

## PHASE TRANSITIONS AND MICROSCOPIC ENVIRONMENTS IN TIH<sub>2</sub>PO<sub>4</sub> (TDP) AND TIH<sub>2</sub>AsO<sub>4</sub> (TDA) SYSTEMS

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Nuclear magnetic resonance has been employed to study the phase transitions and microscopic structures in TIH<sub>2</sub>PO<sub>4</sub> (TDP) and TIH<sub>2</sub>AsO<sub>4</sub> (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 <sup>1</sup>H NMR-<sup>75</sup>As NQR cross relaxation in TDA attributed to a ferroelastic glassy nature was also observed. Besides, our high resolution <sup>31</sup>P NMR measurement further elucidated the nature of the microscopic environments and the phase transitions in the TDP system.

**Keywords**      TIH<sub>2</sub>PO<sub>4</sub>; TIH<sub>2</sub>AsO<sub>4</sub>; NMR; Phase transitions;  
Microdomains

## 1. INTRODUCTION

$\text{TiH}_2\text{PO}_4$  (TDP) and  $\text{TiH}_2\text{AsO}_4$  (TDA) are interesting hydrogen-bonded systems that undergo two major phase transitions [1]. While they are closely related to the KDP ( $\text{KH}_2\text{PO}_4$ ) type crystals, the very short hydrogen bond lengths and the very heavy mass of the  $\text{Ti}^+$  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  $^{31}\text{P}$  high resolution NMR measurements.

## 2. EXPERIMENT

Polycrystalline TDA and TDP samples were used in this work for the NMR measurements. The laboratory frame  $^1\text{H}$  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  $^{31}\text{P}$  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,  $M(t) = M_o \exp(-(t/T_{1\rho})^{1-n})$ , which can be attributed to a random distribution of the correlation time [5]. The

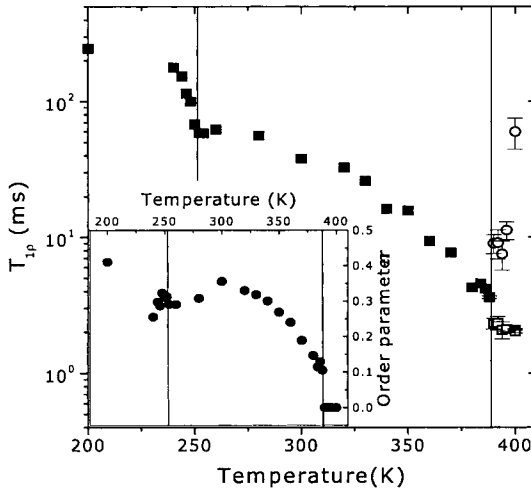


FIGURE 1 Temperature dependence of the rotating frame spin-lattice relaxation time  $T_{1\rho}$  in TDA. The inset shows the temperature dependence of the exponent  $n$ .

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  $\text{PO}_4/\text{AsO}_4$  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  $^1\text{H}$  NMR- $^{75}\text{As}$  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  $^1\text{H}$  NMR [6].

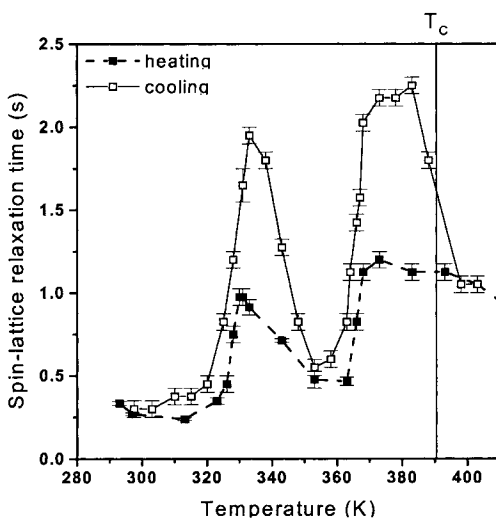
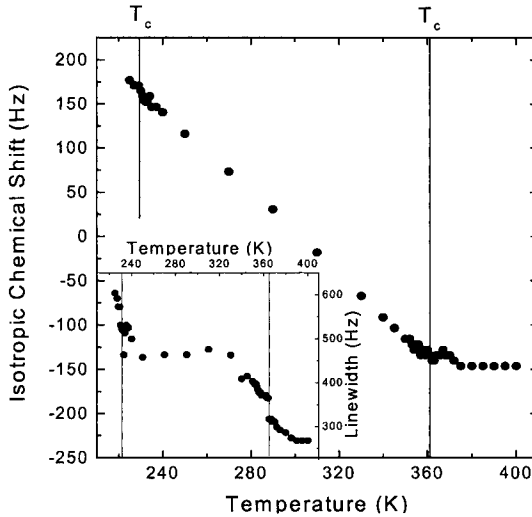


FIGURE 2 Temperature dependence of the spin-lattice relaxation time in TDA measured at 13.5 MHz upon heating and then cooling.

As the 13.5 MHz  $^1\text{H}$  NMR relaxation in fact sensitively reflects the  $^{75}\text{As}$  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  $^{75}\text{As}$  NQR is expected to depend on the distortion of the  $\text{AsO}_4$  tetrahedra, and the thermal hysteresis of the cross relaxation in Fig. 1 is attributed to that of the spontaneous distortion of the  $\text{AsO}_4$

tetrahedra, or, possibly to the ferroelastic glassy nature in the TDA system.



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FIGURE 3 Temperature dependence of the  $^{31}\text{P}$  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  $^{31}\text{P}$  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  $\text{PO}_4$  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  $\text{PO}_4$  tetrahedra in the ferroelastic phase. A strong deformation of the  $\text{PO}_4$  tetrahedra observed in the isotropic chemical shift appears to be responsible for the inhomogeneity.

In summary,  $\text{TiH}_2\text{PO}_4$  and  $\text{TiH}_2\text{AsO}_4$  systems were investigated by means of  $^1\text{H}$  NMR spin-lattice relaxation measurements as well as high resolution  $^{31}\text{P}$  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  $\text{PO}_4/\text{AsO}_4$  tetrahedra and a random distribution of the proton double wells.

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