature of $(\text{NH}_4)_2\text{ZrF}_6$. With further increase in temperature, the width of the line has decreased, and around 340 K, a new transformation of the signal starts and completes above 400 K by the observation of an asymmetric narrow line with a fine structure. The phase transformation of AHFZ in the temperature range of 410–415 K has not changed the line shape. Hence, the analysis of the ^{19}F T_1 is similar to that of the proton. Both decrease in T_1 and narrowing of the NMR signal may be attributed to the diffusion of both ammonium and fluorine ions through the lattice. High ionic conductivity above 400 K observed by Kavun et al. [11] supports this assumption and is attributed to the sublattice movement of F ions. The observed maximum in fluorine T_1 in the present study around room temperature may be attributed to the competition between the diffusion and the reorientational motion.

The ^{19}F T_1 data in the region of 200–106 K also appears to follow Eq. (2) and fitting of the linear portion of the ^{19}F T_1 data in this region gives an activation energy of 13 ± 1 kJ/mol and is attributed to the reorientation of the ammonium group. Hence, it is concluded that the ammonium ion reorientations are rate-determining and the fluorines relax to the lattice mainly by the random modulations of the H–F dipole–dipole interactions due to the NH_4 motion. Several authors have observed a similar behavior in a number of compounds, for example, Watton et al. [22] in $(\text{NH}_4)_2\text{TiF}_6$ and McDowell et al. [34] in $(\text{CH}_3)_3\text{NPF}_5$, and have explained their results in a similar manner. We have recently [35] observed a similar cross relaxation between ^1H and ^{19}F in $(\text{CH}_3)_4\text{NPF}_6$. Indeed, in the present compound, Kavun et al. [11] have also observed that the ^{19}F second moment reaches the rigid lattice limit at a much higher temperature of about 250 K. Figure 4 shows fitting of Eq. (2) to the ^1H T_1 data and the simulated graph of the BPP curve for the ^{19}F T_1 data in the same temperature range.

Fluorine T_1 data in the region of 106–20 K are also attributed to the onset of the ammonium ion motion as the second moment studies of the same compound have shown that the fluorine motions freeze at much higher temperatures at least in the NMR timescale.

5 Conclusion

The present investigation reveals that in AHFZ the ammonium ion plays a major role in the relaxation mechanism. At higher temperatures, the compound shows the diffusion of both ammonium and fluorine sublattices, which is also supported by other techniques. A sharp increase of FID duration and a sudden increase of the relaxation rate around 395 K also supports the diffusion of ions. Further, this investigation reveals that the reorientational motion of the ammonium ion also is responsible for the fluorine relaxation. Another important observation is that even at low temperatures, fluorine nuclei relax due to the quantum rotational tunneling of the ammonium ion.

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