

^1H NMR study of proton motions in thallium-deficient TiH_2PO_4

Jong Hyun Kim and Cheol Eui Lee*

Department of Physics, Korea University, Seoul 136-701, Korea

Kwang-Sei Lee

Department of Physics, Inje University, Kimhae 621-749, Korea

(Received 26 May 1995; revised manuscript received 13 September 1995)

We have studied a thallium-deficient TiH_2PO_4 (TDP) sample in the temperature range 130–400 K using 200 MHz ^1H pulsed NMR. The line shape consists of a broad and a sharp line, corresponding to the TDP phase and a thallium-deficient phase, respectively. The rotating frame spin-lattice relaxation was shown to consist of two separate components each corresponding to the two line shape components, and to sensitively reflect the phase transitions and the proton motions.

I. INTRODUCTION

Thallium dihydrogen phosphate (TiH_2PO_4 , abbreviated as TDP hereafter) is closely related to the KH_2PO_4 (KDP)-type crystals. The KDP-type crystals are the typical hydrogen-bonded materials undergoing structural phase transitions accompanied by ferroelectricity or antiferroelectricity. In these crystals, it is known that protons in double-well potentials on the hydrogen bonds undergo a phase transition accompanied by displacements in the heavy atom, K, P, O, structure. One of their outstanding phenomena is the proton-deuteron “isotope effect”¹ that raises the transition temperature by about 100 K and decreases the pressure dependence of this transition temperature.²

TDP undergoes two major structural phase transitions and three more complex phase transitions.^{3–7} The room-temperature phase (phase II) is known to be paraelectric and ferroelastic, while the low-temperature phase (phase III) is believed to be antiferroelectric from the polarization-electric field double hysteresis loops of its deuterated analog TlD_2PO_4 .⁸ Thus, the antiferroelectric phase transition in TDP corresponds to the ferroelectric phase transition in KDP.

The high-temperature phase (phase I) is known to be paraelectric and paraelastic.⁵ TDP has a monoclinic crystal structure in phases II and III, while phase I has an orthorhombic structure. The II-III phase transition is associated with a doubling of the primitive cell along the a and b axes.⁹ The II-III phase transition occurs around 230 K (T_c) and is known to be of weak first order,^{1–3} while the I-II phase transition occurs around 357 K (T'_c) and is known to be of second order.^{4–6}

TDP has three different crystallographic hydrogen bonds as determined by x-ray and neutron scattering, and a crystal structure of TDP illustrating the three inequivalent H sites can be found in the literature.^{4,7,9} The two shorter bonds, 0.243 nm and 0.245 nm, respectively, are centrosymmetric and form zigzag chains along the c axis. Protons of these bonds are at special positions at a center of inversion and undergo an order-disorder phase transition through the phase transition temperature T'_c . The longest bond, 0.25 nm, is asymmetric along the b axis and the protons are at a general

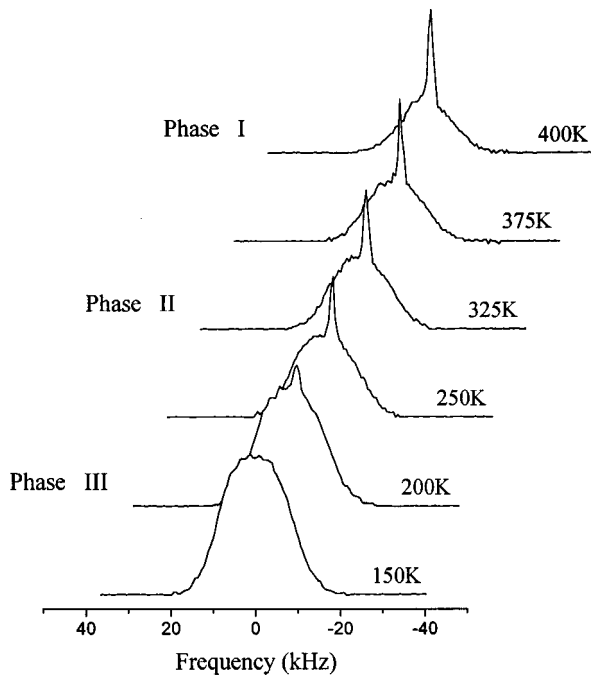
position and are ordered both above and below T'_c . The very short hydrogen bond lengths and the very heavy mass of Tl^+ ion are peculiar to the TDP, different from the KDP-type crystals. These features play an important role in phase transitions of the TDP.

Protons play a main role in the physical properties and the phase transition mechanism in the KDP-type hydrogen-bonded ferroelectrics in any model, and nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) studies are essential in probing the proton motions. Few NMR reports on the TDP are found,¹⁰ while NMR experiments for KDP have been a subject of much interest.¹¹

In the present work, we carried out ^1H line shape and the rotating-frame spin-lattice relaxation measurements of a thallium-deficient TDP sample in order to probe the ultralow-frequency components of the spectral density for the proton motions. The experimental results are discussed in the view of the thermally activated interstitial proton dynamics.

II. EXPERIMENTAL DETAILS

A thallium-deficient polycrystalline TDP sample was made by the reaction Tl_2CO_3 and H_3PO_4 in an excessively acidic aqueous solution and investigated using a 200 MHz ^1H pulsed NMR (Bruker MSL 200) spectrometer. An elemental analysis confirmed the thallium deficiency, and the TDP phase transitions were reflected in the dielectric constant measurements, which indicates that basically the sample has the TDP structure which is known in the literature. The Tl deficiency δ for the $\text{Tl}_{1-\delta}\text{H}_2\text{PO}_4$ sample was determined to be 0.15. The nature of the thallium-deficient phase is not known. The $T_{1\rho}$ data were obtained by applying a 90° pulse, immediately followed by a long spin-locking pulse, phase shifted by 90° with respect to the 90° pulse. The width of the 90° pulse used for the $T_{1\rho}$ was 4.7 μs , which gives the frequency of the rotating frame, $\omega_1 = 2\pi \times 53.2$ kHz. The $T_{1\rho}$ data were obtained by varying the length of the spin-locking pulse. The line shapes were obtained by the 90° - τ - 90° solid echo sequence, with a 90° pulse of 0.7 μs .

FIG. 1. ^1H NMR line shapes at various temperatures.

III. RESULTS AND DISCUSSION

The line shapes at various temperatures are shown in Fig. 1. At low temperatures the line shape consists mostly of a Gaussian line with a linewidth of about 15 kHz, comparable to that of the TDP phase. A narrow Lorentzian peak, attrib-

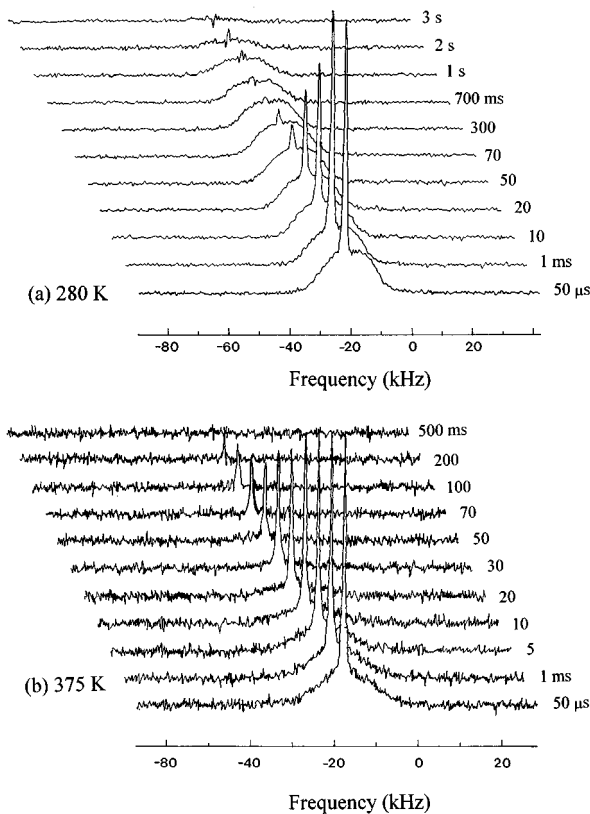


FIG. 2. Fourier-transformed signals following various spin-locking pulse lengths at 280 K (a) and at 375 K (b).

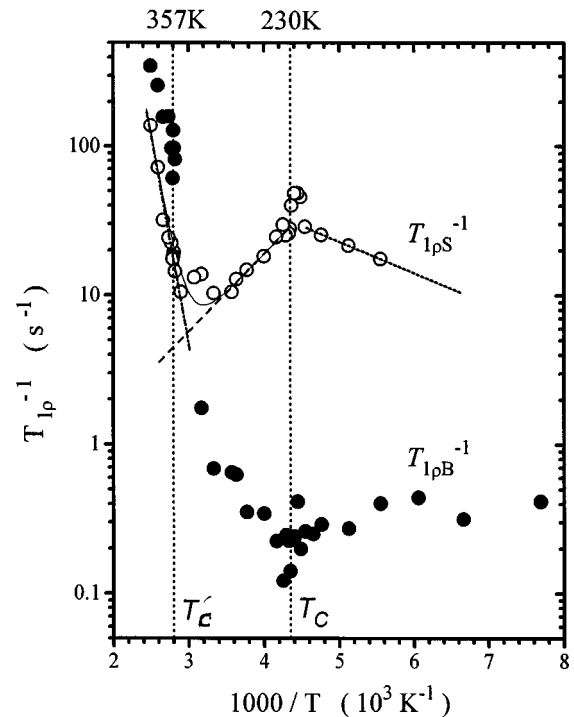


FIG. 3. Temperature dependence of the rotating-frame spin-lattice relaxation rates.

uted to the interstitial proton motions from the thallium-deficient phase such as diffusion or hopping, grows with increasing temperature, corresponding to the growth of the number of "free" protons on increasing temperature.¹² It is seen that the NMR results on the proportion of the two phases are compatible with measured stoichiometry. The two separate components are expected to show distinct relaxation behaviors.

The rotating-frame relaxation data were well fitted into a double-exponential form at all temperatures, giving two rate constants $T_{1\rho S}^{-1}$ and $T_{1\rho B}^{-1}$. The two rate constants correspond to the sharp and broad lines, respectively, as shown in Fig. 2. Figure 3 shows the rotating-frame spin-lattice relaxation rates as a function of the inverse temperature. Both the $T_{1\rho S}^{-1}$ and the $T_{1\rho B}^{-1}$ show sharp transitions around T_c . The $T_{1\rho S}^{-1}$ is only weakly temperature dependent below T_c , but shows a rapid increase with increasing temperature above T_c .

In the simple NMR theory, the general behavior of the relaxation rate for random motions of the Arrhenius type with a correlation time τ_C is described in terms of three regimes: fast, intermediate, and slow motion regimes. For the fast motion regime, namely, for $\tau_C^{-1} \gg \omega_L$, $T_{1\rho}^{-1} \sim \tau_C = \tau_0 \exp[+E_d/k_B T]$, and for the slow motion regime, namely, for $\tau_C^{-1} \ll \omega_L$, $T_{1\rho}^{-1} \sim \tau_C = \tau_0 \exp[-E_d/k_B T]$, where ω_L is the Larmor frequency and E_a is the activation energy. We can calculate the corresponding activation energies from the linear dependence of the relaxation rates in the semilog graph in Fig. 3. In phase III, the activation energy calculated from the slope of the straight line segment of the $T_{1\rho S}^{-1}$ is 0.042 eV, corresponding to a slow motion regime of the proton motions. In phase II, it is 0.10 eV below around 300 K, corresponding to a fast motion regime of the $T_{1\rho S}^{-1}$. The activation energy increases to 0.67 eV in the high-temperature

regime of phase I. Thus, distinct activation energies for the interstitial proton motions are observed in each of the TDP phases. This indicates that the TDP phases are reflected in the interstitial proton motions. In other words, the lattice environments of the distinct TDP phases affect the interstitial proton motions, although the nature of the proton motions is not clearly understood.

The interbond activation energy in the high-temperature regime of $T_{1\rho}$ was calculated to be 0.76 eV. This value is somewhat greater than that of 0.64 eV in KDP, and is consistent with previous observation that the interbond activation energy for the hindered rotation of the H_2PO_4 groups increases with the size of the cation, which controls this re-orientation process.¹³

IV. CONCLUSIONS

We have studied a thallium-deficient polycrystalline sample of TIH_2PO_4 in the laboratory and rotating frames

using 200 MHz ^1H pulsed NMR. The line shapes consist of two distinct components, each arising from the TDP phase and apparently interstitial protons. The rotating-frame spin-lattice relaxation rate is also characterized by two rate constants corresponding to the two separate line shape components. Each TDP phase was characterized by distinct activation energies for the interstitial proton motions. The interbond activation energy for the TDP phase was also obtained and compared with that in KDP in relation to structure.

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 (BSRI-95-2410 and -2411). Thanks are due to K. S. Hong at the Korea Basic Science Institute, and K. W. Lee and C. H. Lee for valuable discussions.

*Author to whom all correspondence should be addressed.

¹J. Bousquet, M. Diet, A. Tranquard, G. Coffy, and J. R. Vignalou, *J. Chem. Thermodyn.* **10**, 779 (1978).

²N. Yasuda, S. Fujimoto, T. Asano, H. Shimizu, K. Yoshino, and Y. Inuishi, *Jpn. J. Appl. Phys.* **18**, 1607 (1979).

³T. Masuo and H. Suga, *Solid State Commun.* **21**, 923 (1977).

⁴R. J. Nelmes, *Solid State Commun.* **39**, 741 (1981).

⁵H. Yoshida, M. Endo, T. Kaneko, T. Osaka, and Y. Makita, *J. Phys. Soc. Jpn.* **53**, 910 (1984).

⁶K. Hanazawa, M. Komukae, T. Osaka, Y. Makita, M. Arai, T. Yagi, and A. Sakai, *J. Phys. Soc. Jpn.* **60**, 188 (1991).

⁷B. Pasquier, N. Le Calve, S. A. Homsí-Teier, and F. Fillaux, *Chem. Phys.* **171**, 203 (1993).

⁸N. Yasuda, S. Fujimoto, and T. Asano, *Phys. Lett.* **76A**, 174 (1980).

⁹R. J. Nelmes and R. N. P. Choudary, *Solid State Commun.* **38**, 321 (1981).

¹⁰N. Nakamura, *Ferroelectrics* **78**, 191 (1988).

¹¹R. Blinc and B. Zeks, *Ferroelectrics* **72**, 193 (1987).

¹²C. Lee, D. White, B. H. Suits, P. A. Bancel, and P. A. Heiney, *Phys. Rev. B* **37**, 9053 (1988).

¹³R. Blinc and J. Pirš, *J. Chem. Phys.* **54**, 1535 (1971).