

Anomalous Larmour Frequency Dependence of Proton Spin–Lattice Relaxation Time (T_1) in the Ferroelectric Glycine Phosphite

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We report here the results of our ^1H NMR spin–lattice relaxation time (T_1) studies in glycine phosphite which is ferroelectric below 224 K. The experiments have been carried out in the temperature range from 200 to 419 K and at two Larmour frequencies of 11.40 and 23.56 MHz. We have noticed a Larmour frequency dependence of T_1 on the high-temperature side of the T_1 minimum. A model is proposed based on the BPP theory to explain the observation.

1. Introduction

Glycine phosphite (abbreviated as GPI) is one of the many inorganic addition compounds that can be formed using amino acids. Most of these addition compounds show interesting properties. Some well known ferroelectric addition compounds formed with the amino acid glycine ($^+\text{NH}_3\text{CH}_2\text{COO}^-$) are triglycine sulphate (TGS), selenate (TGSe), tetrafluoroberrylate (TGFBer) and diglycine nitrate (DGN) [1–4]. Another interesting group, which is formed by the α -amino acid betaine ($(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COO}^-$), includes among others, betaine phosphate (BP) which is antiferroelectric, betaine phosphite (BPI) and betaine arsenate (BA) which are ferroelectric and betaine calciumchloride dihydrate (BCCD) which exhibits a number of phases including incommensurate ones [5–8].

GPI (like other addition compounds mentioned above) belongs to the family of hydrogen bonded crystals. At room temperature it is monoclinic with space group $\text{P}2_1/a$ and the unit cell dimensions are $a = 0.9792$ nm, $b = 0.84787$ nm, $c = 0.7411$ nm with $\beta = 100.43^\circ$ and $Z = 4$ [9]. The structure consists of a layered arrangement of planes containing infinite $[\text{H}(\text{HPO}_3)]_n^-$ chains, alternating with planes built by the organic cations, both layers developing parallel to the b – c plane. The chains of HPO_3 tetrahedra are connected by strong hydrogen bonds and are directed along the c -axis.

GPI undergoes a ferroelectric phase transition at about 224 K [10]. The spontaneous polarisation appears along the b -direction which is perpendicular to the hydrogen-bonded chains of the phosphite anions. This is not so in the case of BPI or caesium dihydrogen phosphate where the hydrogen-bonded chains are parallel to the ferroelectric axis [11, 12]. However, in ferroelectric potassium dihydrogen phosphate (KDP), the hydrogen bonds are perpendicular to the ferroelectric axis.

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Dielectric, infrared, Raman, EPR and DSC measurements have indicated that the ferroelectric phase transition in GPI is of second order and belongs to the order–disorder type [10, 13, 14]. Tritt-Goc et al. [15] have measured the proton NMR spin–lattice relaxation time (T_1) as a function of temperature, at 90 MHz, to understand the role of glycinium cations in the ferroelectric transition in GPI. The main feature in the variation of T_1 with temperature is the observation of a T_1 minimum at 294 K.

We have taken up the T_1 measurements in GPI as a part of our programme to study proton dynamics in the “orientational glass” state exhibited by the mixed systems of GPI and BP. Surprisingly, the spin–lattice relaxation time versus $1000/T$ plot in GPI has exhibited a frequency dispersion on the high-temperature side of the T_1 minimum. We present here our experimental results and a model to explain the observed T_1 dispersion.

2. Experimental Details

Polycrystalline samples of GPI were grown by slow evaporation at 308 K from aqueous solution containing glycine and phosphorous acid in the ratio 1:1. The samples were purified by recrystallisation. The d -spacings obtained using the powder X-ray diffraction technique agreed well with the published crystal structure data [9]. For our experiments, the polycrystalline sample was powdered and sealed in a glass tube after evacuation. ^1H NMR spin–lattice relaxation times were measured at two Larmour frequencies, 11.40 and 23.56 MHz, using a home made pulsed NMR spectrometer working in the range 3–30 MHz. A π – τ – $\pi/2$ pulse sequence was employed for the T_1 measurements. The recovery of the magnetization followed a single exponential in the temperature range studied (210 to 419 K). Above 419 K the sample melts. The onset of melting could be seen by a large increase in the duration of the free induction decay (FID) signal. The melting temperature observed in our experiments matched with that obtained from DSC experiments. The temperature of the sample was controlled using a nitrogen gas flow arrangement and measured using a Pt-100 sensor.

3. Results and Discussion

Figure 1 shows the plot of spin–lattice relaxation time (T_1) versus $1000/T$ at the two Larmour frequencies 11.40 and 23.56 MHz. T_1 passes through a minimum as the temperature is decreased. The minimum in T_1 is at $T = 262$ K ($1000/T = 3.82$ K $^{-1}$) and has a value of 10.8 ms at 11.40 MHz. At 23.56 MHz the T_1 minimum occurs at 276 K ($1000/T = 3.62$ K $^{-1}$) and has a value of 21.7 ms. An interesting feature seen in Fig. 1 is the Larmour frequency dependence of T_1 at temperatures above that of T_1 minimum, till the highest temperature reached (419 K). The T_1 increases with decreasing temperature below the T_1 minimum till the lowest temperature studied. The T_1 dispersion on the low-temperature side of the T_1 minimum is as expected from the BPP theory [16].

In an earlier ^1H NMR spin–lattice relaxation work in the same system by Tritt-Goc et al. [15] at a single Larmour frequency of 90 MHz, the spin–lattice relaxation behaviour has been explained by assuming that the reorientation of the NH_3^+ relaxes all the protons via spin diffusion in the entire temperature range from 195 to 420 K. However, the model used by Tritt-Goc et al. could not explain our T_1 results, especially the T_1 dispersion observed on the high-temperature side of the T_1 minimum. The expression

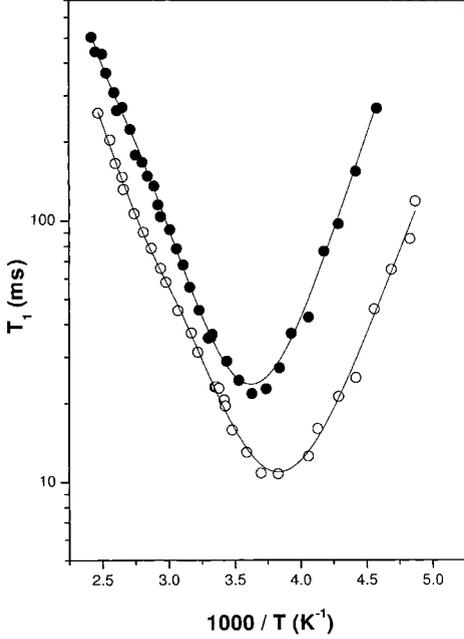


Fig. 1. ^1H NMR spin-lattice relaxation time in GPI as a function of temperature. Open circles correspond to 11.40 MHz and solid circles correspond to 23.56 MHz. Lines denote the theoretical fit to Eq. (3)

for the proton spin-lattice relaxation rate used by Tritt-Goc et al. [15] is given as

$$\frac{1}{T_{\text{1NH}_3}} = \frac{3}{8} D \left(\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right), \quad (1)$$

where $\tau_c = \tau_{c0} \exp\left(\frac{E_0}{kT}\right)$ and $D = \frac{9}{20} \left(\frac{\mu_0}{4\pi}\right)^2 \times \gamma^4 \hbar^2 r^{-6}$. The factor 3/8 in Eq. (1) arises from spin diffusion and in GPI the three protons belonging to the NH_3^+ group, relax the total number of eight protons in the molecule. τ_c is the correlation time of the NH_3^+ group, which is assumed to follow the Arrhenius behaviour, E_0 is the activation energy and D is the relaxation constant for the NH_3^+ group reorientation. Equation (1)

predicts a Larmour frequency independent behaviour for T_1 on the high-temperature side of the T_1 minimum, if $\omega_0 \tau_c \ll 1$.

The T_1 minimum due to reorientation of the NH_3^+ group alone without spin diffusion will be 5.5 and 11.4 ms at the two frequencies of our study and these are half of the values that have been observed. This can occur if there are inequivalent reorienting groups in the system contributing to relaxation [17, 18]. It is known that if the number of “a” type groups is N_a and the number of “b” type groups is N_b , then the effective relaxation rate due to these inequivalent groups is given as

$$\frac{1}{T_1} = \left(N_a \frac{1}{T_{1a}} + N_b \frac{1}{T_{1b}} \right) \frac{1}{N_a + N_b}. \quad (2)$$

We tried to explain our data at 11.40 and 23.56 MHz using Eq. (2) and the best fit T_1 values do not agree with the observed values for both the cases of $N_a = N_b$ and $N_a \neq N_b$. We have also considered the possibility of inequivalence with spin diffusion but could not explain the observed experimental data. Vibrational studies also support the absence of inequivalent glycinium cations in the paraelectric state of GPI [13].

We have modified the model in the following way to explain our observations (Fig. 1). We propose that in addition to the reorientation of the NH_3^+ group, the flip motion of the glycine group ($\text{NH}_2\text{CH}_2\text{COOH}$) about the long axis of the GPI molecule may also contribute to the relaxation of the protons particularly at higher temperatures. The relaxation will be dominated by the NH_3^+ group reorientation at lower temperatures and at higher temperatures where $\omega \tau_{\text{NH}_3} \ll 1$, the 120° flip of the $\text{NH}_2\text{CH}_2\text{COOH}$ group could contribute significantly to the relaxation. The effect of 120° flip in GPI is also seen in the second moment experiments carried out by Tritt-Goc et al. [15]. Similar

observations where the flip of the entire molecule contributing to the relaxation have been reported earlier in the literature [20, 21]. We give below the expression for the proton NMR spin–lattice relaxation rate due to the combined effect of NH_3^+ reorientation and 120° flip of $\text{NH}_3\text{CH}_2\text{COOH}$ group along with spin diffusion,

$$\frac{1}{T_1} = \frac{3}{8} D \left(\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right) + \frac{2}{8} F \left(\frac{\tau_i}{1 + \omega_0^2 \tau_i^2} + \frac{4\tau_i}{1 + 4\omega_0^2 \tau_i^2} \right), \quad (3)$$

where τ_c and τ_i are the correlation times for the NH_3^+ group reorientation and $\text{NH}_3\text{CH}_2\text{COOH}$ group flip motion, respectively. Both correlation times are assumed to follow the Arrhenius behaviour. D and F represent the relaxation constants for the NH_3^+ group reorientation and $\text{NH}_3\text{CH}_2\text{COOH}$ group flip motion, respectively. The factors $3/8$ and $2/8$ come from spin diffusion. The constant D is as given in Eq. (1) and F is given by [21],

$$F = \frac{27}{40} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma^4 \hbar^2}{R^6} \sin^2 \alpha, \quad (4)$$

where α is the flip angle, R is the inter-proton distance between the protons attached to the CH_2 group and the NH_3 group.

We have done a least-squares fitting of the T_1 versus $1000/T$ data to Eq. (3) and the best fit is shown in Fig. 1, and the best fit parameters obtained at 11.40 and 23.56 MHz are given in Table 1. The correlation times obtained for the reorientation and flip motion compare well with those reported in literature [20]. The activation energy of 26.8 kJ/mol for the NH_3^+ group reorientation (which agrees with that reported by Tritt-Goc et al.) is relatively high compared to those in other glycine compounds like TGS, TGSe etc. [19, 22, 23]. Tritt-Goc et al. [15] have attributed this high value to the relatively strong hydrogen bonds in GPI compared to other glycine systems. The high value of 45.6 kJ/mol for the activation energy of the flip of $\text{NH}_3\text{CH}_2\text{COOH}$ group is also to be expected and therefore this motion comes into play only at higher temperatures. Similar values of activation energy for the flip motion have been reported in other systems like thiourea, hydraziniumnitrate etc. [20, 21]. The value of inter-proton distance in the NH_3^+ group calculated using the relaxation constant D is 1.69 Å and it matches well with the value of 1.70 Å obtained from neutron diffraction experiments in amino acids [24]. We have not observed any distinct T_1 minimum due to the flip motion. But a careful look at the spin–lattice relaxation behaviour (Fig. 1) in the higher temperature region at 11.40 MHz shows a weak indication around 370 K. As the flip motion is a high activation energy motion, the motional frequencies may not be very high and it is

Table 1
Motional parameters of GPI obtained using Eq. (3) (at 11.40 and 23.56 MHz)

τ_{c0}	$(5.2 \times 10^{-14} \pm 3.6 \times 10^{-14})$ s
τ_{i0}	$(1.9 \times 10^{-15} \pm 0.72 \times 10^{-15})$ s
E_0	(26.8 ± 1.8) kJ/mol
E_i	(46 ± 0.16) kJ/mol
D	$1.25 \times 10^{10} \text{ s}^{-2}$
F	$0.04 \times 10^{10} \text{ s}^{-2}$
α	$120^\circ \pm 7^\circ$

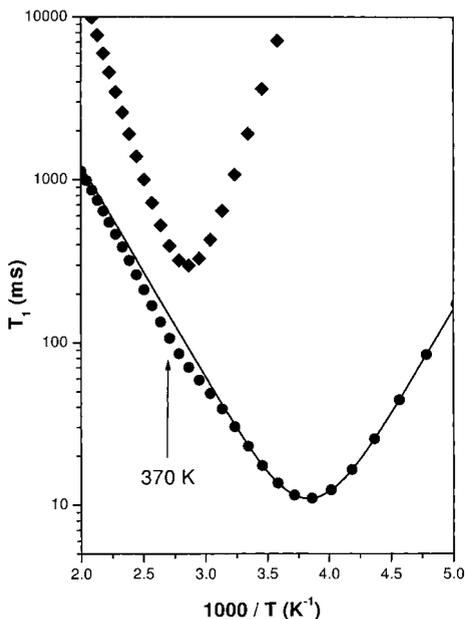


Fig. 2. Simulated T_1 versus $1000/T$ plot at 11.40 MHz using Eq. (3). Diamonds and line represent simulated T_1 data for 120° flip motion of glycine molecule and NH_3 group reorientation, respectively. Solid circles represent the combined effect of flip and reorientation

expected to show up significantly only at lower Larmour frequencies. Figure 2 shows the simulated T_1 versus $1000/T$ curve using the motional parameters from Table 1 at 11.40 MHz, for reorientational motion, flip motion and combined motion of reorientation and flip. The arrow indicates the approximate temperature at which the T_1 minimum is expected due to the flip motion. As the Larmour frequency increases the T_1 minimum from the flip motion shifts to higher temperatures. The data of Tritt-

Goc et al. were obtained at a much higher Larmour frequency of 90 MHz where the flip motion of the glycine group as a whole is not very effective and hence could be explained on the basis of NH_3^+ reorientation alone in the range of temperature studied. $\omega_0\tau_i$ at 11.40 and 23.56 MHz do not satisfy the condition $\omega_0\tau_i \ll 1$ at higher temperatures and this explains the T_1 dispersion in the data at higher temperatures.

It would be interesting to compare the behaviour of T_1 near T_c in GPI ($T_c = 224$ K) and other glycine compounds which exhibit ferroelectric transitions. In triglycine sulphate (TGS, $T_c = 320$ K), selenate (TGSe, $T_c = 295$ K), tetrafluoroberrylate (TGFBc, $T_c = 343$ K), partially deuterated TGS ($T_c = 333$ K) and potassium dihydrogen phosphate (KDP, $T_c = 123$ K) the transition from the paraelectric phase to the ferroelectric phase has been found to be accompanied by a rather sudden decrease in the proton spin-lattice relaxation time [19, 25]. KDP is compared here due to its similarity with GPI in the direction of spontaneous polarisation. In the TG systems a sudden change in T_1 near the transition temperature indicates a direct involvement of protons in the ferroelectric transition. In GPI also a large isotopic effect (98 K) on T_c points towards the essential role of the interphosphite hydrogen bonds in the phase transition mechanism. However, the proton T_1 varies smoothly with temperature near the ferroelectric transition temperature of 224 K [15] indicating that the dynamics of the protons in the hydrogen bonds are fast for the NMR T_1 time scale. This fast proton jump in the interphosphite hydrogen bond also could be the reason for a lower ferroelectric transition temperature in GPI compared to the other ferroelectrics mentioned above [26]. Vibrational spectroscopic studies show that normal $\text{H}_2\text{PO}_3^{1-}$ anions appear in the paraelectric and ferroelectric phases, confirming that the protons in the interphosphite hydrogen bonds are dynamically disordered in the time scale of vibrational spectroscopy [13]. These studies also suggest that the dynamical disorder of interphosphite hydrogen bonds is coupled to the motions of glycinium cations. The above statement is well sup-

ported by the splitting of some glycinium bands in the ferroelectric phase where the interphosphite hydrogen bonds settle to one of the positions in the time scale of vibrational spectroscopy. As stated above, the motion of these protons appears to be too fast ($\omega_0\tau_c \ll 1$) to be observed by the NMR T_1 measurements.

4. Conclusion

We have observed a Larmour frequency dependence in the spin–lattice relaxation time behaviour in GPI on the high-temperature side of the T_1 minimum. The presence of inequivalent glycinium cations could not explain our observed results and an attempt has been made to explain this by invoking the 120° flip motion of $\text{NH}_2\text{CH}_2\text{COOH}$ group about its long axis, in addition to the NH_3^+ reorientation. The motional parameters obtained match well with those obtained in earlier studies. No significant change in T_1 behaviour could be observed at T_c .

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