PHASE TRANSITIONS AND MICROSCOPIC ENVIRONMENTS IN
\( \text{TlH}_2\text{PO}_4 \) (TDP) AND \( \text{TlH}_2\text{AsO}_4 \) (TDA) SYSTEMS

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Nuclear magnetic resonance has been employed to study the phase
transitions and microscopic structures in \( \text{TlH}_2\text{PO}_4 \) (TDP) and \( \text{TlH}_2\text{AsO}_4 \)
(TDA) systems. The phase transitions were sensitively reflected in the
rotating frame spin-lattice relaxation probing the ultra-slow
microdomain motions. A prominent thermal hysteresis in the \(^1\)H NMR-
\(^{75}\)As NQR cross relaxation in TDA attributed to a ferroelastic glassy
nature was also observed. Besides, our high resolution \(^{31}\)p NMR
measurement further elucidated the nature of the microscopic
environments and the phase transitions in the TDP system.

**Keywords** \( \text{TlH}_2\text{PO}_4 \); \( \text{TlH}_2\text{AsO}_4 \); NMR; Phase transitions;
Microdomains
1. INTRODUCTION

TlH$_2$PO$_4$ (TDP) and TlH$_2$AsO$_4$ (TDA) are interesting hydrogen-bonded systems that undergo two major phase transitions [1]. While they are closely related to the KDP (KH$_2$PO$_4$) type crystals, the very short hydrogen bond lengths and the very heavy mass of the Tl$^+$ ion are peculiar to these systems [2]. These features play an important role in the phase transitions. In TDP and TDA the low-temperature (II-III) antiferroelectric phase transition occurs at $T_c=230$ K and $T_c=251$ K, and the high-temperature (I-II) ferroelastic phase transition at $T_c'=364$ K and $T_c'=391$ K, respectively. In our previous publications we have given a detailed description of the systems and revealed the nature of the phase transitions and the microdomain structures [3,4]. In order to elucidate the microscopic environments in the TDP and TDA systems, we have employed laboratory and rotating frame proton spin-lattice relaxation measurements as well as $^{31}$P high resolution NMR measurements.

2. EXPERIMENT

Polycrystalline TDA and TDP samples were used in this work for the NMR measurements. The laboratory frame $^1$H NMR measurements were made at 13.5 and 45 MHz, and the rotating frame spin-lattice relaxation measurements were made using a 200 MHz spectrometer at the rotating frame frequency of 55 kHz. The high resolution $^{31}$P magic angle spinning (MAS) NMR measurements for TDP were made at the Larmor frequency of 243 MHz at the spinning frequency of 3 kHz.

3. RESULTS AND DISCUSSION

While the phase transitions were not well reflected in the laboratory
frame spin-lattice relaxation in the TDP and TDA systems, they were sensitively reflected in the rotating frame spin-lattice relaxation as shown in Fig. 1, indicative of ultra-slow motions, as previously reported [3,4]. The spin-lattice relaxation pattern below the ferroelastic phase transition temperature was not single-exponential but was well fitted by a stretched-exponential form, \( M(t) = M_o \exp\left(-\left(t/T_{1p}\right)^{1-n}\right) \), which can be attributed to a random distribution of the correlation time [5].

![Temperature dependence of the rotating frame spin-lattice relaxation time T1p in TDA. The inset shows the temperature dependence of the exponent n.](image)

random distribution of the correlation time can be ascribed to a random distribution of proton double wells, which may be explained by the random distortion of PO4/AsO4 tetrahedra as will be further discussed in the following.

In Fig. 2 is shown the temperature dependence of the spin-lattice
relaxation time for the TDA sample measured at 13.5 MHz upon heating and then cooling. An apparently complex temperature dependence can be attributed to the $^1$H NMR-$^{75}$As NQR (nuclear quadrupole resonance) cross relaxation, for which two minima in the spin-lattice relaxation time are expected at around 310 and 350 K due to the lifting of the NQR frequency degeneracy in the magnetic field of 13.5 MHz $^1$H NMR [6].

![Graph showing temperature dependence of spin-lattice relaxation time in TDA measured at 13.5 MHz upon heating and then cooling.](image)

FIGURE 2  Temperature dependence of the spin-lattice relaxation time in TDA measured at 13.5 MHz upon heating and then cooling.

As the 13.5 MHz $^1$H NMR relaxation in fact sensitively reflects the $^{75}$As NQR relaxation, which in turn is dictated by the electric field gradient (EFG) distribution, the pronounced thermal hysteresis observed in Figure 2 can readily be attributed to that in the microscopic environments represented by the EFG distribution. The strength of the EFG tensor probed by $^{75}$As NQR is expected to depend on the distortion of the AsO$_4$ tetrahedra, and the thermal hysteresis of the cross relaxation in Fig. 1 is attributed to that of the spontaneous distortion of the AsO$_4$
tetrahedra, or, possibly to the ferroelastic glassy nature in the TDA system.

![Diagram](image)

**FIGURE 3** Temperature dependence of the $^{31}$P isotropic chemical shift in TDP. The inset shows the linewidth, which shows marked linewidth changes through the phase transitions.

Figure 3 shows the temperature dependence of the $^{31}$P isotropic chemical shift in TDP upon heating. The isotropic chemical shift shows a drastic temperature dependence including sign inversion in the ferroelastic phase. From the temperature independence of the average isotropic chemical shift, the ferroelectric transition in KDP was concluded to be a pure structural one with no change in the electronic structure [7]. On the other hand, the strong temperature dependence of the isotropic chemical shift in TDP is indicative of an electronic instability due to a strong deformation of the PO$_4$ tetrahedra in the ferroelastic phase. Marked linewidth changes through the phase transitions shown in the inset in Fig. 3 elucidates an evolution of
inhomogeneous environments around the PO₄ tetrahedra in the ferroelastic phase. A strong deformation of the PO₄ tetrahedra observed in the isotropic chemical shift appears to be responsible for the inhomogeneity.

In summary, TlH₂PO₄ and TlH₂AsO₄ systems were investigated by means of $^1$H NMR spin-lattice relaxation measurements as well as high resolution $^{31}$P NMR measurements. As a result, a strongly inhomogeneous nature of the microscopic environments in the systems was revealed, which can be attributed to the distortion of the PO₄/AsO₄ terahedra and a random distribution of the proton double wells.

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REFERENCES