

## Rotating-frame nuclear magnetic relaxation in $\text{TiH}_2\text{PO}_4$

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(Received 6 February 1996; revised manuscript received 28 August 1996)

A  $\text{TiH}_2\text{PO}_4$  single crystal was studied by means of the rotating-frame NMR measurements and the results were compared with our recent work on a  $\text{TiH}_2\text{AsO}_4$  polycrystalline sample. When the data were fitted in the same manner, similar overall features were observed, whereas anomalies at the antiferroelectric phase transition were much more pronounced. On the other hand, a double-exponential fit at all temperatures suggests that both of the domain structures participate in the antiferroelectric phase transition, whereas only one of them undergoes the ferroelastic phase transition. The domain structure that does not undergo the ferroelastic phase transition shows a differential anomaly in the spin-lattice relaxation at the critical temperature, which appears to be characteristic of an order-disorder transition. [S0163-1829(97)03417-6]

### I. 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.<sup>1-6</sup> 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  $\text{Ti}^{4+}$  ion are peculiar to these systems.<sup>1,2,7,8</sup> These features play an important role in the phase transitions. In TDP the low-temperature (II-III) antiferroelectric phase transition occurs at  $T_c = 230$  K,<sup>3,4</sup> and the high-temperature (I-II) ferroelastic phase transition at  $T'_c = 364$  K.<sup>5,6</sup> Recently we have investigated the ultralow-frequency dynamics in a powder sample of TDA using the rotating-frame  $^1\text{H}$  NMR spin-lattice relaxation measurements.<sup>9</sup> In the previous publication we have given a detailed description of the systems and revealed the nature of the phase transitions and the microdomain structures.

While TDA and TDP have similar structures and are expected to show similar general properties, it would be interesting and informative to actually carry out a comparative study of these isomorphous systems. This would provide further valuable information on the nature of the microscopic properties and dynamics, and microstructures of these systems. In addition, this would throw some additional light on the validity of our interpretation of our data on the TDA. It is indeed the purpose of this paper to perform similar measurements on a TDP single-crystal sample as well as a polycrystalline sample, in order to compare the results with those on the polycrystalline TDA system and obtain a clearer picture and insight than from the earlier investigations on TDA.

### II. EXPERIMENT

A single-crystal sample of TDP as well as a polycrystalline sample was made and investigated in this work using a 200 MHz  $^1\text{H}$  pulsed NMR spectrometer. The experimental conditions were identical to those in our recent TDA work.<sup>9</sup> The rotating-frame spin-lattice relaxation data at the

frequency of the rotating frame,  $\omega_1/2\pi = 53.2$  kHz, were obtained in the temperature range 150–400 K.

### III. RESULTS AND DISCUSSION

The single-crystal sample showed no angular dependences and gave line shapes and rotating-frame spin-lattice relaxation that are identical to those in the polycrystalline sample. The fact that our data on the TDP single crystal were identical to those on a polycrystalline sample supports our interpretation that microscopically TDP single crystals as well as the polycrystalline samples consist of ferroelastic microdomains smaller than the grain sizes of the polycrystalline sample.

Figure 1 shows the FWHM (full width at half maximum) linewidth of the TDP line shape. While the low-temperature phase transition at  $T_c$  is accompanied by a slight decrease of the linewidth, a rapid decrease is observed around the high-temperature transition at  $T'_c$ , indicating the presence of motional narrowing at high temperatures.

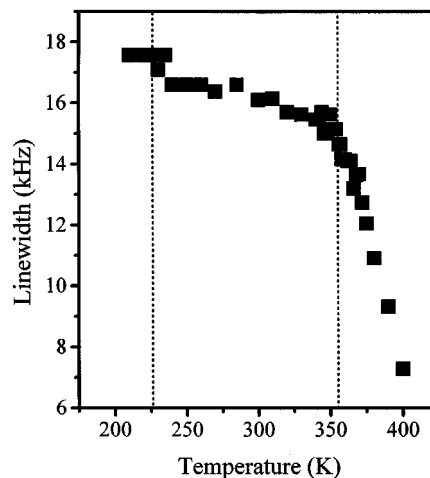


FIG. 1. Temperature dependence of the FWHM linewidth of TDP.

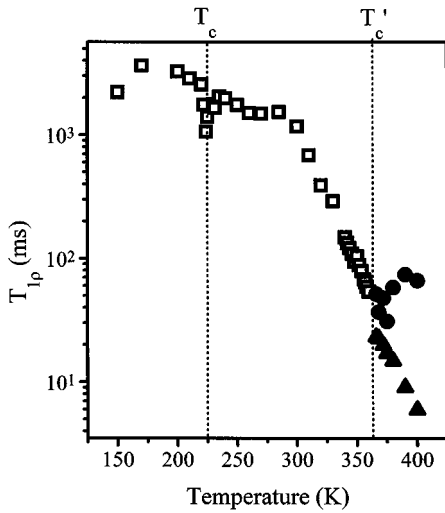


FIG. 2. Temperature dependence of the rotating-frame spin-lattice relaxation times. The open squares were obtained by the stretched-exponential fitting, and the solid circles and the solid triangles by a double-exponential fitting.

The rotating-frame relaxation data obviously deviated from the simple single-exponential form. In the high-temperature phase I they obviously showed a double-exponential pattern, giving two time constants, as in the case of TDA.<sup>9</sup> However, in phases II and III below  $T'_c$ , they were fitted into the stretched-exponential-type or a double-exponential form with equal accuracy, unlike the TDA case where only the stretched-exponential obviously gave reasonable fits. Both of the results will be discussed in this work.

The temperature dependence of the rotating-frame spin-lattice relaxation times obtained by the stretched-exponential fit,  $M(t) = M_0 \exp[-(t/T_{1\rho})^{1-n}]$ , below the high-temperature phase transition temperature and by a double-exponential fit above that temperature is shown in Fig. 2. While they are shown to be longer than those in TDA by an order of magnitude, and the anomalies around  $T_c$  are much more pronounced, the overall pattern is similar to that in TDA.<sup>9</sup> We now discuss the anomalies around the phase transition temperatures, especially around  $T_c$ . As no soft phonon modes are reported in TDP (Refs. 2 and 10) and our 45-MHz laboratory-frame spin-lattice relaxation showed no particular anomalies around the transition temperature, the anomalies observed in the kHz range are indicative of the contribution of a central peak in the spectral density with a very small linewidth.<sup>11-13</sup> Then the different degree of anomalies can be understood in terms of the relative linewidths of the central peak in TDA and TDP. In other words, if the probing frequency is away from the center of the central peak, the anomalies will be weaker or will not be shown. On the contrary, when the probing frequency is closer to the center of the central peak, the anomalies will be more pronounced. This argument enables us to compare the relative central peak contributions in TDA and TDP; the probing rotating-frame frequency, 53.2 kHz, appears to be closer to the center of the central peak in the TDP case.

As discussed in our previous work on TDA,<sup>9</sup> the stretched-exponential relaxation is characteristic of a random distribution of the correlation time  $\tau_c$ ,<sup>14</sup> and can be under-

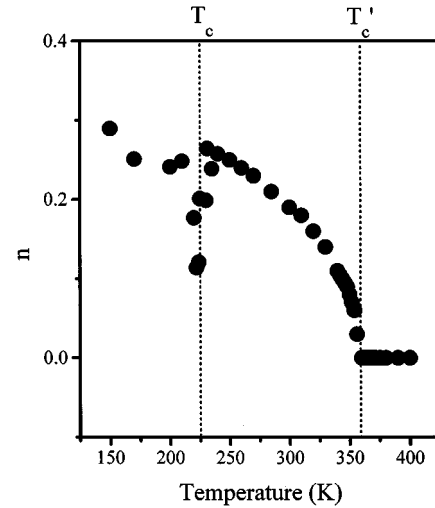


FIG. 3. Temperature dependence of the exponent  $n$ .

stood in terms of a distribution of ferroelectric microdomains, which will result in a distribution of the proton double wells each with a characteristic correlation time for the proton motions.<sup>9</sup> The temperature dependence of the exponent  $n$  for the stretched-exponential fit, which was defined as an order parameter for the proton double-well distribution in the TDA work, is shown in Fig. 3. It is shown that  $n$  also reflects the critical phenomena around the phase transition temperatures. Again, anomalies around the  $T_c$  are much more pronounced than in TDA, whereas the temperature dependence of  $n$  of  $(T'_c - T)^{0.5}$  below  $T'_c$  is similar to that in TDA.

As in TDA, the double exponentiality above the ferroelastic phase transition temperature is indicative of two types of ferroelastic domain structure.<sup>6,9</sup> In the context that  $n$  represents the degree of ferroelastic microdomain distribution, the fact that it shows anomalies at  $T_c$  would indicate that an abrupt change in the microdomain distribution accompanies the antiferroelectric phase transition. As in the case of TDA Fig. 3 shows that the behavior of the exponent  $n$  as an order parameter is confined in the phase II and does not extend down to the low-temperature phase III.

The temperature dependence of the rotating-frame spin-lattice relaxation times  $T_{1S}$  and  $T_{1L}$  from the double-exponential fitting at all temperatures is shown in Fig. 4. The two distinct spin-lattice relaxation times show comparable temperature dependences in the noncritical regions. The difference in their absolute values may arise from the difference of the noncritical contribution to the spin-lattice relaxation rate presumably originating from the proton-phonon coupling.

In Fig. 4, both of the spin-lattice relaxation times  $T_{1S}$  and  $T_{1L}$  show critical fluctuations near the antiferroelectric transition temperature  $T_c$ . On the other hand, only the longer spin-lattice relaxation time  $T_{1L}$  shows apparent anomalies around the ferroelastic phase transition temperature  $T'_c$ . As only one of two distinct domain structures in TDP is known to undergo the ferroelastic phase transition at  $T'_c$ ,<sup>6</sup> this seems to indicate that the two distinct spin-lattice relaxation times arise from the two separate domain structures in TDP. In other words, the  $T_{1L}$  showing apparent anomalies at  $T'_c$  can

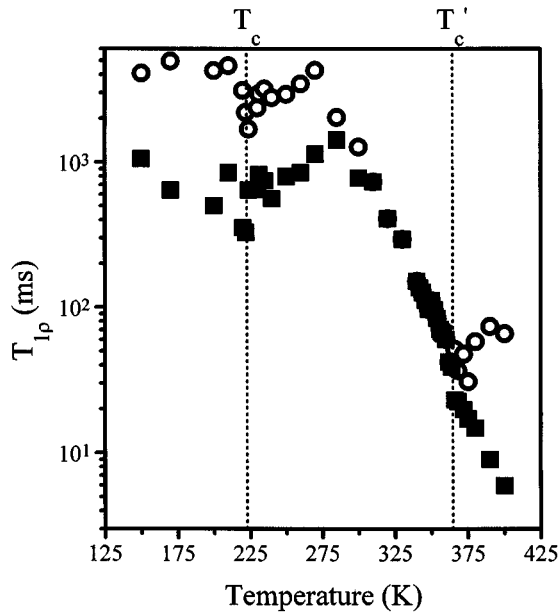


FIG. 4. Temperature dependence of the rotating-frame spin-lattice relaxation times obtained by a double-exponential fitting. The open circles indicate the longer spin-lattice relaxation time  $T_{1L}$  and the solid squares the shorter spin-lattice relaxation time  $T_{1S}$ .

be assigned to the domain structure undergoing the ferroelastic phase transition, whereas the  $T_{1S}$  can be assigned to the other one that does not undergo the ferroelastic phase transition.

While Fig. 4 shows no apparent anomalies in  $T_{1S}$  associated with the ferroelastic transition temperature  $T'_c$ , the derivative of  $T_{1S}^{-1}$  in Fig. 5 with respect to the temperature shows an anomaly around the transition. This seems to indi-

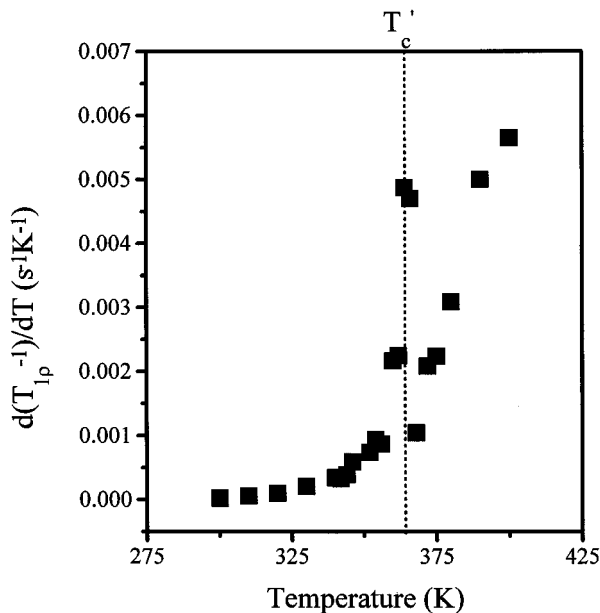


FIG. 5. The derivative of  $T_{1S}^{-1}$  with respect to the temperature around the ferroelastic phase transition temperature.

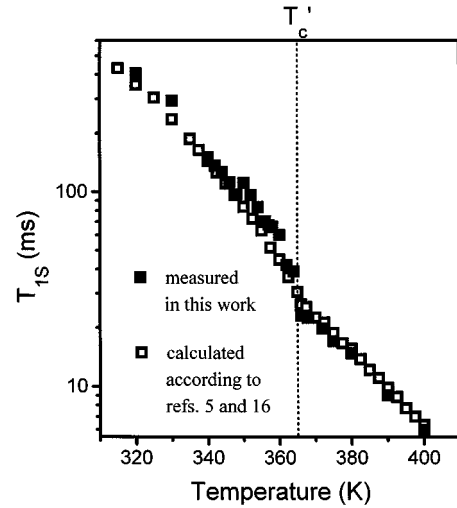


FIG. 6. The  $T_{1S}$  measured in this work (solid squares) and  $T_{1\rho}$  calculated according to Eq. (1) using the previously reported thermal expansion data (open squares) as functions of temperature.

cate that the domain structure that does not undergo the ferroelastic phase transition also undergoes some kind of physical changes around  $T'_c$ . In the compressible Ising model the spin-lattice relaxation time was directly given in terms of the linear thermal expansion.<sup>15,16</sup> Then a  $\lambda$ -like variation in the lattice constants, usually found at a typical order-disorder transition, will result in a discontinuity in  $dT_{1S}^{-1}/dT$ . In fact, an order-disorder nature of the I-II transition was revealed in our previous work,<sup>9</sup> and a  $\lambda$ -like variation in the lattice constants was previously observed in TDP at  $T'_c$ .<sup>4</sup> Thus while  $T_{1S}$  does not show an anomaly attributable to the ferroelastic phase transition, its differential anomaly at  $T'_c$  can be characteristic of the order-disorder transition for the domain structure not participating in the ferroelastic transition. Of course, *both* domain structures are believed to undergo an order-disorder transition at  $T'_c$ . It is possible in some cases that the spin-lattice relaxation time does not show an apparent slowing down at an order-disorder transition, but shows a differential anomaly, as in the current case, and as previously observed at the order-disorder transition in  $\text{NH}_4\text{Cl}$ .<sup>16</sup>

Now we can make a simple model calculation for the  $T_{1S}$  around  $T'_c$ . According to Michel's derivations,<sup>16</sup> the proton rotating-frame spin-lattice relaxation time  $T_{1\rho}$  in compressible Ising lattices can be related to the anomalous thermal expansion  $\Delta L/L$  as, in the limit  $\omega_0\tau_c \gg 1$ ,

$$T_{1\rho} = A\omega_0^2[1 - b(\Delta L/L)], \quad (1)$$

where  $A$  and  $b$  are the constants related to the properties of the lattice, and  $\omega_0$  is the Larmor frequency. Then  $T_{1\rho}$  can be calculated using Eq. (1) according to the previously reported thermal expansion data (from Ref. 5) for TDP. Figure 6 shows our  $T_{1S}$  data and  $T_{1\rho}$  calculated according to Eq. (1) using the fitting parameters of  $A = 0.5 \text{ s}^3$  and  $b = 0.3$ , which are assumed to be independent of temperature. Indeed, an excellent agreement is observed in Fig. 6.

## ACKNOWLEDGMENTS

This work was supported by the Korea Science and Engineering Foundation through the RCDAMP at Pusan National

University and by the Ministry of Education (Grant Nos. BSRI-96-2410 and -2411). Thanks are due to the Korea Basic Science Institute for technical assistance.

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